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FIFTH
INTERNATIONAL CONFERENCE
ON
LANGMUIR-BLODGETT
FILMS

LB5 1991

August 26-30 , 1991
Cité des Sciences et de l'Industrie
PARIS
FRANCE

Abstracts Booklet

ORGANIZATION

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Service de Chimie Moléculaire ; Bât. 125
CEN Saclay
91191 Gif sur Yvette Cedex . France

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La Conférence Internationale sur les Films de Langmuir-Blodgett est placée sous le haut patronage

de la ville de Paris
de la Société Française de Chimie

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TIME SCHEDULE

Time	Sunday 25	Monday 26	Tuesday 27	Wednesday 28	Thursday 29	Friday 30
8.00		Registration	Oral session C	Oral session F	Oral session G	Oral session I
9.00		Oral session A				
10.00						
11.00						Oral session J
12.00						
13.00		Lunch	Lunch	Lunch	Lunch	Lunch
14.00						
15.00		Poster session	Poster session	Poster session	Oral session H	Poster session
16.00		Oral Session B	Oral Session D	Oral Session E		Oral session J
17.00	Registration					
18.00						
19.00	Get-together party					
20.00			3-D movie			
					Conference banquet	

The 5th International Conference on Langmuir-Blodgett Films

Sunday, August 25 - Friday, August 30, 1991
Paris (France)

Preliminary Program

Sunday, August 25

Registration (16.00-20.00)

Get-together party (18.00-20.00)

Oral Presentations

Monday, August 26

OA (8.45)
Opening address
A. Barraud

AI (9.00) *Invited*
Molecular information processing and molecular electronic devices
J. De Rosnay

AO1 (9.45)
The LB deposition as a colloid stability problem
J.G. Petrov

10.15 Coffee break

AO2 (10.45)
Surface potentials of LB alternating layer structures
R.H. Tredgold, P. Hodge, Z. Ali-Adib, D. Dunne, S.D. Evans

AO3 (11.05)
Flow and orientation of rod-like macromolecules in the LB-process
S. Schwiegk, T. Vahlenkamp, Y. Xu, G. Wegner

AO4 (11.25)
Structural changes in lipid-monolayers during the LB transfer due to substrate-layer interactions
K. Spratte, H. Riegler

AO5 (11.45)
Aspects of LB trough design: computerization, surface pressure measurement, unevenness of motion, generated vibrations
G.R. Ivanov, K.G. Kostadinov, A.G. Petrov

12.05 Lunch

14.00 Poster Session

BI (15.15) *Invited*
Supramolecular engineering based on self-assembling monolayers and bilayers
T. Kunitake

BO1 (16.00)
Photoelectric properties of domain arrays in porphyrin LB films
M. Yoneyama, A. Fujii, S. Maeda, T. Murayama

BO2 (16.20)
Multilayer phase transition of a liquid-crystal film on an air/water interface
J.Z. Xue, M.W. Kim

16.40 Coffee Break

BO3 (17.10)
Investigation of fatty acid monolayers at the air/water interface using a reflectance-measuring technique and a phase-contrast microscope
T. Takoshima, A. Masuda, K. Mukasa

BO4 (17.40)
Fusion of phospholipid vesicles with Langmuir lipid monolayer
S.F. Sui, S.P. Wang

BO5 (18.00)
Charge-transfer complex formation in monolayers at the air/water interface
R.C. Ahuja, M. Matsumoto, D. Möbius

BO6 (18.20)
Reflectometry under the Brewster angle as a tool to determine film thickness, headgroup influence and macroscopic inhomogeneities of monolayers at the air/water interface
D. Hönig, D. Möbius

BO7 (18.40)

Water permeation through two-component monolayers of polymerized surfactants and octadecanol

C.J. Drummond, P. Elliott, D.N. Furlong, G.T. Barnes

Tuesday, August 27

CI (8.30) *Invited*

Spectral hole-burning in LB films

M. Orrit, J. Bernard, H. Talon, A. Mouhsen

CO1 (9.15)

Efficient rectified photocurrent from purple membrane LB films at the electrode-aqueous electrolyte interface

Ts. Miyasaka, K. Koyama

CO2 (9.35)

Energy and electron transfer in LB films of cofacial porphyrins-phthalocyanins hetero dimers : a time-resolved study

J.F. Lipskier, T.H. Tran Thi, S. Palacin, S. Gaspard, D. Houde, C. Pepin

CO3 (9.55)

Guided-wave frequency-doubling in LB film waveguides

C. Bosshard, M. Küpfer, M. Flörsheimer, P. Günter

10.15 Coffee Break

CO4 (10.45)

The photoinduced transformation of nonlinear optical properties in organic monolayers

O.A. Aktsipetrov, A.V. Maximychev, E.D. Mishina, T.V. Murzina, A.V. Petukhov

CO5 (11.15)

Optical bistability in the optical waveguides coated with nonlinear LB films

Y.L. Li, J.Q. Fan, Y. Fan, A.D. Lu, X.M. Pang, D.P. Jiang, G.H. Gin, L. Zhang, H. Wang, Y.L. Song

CO6 (11.35)

Photochemical modulation of second order nonlinear optical properties of alternate LB films containing Ru(II)-bipyridine complexes

T. Nagamura, H. Sakaguchi, T. Matsuo

CO7 (11.55)

Second-order nonlinear optical LB films of pyrazine derivatives

M. Era, H. Kawafuji, T. Tsutsui, S. Saito, Ka. Takehara, Ke. Takehara, K. Isomura, H. Taniguchi

12.15 Lunch

14.00 Poster Session

DI (15.30) *Invited*

New trends and prospects in conducting LB films

M. Vandevyver

DO1 (16.15)

New developments in the LB manipulation of electroactive polymers

J.H. Cheung, E. Punkka, M. Rikukawa, R.B. Rosner, A.T. Royappa, M.F. Rubner

16.35 Coffee Break

DO2 (17.05)

The homodoping strategy towards LB conducting films: mixture of amphiphilic octadecyl TCNQ with various semi-amphiphilic TCNQ salts

J.P. Bourgoin, A. Ruaudel-Teixier, M. Vandevyver, M. Roulliay, A. Barraud, M. Lequan, R.M. Lequan

DO3 (17.25)

Electron transport across organic quantum wells: new results on amphiphilic phthalocyanines

K.J. Donovan, K. Scott, R.V. Sudiwala, E.G. Wilson, R. Bonnett, R.F. Wilkins, D.A. Batzel, M.E. Kenney, R. Paradiso

DO4 (17.45)

Electrical properties of LB films of a Ni(dmit)$_2$ charge-transfer complex

C. Pearson, A.S. Dhindsa, M.R. Bryce, M.C. Petty

DO5 (18.05)

Conducting LB films of binary mixtures of donor and acceptor molecules

S.V. Ayrapetiants, T.S. Berzina, S.A. Shikin, V.I. Troitsky

19.00 3-D movie performance
at La Géode

Wednesday, August 28

FI (8.30) *Invited*

Possible applications for LB films

M.C. Petty

FO1 (9.15)

LB films based chemical sensors using second-harmonic generation

S. Draxler, M.E. Lippitsch

FO2 (9.35)

Pyroelectric organo-ruthenium LB films

M.W. Poulter, G.G. Roberts, J. Costello, S.G. Davies

FO3 (9.55)
Non-linear optics: the strongest second harmonic intensity so far from a multilayered LB film structure
G.J. Ashwell

10.15 Coffee Break

FO4 (10.45)
Conducting polymer LB films. Applications to bioelectronics
T.A. Skotheim, L. Boguslavsky, P.D. Hale, H.S. Lee, X.Q. Yang, Y. Okamoto

FO5 (11.05)
LB conducting films of TCNQ and BEDT-TTF derivatives applied to gas sensing: detection ranges and gas diffusion
S. Clemendot, J.P. Bourgoin, G. Derost, M. Vandevyver, A. Ruaudel-Teixier, A. Barraud

FO6 (11.35)
Metal ion sensor based on dioctadecyldithiocarbamat-metal complex induced energy transfer
W. Budach, R.C. Ahuja, D. Möbius

FO7 (11.55)
The effect of the external DC electric field on pyroelectric response of azocompound-based LB films
V.V. Lazarev, N.N. Davydova, V.A. Hkavrichev, S.P. Palto, S.G. Yudin

12.15 Lunch

14.00 Poster Session

FO8 (15.30)
Separation of toxic and acid gases from methane in LB films
P. Stroeve, P.J. Bruinsma, C. Sturesson, R. Koren, G.J.R. Spooner, L.B. Coleman

EI (15.50) *Invited*
Electrochemical studies of self-assembled monolayers
M.S. Wrighton, I. Fritsch-Faules, E. Wollman, D. Frisbie

16.35 Coffee Break

EO1 (17.05)
Electrochemistry at the air/water interface. Lateral diffusion and phase transitions in Langmuir monolayers of octadecyl ferrocene amphiphiles
D.H. Charych, M. Majda

EO2 (17.35)
Homo-epitaxy of diacetylene vapor deposition film on an oriented Langmuir monolayer
Y. Tomioka, S. Imazeki

EO3 (17.55)
Polymerization of 2-alkyl anilines on the LB trough: real time investigation of the polymerization of a conducting polymer confined to two dimensions
R.S. Duran, H.C. Zhou

EO4 (18.15)
Deep-UV photochemistry of chemisorbed monolayers: fabrication of patterned co-planar molecular assemblies
J.M. Calvert, J.M. Schnur, P.E. Schoen, M.C. Peckerar, M.S Chen, W.J. Dressick, C.S. Dulcey, J.H. Georger Jr

Thursday, August 29

GI (8.30) *Invited*
Recent developments in surface analysis of synthesized molecular overlayers
A. Benninghoven

GO1 (9.15)
Spectroscopic properties of trichromophoric molecules incorporated in LB films
D. Meerschaut, M. Van der Auweraer, W Kools, F.C. De Schryver

GO2 (9.35)
LB mono and multilayers of poly(isocyanide)s with different sidechains
M.N. Teerenstra, E.J. Voremkamp, A.J. Schouten, R.J.M. Nolte

GO3 (9.55)
Langmuir-Blodgett-Kuhn multilayer assemblies of liquid-crystalline-azo-dye-sidechain polymers
M. Sawodny, A. Schmidt, R. Reiter, C. Urban, H. Ringsdorf, W. Knoll

10.15 Coffee Break

GO4 (10.45)
Creation and structural comparison of ultrathin film assemblies: transferred freely-suspended films and LB films of liquid crystals
G. Decher, J. Maclennan, J. Reibel, U. Sohling

GO5 (11.15)
Inelastic electron tunneling spectroscopy investigation of monolayers and films of fatty acids and chlorophyll *a*
S. Gauvin, R.M. Leblanc

GO6 (11.35)
Electron spin resonance in LB films of a merocyanine dye and its isotope-substituted analogs
S. Kuroda, K. Ikegami, Y. Tabe, K. Saito, Mi. Saito, M. Sugi, S. Yasui

GO7 (11.55)
Defect annealing rate in monolayers displaying a smectic-L phase
A.M. Bibo, I.R. Peterson

12.15 Lunch

HI (14.00) *Invited*
Atomic scale probes and their applications to organic molecules
G. Binnig

HO1 (14.45)
Nonlinear optical techniques to probe molecular ordering at liquid interfaces
V. Vogel, R. Superfine, C.S. Mullin, X.D. Xiao, Y.R. Shen, M.W. Kim

HO2 (15.15)
Characterization of LB monolayers using polarization modulated FTIR spectroscopy
D. Blaudez, T. Buffeteau, B. Desbat, M. Orrit, J.M. Turlet

HO3 (15.35)
Structural investigations of donor-acceptor-substituted polyenes
T. Wagner, S. Hagen, S. Roth, S. Akari, K. Dransfeld

HO4 (15.55)
Parallel arrangment of fatty acid molecules in the film deposited at a lower surface pressure
H. Matsuda, E. Kishi, R. Kuroda, O. Albrecht, K. Eguchi, K. Hatanaka, T. Nakagiri

16.15 Coffee Break

HO5 (16.45)
Molecular rearrangments associated with the interactions of monolayers and bilayers
C.A. Helm, Y.L. Chen, J. Israelachvili

HO6 (17.15)
Direct observation of molecular structure and dynamics in self-assembled organic monolayers
J.P. Rabe, S. Buchholz

HO7 (17.35)
Scanned probe microscopy of thin organic films
H. Fuchs, L. Eng, W. Schrepp

HO8 (17.55)
The structure of phospholipid monolayers at water surfaces at molecular resolution: a neutron reflectivity study
D. Vaknin, K. Kjaer, J. Als-Nielsen, M. Lösche

20.00 Conference Banquet

Friday, August 30

II (8.30) *Invited*
Tiling the plane with proteins
K. Ulmer

IO1 (9.15)
Ion channel transduction in LB lipid membranes
T.L. Fare, D.A. Stenger, D.H. Cribbs, K.M. Rusin, P.P. Bey Jr, C G. Silvestre , C.A. Palmer

IO2 (9.35)
Oriented IgG layer onto LB films of protein A
I.V. Turko, I.S. Yurkevich, V.L. Chashchin

IO3 (9.55)
Lateral proton conduction along lipid monolayers spread at the air/water interface
J. Teissié, M. Prats, B. Gabriel

IO4 (10.15)
Co-planar patterns of self-assembled monolayers for selective cell adhesion and outgrowth
J.H. Georger Jr, C.S. Dulcey, D.A. Stenger, T.L. Fare

10.35 Coffee Break

JO1 (11.05)
Molecular engineering at the air/water interface: building up designed super molecular assemblies with amphiphilic porphyrins
F. Porteu, S. Palacin, A. Ruaudel-Teixier, A. Barraud

JO2 (11.35)
Self-assembly of avidin-biotin monolayers and multilayers
H. Morgan, D.M. Taylor, C.D'Silva

JO3 (11.55)
Selective substrate binding to guanidinium and urea functionalized monolayers
D. Sasaki, T. Kawahara, Y. Ikeura, K. Kurihara, T. Kunitake

12.15 Lunch

14.00 Poster Session

JI (15.15) *Invited*
Supramolecular chemistry: from molecular recognition towards molecular devices and self-organization
J.M. Lehn

JO4 (16.00)
Molecular recognition in mono and multilayers: biotin-streptavidin systems and analogs
M. Hoffmann, W. Müller, H. Ringsdorf, E. Rump

JO5 (16.20)
Photochromism of spiropyran on supermolecular assemblies
S. Xiao, Z. Lu, R. Zhu, Y. Wei

CA (16.40)
Closing address
H. Kuhn

Poster presentations

Session A

LB film fabrication : instruments and monolayer transfer

AP1
An approach to improving the homogeneity of polymer monolayers
J.B. Peng, G.T. Barnes, A. Schuster, H. Ringsdorf

AP2
A novel alternating-layer trough
L.S. Miller, P.J. Stone

AP3
Molecular orientations of substituted phthalocyanato-polysiloxanes in LB film
K. Yase, S. Schwiegk, G. Lieser, G. Wegner

AP4
Synthesis of polysiloxane films with various microstructures in matrices of synthetic bilayer membranes
K. Sakata, T. Kunitake

AP5
Orientation of polyimide LB films in plane direction
M. Kakimoto, Y. Nishikata, K. Komatsu, Y. Imai

AP6
Theory of flow orientation effects in LB films
M. Sugi, Y. Tabe, K. Ikegami, S. Kuroda, K. Saito, M. Saito

AP7
A new, non-destructive, simple and fast method to visualize submicron defects in Lb films
O. Albrecht, H. Matsuda, K. Eguchi, T. Nakagiri

AP8
Quasi two-dimensional order in LB films
O. Albrecht, H. Matsuda, K. Eguchi, T. Nakagiri

AP9
Monolayer stability and multilayer formation of insoluble monolayers of ionizing materials
R. Aveyard, B.P. Binks, P.D.I. Fletcher

AP10
Mono and multilayers made from discotic liquid crystals
L. Haußling, O. Karthaus, C. Mertesdorf, T. Plesnivy, H. Ringsdorf, C. Urban

AP11
Optimizing LB-multilayer films of 2-docosylamino-5-nitropyridine for potential applications in non-linear and integrated optics
G. Decher, F. Klinkhammer

AP12
Interactions between monolayers and metal ions at the air/water interface. Conditions for the transferability as LB multilayers
S. Bettarini, F. Bonosi, G. Gabrielli, G. Martini, M. Puggelli

AP13
Interaction between Langmuir monolayers and hydrophilic solid substrates
M. Engel, H. Riegler

AP14
Preparation and molecular conformation in LB films from fluorescently amine labeled diacyl phosphatidylethanolamines
G.R. Ivanov

AP15
The equipment for preparations of polar and heterogeneous LB films
S.G. Yudin, S.P. Palto, V.A. Khavrichev, S.V. Mironenko, M.I. Barnik

AP16

Transfer ratio in LB films: role of surface charge regulation

A.A. Servida, H.T. Davis, L.E. Scriven

Session B

Monolayers at liquid-gas interface

BP1

X-Ray diffraction of diacetylene monolayers on LiOH/water substrates

K.M. Robinson, J. Adin Mann Jr

BP2

Modelling the surface potential-area dependence of a stearic acid monolayer

O.N. Oliveira Jr, D.M. Taylor, H. Morgan

BP3

The "time of observation" of π-A isotherms III. Studies on the morphology of arachidic acid monolayers observed by transmission electron microscopy of replica samples of one-layer LB films

T. Kato, Ta. Tanaka, K. Iriyama, T. Araki

BP4

Surface modes on polymer solution by surface light scattering techniques

B.H. Cao, M.W. Kim

BP5

Detection of the optical molecular switching in monolayers by the displacement current measurement

Y. Majima, H. Naruse, M. Iwamoto

BP6

Quantitative evaluation of the dynamic characteristics of phospholipid monolayer

M. Makino, K. Yoshikawa, T. Ishii

BP7

A living monolayer of lipid showing well-regulated displacement current measurement

M. Iwamoto, Y. Majima, A. Watanabe, T. Araki, K. Iriyama

BP8

Investigation of molecular layers on a liquid surface with light scattering

A.F. Maznichenko, A.V. Nabok, B.A. Nesterenko, Y.M. Shirshov, A.V. Maksimychev, N.G. Rambidi

BP9

Monolayers of some pyramidic liquid crystals on water subphase

A. ElAbed, A. Hochapfel, H. Hasmonay, J. Billard, H. Zimmermann, P. Peretti

BP10

Capillary waves: a new monolayer characterization technique using an old method

K. Miyano, K. Tamada

BP11

Effect of thermal treatment on crystal growth of surface monolayer

M. Shimomura, K. Fujii T. Shimamura, K. Kasuga, E. Shinohara, Y. Nagata, M. Matsubara, K. Koshiishi

BP12

Detection of the dynamic behavior of monolayers at the air/water interface by the developed displacement current measurement

M. Iwamoto, Y. Majima, A. Watanabe

BP13

Bidimensional mixtures of biological lipids at the air-water interface

F. Bonosi, G. Gabrielli, E. Margheri

BP14

Theoretical contribution to isotherm of spread monolayer

C.W. Yuan, Y. Wei

BP15

Monolayers of branched-chain phospho lipids

G. Brezesinski, W. Rettig

BP16

LB films of archeabacterial lipid models: 1,1'-polymethylenebis (2-alkyl-*sn*-glycero-3-phospho choline)

K. Yamauchi, A. Moriya, M. Kinoshita

BP17

A LB monolayer with a controllable degree of polarity

J.M. Berg, K.G. Nordli Börve, P.M. Claesson

BP18

Polymeric gegenions induced variability and mobility of amphiphilic supramolecular structures at the air/water interface and on solid substrates

L. Chi, C. Erdelen, R. Johnston, L. Jullien, H. Ringsdorf

BP19

Bulk and monolayer behavior of a ferroelectric liquid crystalline monomer and polymer

W. Rettig, J. Naciri, R. Shashidhar, R.S. Duran

BP20

A new possible approach for interpreting surface pressure-area isotherms

G.F. Leal Ferreira, O.N. Oliveira Jr

BP21

Edge energy at the interface liquid expanded-liquid condensed phase of insoluble monolayers and the sloping of the plateau of the π-A isotherms in the area of the transition betwen these phases

L. Bivas, I. Panayotov, A. Bois

BP22

Bending elastic modulus of monolayers at oil-water interfaces

H. Kellay, J. Meunier, B.P. Binks

BP23

Observation of first-order phase transition in Langmuir monolayers without fluorescent probes

S. Henon, J. Meunier

BP24

Investigation of the phase transitions and anisotropy of behenic acid at the air-water interface by ellipsometry

M. Paudler, J. Ruths, H. Riegler

BP25

UV study on the interaction of amphiphiles having heterocyclic chromophore

Ke. Takehara, K. Isomura, H. Taniguchi

BP26

Thermodynamic study on phase transition in mixed monolayers of cholesterol, lecithin and lithocholic acid

M.J. Galvez-Ruiz, M.A. Cabrerizo-Vilchez

BP27

2D molecular engineering of amphiphilic dithioTTF derivatives

A. Ruaudel-Teixier, M. Vandevyver, A. Barraud, P. Delhaes, E. Dupart, J.P. Morand, I. Favier, T. Albrand

BP28

The influence of chemical modification of lecithin molecules on the dipole and surface components of boundary potential in monolayers

V.S. Gevod, O.S. Ksenzhek, I.L. Reshetnyak

BP29

Langmuir monolayers formed by mesogenic molecules and translationally ordered mesophases with amphiphilic dopants: a comparative study

L.N. Lisetski, L.A. Batrachenko, I.P. Krainov

BP30

Incorporation of non-amphiphilic compounds into host-monolayers

W. Cordroch, D. Möbius

BP31

Ordered domains in a Langmuir monolayer: structure, growth and nucleation

P. Muller, F. Gallet

Session C

Optical properties

CP1

LB films of NLO-dyes with chiral centres in matrices of amylose-esters

M.A. Schoondorp, A.J. Schouten, J.B.E. Hulshof, E.P. Schudde, B.L. Feringa

CP2

LB films of fluorinated polymers for nonlinear optics

H. Hsiung, J. Rodriguez-Parada, R. Beckerbauer, M. Kaku, W. Tam

CP3

Theoretical study on the effect of heterocycles reinforcing the layered structure

K. Isomura, Ke. Takehara, H. Taniguchi

CP4

Excitation energy transfer between J-aggregates of cyanine dyes in LB films and liposomes

T. Sato, Y. Yonezawa, H. Kurokawa, M. Kurahashi, H. Hada

CP5

Aggregates of some spiropyrans with a hydrophobic chain

A. Miyata, D. Heard, Y. Unuma, Y. Higasigaki

CP6

Second harmonic generation in LB multilayers of stilbazium salt polystyrene

L. Liu, J. Zheng, W. Wang, Z. Zhang, Y. Fang, F. Tao, L. Xu

CP7

Electric field poling of composition modulated polymeric films

T. Morita, B.G. Higgins, A. Knoesen, S.T. Kowel

CP8

Quantum efficiencies of photo-electric conversion of triad molecular photodiodes

M. Sakomura, M. Fujihira

CP9

Photo-amplified strorage optical memory with polyion complexed pyrene LB films

M. Fujihira, T. Kamei

CP10
Second harmonic generation from mixed LB films of N-acyl-*p*-nitroaniline and its homologous amphiphile

Y. Miyamoto, K. Kaifu, T. Koyano, M. Saito, M. Kato, K. Kawamura

CP11
The role of the central metal in phthalocyanine LB films studied by hole burning

F. Adamec, M. Ambroz, P. Balog, E. Brynda, J. Dian, M. Vacha, J. Hala

CP12
Excited energy transfer in LB films studied by hole burning spectroscopy

J. Hala, F. Adamec, M. Ambroz, E. Brynda, J. Dian, V. Kapsa, M. Vacha

CP13
LB multilayers from polymers for low loss planar-waveguides

W. Hickel, G. Appel, D. Lupo, W. Praß, U. Scheunemann

CP14
Structure and nonlinear optical properties of LB films formed from *p*-nitroaniline derivatives

M. Bishop, J.H.R. Clarke, L.E. Davis, T.A. King, F.R. Mayers, A. Mohebati, R.W. Munn, M.M. Shabat, D. West, J.O. Williams

CP15
Second harmonic generation in LB films of preformed polymers

T. Verbiest, C. Samijn, A. Persoons

CP16
Polymeric multilayers for NLO-applications

A. Laschewsky, W. Paulus, H. Ringsdorf, A. Schuster

CP17
Polymerizable non-linear optical LB films based on 2-(21-docosenyl) amino-5-nitropyridine

Q. Tang, S.A. Zahir, C. Bosshard, P. Günter

CP18
Orientational investigation of 2-docosyl amino-5-nitropyridine and derivatives by nonlinear optical techniques

C. Bosshard, M. Küpfer, M. Flörsheimer, P. Gunter, Q. Tang, S.A. Zahir

CP19
The characterization of LB films of polymers containing NLO molecules in the side chain

T. Takahashi, Y.M. Chen, P. Miller, L. Samuelson, D. Galotti, B.K. Mandal, J. Kumar, S.K. Tripathy

CP20
Syntheses and LB films formation of donor-acceptor organic compounds

D. Zhu, C. Yang, Yu. Liu, Y. Xu

CP21
Studies on nonlinear optical properties of LB films formed from azobenzocrown ether derivatives

Z.Q. Yao, P. Liu

CP22
Synthesis and LB films deposition of syndioregic stilbazolium polymers

J.M. Hoover, R.A. Henry, G.A. Lindsay, M.P. Nadler

CP23
Dye fluorescence kinetics of LB films

A.G. Vitukhnovsky, M.I. Sluch, J.G. Warren, M.C. Petty

CP24
Nonlinear optical polyamide films derived from L-amino acids

G.A. Lindsay, R.A. Henry, J.M. Hoover, M.P. Nadler, R.A. Nissan, M.D. Seltzer, J.D. Stenger-Smith

CP25
Electrochromism in mixed LB films containing rare-earth bisphthalocyanines

B. Lukas, D.R. Lovett, J. Silver

CP26
The photoexcited states of rhodamine and anthracene in mixed LB films

E. Vuorimaa, M. Ikonen, H. Lemmetyinen

CP27
Waveguiding in polymer/LB film sandwich structures

J.P. Cresswell, G.H. Cross, M.C. Petty, D. Bloor, W.J. Feast

CP28
Studies on electroluminescence of LB films

Y. Hua, J. Peng, D. Cui, L. Li, Z. Xu, X. Xu, Z.Q. Yao, X. Chen

CP29
Photochromic effect of spiropyrans and spirothiopyrans

X. Ma, Y. Huang, W. Zhao, W. Zhang, Z. Du, M. Fan, Z. Zhu

CP30
Second harmonic generation in mixed carotenoid-fatty acid and carotenoid-cyclodextrin LB films

S. Palacin, V. Dentan, M. Blanchard-Desce, I. Ledoux, A. Barraud, J.M. Lehn, J. Zyss

CP31

Novel organic luminophores for LB multistructures

M.A. Afanasyeva, N.Y. Voronkina, I.P. Krainov, S.F. Kramarenko, V.V. Lyakh, N.A. Popova, A.V. Tolmachev

CP32

Oxygen induced fluorescence quenching of pyrene labeled phosphatidylcholine in matrix monolayer at the gas/water interface

R.C. Ahuja, D. Möbius

CP33

Surface coverage by wetting with amphiphilic dyes by adsorption or by LB technique: a comparative study using second harmonic generation

M. Pinnow, G. Marowsky, F. Sieverdes, D. Möbius, C. Kröhnke, D. Neuschäfer

CP34

IR analysis of LB films for non-linear optics

H.P. Haerri, Q. Tang, S.A. Zahir, B. Tieke

CP35

LB film formation and characterization of a new tris-chromophore non-linear optical oligomer

R.M. Swart, E.S. Froggatt, A.N. Burgess, A. Eaglesham, B. Cook, D. Louden, D.P. Devonald, M.G. Hutchings, S. Allen, T.G. Ryan

Session D

Electrical and dielectrical properties

DP1

Measurements of rate constants of photoinduced electron transfer from various ferrocene derivatives to an excited $Ru(bpy)_3^{2+}$ derivative in heterogeneous LB films

M. Fujihira, M. Yanagisawa, T. Kondo, K. Suga

DP2

Device structures for the electrical characterization of LB films of conducting polymers

E. Punkka, M.F. Rubner

DP3

Photogenerated charge storage in hetero LB films including steroidal TCNQ, Cu phthalocyanine and steroidal *p*-phenylenediamine

K. Naito, A. Miura, M. Azuma

DP4

Fast in-plane photoconduction in LB multilayers of polydiacetylenes

K.J. Donovan, R.V. Sudiwala, E.G. Wilson

DP5

Fabrication of electrically conductive LB films comprised of poly (3-hexyl thiophene) and nickel tetra-*tert*-butyl phthalocyanine

M. Rikukawa, M.F. Rubner

DP6

Electrical transport properties of Josephson junctions with a Nb/Au/PI/(Pb-Bi) structure

T. Kubota, M. Wada, M. Iwamoto, H. Noshiro, M. Sekine

DP7

Electrooxidation of dioctadecylthioethylene dithiotetrathiofulvalene LB films

J.P. Morand, L. Brzezinski, M.C. Lopez

DP8

Electronic and optical studies with LB transistors

J. Paloheimo, H. Stubb, P. Yli-Lahti, P. Dyreklev, O. Inganäs

DP9

Monolayer characterization and multilayer deposition of conducting LB films

D.M. Taylor, S.K. Gupta, A.E. Underhill, C.E. Wainwright

DP10

Photo-induced electron transfer in molecular heterojunction using flavin-porphyrin LB multilayers

S. Isoda, S. Ueyama, Y. Hanazato, H. Kawakubo, M. Maeda

DP11

Control of photochemical switching phenomena by chemical modification

H. Tachibana, Y. Nishio, T. Nakamura, M. Matsumoto, E. Manda, H. Niino, A. Yabe, Y. Kawabata

DP12

Preparation of polyimide LB films possessing triphenylamine unit and application to photodiodes

S. Fukui, Y. Nishikata, M. Kakimoto, Y. Imai, K. Nishiyama, M. Fujihira

DP13

The synthesis and characterization of novel polysiloxane LB films

T. Richardson, G.G. Roberts, S. Holder, D. Lacey

DP14

Molecular orientation in conductive LB films of a charge-transfer complex

K. Ikegami, S. Kuroda, Y. Tabe, K. Saito, Mi. Saito, M. Sugi, T. Nakamura, H. Tachibana, M. Matsumoto, Y. Kawabata

DP15
Electronic transport in LB films of metal-$(dmit)_2$
Y.F. Miura, M. Takanaga, A. Kasai, T. Nakamura, M. Matsumoto, Y. Kawabata

DP16
"Superlattices" prepared from dielectric and two-component conducting LB layers
T.S. Berzina, L.A. Feigin, R. Micheletto, F. Rustichelli, V.I. Troitsky, S.L. Vorobyova, L.G. Yanusova

DP17
Identification of the process producing observed rectifying characteristics of M/LB/M structures
A.S. Martin, J.R. Sambles, G.J. Ashwell

DP18
Conducting LB films of new tetrathiafulvalene derivatives
T.S. Berzina, V.Yu. Khodorkovsky, O.Ya. Neilands, V.I. Troitsky

DP19
Molecular orientation-pyroelectricity relationships in alternate LB films
T. Takenaka, T. Kamata, J. Umemura, N. Koizumi

DP20
Pyroelectric behaviour of synthetic biomembrane structures
M. Petty, M.C. Petty, J. Tsibouklis, W.J. Feast, Y. Song, J. Yarwood

DP21
The QTS studies on metal/LB film/GaAs structures
D. Barancok, J. Cirak, M. Haluska, P. Tomcik

DP22
Structural properties of conducting LB films based on $(NDTA)_2(dmit)_2$
K. Tian, T.J. Li, A. Ruaudel-Teixier, A. Barraud

DP23
Time-resolved photovoltage spectroscopy of lipid-free CuTsPc multilayers on *p*-Si(111)
Le. Jiang, W. Liu, D. Wang, Y. Bai, T.J. Li, L. Han, H. Fei

DP24
LB films based on 1,2-dithiolium-TCNQ radical anion
O. Fichet, V. Gionis, J. Amiell, B. Agricole, P. Delhaes, D. Ducharme, A. Perrier, R.M. Leblanc

DP25
Photoelectric properties of LB films containing amphipatic porphyrin and carbazole
T. Nagamura, K. Toyozawa, S. Kamata

DP26
Photoinduced variations of internal electric field in LB films with azodye monolayer
S.P. Palto, M.I. Barnik, V.A. Khavrichev, N.N. Davydova, S.G. Yudin

DP27
Photoinduced electron transfer in monolayers at the air/water interface
G. Caminati, R.C. Ahuja, M. Matsumoto, D. Möbius

DP28
Piezoelectricity in LB films
P.E. Dunn, M. Poulter, G.G. Roberts

Session E
Chemistry in mono and multilayers

EP1
Isomerization of (α-naphtyl)(n-chlorphenyl) ethylene solution by the ruthenium complex LB film
D.A. Styrkas, I.K. Lednev, M.V. Alfimov

EP2
Penetration kinetics of cis-diammine dichloroplatinum II loaded nanoparticles in lipid monolayers as membrane model of reticuloendothelial system
M.A. Egea, M.L. Garcia, M. Espina, O. Valls, M.A. Alsina

EP3
An in situ investigation of the photopolymerization of diacetylene LB films
S.M. Repinsky, V.N Kruchinin, L.L. Sveshnikova, I.N. Domnin

EP4
LB films of hexadecylvinyl dimethyl ammonium chloride and their ozone sensitivity
I. Vikholm

EP5
The polymerization of monolayers and LB multilayers of some unsaturated fatty acids
J. Peltonen, H. Pingsheng, M. Linde'n, J. Rosenholm

EP6
Electrochemistry of viologen-containing LB film prepared by polyion complex technique
M. Shimomura, K. Kasuga, T. Tsukada

EP7
Photoinduced proton transfer in LB films
M. Fujihira, Y. Niedome

EP8

Control of photochromism of diacetylene LB films by polyion complexation

K. Nishiyama, M. Kurihara, M. Fujihira

EP9

Electrocatalytic reduction of CO_2 on modified electrode with LB films of long alkyl substituted nickel cyclam complexes

U. Akiba, Y. Nakamura, K. Suga, M. Fujihira

EP10

Photochemical switching of electrochemical processes on modified electrode with ionic spiropyran LB films

K. Nishiyama, K. Matsumura, M. Fujihira

EP11

Photopolymerization of ω-tricosenoyl derivative of ß-cyclodextrin in LB films

K. Fukuda, Y. Shibasaki, H. Nakahara, W. Tagaki, H. Takahashi, Y. Kawabata

EP12

Preparation and properties of polyamine LB films

T. Suwa, Y. Nishikata, M. Kakimoto, Y. Imai

EP13

Oriented polypeptide monolayers by rapid spontaneous condensation of amphiphilic amino acid esters at the air/water interface

Ts. Miyasaka, N. Nishikawa, M. Ono

EP14

Diffusion process in LB multilayers of hairy rod molecules

M. Schaub, K. Mathauer, S. Schwiegk, P.A. Albouy, G. Wegner

EP15

X-Ray photoelectron spectroscopy study of monomolecular films of Q-state non-stoichiometric lead sulfide in LB films

X.G. Peng, Q. Wei, Y.S. Jiang, X.D. Chai, T.J. Li, J.C. Shen

EP16

A study of properties of 10,12-tricosadiynoic acid LB film

Y. Bai, Li. Li, Y. Wang, J. Yang, D. Tang, M. Gong

EP17

The preparation and properties of CdS colloid LB films

Z.J. Zhang, Z. Du, X. Ma, C. Zhao, Z. Jin, Z. Zhu

EP18

Inorganic monolayers inserted in an LB matrix

H. Perez, A. Ruaudel-Teixier, M. Roulliay

EP19

Electrical properties of copper sulfide semiconductors inserted in LB films

J. Leloup, A. Ruaudel-Teixier, A. Barraud

EP20

Scanning tunneling microscopic, optical and scanning tunneling spectroscopic characterization of size-quantized cadmium selenide particulate films *in situ* generated at monolayer interfaces

X.K. Zhao, L.D. McCormick, J.H. Fendler

EP21

Two-dimensional structures in polymerized monomolecular films

R. Rolandi, S. Dante, A. Gussoni, L. Maga, M. Robello

Session F

Short and long term applications

FP1

Qualitative characterization of enzyme adsorbed to L-film and its application to an urea sensor

S-i. Arisawa, R. Yamamoto

FP2

Relationship between structure and function of a built-up film of amphiphilic Ni phthalocyanine responsible for NO_2

K. Iriyama, T. Araki, N. Shimada, S. Yokoi, Y. Ozaki, T. Iwasaki

FP3

Pattern formation and photophysical applications of LB multilayers based on polyglutamates

K. Mathauer, A. Mathy, M. Schaub, C. Bubeck, G. Wegner

FP4

Polydiacetylene mono and multilayer LB films as E-beam resists: SEM and Raman images

R.V. Sudiwala, C. Cheng, D.N. Batchelder

FP5

The biomimetic property of gas-sensitive films for odorants constructed by the LB technique

M. Ohnishi, C. Ishimoto, J. Seto

FP6

Properties of liquid-crystal cells of pyrolized polyimide LB films

T. Akatsuka, H. Tanaka, J. Toyama, T. Nakamura, M. Matsumoto, Y. Kawabata

FP7

Fabrication of fine patterns by positive-working resists using a polyimide LB film system

M. Iwamoto, S. Kasahara, K. Iriyama, Y. Nishikata, M. Kakimoto, Y. Imai

FP8
Transduction of chemical signals to optical signals by using multilayer-deposited optical fiber
N. Higashi, T. Yamamoto, M. Niwa

FP9
Organic electroluminescent device with cyanine dye LB film as an emitter
M. Era, C. Adachi, T. Tsutsui, S. Saito

FP10
Hybrid gas detector of squarylium dye LB film deposited on a quartz oscillator
M. Furuki, L. Sun Pu

FP11
Gas detection in the ppb-range with a new high frequency, high sensitivity SAW device
M. Rapp, D. Binz, I. Kabbe, M. von Schickfus, S. Hunklinger, H. Fuchs, W. Schrepp, B. Fleischmann

FP12
Preparation of cyanoacrylate LB films and their UV and electron resist applications
N.K. Matveeva, Yu.S. Bokov

FP13
An optical biosensor principle based on fluorescence energy transfer
H.U. Siegmund, A. Becker, H. Ohst, K. Sommer

FP14
Gravimetrical biosensors based on LB films of immunoglobulin
T.B. Dubrovsky, V.V. Erokhin, R.L. Kayushina

FP15
LB resists of diazonaphthoquinone novolac resin made by a new horizontal deposit method
Z. Lu, S. Xiao, Y. Wei

FP16
A gas sensor fabricated with FET and LB film of porphyrin
C. Gu, L. Sun

FP17
Prototype of gas sensor based on LB conducting films
S. Clemendot, L. Henrion, G. Derost, H. Perez, A. Barraud, A. Ruaudel-Teixier

FP18
Elaboration of a glucose biosensor based on LB technology
C. Fiol, J.M. Valleton, N. Delpire, G. Barbey, A. Barraud, A. Ruaudel-Teixier

FP19
LB films as radiation sensitive layers for the use of microlithography
D.V. Nicolau

Session G

Characterization

(structural and other)

GP1
Cellular automata formalism as a method in membranology
K. Kubica, J. Kuczera

GP2
Differential X-Ray reflectometry of imperfect LB films
A.P. Kirilyuk, V.N. Bliznyuk, V.V. Shilov

GP3
Electronic structure of nitrogen square planar complexes in LB films
S. Carniato, H. Roulet, G. Dufour, S. Palacin, A. Barraud, P. Millié, I. Nenner

GP4
Optical properties of LB films: a multiple-angle reflectometric investigation
P.J. Travers, L.S. Miller, R.S. Sethi, D. Skinner

GP5
Secondary ion mass spectrometry studies of mixed arachidic acid and barium arachidate LB films
G. Bolbach, M. Plissonnier, R. Galera, J.C. Blais, G. Dufour, H. Roulet

GP6
LB films assembly of Cu phthalocyanine derivatives substituted by methacrylate oligomer chains
K. Naito, A. Miura, M. Azuma

GP7
Infrared and inelastic electron tunneling spectroscopy of adsorption LB films
S. Kuniyoshi, C. Okazaki, K. Kudo, Ku. Tanaka

GP8
Influence of substituents on in-plane dichroism in LB films of phthalocyanine derivatives
Ki. Ogawa, H. Yonehara, E. Maekawa

GP9
2D ordered LB films of stearic acid on semiconductor substrates
B.A. Nesterenko, V.V Milenin; O.Yu. Gorkun, A.A. Stadnik, Z.I. Kazantseva, A.V. Nabok

GP10
TEM studies on LB films of copolymer of phenyl *p*-nitroazo acrylate

E. Zhou, M. Li, X. Zhao, D. Yan, C.C. Yang, X. Tang

GP11
Structural evaluation of LB films of some amphiphilic phthalocyanines using infrared spectroscopy

M.A. Chesters, M.J. Cook, S.L. Gallivan, D.A. Miles, J.M. Simmons, D.A. Slater

GP12
Soliton mechanism of optical anisotropy photoinduction in LB films

Yu.B. Gaididei

GP13
The properties and structural characteristics of LB films formed from metalloporphyrin complexes with differential alkyl chains

Yu. Liu, J. Lin, X. Feng, J. Mu, K. Yang

GP14
Absorption properties and structure changes caused by the pre-annealing in polydiacetylene LB films

E. Kaneko, M. Shibata, S. Kobayashi

GP15
Structural studies of LB poly-3-BCMU films

G. Gabrielli, D. Grando, M. Nocentini, G. Sbrana, S. Sottini

GP16
LB films of polyheterocyclic compounds with long alkyl chains

H. Nakahara, K. Fukuda, M. Ikeda, K. Kitahara, H. Nishi

GP17
Grazing incidence X-Ray diffraction study of Langmuir and LB monolayers of arachidic acid

T. Matsushita, A. Iida, K. Takeshita, K. Saito, S. Kuroda, K. Oyanagi, M. Sugi, Y. Furukawa

GP18
Structural characterization of polyion complex LB films of perfluoroundecanoic acid-polyethyleneimine

K. Kobayashi, K. Takaoka, S. Ochiai, Y. Taru, M. Takasago

GP19
Aggregation control of photochromic spiropyrans in LB films

I. Hibino, K. Moriyama, M. Suzuki, Y. Kishimoto

GP20
LB films of polymers with chromophoric side chains

T.L. Penner

GP21
Orientation of porphyrins without long alkyl chains in mixed LB films with cadmium icosanoate

R. Azumi, M. Matsumoto, Y. Kawabata, S. Kuroda, M. Sugi, L.G. King, M.J. Crossley

GP22
Analytical surface spectroscopy of phospholipid LB films

R. Linton, V. Guarisco, J.J. Lee, B. Hagenhoff, A. Benninghoven

GP23
A novel range of potentially electroluminescent materials for LB deposition

A.J. Hudson, T. Richardson, G.G. Roberts, R.A.W. Johnstone

GP24
Fourier transform infrared spectroscopy studies on model biological membranes deposited by the LB technique

M.H. Vaughan, J. Yarwood, E.S. Froggatt, R.M. Swart

GP25
Studies of alternating LB films prepared from preformed polymers

P. Davis, P. Hodge, Z. Ali-Adib

GP26
Thermally induced phase transitions in multilayers of Cd arachidate

P. Tippmann-Krayer, R. Kenn, H. Möhwald, K. Kjaer, J. Als-Nielsen

GP27
FTIR metal overlayer ATR spectra of LB films of 12-hydroxystearic acid and its cadmium salt

T. Hasegawa, J. Umemura, T. Takenaka

GP28
In-plane orientation of a dodecyloxy substituted triaryl pyrylium salt by the LB method

C. Ecoffet, D. Markovitsi, M. Vandevyver, A. Barraud, M. Veber, C. Jallabert, H. Strzelecka

GP29
FTIR studies of conducting LB films of *o*-hexadecylthiocarboxy tetrathiafulvalene (HDTTTF)

Y.P. Song, A.S. Dhindsa, M.R. Bryce, M.C. Petty, J. Yarwood

GP30
The structure and stability of metal surfaces modified by silane LB films

M. Wolpers, M. Stratmann, H. Viefhaus, H. Streckel

GP31
Resonance Raman and infrared studies on LB films of some cyanine dyes
Y. Ozaki, N. Katayama, Y. Fujimoto, T. Araki, K. Iriyama

GP32
Characterization of LB overlayers by time-of-flight secondary ion mass spectrometry (TOF-SIMS)
B. Hagenhoff, A. Benninghoven, H.U. Siegmund, D. Holtkamp

GP33
The characterization of two copper phthalocyanine LB films and their gas-sensitive properties
A. Lu, T.J. Li, D.P. Jiang, Z. Zhu, Y.J. Li, X.M. Pang, Y. Fan

GP34
Stereoregularity effects of PMMA on the monolayer characteristics at the air-water interface and on the LB films
J.J. Kim, S.D. Jung, W.Y. Hwang, D.L. Bae, K.J. Lee, J.D. Kim

GP35
Studies on synthesis of PMACME-AN-1 and character of LB films
Y. Zhao, M. Gao, X. Dong, H. Wang, T.J. Li, X. Tang

GP36
Spectral characterization of the LB films of copper phthalocyanine derivatives
Y. Zhou, Yan. Wang, X. Wang, G. Lin, S. Xi

GP37
Stabilization of layered structure of poly(vinyl octal) LB films studied by interlayer energy transfer method
S. Ito, T. Ueno, M. Yamamoto

GP38
Molecular orientation of photogenerated radicals in novel photoelectrochromic LB films
T. Nagamura, Y. Isoda, K. Sakai

GP39
Structure of the Langmuir films from amphiphilic polyimides
V. Tsukruk, N. Mischenko, E. Scheludko, I.P. Krainov, A. Tolmachev

GP40
A new kind of amphiphilic polymers: "duckweed" and "reversed duckweed" types of LB films
J.C. Shen, X. Zhang, R. Zhang, X. Cha, R. Yin

GP41
LB films of crown ether containing biphenyl mesogenic groups
X. Zhang, Z. Lin, J.C. Shen, X. Tang

GP42
The formation and characterization of aggregates of LB cyanine films
L.L. Sveshnikova, V.V. Shelkovnikov, J.U. Seljunina

GP43
Polar multilayer LB films of *p*-octadecyloxyazobenzene-*p'*-sulphamide
V.R. Novak, I.V. Myagkov, Yu.M. Lvov, L.A. Feigin

GP44
Phonon conduction process in LB films
Y. Hiki, S. Ozawa

GP45
Characterization of polyalkylthiophene based LB films
A. Bolognesi, S. Destri, W. Porzio, G. Bajo, R. Paradiso

GP46
On the structure of mixed LB films of two different fatty acid salts
S. Dante, V. Erokhin, F. Rustichelli

Session H
Modern investigation methods

HP1
Visco-elastic properties of thin films probed with a quartz crystal resonator
D. Johannsmann, F. Embs, K. Mathauer, C.G. Wilson, G. Wegner, W. Knoll

HP2
Interfacial recognition reactions as seen by fluorescence-, surface plasmon- and atomic force microscopy
F.J. Schmitt, A. Weisenhorn, P. Hansma, W. Knoll

HP3
Electro-optical spectroscopy on aggregated chromophore systems in LB films
G. Grewer, M. Lösche

HP4
Langmuir monolayers of perfluoroalkyl-terminated amphiphiles studied by optical second harmonic generation
H. Hsiung, R. Beckerbauer

HP5
Imaging of the lateral structure of LB films by metal decoration and polarization microscopy
C. Bubeck

HP6
Angle-resolved photoemission from LB films of copper tetrakis (n-butoxycarbonyl) phthalocyanine

N. Ueno, K. Kamiya, Ki. Ogawa, H. Yonehara, M. Takahashi, H. Nakahara, K. Seki, K. Sugita, K. Fukuda, H. Inokuchi

HP7
Direct measurements of surface forces between monolayers of poly(methacrylic acid) amphiphiles

K. Kurihara, N. Higashi, M. Niwa, T. Kunitake

HP8
Perfectness and blocking property of LB films on platinum electrode investigated by cyclic voltammetry and scanning tunneling microscopy

Z. Ma, C. Zhu, S. Pang, Q. Chen, Lo. Jiang

HP9
Monolayer and multilayer film characterization using surface plasmon resonance

S.J. Cooke, G.G. Roberts

HP10
Scanning optical microscopy of LB films

A.J. Hudson, G.G. Roberts, T. Wilson

HP11
Optical characterization of highly absorbing LB films using ATR techniques

C.R. Lawrence, J.R. Sambles

HP12
Two-dimensional organic crystalline films studied by tunneling microscopy

W.M. Heckl, D.P.E. Smith, H. Klagges

HP13
Direct measurement of the forces between ganglioside bilayers deposited on mica substrates

P.F. Luckham, J.E.C. Wood, R.M. Swart

HP14
Symmetry and orientational structure in hemicyanine monolayer by surface SHG and absorption spectrum

K. Kajikawa, K. Shirota, H. Takazoe, A. Fukuda

HP15
Molecular graphics in the study of the structure of LB films

Z. Ai, Y. Wei

HP16
Evaluation of horizontal lifting method of LB films by using a quartz crystal microbalance

Y. Okahata, Ke. Tanaka, K. Ariga

Session I

Biological and biomimetic aspects, BLM

IP1
Pulmonary surfactant protein SP-C and phosphatidylcholines in bilayers and monolayers

K.M.W. Keough, G. Simatos, J. Perez-Gil, K. Nag, M.R. Morrow

IP2
Simultaneous electrical and optical interferometric measurements of pressure and applied potential induced bilayer lipid membrane deformation

G. Picard, N. Denicourt, J.H. Fendler

IP3
Design and properties of Langmuir films of photosensitive proteins

S.Yu. Zaitsev, N.A. Kalabina, E.P. Lukashev, A.A. Kononenko, N.G. Abdulaev, V.P. Zubov

IP4
Interfacial thermodynamics and activity of IgG monolayers

A. Schirone, C. Ristori, D. De Rossi, A. Ahluwalia

IP5
Surfactin: interfacial properties and interactions with membrane lipids in mixed monolayers

R. Maget-Dana, M. Ptak

IP6
Interfacial films of the membrane protein: photoreaction unit

M. Hara, Y. Yasuda, J. Miyake

IP7
Preparation of LB films of the photosynthetic proteins

Y. Yasuda, H. Sugino, M. Kumei, Y. Hirata, J. Miyake, M. Fujihira

IP8
Adsorption of protein at the air/buffer interface: evidence for lateral interfacial diffusion

J. Teissié, R. Douillard

IP9
Incorporation of membrane proteins into lipid surface monolayers: characterization by measurements of isotherms and by electron microscopy

M. Schönhoff, M. Lösche

IP10
Photoelectric response of black lipid membranes incorporating amphiphilic azobenzene derivative

Y. Yonezawa, H. Fujiwara, T. Sato

IP11
Characterization of monolayers and LB film of dry and wet chlorophyll *a*
G. Munger, R.M. Leblanc, B. Zelent, A.G. Volkov, M.I. Gugeshashvili, J. Gallant, H.A. Tajmir-Riahi, J. Aghion

IP12
Interaction of cytochrome *c* and ribonuclease with phospholipid monolayers
M. Saint-Pierre-Chazalet, C. Fressigné, F. Billoudet, M.P. Piléni

IP13
A Fourier transform infrared spectroscopic investigation of hydrophobic peptides in lipid environment: a monolayer study
A. Dhathathreyan, R. Jayakumar, A.B. Mandal, T. Ramasami

IP14
Drugs in biomimetic models: a monolayer study of the interaction between a phospholipid and two antibiotics, lasalocid and monensine
A. Hochapfel, H. Hasmonay, M. Jaffrain, P. Peretti

IP15
Application of two-dimensional crystallization of proteins on planar lipid films to structure determination by electron crystallography
A. Brisson, G. Mosser

IP16
Physicochemical properties of hepatitis B peptide fragments at an air/water and lipid/water interface
M.A. Alsina, F. Rabanal, M.A. Busquets, F. Reig, I. Haro

IP17
Two-dimensional crystallization of muscle protein actin by adsorption to charged lipid monolayer
A. Tomioka, H.O. Ribi, T. Furuno, H. Sasabe, K. Miyano, T. Wakabayashi

IP18
The protein concentration of IgG mixed films deposited on waveguides
B. Lu, W.B. Shi, Y. Wei

IP19
Factors determining stability of bacteriochlorophyll monolayers
L.N. Raser, L.L. Thomas, J.H. Kim, T.M. Cotton, R.A. Uphaus

IP20
Chemically driven phase separation in black lipid membranes and its coupling to membrane functions
J. Spinke, W. Knoll

IP21
Immobilisation of enzyme on electrode modified by an hydrophobic self-organized structure: mediation of the catalytic activity of an hydrogenase via lateral diffusion of an electroactive amphiphile
T. Parpaleix, M. Majda, C. Bourdillon

IP22
Improvement of enzymatic activity and lifetime of LB films by using submicron SiO_2 particles
F.Q. Tang J.R. Li, Lo. Jiang

IP23
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Session AO

LB film fabrication : instruments and monolayer transfer

AI

MOLECULAR INFORMATION PROCESSING AND MOLECULAR ELECTRONIC DEVICES

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One of the most promising areas of molecular information processing results from the convergence of microelectronics, solid state physics, and molecular biology. This hybrid technology is leading to the development of molecular electron devices (MED). Technological breakthroughs in this area are opening the way to the development of "chemical computers". Such long term applications were discussed during several meeting and workshops in the past years. Molecular electron devices could represent a significant breakthrough for computers in the next 30 years. From the tube era (40s to 60s), to the transistor era (60s to 80s), we are now entering into the molecular electron devices era (80s to 2000 and beyond). The challenge is enormous. We need to start from scratch and reinvent all the components of present day micro-electronics.

First, engineers have to work on a switch, able to shift information in one stage or another. By interrogating this component, one should be able to find out in which stage the switch is. The development of a molecular switch will be equivalent to the discovery of the transistor.

The second major achievement will be the building of a true memory with different switches, that is, an array of molecules which could undergo reversible alterations, and therefore can be reused.

The third major step is to construct molecular wires, able to transport information through distances , like conjugated chains of carbon atoms on which solitons move rapidly in order to connect switches and memories .

The fourth step will be represented by the assembly of switches, memories and wires in three-dimensional structures or arrays, organized in assemblies of modules at several levels of communication and interconnections, able to perform coordinated functions.

This is where one of the major breakthroughs of the new molecular engineering techniques will come into play : from the properties of atoms and molecules, the system will self-assemble in highly organized structures, putting atoms, molecules, and macromolecules into place, in order to perform dedicated functions. At this step, immunology techniques could be used to fit molecules at predetermined spots, or to deposit heavy metals which could be used as conductors at other levels of communications.

Finally, the system should be reparable. Modules which do not perform correctly will have to be detected, corrections made, and sometimes a device replaced. These types of self-repairing automata already exist in biological systems. We begin to understand how they function at the molecular level, and how they self-assemble. Other supramolecular assemblies, like the quantosome, the photosome, the oxysome are small self-contained factories which perform important functions for the cell. These minute devices are packed with an enormous amount of molecules and information. We are slowly starting to understand their structures, and able for the first time to copy them. But we still have to learn more from nature's design, understand how nature operates, and then translate what we have learnt into the new micromachines.

In order to make ultramicrocircuits, several laboratories are trying to synthesize proteins which do not exist in nature. Such syntheses are feasible using present day genetic engineering techniques, automatic gene and protein synthesis, and computer reproductions of the bi and tridimensional structures of amino acid sequences. It is likely that from this research a large variety of molecular electronic devices and ultramicrocircuits could be conceived and manufactured. They could be rendered biocompatible, thus allowing the production of implantable logic circuits, offering the prospect of direct interface between the central nervous system of animals or human beings and computers; Such biocompatible circuits are now being implanted and tested in the brains of rats. Other applications of these ultramicrocircuits could be the production of prostheses for the blind, different transducers, or solar energy converters on soft plastic sheets.

The production and assembly of these molecular circuits can be considered from two different approaches : a "passive" one (successive depositions, etching, grafting, doping) using technologies close to those presently used in the manufacturing of microcircuits ; or an "active" one resulting from the spontaneous "growth" of the molecular circuit. In fact, automatic machines used today for synthesizing and analyzing genes and proteins, offer new models which may inspire the automation of the successive operations of molecular circuit production : growth of polymers, successive washing, reactions with other active groups, blocking, and reactivation of chemical groups.

However, at the level where the presence or absence of a single chemical link can affect the performance of an entire circuit, it is virtually impossible to construct and assemble circuits with traditional macroscopic control techniques. It becomes necessary to use auto-assembly properties of biological macromolecules, observed for instance in Langmuir-Blodgett films or during the auto-organization of viruses or predissociated cellular organelles. In other words, instead of introducing the information from the outside, as we do today with most of our machinery (drill press, lathe, or even car construction robots), we will use information from the biopolymers themselves. Such information stored in the primary sequences of amino acids, allows the three dimensional information stored in the primary sequences of amino acids, allows the three dimensional folding of a protein. It is thus possible to benefit from the properties of biological macromolecules to assemble three dimensional molecular ultramicrocircuits.

Many questions still remain unanswered : will these ultramicrocircuits be repairable? Will we able to selectively break chemical linkages or rearrange them ? Is it still necessary to utilise boolean logic, presently used in all computers ? Will we be inspired by the neuronal networks of the brain ? These circuits presently work, in all probability, in a non-boolean fashion, using parallel processing. To build the logic of the future, the convergence between molecular neurobiology and micro-electronics is in the forefront and it holds great promise.

AO1

THE LANGMUIR-BLODGETT DEPOSITION AS A COLLOID STABILITY PROBLEM

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The Langmuir-Blodgett monolayer deposition is considered as a result of the interaction between the solid/liquid and gas/liquid interface in the three-phase contact zone. Our and literature data on static contact angles θ_0 are interpreted on the basis of the Frumkin-Derjaguin theory (1,2) relating θ_0 to the type of the disjoining pressure isotherm Π (h). "Dry" deposition (without liquid film entrainment) occurs when the disjoining pressure barrier Π_{max} between the hydrophilic groups of the adjacent monolayers has been overcome. The correlation between the irreversibility of the monolayer deposition and the large contact angle values, first observed by Langmuir (3), can also been explained in these framework - they both are related to the deepness of the minimum of the specific Π (h) isotherm of the system.

References :

1. A.N. Frumkin, J. Phys. Chem. (Moscow)12 (1938) 337.
2. B.V. Derjaguin, J. Phys. Chem. (Moscow) 14 (1940) 137.
3. I. Langmuir, Science, 87 (1938) 493.

AO2

SURFACE POTENTIALS OF LB ALTERNATING LAYER STRUCTURES

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LB Multilayers formed from alternating layers of two distinct materials have been extensively studied recently. These systems are all likely to have a net electric dipole associated with each bilayer and these dipoles will reinforce as multilayers are built up producing, as is shown below, a change in apparent surface potential which increases linearly with the number of layers deposited. Studies previously made by us on materials which form Y-layers showed that many LB films exhibit a change of surface potential with thickness which can best be explained in terms of a surface double layer analogous to a Schottky barrier. In a material formed from alternating layers one might expect both these effects to be present. This paper describes the results obtained from an investigation of these phenomena. The materials studied were dipped on bottom electrodes of aluminium deposited *in vacuo* on microscope slides. Surface potential measurements were made by the Kelvin technique. In this method a reading is taken when the electric potentials of the top of the specimen and the bottom of the Kelvin vibrating electrode are equal and thus the field is zero between two surfaces. If the total polarisation of the specimen normal to the upper surface is P then the bound charge associated with this polarisation is given by $\sigma = P$ and

$$P = P_o + \epsilon_o \chi E_s$$

where Po is the polarisation arising from the fixed dipoles, Es is the electric field at the surface and χ is the susceptibility. The field in the specimen resulting from σ is thus given by

$$E = - P_o/\epsilon_o \epsilon$$

where $\epsilon = \chi + 1$ and is the relative permittivity. Thus the potential of the upper surface relative to the bottom electrode will be linearly proportional to the number of bilayers and will differ in sign depending on whether the layers are ABAB... or BABA... . In addition there will be a potential resulting from the Schottky barrier effect which will be quadratic in the thickness and will be independent of the sequence of deposition.

We have carried out experiments using alternating layers of stearic acid and stearylamine which confirm the validity of the analysis given above and allow one to calculate the density of acceptor states in the LB film. We are now extending these studies to other alternating LB systems, in particular those formed from polymers.

AO3

FLOW AND ORIENTATION OF ROD-LIKE MACROMOLECULES IN THE LB-PROCESS

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Rod-like polymers with flexible side chains like Tetra-(methoxy-)tetra-(octoxy-)phthalocyaninato-polysiloxane (PcPS) and Poly-[(γ-methyl-L-glutamate)-co-(γ-n-octadecyl-L-glutamate)] (PG) form stable monolayers on the water surface. These monolayers can be transfered to hydrophobisized glass plates with a transfer ratio near 100%.

Due to the form anisotropy of the molecules supramolecular structures showing a macroscopic anisotropy in the layer plane can be obtained. The orientation of the main axis of the transfered molecules can be correlated to the geometric conditions of the transfer experiment.

The molecules are aligned parallel to the dipping direction, if the transfer gives rise to a convergent flow of the monolayer on the water surface. The molecules show a random orientation on the substrate, if convergent flow conditions are carefully avoided.

The time dependent orientation development during the deposition of the first monolayer may be analyzed theoretically in terms of a two-dimensional liquid-crystal suffering shear deformation.

Orientation effects which may arise from mechanical deformation of the monolayer at the meniscus during transfer to the substrate are negligible as has been shown by direct measurement of the interfacial forces.

AO4

STRUCTURAL CHANGES IN LIPID-MONOLAYERS DURING THE LANGMUIR-BLODGETT TRANSFER DUE TO SUBSTRATE-LAYER INTERACTIONS

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The structural changes of Langmuir monolayers have been studied by fluorescence microscopy during their hydrophilic transfer onto a solid substrate. The monolayers have been doped with minor amounts of fluorescent dye and are imaged in their liquid- condensed/liquid-expanded (LC/LE) coexistence phase. Thus probe-depleted dark LC- domains are visualized in a bright fluorescent LE-matrix. The size and shape of the domains provides information on the local condition of the monolayer.

The observation of dipalmitoylphosphatidylcholine (DPPC) and dimyristoylphosphatidylethanolamine (DMPE) monolayers reveals the substrate-mediated fractional condensation and local phase separation at the three-phase line. It is shown, that the monolayers are preferentially transferred as higher ordered, probe depleted LC-phase during slow ($<2 \mu m/s$) LB-transfers onto SiO_2-substrates. This fractional condensation and/or selective transfer induces an increasing concentration of impurities (i.e. fluorescent dye) in the floating monolayer zone adjacent to the three-phase line. This local impurity-concentration causes the increase of the coexistence pressure, which is detected in the local melting of the domains. The local probe concentration profile depends on the overall probe concentration, the transfer speed, temperature, pressure, etc., and is measured and quantified by image analysis techniques.

With stationary substrates we observe the substrate-mediated pressure deposition of LC-phase and/or the diffusion limited fingering domain growth nucleating at the three-phase line. The substrate-mediated pressure deposition permits the transfer of large areas of LC-phase with unique homogeneity.

The experimental results show that the interaction of the monolayer with its support affects its free energy and thus its equilibrium molecular ordering (e.g. the pressure of the coexistence phase). Hence a molecular rearrangement is observed for slow LB-transfers, where the monolayer interface changes from the aqueous meniscus subphase to the solid support.

Substrate-mediated deposited stripes obtained by slow compression/expansion cycles of increasing maximum pressure (DPPC)

AO5

ASPECTS OF LANGMUIR-BLODGETT TROUGH DESIGN: COMPUTERIZATION, SURFACE PRESSURE MEASUREMENT, UNEVENNESS OF MOTION, GENERATED VIBRATIONS

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The old problem of the influence of motion unevenness of barrier and substrate holder of Langmuir-Blodgett (LB) troughs and the generated within the trough vibrations on the film at the air-water interface and deposited structures was completely forgotten in recent years. The disadvantages of computerization were misregarded and its full potential was not used.

Here our experience in designing a new generation of research LB troughs is presented. The trough is entirely computer controlled with digital and analogue (master and slave) velocity control feed back loop and on-line monitoring of the unevenness of motion. The software productivity is 18 readings per second from all four transducers with IBM PC/AT computer. Four principally different translational drive units are constructed. One of them is realized by redundancy of drives impedance control i.e. stiffness and damping of the barrier are changed. A new methodology for their evaluation is applied. It comprises independent and simultaneous monitoring of three different parameters i.e. drive motor velocity, output link velocity and output link vibrations (see Fig. 1). Our trough features incremental line positional sensors with absolute accuracy below 0.005 mm attached directly to the output link; speed range in excess of 1 : 10000; microprocessor Pt 100 thermometer. Wilhelmy type surface pressure transducer connected to Lock-in amplifier is compared with zero position one. The interbalance between digital and analogue is discussed in relation to velocity control and surface pressure control feed back loops.

We thank the 22 scientists from 8 institutions who participated in final design and evaluation. This project was partly supported by the Bulgarian Ministry of Science and Higher Education under contract No 587.

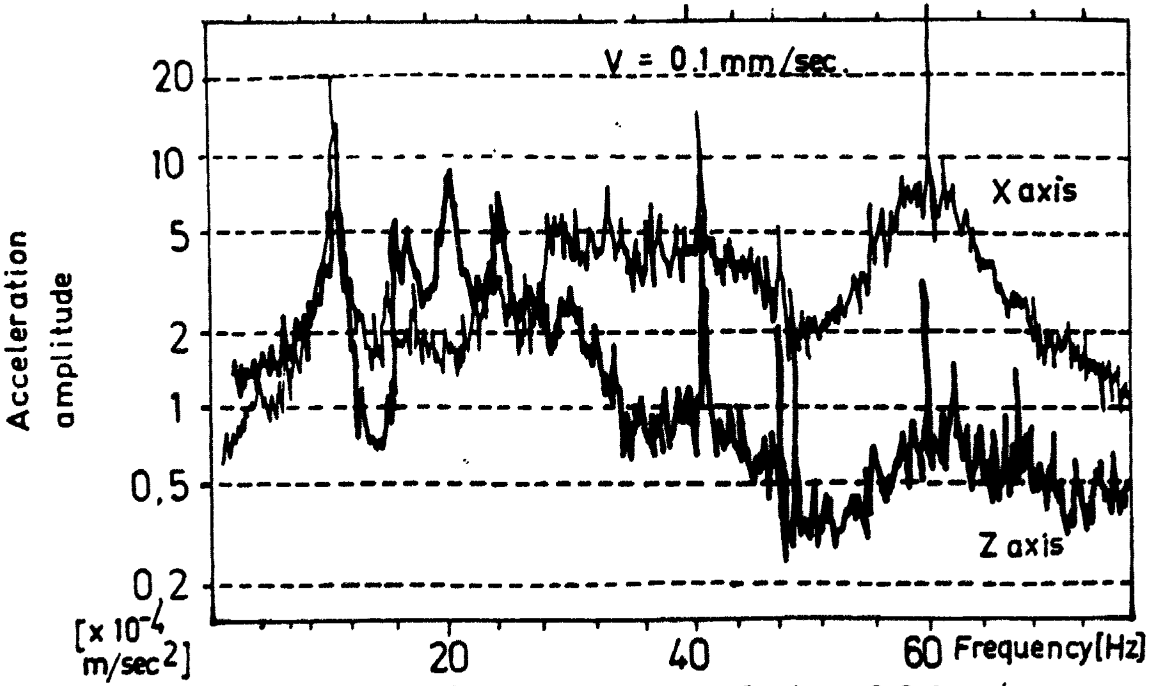

Fig. 1. Acceleration spectra of the barrier at velocity of 0.1 mm/sec.

Session BO

Monolayers at liquid-gas interface

BI

Supramolecular Engineering Based on Self-Assembling Monolayers and Bilayers

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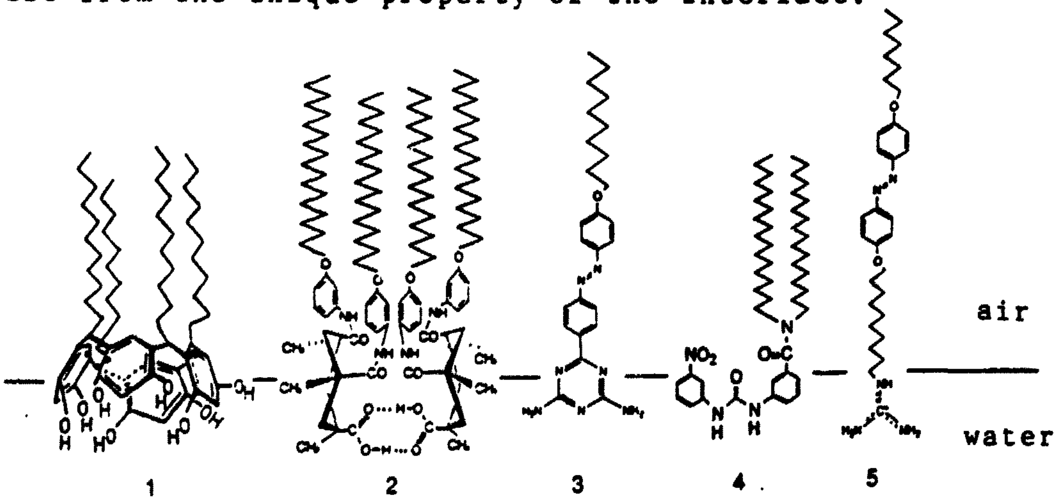
Novel molecular functions are conveniently designed by taking advantage of self assembling properties of monolayers and bilayers. Some of our recent progresses in this field are summarized. A common theme is to design macroscopic organization on the basis of microscopic (molecular) organization.

1. Molecular Recognition by Surface Monolayers.

Molecular recognition via specific hydrogen bonding has been extensively studied as host guest interactions in organic media. We found that hydrogen bonding interactions play important roles even at the air-water interface which is exposed to the subphase water.1) Fig. 1 illustrates examples of functionalized monolayers which we have prepared. They bind specifically respective aqueous substrates at low concentrations. For instance, a Kemp's triacid derivative aligns in a dimeric form (2) and is capable of specific binding of nitrogen aromatics and amino acids. The monolayer of a guanidinium derivative (5) can bind ATP selectively. The mode of molecular recognition can be confirmed by FT-IR and XPS spectroscopies of transferred films. Enhanced binding must arise from the unique property of the interface.



2. Preparation of Highly Stabilized BLM's.

Black lipid membranes (BLM) have been used as biomembrane mimics: however, their uses are limited due to short lifetimes. We found that stable BLM's were formed from various synthetic amphiphiles which spontaneously produced aqueous bilayer dispersions.2) The lifetime exceeds one day in several cases. Conventional permeation experiments can be conducted because of this improved stability.

3. Controlled Orientation of Bioactive Molecules in Synthetic Bilayer Membranes.

Component amphiphiles in the bilayer assembly assume well-defined orientations. Certain guest molecules are incorporated into bilayers in ways that reflect the assembly of the matrix bilayer. The orientation of negatively-charged porphyrins in matrices of ammonium bilayers is determined by optimized electrostatic interactions.3) Molecular orientation of myoglobins and other heme proteins in bilayers can be controlled similarly.4)

4. Cast Films of Synthetic Bilayers as Molecular Templates.

Aqueous synthetic bilayers are cast into free-standing multilayer films. Alkoxysilanes incorporated into the regular interbilayer space of the cast film can be hydrolyzed and condensed to form silicate layers.5) Multilayered, ultrathin (20 Å) silicate films are obtainable upon extraction of organic matrices. This approach is extended to formation of aluminosilicates. An ion exchange technique has been used to attain even finer control.

References

1) K. Kurihara, K. Ohto, T. Tanaka, Y. Aoyama, T. Kunitake J. Am. Chem Soc., in press.
2) S. Kato, T. Kunitake, Chem. Lett., in press.
3) Y. Ishikawa, T. Kunitake, J. Am. Chem. Soc., in press.
4) I. Hamachi, S. Noda, T. Kunitake, J. Am. Chem. Soc., 112, 6744(1990).
5) K. Sakata, T. Kunitake, J. Chem. Soc., Chem. Commun., 504(1990).

PHOTOELECTRIC PROPERTIES OF DOMAIN ARRAYS IN PORPHYRIN LB FILMS

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Practical applications of LB films, especially to microelectronic devices, require a careful control of the two-dimensional textures of spread monolayers. This task involves the study of experimentally correlating the functional properties of the monolayers with their microstructures, which is quite important but seems to have been rather neglected so far. Here we discuss the formation of porphyrin domain arrays at the air-water interface together with the domain-level characterization of the photoelectric properties of LB films containing these arrays.

The system studied is a mixed monolayer containing 5-(4-N-decyl-pyridinium)-10,15,20-tri-p-tolyl porphyrin (C_{10}PyTTP) as a highly photovoltaic compound and arachidic acid(C_{20}) as an insulating matrix component. Fluorescence microscopic observations reveal that C_{20} forms small crystalline domains (<10 μm) in an as-spread monolayer on pure water while C_{10}PyTTP forms nearly circular domains of finite size after repeated compression and expansion of the monolayer. The porphyrin domains are of rather uniform size with their mean diameter strongly depending on the molar mixing ratio of C_{10}PyTTP and C_{20}. For example, a mean diameter of 50 μm is obtained for 1:10 mixtures. The domains are separated from each other by C_{20} crystallites, making an array-like pattern at the air-water interface.

These microstructures are successfully transferred onto solid substrates, and Schottky type photovoltaic cells (Al/porphyrin layer/covering layer/Ag) are fabricated. Their photoelectric properties are investigated on the domain level by measuring short-circuit photocurrent (Isc) under illumination of a focused light (~20 μm). Lateral distributions of Isc are monitored by scanning the light across the cell surface. The obtained Isc shows a large fluctuation depending on the position of illumination, indicating that the porphyrin domains function as photodiode arrays.

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BO2

MULTILAYER PHASE TRANSITION OF A LIQUID CRYSTAL FILM ON AN AIR/WATER INTERFACE

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Abstract

Thin liquid crystal(LC) films show very interesting physical phenomena and have been studied by many researchers. We study the phase behavior of thin film of Octylcyanobiphenyl(8CB) at the air/water interface by simultaneously measuring the molecular alignment and the static pressure as a function of density. The density of the liquid crystal molecules on the interface is changed either by adding in more liquid crystals and /or by compressing the sample surface. We find that when the density is very low, the LC is in "gas" phase, molecules either lie parallel to the interface or form patches with their director roughly perpendicular to the interface. Increasing in the density results in quantized growth of liquid crystal layers which are parallel to the interface. This layer growth apparently strongly depends on the interface interactions between the LC molecules and water. We also study this surface induced ordering when the temperature is changed in the range where the bulk LC will go from isotropic phase to crystal phase. Ellipsometry and the surface balance techniques are used in the studies.

BO3

Investigation of Fatty Acid Monolayers at the Air-water Interface Using a Reflectance-measuring Technique and a Phase Contrast Microscope

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We newly developed two techniques to investigate the aggregation structure of monolayers at the air-water interface.

Reflectance-measuring technique

Using this technique, we investigated the aggregation structure of fatty acid (C_{12}~C_{22}) monolayers at the air-water interface without using fluorescent probes. It is found that the aggregates (domains) grow even below 0.1mN/m, and the size of the domains increases with the alkyl-chain length up to arachidic acid, but it decreases in behenic acid.

Fig.1 shows a typical example of the time dependence of the reflectance in arachidic acid on a water subphase. The reflection spectra from a clean water surface was monitored for 5 min. then the sample solution was spread (a). We waited for 10 min (b-c) to evaporate the solvent (chloroform), and the compression was started (c). Below 25Å2/molecule (d-e) which means in condensed monolayer, the reflectance increases continuously with increasing surface pressure. An occasional increase in reflectance is observed even below 0.1mN/m (b-d). Since the reflectance increases continuously in condensed monolayer, the occasional increase suggests the growth of condensed domains at very low surface pressure. The intensity and the period of the variation in reflectance at very low surface pressure increase with the alkyl-chain length up to arachidic acid. But in behenic acid little variation in reflectance is observed at very low surface pressure. It is considered that the period of the variation reflects the size of domains, because the compression speed is constant. Therefore, it is concluded that the size of domains at very low surface pressure increases with increasing the alkyl-chain length from myristic acid to arachidic acid, but it decreases in behenic acid.

Phase Contrast Microscope

We found that the aggregation structure of monolayers at the air-water interface can be visualized using a phase contrast microscope. Using this technique, we first observed the domain morphology in fatty acid (C_{14}~C_{24}) monolayers directly and in real-time without using fluorescent probes.

Fig.2 shows a typical example of visualized domains at very low surface pressure in arachidic acid. In our experimental set up, dark regions in the picture are domains. In the upper part of the picture one can see the passing time from the spreading of the sample solution. From the direct observation of domains in fatty acid monolayers, it is confirmed that

(1) domains grow in several seconds after the spreading
(2) isolated domains fuse together to form larger domains in several minutes after the spreading
(3) the size of domains increases with the alkyl-chain length up to arachidic acid, but it decreases in behenic acid and lignoceric acid.

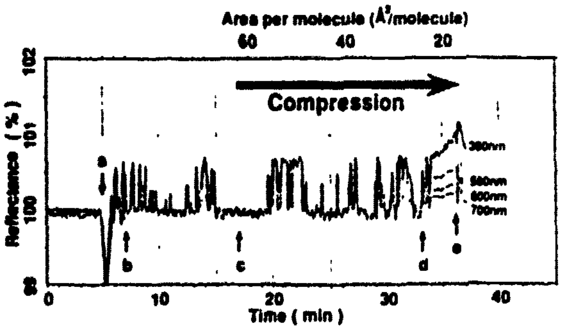

Fig. 1 Time dependence of the reflectance in arachidic acid

Fig.2 Visualized domains in arachidic acid

B04

FUSION OF PHOSPHOLIPID VESICLES WITH LANGMUIR LIPID MONOLAYER

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The interactions between biological membranes involve some major matters of membrane biophysics, such as membrane adhesion and fusion, exocytosis and endocytosis, lipid exchange and so on. As a model, lipid vesicles or liposomes have been widely used in the study of inter-membrane interactions. The present review, however, is devoted to investigate the interactions of phospholipid vesicles with Langmuir lipid monolayer, which may furnish another model system to study inter-membrane interactions. In fact, the radius of curvature of secretion vesicles created by celluar biochemical processes (very small vesicles) is much smaller than that of the inner monolayer of cell membrane. The problem of interactions of these small vesicles with the cytoplasmic-side monolayer of plasma membrane, therefore, may be approximately treated as an interaction of very small vesicles with a planar lipid monolayer

Pure and mixed phospholipid monolayers were prepared at air / water interface. The π-A isotherms coming from same lipid monolayer but different subphase (with and without lipid vesicles) were compared. After special calibration to correct the molecular average area, a quantitive information of lipid molecular transfer from vesicle into Langmuir film was obtained. In case the change of molecular average area is not sensitive to molecular composition, a molecular transfer rate C. maybe approximately described as:

$$C = \frac{A(\pi) - A_0(\pi)}{A_0(\pi)} \times 100\%$$

where $A(\pi)$ and $A_0(\pi)$ are the film area after and before vesicle fusion respectively.

The effects of vesicle dimension, vesicle phase and surface charge on the fusion of phospholipid vesicles with Langmuir lipid monolayer were analyzed, which showed that these factors strongly affected the fusion process.

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BO5

Charge-Transfer Complex Formation in Monolayers at the Air/Water Interface

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Many of the organic conducting materials are based on the charge-transfer (CT) complexation of the two components involved. We have investigated the formation of such complexes in monolayers at the air/water interface using the amphiphilic cyanine dye N,N´-dioctadecyl-oxacyanine perchlorate (S9) as donor and octadecyl tetracyanoquinodimethane(C18TCNQ) as acceptor components. UV-VIS surface reflection and fluorescence techniques were employed to investigate the complexation process.

The absorption spectrum of the chloroform solution of S9 and C18TCNQ(1:1) does not show any extra bands. However, when the solution is spread at the air/water interface the surface reflection spectrum shows a new broad band with a maximum at 480nm which we have ascribed to the CT transition between S9 and C18TCNQ. The CT band shows bathochromic shifts with increasing surface pressure. Progressive dilution of the 1:1 monolayer with matrix molecule (DMPC) leads to a decrease in the CT band intensity until at 1:1:5 molar ratio of the components no CT band is seen. The CT complex formation is also reflected in the surface potential-area isotherms. Upon direct excitation of the CT band at 480nm or via excitation of the donor (365nm) a broad band fluorescence emission with maximum at 560nm was observed. The excitation spectrum of the CT band closely resembles the reflection spectrum. The fluorescence quantum yield increases with decreasing temperature. The fluorescence intensity normalized (at constant surface density)-area isotherms show that the CT band intesity increases continuously with increasing surface pressure, whereas the donor fluorescence intensity decreases sharply above 25mN/m. The results are analyzed in terms of Mulliken CT model.

BO6

Reflectometry under the Brewster angle as a tool to determine film thickness, headgroup influence and macroscopic inhomogeneities of monolayers at the air/water interface.

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For the characterization of monolayers at the air/water interface one commonly uses either normal incident light reflection, ellipsometrical or fluorescence methods. We developed a simple, easy-to-handle method without probe molecules: a p-polarized light beam of 1mm diameter from a diode laser (670nm) is incident under the Brewster angle of the pure water surface. The reflected light intensity is measured by a small photomultiplier. The Brewster angle offers the advantage of very low (theoretically zero) background signal from the pure water. The reflectivity is enhanced some hundred percents by compressing a monolayer of a common matrix substance (i.e. arachidic acid). Fig.1-3 illustrate some of the abilities of this simple method concerning film thickness and monolayer deposition control.

Fig.1 A typical reflection isotherm. The steep increase in intensity is due to a compact island drifting under the light spot. Inhomogeneities of the monolayer are observed.

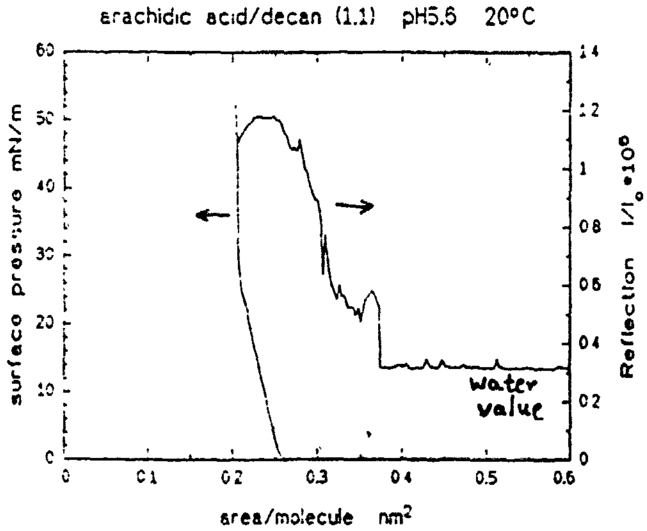


Fig.2 The maximum reflection enhancement versus chain length for fatty alcohols.

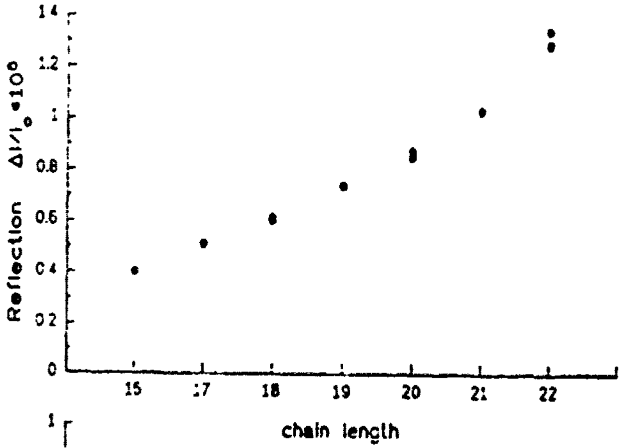
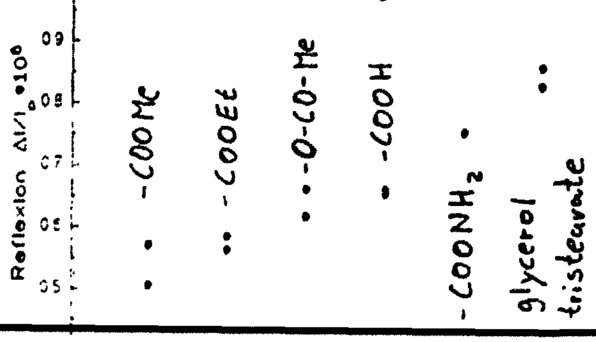


Fig.3 The influence of headgroups on maximum reflection for stearyl chains (n=18). The isotherms vary strongly in shape for the different substances.



B07

WATER PERMEATION THROUGH TWO-COMPONENT MONOLAYERS OF POLYMERISED SURFACTANTS AND OCTADECANOL

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Surface pressure-area (π-A) isotherms and resistances to water evaporation (r) have been measured for monolayers of poly(octadecyl methacrylate), poly(octadecyl acrylate) and poly(vinyl stearate). For each polymer, there were several samples of different molar mass and polydispersity. All samples were polymerised before spreading at the air/water interface. The Langmuir-Schaefer method was employed to measure evaporation resistances.

The π-A and r data for the polymerised surfactants suggest that, at least in the weight average molar mass range of 60 to 900 kg mol^{-1} and polydispersity range of 2 to 9, monolayer properties do not depend on molar mass or polydispersity. The evaporation resistances of the polymerised surfactants ($r < 0.5$ s.cm^{-1} at 20 mN/m and 20°C) are significantly lower than that of octadecanol ($r = 2.87$ s.cm^{-1} at 20 mN/m and 20°C).

π-A isotherms and r have also been measured for mixed octadecanol/poly(octadecyl methacrylate), octadecanol/poly(octadecyl acrylate) and poly(vinyl stearate)/poly(octadecyl acrylate) monolayers. For these two-component systems, excess areas and excess free energies of mixing, calculated by the Goodrich method, were determined from the π-A isotherms. Significant deviations from ideal mixing occur with both the octadecanol/poly(octadecyl methacrylate) and the octadecanol/poly(octadecyl acrylate) systems. With evaporation resistance, ideal mixing is thought to correspond to a linear relationship between $\ln(r)$ and composition (x). The data for the octadecanol/poly(octadecyl methacrylate) show negative deviations from this relationship whereas the results for octadecanol/poly(octadecyl acrylate) show positive deviations, and for mole fractions of octadecanol > 0.3 the values of r are close to that of pure octadecanol.

These results have been used to compare two theories of monolayer permeation, viz. the energy barrier theory of Langmuir and Schaefer and the accessible area theory of Barnes, Quickendon and Saylor.

Session CO

Optical properties

SPECTRAL HOLE-BURNING IN LANGMUIR-BLODGETT FILMS

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Conventional spectroscopy was applied long ago to LB films by Kuhn and his group : these experiments provided such information as molecular parameters, position of dye molecules from energy or electron transfer measurements, orientation of transition dipole moments, etc. Our aim here is to show the interest of high-resolution studies of LB films.

At low temperatures, the spectra of solid solutions are inhomogeneously broadened : the narrow (from 0.001 to 0.1 cm^{-1}) homogeneous zero-phonon lines of individual molecules are spread over the much broader (from 10 to 1000 cm^{-1}) absorption band of the solution. Among various time-resolved and spectral methods used to measure the homogeneous width in solid solutions, the spectral hole-burning is most widely used because it applies to many solute-matrix couples [1]. As the homogeneous broadening arises from population and coherence loss, the hole width is a probe for fast energy transfer (e.g. in photosynthetic centers) and for the low-temperature dynamics around the absorbing molecules. Also, a narrow spectral hole is much more sensitive to external perturbations (electric or magnetic fields, pressure and strain, etc.) than the broad band in which it is burnt.

Recording spectral holes burnt in monolayers is difficult because of the weak number of active dye molecules. Moreover, whenever the matrix dynamics is to be measured, energy transfer should be avoided by keeping the dye concentration very low. In our setup, we applied the very sensitive fluorescence excitation method to a stack of thin plates covered with the LB film [2]. Hereafter, we describe several hole-burning experiments in LB films.

i) dielectric image effect

Dye molecules imbedded in a surface monolayer are affected by a medium change across the surface. A convenient way to achieve this at helium temperatures is to immerse the sample in superfluid helium. Due to the liquid's polarization, the molecular transition frequencies are red-shifted by a few hundredths of a cm^{-1}. We detected this red shift using a narrow spectral hole [2]. Similar experiments could be devised using holes as surface probes.

ii) Stark effect

The change in hole shape after application of a static electric field (Stark effect) may be related through the molecular structure to the orientation of the chromophore axes of the absorbing molecules in the film (including their direction, which is not given by absorption spectra). Using a fatty acid multilayer doped with an amphiphilic cyanine dye, we have shown that the short chromophore axis lies nearly parallel to the surface [3]. In the case of centrosymmetric molecules, a linear Stark effect indicates that microscopic internal fields break the molecular symmetry. Stark measurements could thus be related to the internal field in LB films.

iii) Surface dynamics

We studied the temperature dependence of the hole width in LB assemblies where the dye occupied different positions with respect to the surface and substrate. When the dye is close to the surface (i.e. in the two last monolayers) the hole width remains large at the lowest temperature studied (1.7 K). We attribute this unexpected result to a specific low-temperature motion taking place in the surface monolayer. As is known from other techniques, especially infra-red absorption, the last (surface) layer is less ordered than the bulk ones. The low-T motion could perhaps be related to the structure of the surface layer. We hope further work will give us insight into this problem.

References :

[1] W. E. Moerner, editor, Persistent Spectral Hole-Burning : Science and Applications, Springer (1988).

[2] M. Orrit, J. Bernard and D. Möbius, Chem. Phys. Lett. 156 233 (1989).

[3] M. Orrit, J. Bernard, A. Mouhsen, H. Talon, D. Möbius and R. I. Personov, submitted to Chem. Phys. Lett. (1991).

CO1

EFFICIENT RECTIFIED PHOTOCURRENT FROM PURPLE MEMBRANE LB FILMS AT THE ELECTRODE-AQUEOUS ELECTROLYTE INTERFACE

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Bacteriorhodopsin (bR)-containing purple membrane (PM) was purified from *Halobacterium halobium* and its LB films were prepared on an SnO_2 electrode. A photochemical cell was constructed by dipping the PM-coated electrode in an aqueous KCl electrolyte together with a counter electrode and a reference electrode, where the thin PM layer placed between the electrode and electrolyte was to function as a photosensitive interface.

Visible light irradiation to the PM film caused a photocurrent in an external circuit with a time response profile as shown in Fig. 1. The action spectrum of the photocurrent coincided with the absorption spectrum of bR (Fig. 2). The magnitude of photocurrent depended significantly upon the electrode potential applied to the SnO_2 electrode but was always rectified in cathodic direction showing marked enhancement under cathodic polarization of the electrode. The pH of the electrolyte highly affected this potential dependence profile and the maximal photocurrent response was obtained in a neutral pH region which agrees with the pH dependence of the proton pump activity of bR. The pH dependence as well as a fact that the photocurrent was strongly quenched by any kind of buffering agent added in electrolyte, support that the photoresponse arises from the light-driven proton transfer in bR.

Of important performance in this type of solid-liquid junction photocell is that a highly efficient and stable photocurrent can be obtained with only a few number of PM monolayers. A sandwich type bR photocell was also constructed using a thin layer polymer electrolyte containing agar, gelatin, CM-chitin, etc., which enabled to fabricate a lateral array of small photocells (pixels) on a substrate. Based on this technique, we were successful to develop an image sensing device with 64 bR photo-pixels, which proved to have a unique sensing function similar to those found in visual perception.

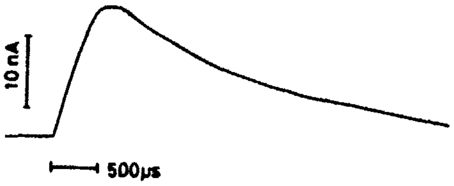

Fig. 1 Time response by flash excitation.

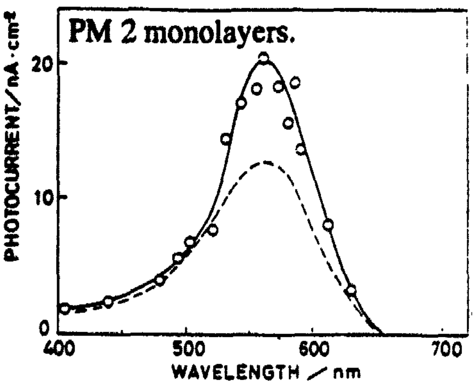

Fig. 2 Photocurrent spectrum

CO2

ENERGY AND ELECTRON TRANSFER IN LANGMUIR-BLODGETT FILMS OF COFACIAL PORPHYRINS-PHTHALOCYANINES HETERODIMERS: A TIME-RESOLVED STUDY.

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L.B. films of semi-amphiphilic porphyrin-phthalocyanine heterodimers have been prepared and characterized. ESR anisotropy and linear U.V.-vis. dichroïsm show that the macrocycles are superimposed face to face, with their mean plane parallel to the substrate plane (fig.1).The photochemistry of such films has been investigated in details by time-resolved absorption spectroscopy from the sub-picosecond to the microsecond time domain in comparison with similar dimers in dilute solutions. It is shown that selective excitation of the porphyrin moiety with visible laser light results either in the migration of the excitation energy towards the phthalocyanine, or in the transfer of one electron between the two chromophores. By an adequate choice of the metal center(s) of the two components, one is able to direct efficiently the dominant deactivation pathway towards either of these photophysical processes.

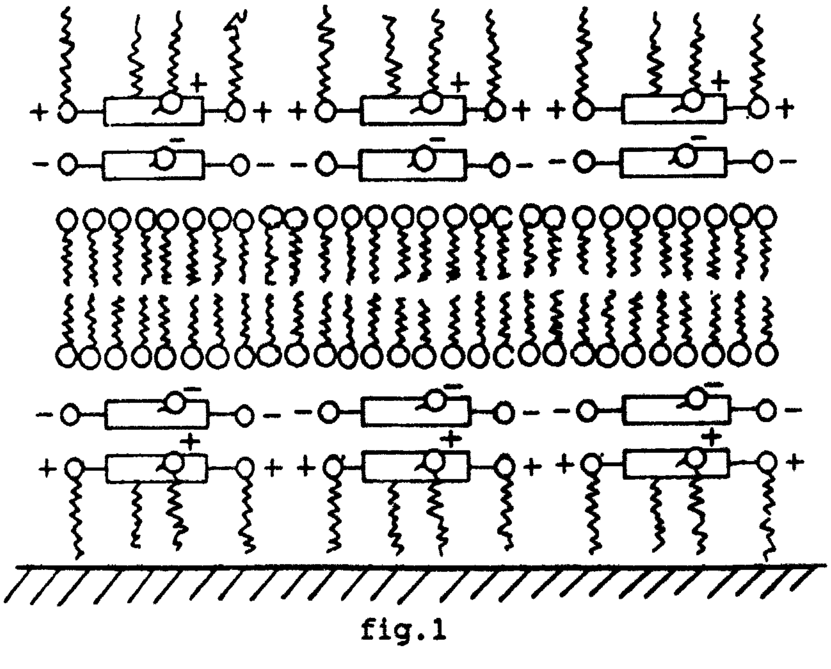

fig.1

CO3

GUIDED-WAVE FREQUENCY-DOUBLING IN LANGMUIR-BLODGETT FILM WAVEGUIDES

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2-docosylamino-5-nitropyridine (DCANP) is a molecule displaying strong nonlinear optical effects in Langmuir-Blodgett (LB) films. Its linear and nonlinear optical properties have been described in [1| and [2]. Due to its ability to form multilayers of high optical quality waveguiding in these films was observed [2].

We now report for the first time guided-wave second-harmonic generation in nonlinear optically active LB films. Phase-matched frequency-doubling was observed in LB films of DCANP by using the Cerenkov-type configuration. This method is simpler than phase-matching of guided modes where very strict conditions on the waveguide thickness are required and where both fundamental and second-harmonic waves have to be guided. In Cerenkov-type phase-matching, however, only the fundamental beam is guided in the layer whereas the second-harmonic beam is radiated into the substrate. The charge-transfer axis of the DCANP molecules lies in a plane parallel to the dipping direction. Therefore the largest nonlinear optical coefficient d_{33} could be used with TE modes. Experiments at different wavelengths and waveguide dimensions and efficiency studies of the frequency-doubling process were performed. In addition the dipping process was adjusted for optimized waveguiding.

[1] G. Decher, B. Tieke, C. Bosshard and P. Günter, Ferroelectrics **91**, 193-207 (1989)

[2] Ch. Bosshard, M. Küpfer, P. Günter, C. Pasquier, S. Zahir and M. Seifert, Appl. Phys. Lett. **56** (13), 1204-1206 (1990)

CO4

THE PHOTOINDUCED TRANSFORMATION OF NONLINEAR OPTICAL PROPERTIES IN ORGANIC MONOLAYERS

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The generation of optical second harmonic (SH) was investigated in Langmuir-Blodgett films of 4-nitro-4'-oktodecilasobenzole (NAB) and bacteriorhodopsine (BR). The research was carried out while reflecting the pulse radiation of **YAG:Nd**$^{3+}$-laser at 1064 nm from the film or passing through it. It was discovered that LB NAB monolayered films demonstrated a significant anisotropy in nonlinear-optical properties; the dependence of the second harmonic intensity $I_{2\omega}$ on rotational asimutal angle Φ $I_{2\omega}(\Phi)$ had two maxima spaced at the distance of π. These properties changed dramatically while illuminating the film by Ar^{+}-laser polarized radiation at 514 nm. The new dependence $I_{2\omega}(\Phi)$ had also two maxima, but their positions could be shifted so that the angle between the new maxima position and the direction of the additional radiation polarization become equal to $\pi/2$.

The SH generation was also studied in LB mono- and multilayered films of BR. The square dependence of the SH intensity on the number of monolayers was observed. Photochromic character of SH in these LB films has not been detected, while electrodeposited films of BR demonstrated strong photochromism - $I_{2\omega}$ decreased twice under the additional illumination of the excited area.

So we have discovered the photoinduced anisotropy of nonlinear properties of LB films and showed that these properties could be changed gradually by additional polarized illumination. The SH generation was also first observed for mono- and multilayered LB films of bacteriorhodopsine.

CO5

OPTICAL BLSTABILITY IN THE OPTICAL WAVEGUIDES COATED WITH NONLINEAR LB FILMS

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Recently, the third order optical nonlinearity and optical bistability of derivatives of phthalocyanine have been found and investigated[1,2].

In this paper, we report, for the first time, that the optical bistability in the optical waveguide coated with nonlinear LB films of copper tera-4-(2,4-ditert-ampylphenoxy) phthalocyanine (tapCuPc) have been observed by 530nm line of YAG Laser at room temperature.

In our experiment. 30 layers of tapCuPc were deposited by the LB technique onto the optical glass waveguide of K^+ ion-exchange and the four layer dielectric waveguide coated with LB films was formed.

530nm line of YAG laser is used as a light source. The input light with 30-40μJ/pulse, pulse width of 50ns and frequency of 2Hz. is coupled into the optical waveguide coated with the LP films by glass prisms.

The input and output beams are conversed into electrical signals and recoreded by storage oscilloscope.

The optical nonlinearity and bistablility are observed in the waveguide with LB films. The threshold of power is about 4μJ and the swithching off time is 1ns. when we remove the LB films coated, no optical nonlinearity is observed in the waveguide.

The machanism of optical bistability in the waveguide coated with LB films is studying.

References

1 Wn.J.W., Heflin, J.R., Norwood, R.A., Wong, K.Y., Zamani-khamiri, O., Garito, A.F., Kalyanaraman,P., and sounik, J., J.Opt. Soc, Am.B6.707(1989).
2. Garito, A.F., and Wu,J.W., conference of 1990. International Topical Meeting on Optical Computing. 9A1. 1(1990).

CO6

PHOTOCEMICAL MODULATION OF SECOND ORDER NONLINEAR OPTICAL PROPERTIES OF ALTERNATE LB FILMS CONTAINING Ru(II)-BIPYRIDINE COMPLEXES

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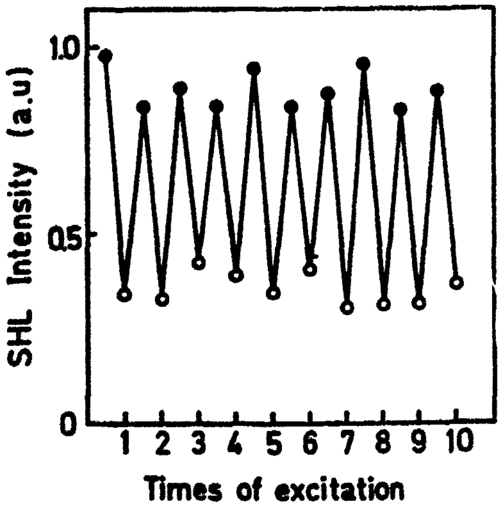
We recently reported that a metal to ligand charge-transfer (MLCT) transition in ruthenium(II)-bipyridine derivatives has the capability of second harmonic generation (SHG) in alternate LB films.[1] Now we report that we can modulate photochemically the SHG of such LB films by a UV laser.[2]

A mixture of (N,N'-dioctadecyl-4,4'-dicarboxamide-2-2'-bipyridine)-bis(2,2'-bipyridine)ruthenium(II) perchlorate (abbreviated to RuC18B) and dioctadecyldimethylammonium bromide (2C18NB) with a molar ratio of 1:4 was deposited alternately with 2C18NB alone at 25 °C and 20 $mN \cdot m^{-1}$ in the presence of dextranesulfate polyanion. Thirty dye layers were deposited on each side of a glass slide treated with a silane coupling agent. The second hamonic signal from LB films irradiated with an Nd:YAG laser at 1064 nm (100 mJ/cm^2) was detected with a photomultiplier through aqueous $CuSO_4$ solution and IRA-25S(IR-cut) filters and a monochromator. In some cases LB films containing Ru(II) complexes were excited by the third harmonic(355 nm, 0.1-10 mJ/cm^2) of an Nd:YAG laser 10 ns before irradiation of a 1064 nm pulse.

The intensity of second harmonic light observed from alternate LB films containing Ru(II) complexes was decreased by exciting at 355 nm. The SHG could be modulated reversibly for many times as shown in Fig. 1 (● without and ○ with 355 nm laser). The extent of the decrease in SHG increased with the intensity of the UV laser, about 50% decrease at 10 mJ/cm^2. The transient absorption of RuC18B upon excitation at 355 nm was resolved into absorption bands of bipyridine anion radical and Ru^{3+} and the depletion of the ground-state MLCT band together with the luminescence above 600 nm. These results clearly indicated the formation of chrage-separated excited state. The decrease of SHG upon UV excitation may be caused by the changes in the orientation of chromophores, the phase matching, and the refractive indices, and by the possible absorption of 532 or 1064 nm light at the excited state. From detailed experiments, we have excluded these possibilities. The observed molulation of SHG can be ascribed to the change in molecular hyper-polarizalibity for the ground and the excited state.



1) H. Sakaguchi, T. Nagamura et al, Chem. Lett., 1715 (1989). 2) idem, submitted to Jpn. J. Appl. Phys. Pt. 2, Lett.

CO7

SECOND-ORDER NONLINEAR OPTICAL LANGMUIR-BLODGETT FILMS OF PYRAZINE DERIVATIVES

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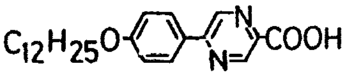
The Langmuir-Blodgett (LB) technique is a promising method for the fabrication of thin films with noncentrosymmetric molecular orientation; one can obtained a noncentrosymmetric LB film, so-called hetero-Y type film, by alternating deposition of two different monolayers.

Pyrazine derivatives (1,2 and 3) have large molecular hyperpolarizability β comparable to that of p-nitroaniline. Moreover, the degree of molecular orientation in the pyrazine derivative LB films is very high. Thus, we expect that high-performance noncentrosymmetric LB films for nonlinear optics will be obtained by use of an alternating deposition of pyrazine derivatives and arachidic acid.

Noncetrosymmetric LB films were fabricated using two-compartment Langmuir through. Monolayers of a pyrazine derivative and arachidic acid were spread on each compartmentalized subphase of a $BaCl_2$ aqueous solution, and then were deposited on fused quartz substrates in up stroke and down stroke, respectively.



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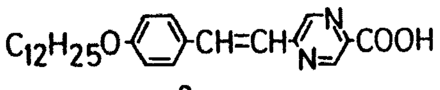

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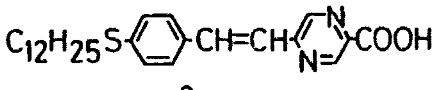

3

Spectroscopic and X-ray diffraction studies on the alternating LB film of 1 proved that molecules were predominantly oriented normal to the film plane in the LB film.

Second-order optical nonlinearity in the LB films was examined by a second-harmonic generation (SHG) measurement using a Q-switched Nd,YAG laser. The SH intensity from the noncentrosymmetric LB films of 1 quadratically increased with the film thickness up to 200 bilayers (1μm). The quadratical dependence demonstrates that the noncentrosymmetric molecular orientation preserved in the LB film with thickness enough for the application to the nonlinear waveguide. From the SH intensity, the second-order susceptibility of the LB film was estimated to be 1×10^{-7} esu.

Second-order optical nonlinearity in noncentrosymmetric LB films of other pyrazine derivatives (2 and 3) will be also discussed in this presentation.

Session DO

Electrical and dielectrical properties

DI

NEW TRENDS AND PROSPECTS IN CONDUCTING LB FILMS

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Since the discovery in 1984 of a method leading to conducting LB films, many kind of conducting films have been fabricated. We present a survey of the state of art in this field. So far, derivatives of well known electroactive nuclei (as TCNQ, TTF or dmit) have been used as brick stone components for that purpose. Methods used to obtain the necessary conditions (in plane crystallization together with mixed valence state) are briefly listed together with the main results obtained to date. Despite the fact that characterization methods for both structural and textural investigations of films are generally available, very often the following questions are still unanswered : are we dealing with true LB films ? To what extent the macroscopically 2D crystallization of films can be checked ? and, more precisely : what is the intrinsic (i.e. local) character of the crystallization (1D or 2D).

In the course of the lecture, we report recent works developped in Saclay in order to obtain one at least of the following properties 1) Highly conducting indeed metal like films, 2) Intrinsically (or local) two dimensional material. 3) Getting a true conducting bilayer.

In a first step, BEDT derivatives possessing two aliphatic chains both grafted at the same end of the electroactif nucleus have been used. Hence in the resulting films, the conjugated systems stand on edge with their long axis perpendicular to the support. After a controlled oxidation by iodine vapour, films are obtained as conducting sheets the dc conductivity of which is close to 0.2 Siemens.cm^{-1} at room temperature.

The point is that such a structure is especially designed to mimic the sheet like molecular array of classical $(BEDT)_2I_3$ highly conducting or even supraconducting bulk crystal. In addition an encouraging result comes from a careful spectroscopical investigation of films : the stoichiometries are basically the same. In contrast, the intrinsic (i.e. local) nature of the conductivity (1 or 2D) is still completely unknown. Moreover the dc conductivity abruptly decreases as the number of superimposed monolayer decreases and a bilayer thick film is found to be an insulator. Such a behaviour is understood in terms of superimposed conducting domains separated by more or less insulating boundaries.

Basically different properties are currently obtained by the use of homodoped TCNQ containing films. The homodoping strategy consists in mixing in the same monolayer neutral amphiphilic octadecyl TCNQ (OD-TCNQ) together with the anion radical semi amphiphilic TCNQ salts for example octadecylsulfonium+ $TCNQ^{\cdot -}$ (ODS-TCNQ). Hybrid stacks are obtained in that way. The average electronic charge of TCNQ (and hence the conductivity) can be accurately adjusted by properly choosing the molecular ratio of the individual components. The corresponding compression isotherm curves exhibit a basically different behaviour from the one of pure anion radical semi amphiphilic salts : no plateau regime attributed to a 2D → 3D crystallisation is observed. This is understood in terms of a strong interaction between neutral $TCNQ^{o}$ and radical anion $TCNQ^{\cdot -}$. In that way electron conducting bilayer thick films can be built very easily. The highest corresponding values of the room temperature conductivity is found to be ca 0,01 Siemens.cm^{-1}.

In this lecture we emphasis the crucial role of IR spectroscopy in investigating conducting films. This is basically related to the extreme sensitivity of IR absorption on interaction between conduction electrons and molecular vibrations of electroactive nuclei. In addition we suggest new prospect arising from in plane oriented films together with the possible diffusion into built up LB films of relatively large electroactive nuclei.

DO1

NEW DEVELOPMENTS IN THE LANGMUIR-BLODGETT MANIPULATION OF ELECTROACTIVE POLYMERS

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New monolayer forming systems based on a number of different electrically conductive polymers have been utilized to fabricate Langmuir-Blodgett (LB) thin films with well defined multilayer organizations. For example, multilayer thin films based on acid functionalized polythiophene and polyaniline molecules have been fabricated from polyion complexes formed between the acid groups of the conjugated polymer and stearylamine. Monolayers of these complexes have been found to form highly anisotropic, well ordered Y-type LB films in which the conducting polymer chains are ionically bound to the head groups of the surface active stearylamine molecules. LB monolayers of unsubstituted polyanilines have also been formed into Z-type multilayer films through the direct manipulation of the emeraldine base form of polyaniline and a small fraction of a processing aid such as acetic acid. In this case, it is possible to form electrically isotropic multilayer films that essentially only contain polyaniline chains. New techniques for the synthesis of electrically conductive chains of polypyrrole in the hydrophilic planes of preformed multilayer LB films have also been developed. All of these new generation conducting polymer based LB films are highly ordered and exhibit electrical conductivities in some cases as high as 10 S/cm. The availability of a wide range of conducting polymer based monolayer systems means that it is now possible to fabricate new thin film heterostructures of conducting polymers with layer sequences that are controlled at the molecular level. The structures and electrical and optical properties of these new LB films and a number of new heterostructures based on them will be discussed.

DO2

THE HOMODOPING STRATEGY TOWARDS LB CONDUCTING FILMS: MIXTURE OF AMPHIPHILIC OCTADECYL TCNQ WITH VARIOUS SEMI-AMPHIPHILIC TCNQ SALTS

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An homodoping strategy leading to conducting LB hybrid films without any further doping treatment is investigated. The method consists of mixing, within the same layer, semi-amphiphilic and amphiphilic derivatives of the same electroactive nucleus (here tetracyanoquinodimethane (TCNQ), which appears as radical anion in the semi-amphiphilic compound and as neutral species in the amphiphilic one).

In recent experiments, the polar head of the aliphatic cation was varied in the semi-amphiphilic compound . The preliminary results, which will be briefly presented, are very close to those previously reported on the mixture octadecyl-dimethyl-sulphonium TCNQ (ODS TCNQ) - octadecyl TCNQ(1). Hence, we believe that this method may be a general one. However, the properties of the hybrid films slightly depend on the nature of the cation. In the present work we compare hybrid films of ODS TCNQ - octadecyl TCNQ on one hand and N-docosyl-pyridinium(NDP) TCNQ-octadecyl TCNQ on the other hand. Both type of films exhibit a similar behaviour at the air-water interface, a high optical quality and a similar variation of the conductivity with the molecular ratio of the amphiphilic and semi-amphiphilic TCNQ derivatives, which monitors the average electronic charge per TCNQ nucleus: the curve of the conductivity of both type of films bears a maximum for a molecular ratio of approximately two amphiphilic neutral TCNQ to one semi-amphiphilic radical anion TCNQ. However, the shape of the curve appears to differ. In addition, for this given 2-1 molecular ratio, the variation of the conductivity per layer with the number of superimposed layers is quite different in the two case: whereas for hybrid films based on NDP TCNQ the conductivity per layer decreases drastically below 6-8 layers, in contrast for the films based on ODS TCNQ the conductivity per layer is almost constant down to one bilayer and remains non zero for a single monolayer. These results will be presented and discussed together with some questions which remain unanswered to date such as: - why does the dc conductivity decrease when the samples are stored in the air at room temperature? - why does it exist a discrepancy between the order of magnitude of the conductivity deduced from the infrared behaviour and the rather low value of the dc conductivity (10^{-2} S/cm in the best case) ?

(1) A.Ruaudel-Teixier, M. Vandevyver, M. Roulliay, J. P. Bourgoin, A Barraud, M. Lequan, R. M. Lequan, J. Phys. D. Appl. Phys. (23), 987 (1990)

DO3

ELECTRON TRANSPORT ACROSS ORGANIC QUANTUM WELLS- NEW RESULTS ON AMPHIPHILIC PHTHALOCYANINES

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Two new phthalocyanine molecules, Tetra-tertiary-butyl phthalocyanine-monosulphonic acid (1) and a two ring phthalocyanine, $(HO)SiPcO{-}SiPc(OSi(n{-}C_6H_{13})_3)$, have been synthesised and demonstrated to be well behaved conjugated ring compounds for forming Langmuir-Blodgett films.

These molecules have been deposited as multilayers and characterised optically and electronically.

Charge transport perpendicular to the plane of the layers has been measured. The results demonstrate that photocreated carriers in the films move across up to 32 layers. The layers can be considered as quantum wells of high electron affinity (the conjugated ring) seperated by regions of low affinity. Initial results suggest that the tunnelling between neighbouring wells is of the order of 1ns for both molecules..

Using a 25 picosecond laser pulse to generate charge on the conjugated region of the molecular layers, subsequent interlayer motion is observed with fast electronics as a build up of charge on electrodes sandwiching the quantum wells. This build up of charge is seen to occur over longer times as the number of layers is increased thus indicating that the charge which is created uniformly in the wells travels across all the layers.

We may define a sensitivity S as the number of electrons circulated in the external circuit per absorbed photon. S varies linearly with (N-1), where N is the layer number. The total charge collected, Q, depends on the product of the quantum efficiency for carrier pair creation, η, the probability that the carrier pair seperate in an applied field, ϕ, and the distance that the charges seperate, s. The value of $\eta\phi s$ is reported and a value for $\eta\phi$ obtained by putting $s = (N-1)a$ where a is the layer seperation.

At high light intensities Q varies as the square root of light intensity, indicating that bimolecular recombination of electrons and holes is occuring during the interwell transport once a critical carrier density is exceeded. Q varies linearly with applied field at low field reflecting the field dependence of the escape probability, $\phi(E)$. At high field this dependence becomes superlinear.

(1) British Patent Application 21/12/90

DO4

ELECTRICAL PROPERTIES OF LB FILMS OF A Ni(dmit)$_2$ CHARGE-TRANSFER COMPLEX

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There is currently growing interest in the production of electrically conducting multilayer Langmuir-Blodgett films. Much of the work has been concerned with charge-transfer complexes of amphiphilic derivatives of electron donors such as tetrathiafulvalene (TTF) and acceptors like tetracyanoquinodimethane (TCNQ). Recently, Nakamura et al[1] have described the formation of thin films of tridecylmethylammonium-Au(dmit)$_2$ complex (H_2dmit = 4,5-dimercapto-1,3-dithiol-2-thione). After doping, these layers exhibited a metallic temperature dependence of conductivity above 200K. We now report a preliminary investigation into the electrical properties of a new Ni(dmit)$_2$ charge transfer complex, namely (N-octadecylpyridinium)$_2$-Ni(dmit)$_2$.

The synthesis and LB film formation of the Ni(dmit)$_2$ complex has been reported previously[2]. Direct current, lateral conductivity was measured, using a two probe technique, over the temperature range 100-300K, both before and after doping with iodine vapour. In both cases the conductivity was found to be thermally activated. Before doping, the current versus voltage characteristic was linear with a room temperature conductivity of 6×10^{-6} Scm^{-1}. The log(current) versus reciprocal temperature behaviour was found to be quite complex showing a number of discrete activation energy regions. After doping, the conductivity was observed to increase with time over a few hours, reaching a maximum in the range 0.2 - 0.8 Scm^{-1}. The current versus voltage characteristics for doped samples generally exhibited a power law behaviour, suggesting the injection of space-charge into the films. The electrical data have been interpreted in terms of ideas put forward by Roberts and Schmidlin[3,4].

References

1. T. Nakamura and Y. Kawabata, Techno Japan, **22**, 8 (1989).
2. A. S. Dhindsa, J. P. Badyal, C. Pearson, M. R. Bryce and M. C. Petty, J.Chem. Soc. Chem. Comm., in press.
3. G. G. Roberts and F. W. Schmidlin, Phys. Rev. **180** 785 (1969).
4. F. W. Schmidlin and G. G. Roberts, Phys. Rev. B **9** 1578 (1974).

DO5

CONDUCTING LB FILMS OF BINARY MIXTURES OF DONOR AND ACCEPTOR MOLECULES

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Conducting films of high quality can be deposited from the surface of pure water when using the mixtures of neutral surfactant donor and acceptor molecules. Conductance arises without doping, and the values of conductivity do not change usually for a long time. Results on the investigation of the multilayers prepared from six different combinations of donor and acceptor molecules are presented here. The donor molecules of heptadecyldimethyltetrathiafulvalene (C_{17}-DMTTF), hexadecylbis(ethylenedithio)tetrathiafulvalene (C_{16}-BEDT-TTF) , and hexadecylethylenedithiopropylenedithiotetrathiafulvalene (C_{16}-EDT-PDT-TTF) in the mixtures with acceptor molecules hexadecyltetracyanoquinodimethane (C_{16}-TCNQ) and 2-heptadecaoxycarbonyltetracyanoanthraquinodimethane (C_{17}-OC-TCNAQ) were used. The relationships between composition of the mixture, conditions of the film preparation, structure of the multilayers obtained on the one hand and electrical properties of the films on the other hand were ascertained. Temperature dependences of conductivity were measured. The changes of structure and morphology under temperature variations were recorded by means of electron diffraction and electron microscopy. Field effect, i.e. variation of conducting film resistance under the electric field influence was studied as well.

Irreversible changes of conductance under annealing at temperatures in the interval between 305 and 320 K for the films of mixtures of donor compounds with C_{16}-TCNQ take place. When annealing of the sample is produced at 305-307 K small decrease of conductance happens. Electron diffracion patterns show that the films become amorphous. Strong increase of conductance occurs if the temperature is maintained at 307-315 K. This is caused by recrystallization of the film and improvement of the crystalline order without deterioration of the multilayer morphology. Decrease of conductance after heating above 315 K occurs due to formation of large crystals, so that finally the film can become discontinuous. Activation energy changes after annealing. This change seems to be caused by modification of boundaries between the crystallites.

Stabilization of conductivity value and its increase for the mixed films of C_{16}-BEDT-TTF and C_{16}-TCNQ occure after a short treatment of the sample in hexane. It appears that two crystalline phases arise in the multilayer. One phase is dissolved in hexane, and the second forms a continuous uniform film without the change of its crystalline structure.

Measuring of field effect permitted us to draw a conclusion about the nature of carriers as well as about their surface concentration and mobility in the films of C_{16}-BEDT-TTF and C_{16}-TCNQ mixture . Output and transfer characteristics of the devices prepared were measured. The carriers are holes. Using a simplified theory the value of mobility was found to be equal to 1 $cm^2/(V \cdot s)$. The surface concentration of carriers equals approximately 10^{-12} cm^{-2} . Temperature dependence of field effect was measured also.

Session EO

Chemistry in mono and multilayers

EI

ELECTROCHEMICAL STUDIES OF SELF-ASSEMBLED MONOLAYERS

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Thiols, disulfides, isonitriles, and dithiocarbamates interact strongly with Au and Pt electrodes. The coordination of redox active molecules to electrode surfaces via such ligating groups leads to the ability to tailor the electrodes for purposes ranging from electrocatalysis to sensor applications. The electrochemical behavior of self-assembled monolayers containing redox active molecules will be reported for assemblies confined to microfabricated Pt or Au microelectrodes. Similar coordination to macroscopic Pt or Au occurs, but the emphasis on the microelectrodes follows from interests in controlling chemistry in very small dimensions.

Two aspects of the characterization of microelectrode-confined molecular assemblies will be covered: (1) surface science characterization (SIMS, Auger, and XPS) to establish the selective binding of the molecules to the Au or Pt and not the insulating substrate and (2) electrochemical studies to establish durability, coverage, and aspects of interfacial phenomena such as electron tranfer rates involving the surface-confined redox center. Many of the surface-confined molecular systems to be considered involve ferrocene derivatives having highly reversible oxidation processes which can be used to assay coverage. When two ferrocene derivatives have different redox potnetials it is possible to use electrochemical techniques to quantitatively assay competitive uptake of the two molecules and to study exchange processes of the surface-confined molecules.

E01

ELECTROCHEMISTRY AT THE AIR/WATER INTERFACE. LATERAL DIFFUSION AND PHASE TRANSITIONS IN LANGMUIR MONOLAYERS OF OCTADECYL FERROCENE AMPHIPHILES.

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A two-dimensional electrochemical experiment has been developed to probe the dynamics of lateral diffusion and charge transport in Langmuir monolayers.

Experiments reported here rely on purposefully designed microelectrodes which can be positioned in the plane of the air/water interface, and which act as line electrodes probing a 2-D system of redox species. Physically, a microelectrode consists of a 500 Å wide, 0.1 cm long band of gold produced by fracturing a section of a glass slide with a 0.1 cm wide strip of gold vapor-deposited on its surface. Before fracturing, the gold and glass surfaces are coated with a self-assembled monolayer of octadecylthiol and octadecyltrichlorosilane, respectively. When positioned at the water surface, the high gradient of wettability between the clean, hydrophilic gold of the micro-band and the hydrophobic, monolayer-coated gold surface defines, along a single line, the coexistance front of three phases. It is this line that plays the role of a one-dimensional electrode addressing a monolayer at the air/water interface. The reduction of dimensionality in these 2-D electrochemical experiments does not effect the shape of 2-D cyclic voltammograms.

Investigations of N-octadecyl-(ferrocene carboxamide), ($C_{18}Fc$) and its dioctadecyl analogue on perchloric acid subphase involved determination of the lateral diffusion coefficients as a function of surface concentration by chronoamperometry. We observed a decrease of D from *ca.* 6×10^{-6} cm^2/s to 2×10^{-7} cm^2/s when the surface concentration of $C_{18}Fc$ was increased from 5×10^{-11} to 3.6×10^{-10} mol/cm^2. This result reflects an expected decrease of monolayer fluidity when it is compressed. The same behavior was observed when a $C_{18}Fc$ monolayer was diluted with octadecylhydroxide ($C_{18}OH$). Further analysis of these data involved the Cohen-Turnbull theory of diffusion in hard-sphere fluids (J. Chem. Phys. 1970, 52, 3038). According to this theory, molecules move with a gas phase velocity, u, whenever fluctuation of density creates a void in a cage of their residence:

$$D = g\, u\, \alpha\, (A^* + A_f/\gamma)\, \exp(-\gamma\, A^*/A_f) \qquad (1)$$

Here, g is a geometric factor; A_f and A^* are the free area per molecule and the critical free area per molecule above which the system behaves purely randomly (gas-like behavior); and γ is a numerical parameter with a value between 0.5 and 1. When $A^* << A_f/\gamma$, equation 1 reduces to a direct proportionality of D and A_f:

$$D = g\, u\, \alpha\, A_f/\gamma \qquad (2)$$

In physical terms the latter limit assumes that no minimum free area is needed for lateral diffusion to take place and the system is fluid at all levels of void area greater than zero.

EO2

Homo-epitaxy of diacetylene vapor deposition film on an oriented Langmuir monolayer

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Polydiacetylenes are well-known as π-conjugated one-dimensional crystalline polymers having attractive properties, e.g., large third-order optical susceptibility and high electron mobility. We have previously reported that a highly inplane-oriented Langmuir monolayer can be easily fabricated using soluble urethane-substituted polydiacetylenes at the air-water interface.[†] The π-conjugated backbone of the polydiacetylene in this monolayer is oriented perpendicularly to the direction of uniaxial compression through its coil-to-rod phase transition at the air-water interface. Further, this highly-oriented monolayer has been confirmed to exhibit relatively good crystallinity. Thus, we expect that this highly-oriented polydiacetylene monolayer is well-suited for substrates of organic epitaxy, especially for fabricating topochemically polymerizable polydiacetylene thin films.

We report here the preparation and characterization of well-oriented thin films of poly-3BCMU grown by epitaxy of its monomer on the highly-oriented poly-3BCMU monolayer as shown in fig.1. Structures and morphology of poly-3BCMU vapor deposition films on the substrate of the highly-oriented monolayer were investigated using polarized absorption spectroscopy, X-ray diffraction, and optical and electron microscopy.

As a result, there was evidence of uniaxial oriented overgrowth "epitaxy", i.e., the π-conjugated backbone of the overgrown poly-3BCMU thin film is aligned in the same direction as that of the underlying oriented poly-3BCMU Langmuir monolayer. The dichroic ratio calculated directly from the ratio of the excitonic peak heights was about 14, as shown in fig.2. The two-dimensional lattice matchings between the interfacing lattice periodicities of the overgrown poly-3BCMU thin film and the underlying poly-3BCMU monolayer were well within the accepted limits for epitaxy. Epitaxial growth in these cases can be thought to result from two-dimensional lattice matchings.

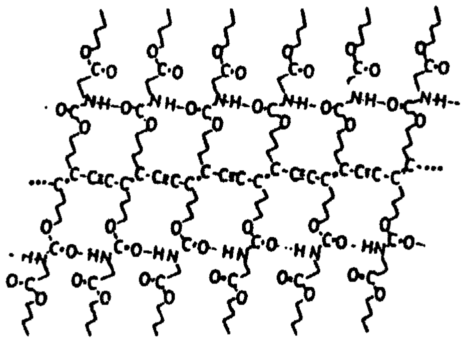

Fig. 1 Structure of poly-3BCMU.

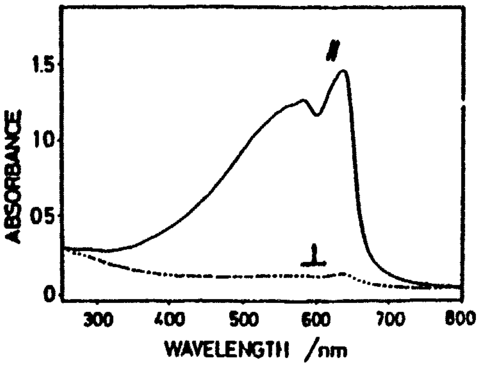

Fig. 2 Polarized absorption spectra.

[†] Y. Tomioka, S. Imazeki and N. Tanaka, Chem. Phys. Lett., 174 (1990) 433.

EO3

POLYMERIZATION OF 2-ALKYL ANILINES ON THE LB TROUGH: REAL TIME INVESTIGATION OF THE POLYMERIZATION OF A CONDUCTING POLYMER CONFINED TO TWO DIMENSIONS

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Polyaniline is a material that has attracted considerable interest recently due, in part, to the fact that it is an air stable electrically conducting polymer. Unfortunately, in the conducting form polyaniline is generally insoluble and infusible making it difficult to characterize. Functionalization of polyaniline with long alkyl side chains makes this polymer soluble in common organic solvents and surface active at air/aqueous interfaces.

We have been studying the behaviour of some 2-alkyl anilines and their polymers at the air/aqueous interface on a LB trough. These monomers can be chemically polymerized on the trough. Furthermore, we have been able to use the trough as a "two dimensional dilatometer" to measure the mean molecular area change and its rate as the polymerization progresses. From this, we have developed methodology to use the LB trough as an analytical tool to study environmental effects on this polymerization reaction.

This paper will discuss the polymerization process of the 2-alkyl functionalized anilines and the effects of such variables as applied surface pressure, temperature, chemical nature of the subphase, etc. on this reaction. The length of the alkyl chain and dipping behavior will also be discussed.

E04

DEEP UV PHOTOCHEMISTRY OF CHEMISORBED MONOLAYERS: FABRICATION OF PATTERNED CO-PLANAR MOLECULAR ASSEMBLIES

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ABSTRACT

Deep UV irradiation is shown to modify organosilane self-assembled monolayer (SAM) films, rendering the surface amenable to further SAM modification. Optical and surface spectroscopies demonstrate a photocleavage mechanism. Patterned UV exposure of the SAM film is used to create alternating regions of intact film and hydrophilic, reactive sites. The exposed regions can undergo a second chemisorption reaction to produce an assembly of SAMs in the same molecular plane with identical substrate attachment chemistry. The UV patterned silane films can also act as a template for selective build-up of molecular units in the *z* direction.

The organosilane monolayer films were also used as imaging layers for optical lithography. The films were irradiated with patterned deep UV light and then selectively metallized using electroless deposition such that a thin metal layer (200-400 Å) is deposited only in the unexposed areas. The film/metal assembly is a plasma-impervious barrier to reactive ion etching which can subsequently be stripped from the substrate after feature definition. Features to 0.25μ line width in polysilicon, and working transistor test structures have been produced using this process. The additively deposited metal can also be employed as an opaque region for mask fabrication or as a conductive path for interconnects.

Session FO

Short and long term applications

FI

POSSIBLE APPLICATIONS FOR LANGMUIR-BLODGETT FILMS

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Almost one quarter of the papers presented at the First International LB Film Conference (held in Durham in 1982) were devoted to applications; this figure has remained at approximately ten per cent for the subsequent meetings. Despite this attention, no large-scale commercial use for either monolayer or multilayer films has emerged. However, the LB is technique is one of the few thin film technologies that actually permits the manipulation of materials <u>at the molecular level</u>. It should therefore be eminently suited to exploitation by workers wishing to engineer interesting materials or build up novel device structures.

A comprehensive review of potential applications for LB films has been given by Roberts(1). In this paper we shall review some of the most recent developments. Of particular note is the increasing interest in the exploitation of biological bilayer and multilayer structures; a number of applications in the area of sensors are currently envisaged. Work continues in many of the application areas identified at previous conferences. For example, relatively thick (> 100 layers) asymmetric films possessing second-order nonlinear optical coefficients may now be routinely produced; and waveguiding has now been demonstrated in active LB structures. The ability of some films of preformed polymers to bridge holes in porous substrates has led to a renewed interest in the area of filtration membranes. 'Real' molecular electronic devices based on LB films remain elusive. Although there have been a number of reports of diode behaviour in monolayer and multilayer films, it has not yet been established unequivocally that this rectification is molecular in origin. (However, the means to address such structures, either optically or electrically, certainly exists.)

Despite the proliferation and diversity of ideas, a number of problems currently frustrate any immediate application for monolayer and multilayer films. These include the poor molecular alignment in many films, intermixing of molecules in some two-component (alternate-layer) systems and, of course, the (lack of) thermal stability of most LB structures. This review will also pay some attention to these important aspects.

Reference

1. G G Roberts, in 'Langmuir-Blodgett Films' (ed G G Roberts), Plenum Press (1990) 317-411

FO1

LANGMUIR-BLODGETT FILM BASED CHEMICAL SENSORS USING SECOND-HARMONIC GENERATION

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This contribution is concerned with the use of second-harmonic generation in Langmuir-Blodgett-films for chemical sensing. As is well known, certain organic molecules have a high second-order optical polarizability, a quantity depending sensitively on the chemical structure of the respective molecule. Modification of those molecules by reversible interactions with chemical species alters the nonlinear-optical response and hence the second-harmonic intensity. This fact may be applied as a new principle for chemical sensing. For this purpose Langmuir-Blodgett films are superior to bulk nonlinear materials with respect to response time as well as ease of manufacturing.

The suitability of this principle is demonstrated by the construction of a nonlinear-optic pH sensor. The sensor element consisted of a fused silica substrate coated with a monolayer of an amphiphilic merocyanine. A simultaneously mode-locked / Q-switched Nd-YAG laser was used as an excitation source. Secondharmonic radiation was detected by a photomultiplier and boxcar integrator. The intensity was measured in comparison with a quartz reference. To study dye orientation, s- and p-polarization was used for excitation as well as in measuring second harmonic radiation. The chromophores turned out to lie rather flat on the surface and to exhibit a spontaneous ordering in domains large compared to the wavelengths involved.

The sensor element was immersed in a buffer solution and brought to pH values between 1 and 11 while measuring second-harmonic generation. A pronounced change in second-harmonic intensity was observed near the pK_a value of the dye, corresponding to a change in β of about one order of magnitude, but no major changes in molecular order. The change was reversible and the film remained stable for many protonation / dissociation cycles. Within ± 1 pH around the pK_a value, pH of the buffer could be determined to 0.1 from the second-harmonic intensity.

FO2

PYROELECTRIC ORGANO-RUTHENIUM LANGMUIR-BLODGETT FILMS

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The pyroelectric effect in non-centrosymmetric Langmuir-Blodgett (LB) films has been widely reported and much of this research has been generated with the anticipation that LB films may one day form the active pyroelectric layer in a commercial, uncooled thermal imaging device. The realisation of this goal will be the result of the systematic characterisation of LB film molecules which have been iteratively engineered to have optimum physical and electrical properties.

The required flexibility in molecular design is exhibited by a class of organo-ruthenium materials formed by complexation between an organo-ruthenium headgroup and cyano terminat liquid crystal molecules. These complexes are inherently thermally stable and form good floating Langmuir monolayers. In addition they possess a ground-state dipole moment so that, when deposited in an alternate, non-centrosymmetric, ABAB.. film structure, resulting multilayer films have a spontaneous polarisation which may give rise to the pyroelectric effect.

The pyroelectric and dielectric properties of a number of organo-ruthenium LB films will be presented and compared with previously published results for other materials in this same class. The results obtained will be used in attempting to understand the physical mechanism responsible for pyroelectricity.

When LB films are incorporated into a device structure other passive dielectric materials may also be used. The properties of the LB films will therefore be studied for a range of substrate configurations which will include polyimide as the passive dielectric. The dynamic pyroelectric effect will also be used to compare the response of films on different substrates and an attempt made to provide agreement between experimental data and a simple thermal model.

FO3

NONLINEAR OPTICS: THE STRONGEST SECOND HARMONIC INTENSITY SO FAR FROM A MULTILAYERED LANGMUIR-BLODGETT FILM STRUCTURE

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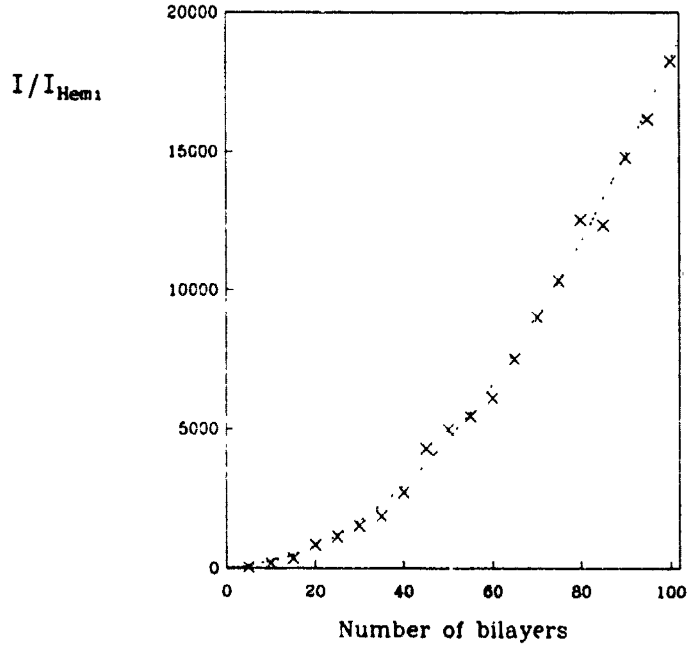
Noncentrosymmetric Langmuir-Blodgett film structures of the hemicyanine dye, $(CH_3)_2N-C_6H_4-CH=CH-C_5H_4N^+-C_{18}H_{37}\ I^-$, interleaved with the two-legged spacer molecule, 4,4'-dioctadecyl-3,5,3',5'-tetramethyldipyrrylmethene hydrobromide, show strong second harmonic generation with an intensity which increases quadratically with the number of layers. The two-legged molecule was specifically designed to alternate with the optically active layers of the one-legged hemicyanine dye, the principle being that the single leg of the dye might penetrate the open hydrophobic legs of the spacer and fasten the interleaving layers (a *"Molecular Zip"*). Ordered noncentrosymmetric structures have been obtained by this method and quadratic enhancement of the second harmonic intensity has been obtained for 200 layer films, the the signal being by far the largest obtained from any Langmuir-Blodgett film structure and 18,300 times the monolayer signal reported by Girling at al. (*Thin Solid Films* **132**, *101, 1985*) for a related hemicyanine dye.



The nonlinear optical properties of two zwitterionic materials of general formula $D^+-CH=C(CN)-C_6H_4-C(CN)_2^-$, where D^+ is either N—hexadecylquinolinium or N—hexadecylpyridinium, will be reported and compared with those of the interleaved dyes. The zwitterions have negative charges in the terminal position and interlayer Coulomb repulsions suppress the more usual Y-type film structures. These materials also show quadratically enhanced second harmonic generation.

F04

CONDUCTING POLYMER LANGMUIR-BLODGETT FILMS. APPLICATIONS TO BIOELECTRONICS.

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The design and fabrication of electroactive Langmuir-Blodgett (LB) films opens the possibility of rational molecular design of organized structures for highly specific applications. We have developed a new class of derivatized conducting polypyrrole Langmuir-Blodgett films with electroactive groups covalently attached to alkyl-pyrroles. Specifically, we have studied copolymers formed by polymerizing mixed 3-alkyl pyrrole and ferrocene-3-alkyl pyrrole (Fc-Py) at the air-water interface, with the subphase containing $FeCl_3$. When the Fc-Py containing film is deposited on an electrode surface, the resulting derivatized electrode can be used for reoxidizing reduced flavin enzymes such as glucose oxidase. The ferrocene moieties are oriented away from the film surface and are able to act as redox mediators to effect charge transfer from the catalytic center of flavin enzymes. The successful demonstration of electronic communication between electroactive LB films and redox enzymes represent an example of molecular design of a bioelectronic system.

FO5

LB CONDUCTING FILMS OF TCNQ AND BEDT-TTF DERIVATIVES APPLIED TO GAS SENSING: GAS DIFFUSION AND DETECTION RANGES.

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LB conducting film of semi-amphiphilic TCNQ derivatives has been proved to be a promising material to develop gas sensors(1). When these films are exposed to phosphine (PH $_3$) in dry air, their conductivity decreases significantly after one minute(2). We investigate gas diffusion in the conducting layers which appears to be an important limiting factor in the detection mechanism.

We have deposited layers of silver docosanoate which is chemically reactive towards phosphine, under the conducting film. The gas-layers interaction is easy to be observed by strong modifications of the infrared absorption peak assigned to the carboxylate group surrounded by Ag^+ ions which decreases after an exposure (10 minutes) to high quantities of gas (> 265ppm in dry air). This observation is interpreted as a reduction reaction leading to reduced silver in the docosanoic acid matrix(3).

The deposition of 20 layers of semi-amphiphilic N-octadecyl-pyridinium,TCNQ onto the test underlayers is easy to be performed. When the films are exposed during 10 minutes to high quantities of phosphine, it is observed that the test underlayer does not react towards the gas (no change in the infrared spectrum) even though the conductivity of the upper conducting layers strongly decreases. This is a direct evidence that only the superficial conducting layers react towards the gas.

In addition, we investigate new conducting LB films of amphiphilic BEDT-TTF derivatives(4) regarding the detection of phosphine. Preliminaries results are presented and compared to those obtained with the LB films based on semi-amphiphilic TCNQ derivatives. The main differences concern the ppm range sensitivity which is achieved without the need of cycling at high quantities of gas. The diffusion test reveals that the underlayers react towards the gas. This a direct evidence that gas diffusion does not limit the response time of this sensor which is as short as a few seconds.

References:

(1): L. Henrion, G. Derost, A. Ruaudel-Teixier, A.Barraud *Sensors and actuators*, 14 (1988) 251-257.
(2): L.Henrion, G.Dersost, A.Barraud, A.Ruaudel-Teixier *Sensors and actuators*,17 (1989) 493-498.
(3): J.Leloup, P.Maire, A.Ruaudel-Teixier, A .Barraud *J. de ChimiePhysique*, 82 (1985), n°6, 695-700.
(4): M. Vandevyver, M.Roulliay, JP.Bourgoin, A.Barraud, JP.Morand, O.Noel *J.of colloid and interface science*, Vol. 141 (February 1991), 456-466.

FO6

Metal Ion Sensor based on Dioctadecyldithiocarbamat-Metal Complex Induced Energy Transfer

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The characterization of dioctadecyldithiocarbamate (DOTC) monolayers at the air/water interface and its complexation with metal ions in the aqueous subphase are reported. Surface pressure-, surface potential-area isotherms and reflection spectroscopy at the air/water interface were used for the detection and characterization of the DOTC- ion complexation. Metal ion complexation leads to metal specific changes in the surface potential, area/molecule and also to either a shift of the DOTC reflection band or the appearance of a new band in the UV-VIS reflection spectrum.

Based on these results we describe a novel and selective technique for the detection of metal ions at the LB-film/aqueous phase interface. The LB-film is made up of a fluorescent oxacyanine monolayer and an adjacent DOTC monolayer, with the metal binding headgroup facing the aqueous phase. Any metal ions present in the aqueous phase lead to the DOTC-metal complex. In case, the complex absorption band overlaps with the fluorescence band of the dye layer, it results in Förster type energy transfer from the dye to the DOTC-metal complex leading to the quenching of the dye fluorescence. The degree of fluorescence quenching and hence the signal depends among other factors on the distance between the donor and acceptor and their respective densities. The specificity of the sensor system may be achieved through the appropriate matching of the fluorescence dye and the corresponding metal-complex. For the specific case of DOTC-copper complex and the used oxacyanine fluorescent dye in the present configuration, Cu^{2+} concentrations down to the nanomolar range could be detected. The response time of the system was ca. 10 seconds.

FO7

THE EFFECT OF THE EXTERNAL DC ELECTRIC FIELD ON PYROELECTRIC RESPONSE OF AZOCOMPOUND-BASED LB FILMS

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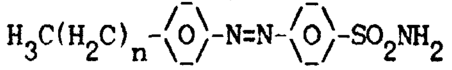
LB films based on azobenzene compounds have been already reported [1] to possess a spontaneous polarization P_s and exhibit piezo- and pyroelectric effects. In this paper we report the effect of the external d.c. electric field applied along a unique polar axis on the pyroelectric response of multilayer films formed by Langmuir-Shaefer method from azobenzene compounds with different hydrocarbon chain lengths:



, n=17,10,9,8,3.

LB film transfer conditions and pyroelectric response measurements have been discribed in detail elsewhere [2]. Fig. 1 demonstrates the effect of applying the external d.c. electric field on the pyroelectric response of 100-layer films.

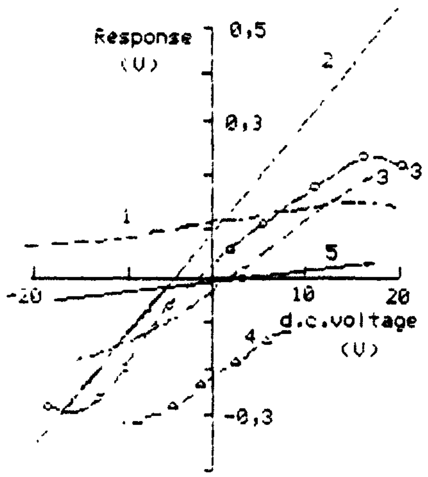
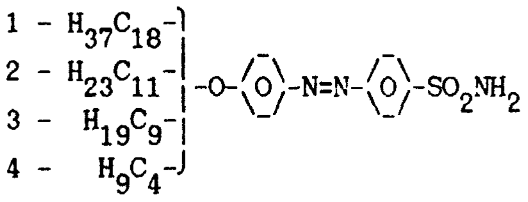
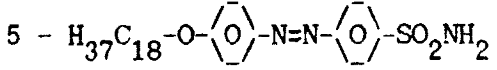


Fig.1. The pyroelectric response vs. d.c. voltage for 100-layer X-type films:



and for 50-bilayer Y-type film



The pyroelectric response verses d.c. electric field characteristics are liniar for all LB films almost up to breakdown fields. For some films (C_{11}, C_9 carbon chain compounds) polarization induced by the external field P_{ind} can be greater than spontaneous polarization P_s that results in icreasing pyroelectric response (P_{ind} in the direction of P_s) or even changing the response sign (the opposite direction of P_{ind}). From the experimental results the spontaneous polarization value can be determined from the relationship: $P_s = \varepsilon_o(\varepsilon - 1)V_o$, where V_o is the external electric field which cancels pyroelectric response. ε is the relative permittivity. For the investigated LB films the magnitude of P_s lies in the range of 10^{-8} $2 \times 10^{-7} C/cm^2$.

References

1 L.M. Blinov, N.N. Davydova, V.V Lazarev and S.G. Yudin Sov Phys. Solid State, 24 (9) (1982) 1523.

2 N.N. Davydova, V.V. Lazarev, V.A. Khavrichev and S.G. Yudin, Sov Biological Membranes, 7 (11) (1990) 1183-1187 (in Russian).

FO8

SEPARATION OF TOXIC AND ACID GASES FROM METHANE IN LANGMUIR-BLODGETT FILMS

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ABSTRACT

Composite membranes for gas separation were fabricated by depositing polymeric Langmuir-Blodgett (LB) films on porous support membranes. Two copolymers, both containing tertiary amines, were utilized as LB materials. The polymers had main-chain and side-group spacers. By bridging over the pores of the porous support, the polymeric LB multilayer acted as a selective barrier to gas diffusion. The gas selectivity of the LB films was demonstrated by measuring the gas permeability of hydrogen sulfide, a toxic and acid gas, carbon dioxide, an acid gas, and methane as a function of temperature. The hydrogen sulfide had the highest permeability of the gases studied. The permeability of carbon dioxide was less than hydrogen sulfide but one order of magnitude higher than that of methane. Fourier Transform Infrared Spectroscopy (FTIR) measurements indicated that when the films were heated the hydrocarbon side-groups of the polymer were irreversibly disordered. The disordering increased the permeabilities of hydrogen sulfide and carbon dioxide relative to methane and the selectivities of the former gases improved. Disordered layers appear to provide better transport properties for the hydrogen sulfide and carbon dioxide than sordered layers.

Session GO

Characterization
(structural and other)

GI

Recent Developments in Surface Analysis of Synthesized Molecular Overlayers

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There exists a number of well established techniques providing information on the chemical composition of the uppermost monolayers of a solid. These techniques are based upon the energy analysis of electrons emitted from such surfaces during primary electron (Auger Electron Spectroscpoy : AES) or photon (Photo Electron Spectroscopy : XPS) bombardment or upon the mass analysis of atomic and molecular species emitted from the surface during its interaction with an ion or laser beam.

AES or XPS supplies mainly information on the elements present in the uppermost atomic layers and additionally some information on the chemical environment of these elements. Lateral resolutions down to the sub-μm - range are capable.

On the other hand surface mass spectroscopy supplies information on the elemental and molecular surface composition by mass analysis of the emitted secondary ions and neutrals. Until recently the mass analysis of the ejected surface species has been carried out by mostly magnetic sector field or quadrupole instruments. More recently high performance time - of - flight mass spectrometers have been applied. These instruments combine an unlimited mass range with high mass resolution and a transmission near 1.

The performance of Time - of - Flight secondary ion mass spectrometry will be treated in detail. The analytical power of this technique concerning sensitiy, quantification, mass range and lateral resolution will be discussed by typical examples. Recent and expected developments will be assessed.

GO1

SPECTROSCOPIC PROPERTIES OF TRICHROMOPHORIC MOLECULES INCORPORATED IN LANGMUIR BLODGETT FILMS

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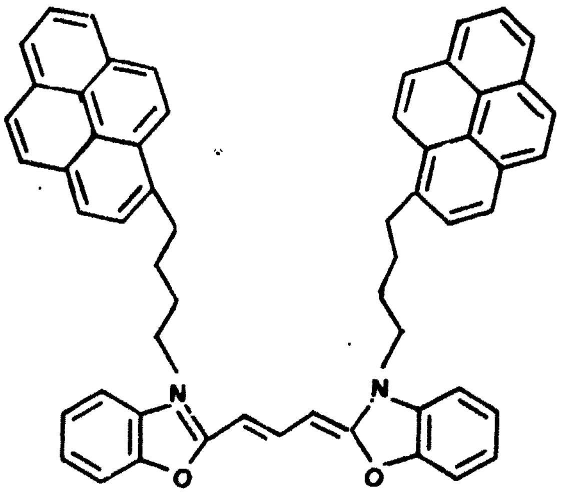
In order to achieve efficient charge transfer in Langmuir-Blodgett films a trichromophoric molecule containing an oxacarbocyanine and two pyrene moieties has been synthesized (compound I). Pressure area diagrams indicate that on a water surface monolayers can be obtained from the pure compound I and from mixtures of compound I and fatty acids. The monolayers can be deposited on quartz substrata.

Between 400 and 550 nm the absorption spectra of the mixed Langmuir Blodgett films of compound I and fatty acids acid resemble those of mixed Langmuir Blodgett films of dioctadecyloxacarbocyanine (compound II) and arachidic acid. Compound I is however characterized by a smaller tendency to form dimers than compound II and the hypsochromic shift of dimers of compound I is smaller than that of dimers of compound II.

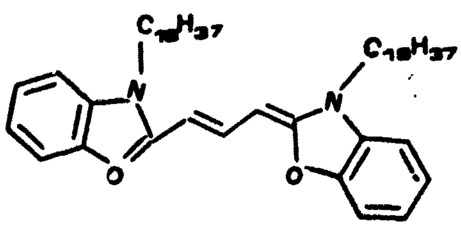
Between 280 and 400 nm the absorption spectra of mixed monolayers of compound I and fatty acids resemble those of mixed monolayers of pyrene-octanoic or pyrenehexadecanoic acid and fatty acids.

Upon excitation of mixed Langmuir Blodgett films of compound I and fatty acids the fluorescence of monomers and aggregates of the cyanine moiety is observed. Excitation at 360 and 480 nm yields identical emission spectra indicating that efficient energy transfer from the pyrene chromophore to the cyanine chromophore occurs

When compound I is diluted with dioleylphosphatidylcholine the absorption and fluorescence spectra indicate a smaller tendency to form dimers or aggregates.



compound I



compound II

GO2

LANGMUIR-BLODGETT MONO- AND MULTILAYERS OF POLY(ISOCYANIDE)S WITH DIFFERENT SIDECHAINS.

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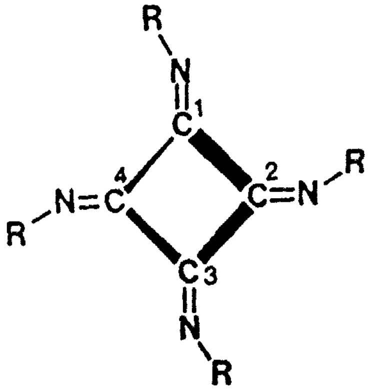
Summary.

In this study poly(isocyanide)s, $[\mathrm{R{-}N{=}C}<]_n$, with different sidechains, R, are used as spreading material to form L-B monolayers at the water-air interface. Poly(isocyanide)s are rigid-rod polymers, which have a stable, helical conformation.



Helical structure of a poly(isocyanide)
(repeat unit C^5 is behind unit C^1, etc.)

One of the aims of this study was to investigate whether this rigid conformation is sufficient to get a stable monolayer on the water surface.

We find, that different poly(isocyanide)s with non-polar aliphatic substituents are unable to form such stable monolayers. On the other hand, poly((S)-1-acetoxymethylethylisocyanide), a polymer which has polar substituents, does form a stable monolayer. So, rigidity of polymer molecules is not a sufficient factor for obtaining stable films and polar moieties which can interact with the water surface are required as well. The monolayer can be transferred onto solid substrates with Z-type transfer. With use of molecular models, ellipsometry and FT-IR spectroscopy the orientation of the polymer rods was studied.

GO3

LANGMUIR-BLODGETT-KUHN MULTILAYER ASSEMBLIES OF LIQUID-CRYSTALLINE-AZO-DYE-SIDECHAIN POLYMERS

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Liquid-crystalline-side-chain-polymers have recently been used for optical data storage by inducing local trans-cis-isomerisations of its azo-benzene side-groups [1]. Only little work was done on azo-dye-LC-systems that can be deposited by the Langmuir-Blodgett-Kuhn (LBK) technique [2,3].

Therefore we investigated a set of LC-polyacrylates with azo-benzene-dye comonomers of different concentration for the possibility of LB-deposition. The homopolymer system transfered onto solid substrates which is known to store optical data peristently [4] is characterized by X-Ray, surface-plasmon and IR-experiments. The π-a diagrams of the copolymer systems show spontanous smectic ordering at the water-air interface described by Gruler et al. [5]. This behaviour was studied with ellipsometry-measurements directly at the water-air interface. The writing and relaxation-process of the investigated systems due to their trans-cis isomerisation of the azo-benzene sidegroup was determined by various experimental techniques. From all our results we can derive a model connecting the microscopic behavoiur of our substances under illumination with the macroscopic structure of the LBK systems.

[1] M.Eich, J.H.Wendorff, B.Reck, H.Ringsdorf, Macromol. Chem. Rap. Comm. 8 59 (1987)
[2] T.Seki, K.Ichimura, Thin Solid films 179 77 (1989)
[3] M.I.Bernik, V.M.Kozenkov, N.M.Shtykov, S.P.Palto, S.G. Yudin, J.of Mol.Elec. 5 53 (1989)
[4] M.Sawodny,A.Schmidt,C.Urban,H.Ringsdorf,W.Knoll, Macromol.Chem.Symp., submitted
[5] B.Rapp,H.Gruler, Phys.Rev.A, 42 2215 (1990)

GO4

CREATION AND STRUCTURAL COMPARISON OF ULTRATHIN FILM ASSEMBLIES: TRANSFERRED FREELY-SUSPENDED FILMS AND LB-FILMS OF LIQUID CRYSTALS

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INTRODUCTION

Amphiphilic liquid crystalline (LC) compounds offer the possibility of obtaining similarly layered ultrathin film assemblies such as LB mono- and multilayers and freely-suspended films (FSFs). The latter ones are prepared by drawing a small amount of material across an aperture in a metal or glass substrate and can be obtained with an area of several square cm. The thickness of these films is comparable to that of LB-films and ranges from two to several hundred layers. In contrast to LB-films they are symmetrical (two film/air interfaces) and they can be obtained as monodomains. Taking advantage of the excellent degree of ordering in FSFs, we have developed a technique to transfer the free films (Fig. 1) onto solid supports, thereby maintaining both the smectic layering and the in-plane structure. The FSFs can be transferred onto the same substrates as LB-films which completes the series of layered assemblies and offers the possibility of comparing all systems, combining the experience from both the LB- and the LC-fields.

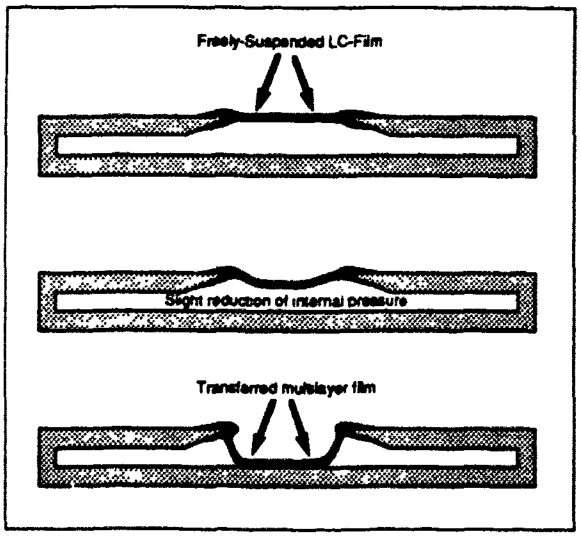
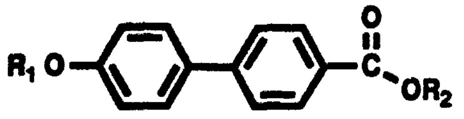


Figure 1: *This side-view drawing schematically depicts the transfer process. Distances are not drawn to scale and the layered structure of the film is not indicated. At the top, a freely-suspended LC-film is spanned across a circular aperture with sharp edges. In the middle, an atmospheric pressure differential is applied, causing the initially flat film to bulge bubble-like towards the lower part of the sample holder. After contact of the free film with the substrate, the coated area quickly spreads until a stable geometry is reached, as shown at the bottom. If the pressure differential is raised even further, the contact line is driven outward again, until the film ruptures. This usually occurs when the area of the transferred film exceeds the area of the original free film.*

RESULTS AND DISCUSSION

We have used different amphiphilic liquid crystalline biphenyl derivatives for the investigation of the various multilayer structures ($R_1 = -C_7H_{15}, -C_8H_{17}$; $R_2 = -H, -CH_3, -C_2H_5$). In all cases the free acid and the methyl esters formed bilayer LB-films and the ethyl esters formed monolayer LB-films. The compound with $R_1 = -C_7H_{15}$ and $R_2 = -CH_3$ shows extremely good deposition behaviour and the LB-films are very well ordered as seen by X-ray scattering (Fig. 2).



Comparison of LB-films and transferred freely-suspended films of compound with $R_1 = -C_8H_{17}$ and $R_2 = -C_2H_5$ shows very interesting results as judged from first experiments. Although the same layer spacing (24 Å) is found in both systems, the melting of the latter one occurs at 110 °C (same as bulk), whereas the LB-film is less stable and starts to melt at 80 °C.

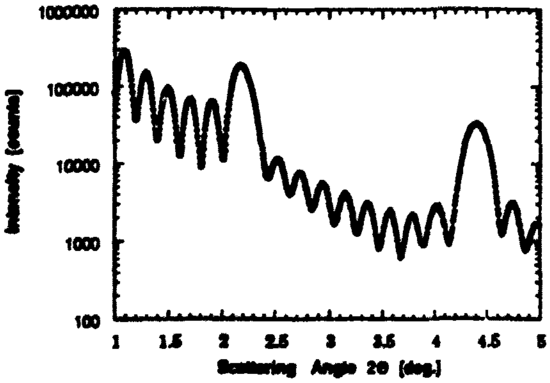


Figure 2: *Small angle region of an X-ray diffractogram of a 10 bilayer LB-film of the methyl ester showing Kiessig fringes and the first two of a total of 21 observed Bragg peaks.*

GO5

INELASTIC ELECTRON TUNNELING SPECTROSCOPY INVESTIGATION OF MONOLAYERS AND FILMS OF FATTY ACIDS AND CHLOROPHYLL *a*

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There are many well established techniques to study the vibrational modes of organic molecules. Among others, we can select IR, FTIR, R, RR, etc., each one having its own set of advantages and drawbacks. Our interest is the behavior of one monomolecular film (Langmuir-Blodgett or autoadsorption) and the above methods are not the best for this purpose. We beleive that Inelastic Electron Tunneling Spectroscopy (IETS) with its high sensitivity can be used with substantial benefits for our investigation. Briefly, the sample is deposited upon the oxide of an Al/Al_2O_3/sample/Pb tunnel junction. An electric potential difference (V) between Al and Pb causes an electronic current (I) by the tunneling mechanism. The second derivative of this I-V curve gives the spectrum. The spectra of autoadsorbed fatty acids with 6 to 11 carbon atoms were initially studied. We also obtained preliminary results concerning chlorophyll *a* in films: (I) Langmuir-Blodgett, (II) autoadsorbed, (III) solid and (IV) rinsed. These spectra are surprisingly simple except in the case of films rinsed with ethanol. We interpret these results in terms of the formation of aggregates.

GO6

ELECTRON SPIN RESONANCE IN LANGMUIR-BLODGETT FILMS OF A MEROCYANINE DYE AND ITS ISOTOPE-SUBSTITUTED ANALOGS

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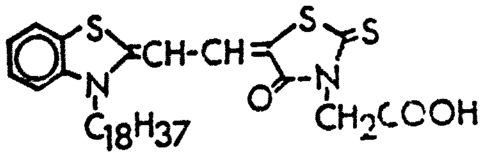
Two kinds of stable radicals exist in LB films of a merocyanine dye having benzothiazole for the donor nucleus (DS in Fig. 1). One of the species exhibits clear nitrogen hyperfine structure in the ESR spectra, the analysis of which revealed a characteristic in-plane orientation of the radical molecules. The results suggested a flow orientation of the J-aggregate from which radicals may originate [1]. Later developed theory of flow orientation during LB dipping process [2] successfully describes the flow orientation effect both in the optical dichroism of J-band [2] and the ESR spectral line shape [3,4]. This coincidence between ESR and optical anisotropies provides new evidence that the radicals originate from J-aggregate.

Based on these observations as well as photo-induced enhancement of ESR intensities, we have previously proposed an intermolecular charge transfer in J-aggregates, producing cation and anion of the dye molecule, as the origin of the observed two radical species. In this paper we examine the model by studying the hyperfine couplings of the dark and photo-induced species using isotope-substituted dye analogues. Since the nitrogen coupling of species A has been already detected, we focused on ^{15}N-substitution of either of the two nitrogens in the molecule as the first step. The results of the substitution for the one in benzothiazole (left-hand side of DS) has been already reported [3,4] The triplet splitting due to ^{14}N was replaced by the doublet splitting due to ^{15}N, showing that the observed coupling of species A arises from this nitrogen which belongs to the dye chromophore; N-C=C-C=C-C=O. The results of the substitution of the other nitrogen in rhodanine acetic acid in this work further confirmed this result; no change of the nitrogen splitting of species A was observed. On the other hand, the spectra of species B showed no distinct change for the former substitution but a small but significant change for the latter substitution, showing that a certain spin density of species B also exists on the dye molecule, as expected.

The anisotropy of the photo-induced signal was compared for the films of unsubstituted and substituted cases. The photo-induced signals showed a similar change as the dark signals upon ^{15}N-substitution, providing new evidence that the dark and photo-induced signals arise from the common species.

ESR spectra of substituted system can be simulated according to the previously reported procedure [1,4]. The anisotropic hyperfine coupling of ^{15}N at the same time provides new intrinsic probe for the study of the molecular orientation [4]. These examples demonstrate that unique microscopic informations of molecular aggregates in LB films can be obtained by ESR spectroscopy when appropriate isotope-substitution is employed.

Fig. 1



DS

1. S. Kuroda et al., J. Phys. Soc. Jpn. 56, 3319 (1987).
2. N. Minari et al., ibid 58, 222 (1989).
3. S. Kuroda et al, Solid State Commun., 71, 333 (1989).
4. S. Kuroda et al, Phys. Rev. B42, in press.

GO7

DEFECT ANNEALING RATE IN MONOLAYERS DISPLAYING A SMECTIC-L PHASE

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Abstract:

In a previous report quantifying the annealing of orientational defects in monolayers of 22-tricosenoic acid on the water surface[1], a significant rate was only observed when the surface pressure was cycled between two values, and not when the monolayer was quiescent. The cycling somehow makes the defects more mobile, but for practical purposes, even this enhanced mobility is an order of magnitude too small. In later work[2], the enhancement was traced to the fact that during the cycling, the monolayer was undergoing a phase transition. Subsequent X-ray diffraction and miscibility investigations have determined that this particular transition is between two hexatic phases, smectic-I (low surface pressure) and smectic-F (high surface pressure), respectively[3-5]. In a theoretical study of hexatic phases[6], Selinger and Nelson have shown that the stresses caused by an orientational defect in one of these phases can locally induce a transition to the other, or to the smectic-L phase which under certain conditions can occur between the regions of stability of I and F.

We report a study of the monolayer defect annealing rate in a mixture of 90% docosanoic acid and 10% ethyl eisosanoate, at a number of surface conditions including I, L and F phases.

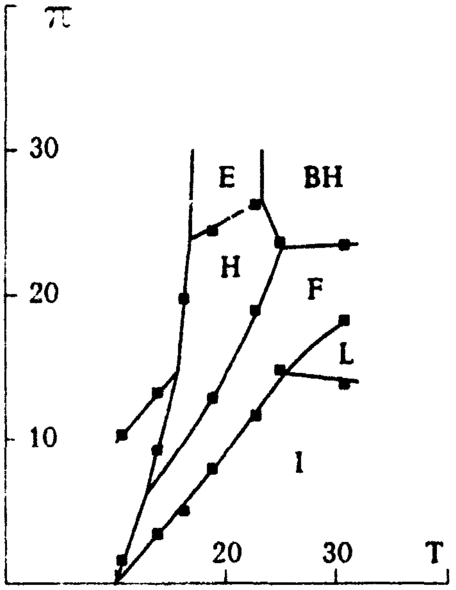

Fig. 1. π-T phase diagram of a docosanoic monolayer with 10% admixture of ethyl eicosanoate, showing smectic categories of mesophases.

1. A.M.Bibo and I.R.Peterson, *Thin Solid Films* **178** (1989) 81
2. A.M.Bibo, Degree Thesis, Joh. Gutenberg University Mainz, 1989
3. A.M.Bibo and I.R.Peterson, *Advan. Mater.* **2** (1990) 309
4. R.M.Kenn, C.Böhm, A.M.Bibo, I.R.Peterson, H.Möhwald, J. Als-Nielsen and K.Kjær, *J. Phys. Chem.* **95** (1991) 2092
5. A.M.Bibo, C.M.Knobler and I.R.Peterson, *J. Phys. Chem.*, in press
6. J.V.Selinger and D.R.Nelson, *Phys. Rev.* **A39** (1989) 3135

Session HO

Modern investigation methods

HI

ATOMIC SCALE PROBES AND THEIR APPLICATION TO ORGANIC MOLECULES

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An overview on scanning tunneling microscopy and force microscopy is given . The application of these techniques to biological samples has not yet resulted in many scientific results . Problems of sample preparation and of possible artefacts in the measurements are discussed . Preliminary results on single living cells and on DNA strands are presented . Clearcut experimental results are obtained when small organic molecules of various kinds form ordered surface layers on a crystalline substrate .

HO1

NONLINEAR OPTICAL TECHNIQUES TO PROBE MOLECULAR ORDERING AT LIQUID INTERFACES

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Recently, nonlinear optical techniques have been shown to provide structural information from liquid interfaces with high surface specificity. In this presentation, second harmonic generation (SHG) and IR-visible sum frequency generation (SFG) will be discussed as challenging new tools to study molecular ordering at liquid interfaces.

Surface adsorption, for example, is a fundamental problem in surface science. Techniques to directly measure the number of surface molecules are rare and their applicability is often limited by difficulties in differentiating signals from the surface and the bulk. Second-order optical processes provide the intrinsic advantage that they are forbidden in systems with inversion symmetry, in the electric dipole approximation, and are necessarily allowed at interfaces. Here, optical second harmonic generation (SHG) is used to probe the surface density and polar ordering of an adsorbate layer of soluble surfactants.

Electron delocalization normal to interfaces can be probed, as induced for example in thin films by the presence of the interface, a chemical reaction etc. We will discuss the effect of the proton and salt concentration in solution on the strength of charge-transfer complexes embedded as molecular probes in insoluble monolayers.

Infrared-visible sum frequency generation (SFG) provides vibrational spectra from single monolayers at liquid interfaces. The focus of this presentation is on the condensed phases of fatty acids, i. e. from 25 - 19 $Å^2$/molecule, where translational ordering and a continuous tilt transition have been observed by x-ray scattering.

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HO2

CHARACTERIZATION OF LANGMUIR-BLODGETT MONOLAYERS USING POLARIZATION MODULATED FTIR SPECTROSCOPY

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Polarization Modulated InfraRed Reflexion Absorption Spectroscopy (PM-IRRAS) is a very powerful and non destructive method to analyse, in situ and within a few minutes, ultrathin molecular films as for instance a single LB layer. It consists in rapidly modulating (62 KHz) between the linear p and s states, the polarization of the electromagnetic field incident at grazing angle onto the surface and in detecting the normalized differential reflectivity (Rp-Rs)/(Rp+Rs). With metallic substrates, due to the enhancement and the high polarization anisotropy of the effective electric field nearby the surface, this method gives IR surface spectra with much better signal to noise ratio than conventionnal IRRAS spectroscopy. Moreover, applying the so-called surface selection rule on such well defined surface spectra, one can get accurate conformational and orientational informations on LB systems.

In this communication, after some experimental details on the method, we present the bases of the quantitative analysis of the PM-IRRAS signal with particular emphasis on its linear behaviour versus the thickness and the extinction coefficient of the LB films; this linearity is very important to connect PM-IRRAS spectra with absorbance spectra. Next, we describe the different steps of the molecular orientation evaluation, comparing the relative band intensities of the PM-IRRAS spectra (subject to surface selection rule) with their bulk sample counterparts. Using an all trans conformational model for the hydrocarbon chain of the LB molecules, the tilt of this chain relative to the surface normal and the rotation around the chain axis may be accurately determined.

Finally, we apply this method to LB monolayers of cadmium arachidate deposited on gold substrate : stacks of several (2 to 8) CdAr layers exhibit well ordered structures and fit the all trans conformational model. The effect of molecular packing (increasing the thickness) on the tilt angle is pointed out. Conversely, single CdAr layer spectra present clear evidence of desorder, that may be interpreted in terms of inhomogeneous structure including domains where the alkyl chains have gauche conformations. More informations on this desorder can be drawn from the study of a deuterated CdAr monolayer inserted into a stack of normal LB layers. Results from such a work, actually in progress, will be also presented.

HO3

STRUCTURAL INVESTIGATIONS OF DONOR-ACCEPTOR-SUBSTITUTED POLYENES

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In this study we report on investigations on Langmuir-Blodgett-films of donor-acceptor substituted polyenes with long aliphatic chains. Monolayer film formation of 7-N,N-dioctylaminophenyl-7,8'-diapocarotene-8'-al (DAPC) has been observed and was characterized on the water surface by pressure-area isothermes. The films were transferred to several substrates like glass, tungsten diselenide (WSe_2), silver coated silicon and glass slides. To determine thickness and dielectric constant surface plasmon resonance (SPR) measurements were applied. The theoretical fit of the SPR results yielded a thickness of 10 Å per monolayer. Molecular resolution of DAPC-molecules has been obtained by scanning tunneling microscope (STM) investigations for the first time. The images revealed structures with two different periodicities: i) periodic structures with spacing of 4-5 Å, indicating the standing aliphatic chains and ii) longly oriented and strongly parallel structures of 22 Å length and 2-3 Å width indicating the conjugated part of the polyenes. These results coupled with UV-Vis and IR spectra show that the conjugated chains are deposited parallel while the aliphatic chains are placed perpendicular to the surface.

HO4

PARALLEL ARRANGEMENT OF FATTY ACID MOLECULES IN THE FILM DEPOSITED AT A LOWER SURFACE PRESSURE

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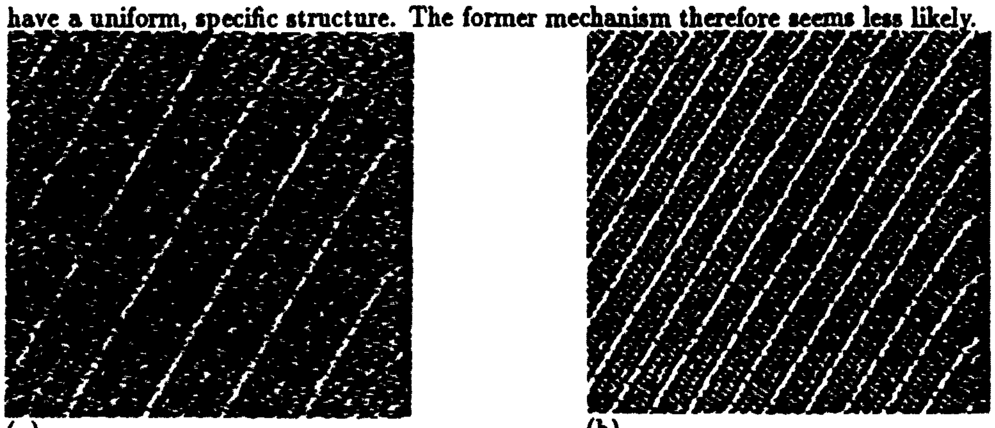
It is widely believed that the LB film deposited at a lower surface pressure, *i.e.* in a rather expanded phase, has a disordered structure. With a scanning tunneling microscope (STM), however, we have found unexpectedly ordered structures in fatty acid films, deposited at a lower surface pressures onto single-crystal substrates such as highly oriented pyrolytic graphite (HOPG) and MoS_2, where the molecules adhere with their long axes parallel to the substrate surface.

This parallel arrangement can be obtained with high reproducibility by the following two procedures: [i] immersing the substrate through the monolayer at the air-water interface and subsequently withdrawing it after removing the monolayer; [ii] immersing and then withdrawing the substrate through the monolayer kept in the L_2 phase.

The typical STM images of behenic acid deposited on HOPG by using above method are shown in Fig. 1. We observed two types of molecular arrangements. One type (Fig. 1a) has two periodicities, 6nm (with sub-periodicity of 3nm) and 0.4nm. The other one (Fig. 1b) has periodicities 3nm and 0.4nm. The wider periodicities of 6nm and 3nm correspond to double and single spacing of the molecular axis, whereas the narrower periodicity of 0.4nm corresponds to the diameter of the molecule. There was no marked difference between the films fabricated either by the method [i] or by the method [ii] while we could not obtain any significant image of films deposited with the conventional method (π=26mN/m, 20°C, L_2' phase), probably because of its thickness. The double spacing structure tended to occur at an early stage during scannings with the STM-tip and it often changed to the single spacing structure with time. The feature on MoS_2 was almost the same as that on HOPG except that the double spacing structure was more stable.

Two possible explanations for the parallel arrangement are presented. First, a porous structure, where the molecules are oriented almost perpendicular, is produced by poor deposition and overturning. Then the scanning of the STM-tip mechanically peels off some molecules and induces a molecular reorientation from perpendicular to parallel. Second, some molecules detach from the substrate during the withdrawal period followed by immediate reorientation of the remaining molecules from a perpendicular arrangement to a parallel one. Extended scanning of a film deposited by the conventional method did not result in a parallel arrangement, which was observed in many cases immediately upon start up of the scanning in films fabricated with the above presented methods. The contact angle of water on films fabricated by method [i] was uniform on the whole film area (75°) but was different from that of the bilayer film fabricated by the conventional method (107°). This indicates that these films intrinsically have a uniform, specific structure. The former mechanism therefore seems less likely.



(a) (b)

Figure 1 STM images of behenic acid on HOPG. 10nm

HO5

MOLECULAR REARRANGEMENTS ASSOCIATED WITH THE INTERACTIONS OF MONOLAYERS AND BILAYERS

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Experiments were carried out on a variety of LB and self-assembled monolayer and bilayer surfaces on mica using the Surface Forces Apparatus technique. The experiments were designed to study the molecular reorientations and mechanisms associated with such dynamic phenomena as (1) adhesion-decohesion hysteresis and contact angle hysteresis, (2) the hydrophobic interaction, and (3) the fusion of two bilayers in water.

We found that hysteresis effects are not simply due to surface imperfections, such as roughness or chemical heterogeneity. Even monolayer-coated surfaces that are initially perfectly smooth and chemically homogeneous can exhibit hysteresis effects. These arise from slow molecular rearrangements and interdigitations occurring at the contacting interfaces as soon as contact occurs between the two surfaces (whether solid-solid or solid-liquid). We have studied three factors that enhance hysteresis: (i) increasing the freedom of the surface molecules to reorder, (ii) increasing the time surfaces remain in contact, and (ii) increasing the speed of separation (or receding). These findings highlight the inherent non-equilibrium nature of most adhesion-decohesion and wetting-dewetting processes, and preliminary results also indicate a correlation between adhesion hysteresis and friction/stiction.

Measurements of the deformations and short-range forces between various bilayers specifically deposited or stressed to expose additional hydrophobic area to the aqueous phase indicate (i) that the hydrophobic attraction is mainly responsible for the direct fusion of bilayers, which may be viewed as a first-order phase transition, (ii) that the hydrophobic attraction can be enhanced by up to two orders of magnitude by stressing bilayers, (ii) that it is associated with fairly slow (~milliseconds) rearrangements of amphiphile/water molecules or the H-bond network in the water gap between two surfaces, and (iv) that the repulsive short-range "hydration" forces between bilayers are not due to solvent structuring effects, as previously thought, but to thermal fluctuation forces (steric-entropic repulsions between mobile surface groups). These findings imply that the hydrophobic interaction between bilayers, vesicles and biological membranes may depend on the osmotic, electrical and other stressed conditions of the membranes as well as on the rates at which the surfaces interact.

HO6

DIRECT OBSERVATION OF MOLECULAR STRUCTURE AND DYNAMICS IN SELFASSEMBLED ORGANIC MONOLAYERS

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Scanning tunneling microscopy has been employed to investigate structure and dynamics of selfassembled organic monolayers on the length scale of 0.1 nm and the time scale of 100 ms. Long chain alkanes (C_{16} through C_{50}), various alkyl–derivatives, including fatty acids, alcohols, and esters, as well as dialkyl–substituted moieties (e.g. didodecylbenzene and dihexadecyloxynaphtalene) are shown to adsorb from organic solutions onto highly oriented pyrolytic graphite with the first monolayer exhibiting lamellar phases in which the molecules are extended and oriented parallel to the basal plane of graphite. Bias dependent imaging allowed to image either preferentially the underlying substrate or the molecular adsorbate, without disrupting the adsorbate layer. Detailed information was obtained on the packing within the monolayer as well as about orientation and commensurability of adsorbate and substrate. Moreover, various defects, involving individual molecules as well as molecularly sharp domain boundaries could be observed and explained on the molecular scale. Finally, fast image recording allowed to directly observe appearance, diffusion and annealing of the defects on the time scale of 100 ms and longer.

HO7

SCANNED PROBE MICROSCOPY
OF
THIN ORGANIC FILMS

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The local surface structure and the electrical properties of thin organic films can be investigated with the novel scanned probe microscopes such as the Scanning Tunneling Microscope (STM) and the Scanning Force Microscope (SFM).

We applied these atomic scale probes to investigate LB films, vacuum deposited organic films as well as polymeric thin films drawn from the melt. With the STM, uncoated monolayers of 22-tricosenoic acid deposited on semiconducting substrates and polyimid films prepared via gas-phase deposition from precursors (ODA, PMDA) were investigated. The experiments indicate the possiblity of the direct imaging of uncoated organic monolayer films deposited onto appropriate substrate materials on the molecular scale. In addition, novel electronic interfacial effects have been observed on discontinuous monomeric and polymeric thin organic films.

With the SFM, drawn polymeric films and LB films have been investigated. This method clearly shows the fibrillar structure of the drawn films. It also allows to study the forces between individual fibrils. The resolution limit for these soft systems is in the range of 1 nm, while on inorganic substrates such as mica, atomic resolution is obtained. On LB films, the SFM allows to measure the surface roughness of multilayer films and to detect defects in the film structure. The scanned probe techniques thus excellently complement conventional averaging surface inspection techniques and provide useful information on the (sub-) molecular scale of uncoated organic surfaces.

H08

THE STRUCTURE OF PHOSPHOLIPID MONOLAYERS AT WATER SURFACES AT MOLECULAR RESOLUTION: A NEUTRON REFLECTIVITY STUDY

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The interaction of proteins with solid interfaces is a key issue in devising functionalized structured surfaces for the application in biophysical research and in materials science. A new approach toward the understanding of the underlying complicated interactions involved in cell-cell recognition processes and toward the construction of sophisticated functional interfaces involves binding studies of proteins to monomolecular surface layers comprising functionalized lipidic species. The molecular structure of such layer systems is of immediate interest as its knowledge is a prerequisite for a controlled composition of model systems and of functionalized devices.

Only recently, synchrotron X-ray reflection and diffraction experiments on surface monolayers from (phospho-) lipids have provided detailed insight into the molecular structure of such model systems, in particular into chain orientation and packing characteristics. Structural features of the head groups exposed to the aqueous phase have been assessed to a lesser degree. For investigations of the lipid head group structure and of proteins associated to lipids from the aqueous phase, neutrons are expected to provide a definite advantage over X-rays in that the contrast of different parts of the system under investigation can be varied in wide ranges.

We have constructed a dedicated liquid-surface neutron reflectometer and have measured the reflectivity from monolayers of chain-perdeuterated DPPC-d_{62} on H_2O and on D_2O subphases. In a new approach to refining a model of the interface structure based on our measurements in combination with older X-ray data on the same monolayer under similar conditions we show that both techniques mutually complement each other. The conclusions drawn from this analysis lead to a definite conception of the interface structure. For the liquid-condensed (LC) phase of DPPC (which is analogous to the $L_{\beta'}$ phase in vesicle dispersions) it is found that the head group is interpenetrated with subphase water (4 ± 2.5 molecules per lipid) and that the average tilt angle of the hydrophobic chains from the surface normal is 33 ± 3 degrees.

Session IO

Biological and biomimetic aspects,
BLM

II

TILING THE PLANE WITH PROTEINS

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101

ION CHANNEL TRANSDUCTION IN LANGMUIR-BLODGETT LIPID MEMBRANES

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ABSTRACT

Multilayers of phospholipid films with VDAC (voltage dependent anion channels) or acetylcholine receptors (AChR) have been deposited onto platinum electrodes using the Langmuir-Blodgett technique. The electrical properties of both suspended and platinum electrode-supported phospholipid bilayers containing VDAC were studied.

For the VDAC-coated electrodes, the VDAC conductance decreased under appropriate biasing conditions due to the voltage sensitive response of the protein. The response was asymmetric with respect to the polarity of the offset voltage, possibly the result of steric hindrance of the protein conformational changes by the electrode surface.

Physical properties of AChR-lipid films were investigated at the air-water interface as a function of surface pressure. The AChR-lipid film were transferred onto electrodes and the conductance on the electrodes was found to decrease upon injection of carbomyl choline. Alternative methods for protein transfer onto the electrode have been considered. The stability and sensitivity of these films will be discussed with respect to biosensor development.

ORIENTED IgG LAYER ONTO THE LANGMUIR-BLODGETT FILMS OF PROTEIN A

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Immunosensors permit to detect trace amounts of chemicals with high sensitivity and specificity. There is a number of problems for further development of this type of biosensors. One of them is the method of IgG immobilization on the surface of suitable detector because the traditional covalent attachment or physical sorption don't allow to immobilize antibodies with high yield and in functional orientation.

Since protein A is known to interact with Fc fragment of IgG molecule, Langmuir-Blodgett films of protein A were used for futher functional orientation of IgG layer.

A surface pressure-area and surface pressure-time curves of protein A at the air-subphase interface show that protein A "drowns" well. We have synthesized N-hydroxysuccinimide esters of stearic and ^{14}C-stearic acids and obtained a number of hydrophobizated proteins A, modified with 1 to 10 hydrophobic tails per protein A molecule. These modified proteins A have been immunologically characterized. The conditions (pH and composition of subphase, surface pressure, the degree of protein A modification, the number of transferred monolayers) of the modified protein A Langmuir-Blodgett films deposition were optimized. It permited to obtain Langmuir-Blodgett films of protein A, which bind ^{125}I-IgG 3-5 times more effective than protein A immobilized on the same substrate chemically with amino silane and glutaric aldehyde.

IO3

LATERAL PROTON CONDUCTION ALONG LIPID MONOLAYERS SPREAD AT THE AIR/WATER INTERVACE

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Membrane solution interfaces are playing a decisive role in the function of biological cells. The movement of protons is very important being involved in the transduction of energy by membranes. One open question is to know if this movement is only perpendicular to the plane of the membrane or if a lateral flow may occur.

Lateral proton facilitated movement along lipid monolayers can be observed by fluorescence spectroscopy. This approach allowed us to demonstrate in 1985 that the movement was much faster along the lipid/water interface than in the bulk phase. These results were confirmed in our further studies using either interfacial fluorescence spectroscopy, surface pressure or surface potential. This conclusion was supported by the observation in other groups of an enhanced electrical conductance along the interface when a monolayer was present. This was in agreement with a much older observation on multilayered system . A fast spectroscopy indirect approach showed a modulation of the surface conduction by the nature of the lipids. All the direct evidences of a facilitated conduction along lipid monolayers were giving an experimental support to the hypothesis of a "microlocalized" pathway for the "chemiosmotic coupling" in energy transducing membranes we mentioned above.

A systematic investigation of this conduction was performed by use of interfacial fluorescence. Continuity of the lipid matrix was a key property of the film. The process was observed whatever the nature of the polar headgroup but was only detected when the state was liquid expanded.

The molecular mechanism responsible for this facilitated interfacial proton movement was proposed to be due to the occurence of an hydrogen bond network between the polar headgroups of the phospholipids and the interfacial water molecules as suggested by D. Chapman more than 20 years ago. This was experimentally supported by the detection of a very steep pH gradient along the interface when the conduction was present, the effect of magnetic field, of Ca on phosphatidylethanolamine monolayers and more directly by the behaviour of deoxy derivatives of ether linked phosphatidylglycerol. The observations that this conductive network is no more effective when the film is in the condensed state can be explained by a dehydration of the interface when the lipids are brought to the Liquid Condensed state or by a conformational change of the polar headgroup region. But this inhibition is specific of the gel state and as biological membranes are always fluid, we may conclude that lipid domains at their surface are putative conduits for proton movement as supposed in the coupling mosaïc model.

CO-PLANAR PATTERNS OF SELF-ASSEMBLED MONOLAYERS FOR SELECTIVE CELL ADHESION AND OUTGROWTH

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ABSTRACT

A recently-developed deep ultraviolet (DUV) photolithographic method has been used to produce high resolution (1-200 μm feature size) patterns of co-planar self-assembled monolayers (SAMs) on solid substrates. In one example, substrates modified with SAMs of a silane-coupled ethylenediamine (EDA) are directly modified by DUV exposure through metallized masks to create exposed areas which are amenable to remodification using a hydrophobic perfluorinated molecule, such as tridecafluorosilane (13F). Contact angle goniometry and UV spectrocopy of these patterned SAMs show that adjacent regions of intact organic functionalities of EDA and 13F residing in the same molecular plane are produced by this technique. Human SK-N-SH neuroblastoma cells plated from growth media on substrates with these SAM patterns show 98% selective cell adhesivity. Explanted neurons, from fetal mouse hippocampus, selectively adhered and restricted their outgrowth of dendrites and axons to 1-20 μm-wide cell-adhesive EDA lines on EDA/13F patterns. The selective adhesion and outgrowth on these SAM patterns of a variety of other cell types will be presented. This presentation will demonstrate that this technique is a simple, yet powerful method for producing co-planar SAMs for cell adhesion and outgrowth. Patterned co-planar SAMs produced using this technique may provide novel devices where the non-random positioning and development of cells is necessary, and will provide more detailed experimental information for the increased understanding of substrate-mediated neuronal development and function.

Session JO

Molecular recognition,
self-assembling systems

SUPRAMOLECULAR CHEMISTRY: FROM MOLECULAR RECOGNITION TOWARDS MOLECULAR DEVICES AND SELF-ORGANIZATION

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Molecular recognition rests on the **molecular information** stored in the interacting species. Together with **catalysis** and **transport**, and in combination with polymolecular organization, it opens ways towards **molecular** and **supramolecular** devices, defined as structurally organized and functionally integrated chemical systems built on supramolecular architectures. The development of such devices requires the design of molecular components performing a given function (*e.g.* photoactive, electroactive, ionoactive, thermoactive or chemoactive) and suitable for assembly into an organized array.

Light-conversion devices as well as approaches towards molecular **electronic** and ionic devices have been investigated.

Of special interest is the possibility to design devices that may form by **molecular self-assembling**.

Supramolecular chemistry has relied on more or less pre-organized molecular receptors for effecting molecular recognition, catalysis and transport processes. A step beyond consists in the design of systems undergoing **self-organization**, i.e. systems capable of spontaneously generating a well-defined supra-molecular architecture by **self-assembling** from their components in a given set of conditions. The information necessary for the process to take place must be stored in the components and performs via selective molecular interactions. Thus, these **programmed molecular systems** operate via molecular recognition.

Several approaches to self-assembling systems have been pursued :

1) the formation of helical metal complexes, the *double-stranded helicates*, that result from the spontaneous organization of two linear polybipyridine ligands into a double helix by binding of specific metal ions;

2) the generation of mesophases and liquid crystalline polymers of supramolecular nature from complementary components, amounting to macroscopic expression of molecular recognition;

3) the molecular recognition directed formation of ordered solid state structures.

Such systems may be able to perform highly selective operations of recognition, reaction, transfer and structure generation for signal and information processing at the molecular and supramolecular levels.

JO1

MOLECULAR ENGINEERING AT THE AIR-WATER INTERFACE : BUILDING UP DESIGNED SUPERMOLECULAR ASSEMBLIES WITH AMPHIPHILIC PORPHYRINS.

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The increased interest showed in the last ten years in the Langmuir-Blodgett (LB) technique results mostly from the unique ability of this technique for the building of well-defined materials . Of particular interest is the opportunity of building up supermolecular assemblies from designed organic molecules under a fully controlled process . Considering the intimate relationship between molecular structure and supramolecular reactivity in the solid state, the collective order provided by the LB technique strongly governs the specific properties of these ultrathin films and their potential applications . Within this field, porphyrins and their derivatives exhibit interesting properties which can be modulated by the structural environment and a geometrical control of the molecular interactions.

So, it seems attractive to study the ability of amphiphilic porphyrins to build new supermolecular assemblies by the LB technique . Our strategy is based on the geometrical control of the intermolecular interactions occurring at the air/water interface between two different amphiphilic molecules . Two macrocycles have been synthesized in this goal : the tetra-4-oxy-(2 docosanoic acid) phenyl porphyrin (P_1) and the tetra-3-docosyl pyridinium porphyrin (P_2) .The aim of the present work is the controlled building of oriented supermolecular assemblies through molecular recognition at the air/water interface between oppositely charged monomers (P_2 bears four positive charges while P_1 bears four ionizable carboxylic functions). Hence, spreading the equimolar mixture $[P_1 + P_2]$ at the air/water interface undergoes the formation and the orientation of self-assembled heterodimers, the structure of which are checked out by convergent spectroscopic techniques such as linear dichroism or anisotropic ESR on copper II derivatives . In that case, the spontaneous heterodimerization arises from a geometrically controlled recognition between the two planar macrocycles which lie together flat on the water surface . However, a slight modification of the amphiphilic macrocycles may prevent the spontaneous formation of face to face dimers at the air/water interface and promote the building of lateral ionic interactions between adjacent macrocycles organized as a planar paving by the Langmuir technique . Hence, when P_2 is replaced by its μ-oxo dimer $(FeP_2)_2O$, no heterodimerization is observed. In this case, the extra macrocycle P_2 plays the role of a bulky axial ligand for the former one and precludes the formation of a face to face heterodimer with P_1. Moreover, infrared spectroscopy indicates that the ionic links between the two oppositely charged porphyrins are still present within the LB structure which becomes totally insoluble in their spreading solvent . These results are in favor of the spontaneous formation of an ionic network occuring at the air/water interface between the oppositely charged porphyrins $(FeP_2)_2O$ and P_1 .

Thus, designed supermolecular assemblies can be built through the geometrical control of intermolecular interactions at the air/water interface . This general strategy provides an elegant and efficient access towards molecular machines .

JO2

SELF-ASSEMBLY OF AVIDIN/BIOTIN MONOLAYERS AND MULTILAYERS

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The assembly of molecular networks is an important goal in the realisation of functional Molecular Electronic systems. As a first step in the fabrication of such networks we have utilised the strong affinity of the protein, avidin, for the biotin ligand. Stoichiometric mixtures of the protein with the bifunctional ligand bisbiotin readily polymerise and the resulting polymer can be spread at the air/water interface and deposited onto substrates using the LB technique. The behaviour of the preformed polymers at the air/water interface will be described and TEM micrographs of the deposited monolayers presented.

In related experiments we have successfully chemisorbed the biotin ligand to an evaporated gold surface. Subsequently, further monolayers of avidin and bisbiotin have been chemisorbed to the biotin layer suggesting that it may be feasible to assemble polymer chains one subunit at a time on a solid surface. The deposition process is monitored by surface potential and surface plasmon resonance techniques. The protein layer makes a positive contribution to the surface potential, consistent with the known excess of positively charged residues on the protein. From surface plasmon resonance studies, the thicknesses of the first biotin and avidin monolayers were found to be consistent with known molecular structure.

JO3

SELECTIVE SUBSTRATE BINDING TO GUANIDINIUM AND UREA FUNCTIONALIZED MONOLAYERS

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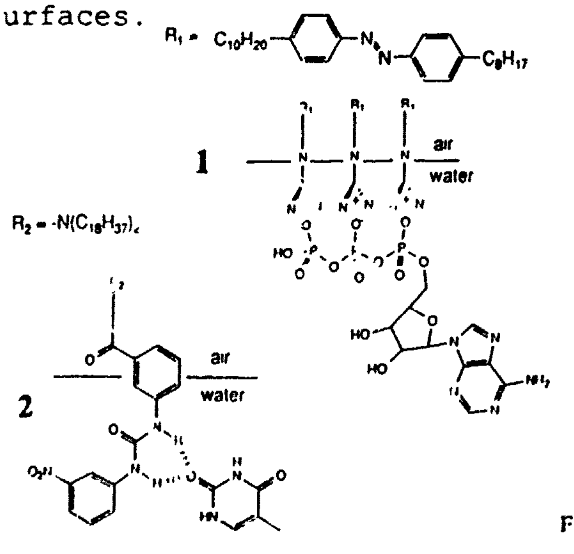
Molecular recognition at the cell surface is an essential phenomenon for the initiation of intercellular and transmembrane processes influencing the cell's direction of growth, defenses, and death. We are currently investigating the aspect of molecular recognition on a membrane surface utilizing synthetic amphiphiles to isolate and study the basic interactions between substrate and membrane receptor. We report here the selective substrate binding on a guanidinium (ionic-type) functionalized monolayer **1** and on a urea (H-bonding) monolayer **2**.

Qualitative as well as quantitative substrate binding for monolayers of **1** and **2** were assessed through several analytical techniques. With monolayers of **2** pressure-area (π-A) isotherms exhibit expansion when proton acceptor substrates are present in the subphase, indicating substrate binding. Interestingly, the monolayer of **1**, studied via UV reflectance spectroscopy as well as π-A isotherms, exhibits amphiphile disorder (expansion) or order (condensation) dependent on the number of interaction points between the substrate and monolayer. Data provided by FTIR spectroscopy of LB films of monolayers of **1** and **2** deposited from substrate laden subphases confirmed substrate binding. Quantitative results were obtained through ESCA of the LB films. Concentration studies (e.g. Fig. 1) of substrates binding to monolayers of **1** and **2** gave binding constants for various substrates. With the ionic properties of **1**, ATP and AMP substrates gave strong Langmuir binding constants of 1.0×10^7 and 3.0×10^6 M^{-1}, respectively. Monolayer of **2** with strong H-bonding ability gave binding constants with thymine at 3.0×10^3 M^{-1}. These binding constants are essential in providing a handle for the design of multifunctional receptor sites at membrane surfaces.



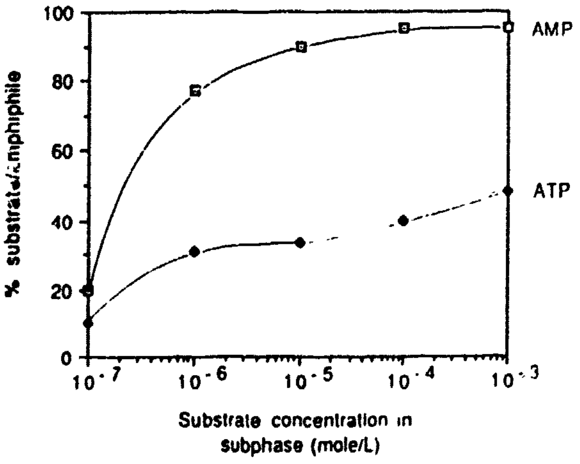


Fig. 1. AMP and ATP substrates bound to monolayer **1** at varying subphase concentrations determined by ESCA analysis.

J04

MOLECULAR RECOGNITION IN MONO- AND MULTILAYERS: BIOTIN-STREPTAVIDIN SYSTEMS AND ANALOGS

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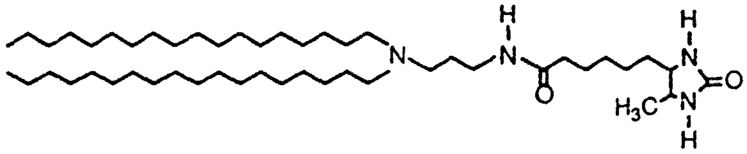
Specific interactions between proteins and membrane incorporated receptors are the basis of signal transduction processes in biological systems. Thus proteins can be valuable components in biosensor applications of LB mono- and multilayers. Incorporation of proteins and their ligand molecules in synthetic LB mono- and multilayers allows the combination of the high specificity of biological recognition processes and the stability respectively functionalizability of synthetic mono- and multilayer systems.

Specific interaction between biotin (vitamin H) and the protein streptavidin in monolayers of synthetic lipids with biotin headgroups results in the formation of highly ordered 2D streptavidin crystals in the plane of the monolayer [1]. Two binding sites of the protein which are still free offer the possibility to further functionalize the streptavidin layer [2]. To proof the applicability of this system for building up proteinaceous multilayer structures a specific stabilization or competitive replacement of the streptavidin layer is investigated.

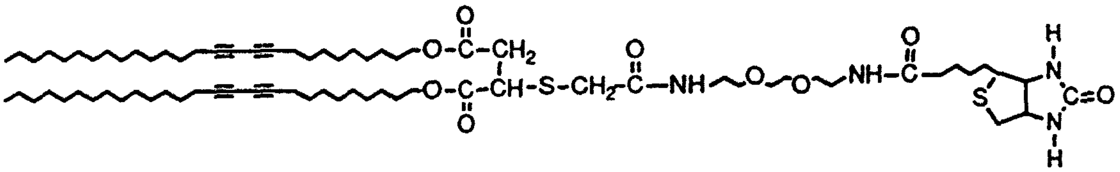
Use of newly synthesized lipids containing desthiobiotin - a biotin analog - (**fig 1**) also leads to formation of 2D-streptavidin crystals. The binding constant of desthiobiotin is two orders of magnitude lower compared to biotin. Thus protein layers can selectively be separated from the lipid monolayer by competetive replacement with biotin.

Fig.1



Stabilization of functional streptavidin layers can be achieved by use of biotin containing amphiphilic polymers, or biotin containing polymerizable amphiphiles. Thus various UV-polymerizable, biotin-containing diacetylene lipids have been synthesized (**fig 2**). They have been shown to form well ordered monomeric and polymeric monolayers which can specifically bind streptavidin. The spectroscopic properties of poly-diacetylenes furthermore offer the possibility to detect very small conformational changes in the polymer backbone such as can be induced by streptavidin binding to the biotin headgroups.

Fig.2



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[1] R.Blankenburg,P.Meller,H.Ringsdorf,C.Salesse;*Biochemistry*,**28** (1989) 8214
[2] M.Ahlers,R.Blankenburg,D.W.Grainger,P.Meller,H.Ringsdorf,C.Salesse,*Thin Solid Films*,**180** (1989) 93. M.Ahlers,W.Müller,A.Reichert,H.Ringsdorf, J.Venzmer, *Angew.Chem.Int.Ed.Engl.* **29** (1990) 1269

JO5

Photochromism of Spiropyran on Supermolecular Assemblies

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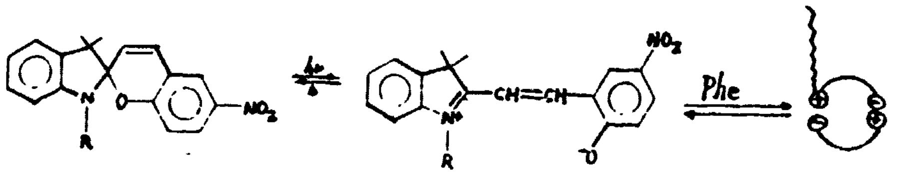
Photochromic systems offer some interesting industrial applications including high density optical memories. Recently there has been an increasing interest in the complex formation of spiropyran which provided a novel approach for improving the light-fastness for imaging and data recording systems.This paper describes firstly the photochromism of supermolecular assemblies(Fig.1) of spiropyran with phenylalanine by using langmuir-Blodgett technique.



SP16: $R=C_{16}H_{33}$, SP18: $R=C_{18}H_{37}$

Fig.1 Formation of supermolecular assemblies

The π-A isotherms for spiropyran spreaded on phenylalanine solutions are similar to those on pure water surface under UV irradiation. The area per SP16(Fig.1) molecule occupied(20A) at high temperature(>34°C) is much smaller than that given by molecular models, suggesting that the hydrophilic photochrome head group comes to lie directly beneath the chain attached to its extremity. A new absorption of merocyanine(SP16) appeared in accumulated LB films on quarts slides and this assigned to assemblies. Furthermore, there is a considerable retardation of the photofading and thermal decoloration rates.

This method can be expected to improve the image stability of recording system.

1.a)Sunamoto,J; Iwamoto,K; Mohri,Y and Kominato, T. J.A.C.S. 104, 5502-5504(1982).

b)L.S.Atabekyan and A.K.Chibisov, J. Photochemistry, 34, 323, (1986).

Session AP

LB film fabrication : instruments and monolayer transfer

AP1

AN APPROACH TO IMPROVING THE HOMOGENEITY OF POLYMER MONOLAYERS

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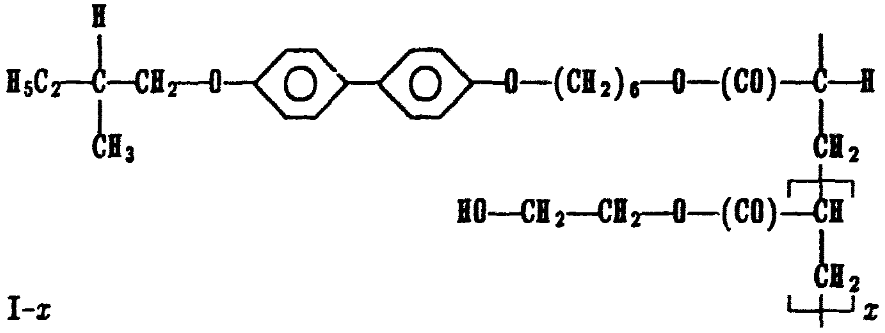
Unlike monolayers of small surfactant molecules, monolayers of polymers usually develop a marked gradient in surface pressure during compression[1,2] because of high viscosity or low diffusion rate. For many purposes it is necessary to improve the homogeneity of polymer monolayers. Our recent results[3] show that the introduction of a simple monomeric surfactant into polymer monolayers may greatly reduce the gradient. However appropriate changes to the chain structure of the polymer might be another approach, and our first attempts are reported here. The molecular design is based on increasing the length and hence the flexibility of the main chain in the repeating unit of the polymer, making it hydrophilic, while keeping the side chain hydrophobic. This would improve the mobility of the side chains on the surface of the water. Typical of the polymers employed is I–*x*, with the unit structure shown:



I-x

where $x = 0$ or 3.

Measurements of surface pressure along the center line of the trough demonstrate that a steep gradient in surface pressure is gradually built up during compression of I–0 monolayers and that once the gradient has formed it does not vanish in 90 minutes although it is reduced by about half. However in the films of I–3 there is a much smaller surface pressure gradient formed during compression. The isotherms of these two polymer monolayers are quite different: for I–0 the isotherm is very steep and the areas indicate close packing of the side chains; in contrast, the isotherm of I–3 has a smaller slope and the areas are substantially larger, approaching the area of I–0 only at high surface pressures. The much greater compressibility of I–3 indicates that its main chain is easy to rearrange, facilitating movement of the side chains. Thus the viscosity of I–3 is much lower than that of I–0 and this leads to much smaller surface pressure gradients on compression.

1. Peng, J. B. and Barnes, G. T., *Langmuir*, 1990, *6*, 578.
2. Peng, J. B. and Barnes, G. T., to be published.
3. Peng, J. B. and Barnes, G. T., to be published.

AP2

A NOVEL ALTERNATING-LAYER TROUGH

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There are two principal designs of Langmuir-Blodgett trough: the constant-perimeter and the sliding-barrier. Conventional constant perimeter troughs often suffer from problems of contamination or difficulty in cleaning the barrier. The design of trough discussed here is based on the 'diamond-barrier' design discussed earlier (Miller et al 1988), but developed for use in an alternating-layer mode as most often utilised for depositing non-centrosymmetric systems for second harmonic generation.

In the present trough, two diamond-barriers are used, so building on the technology developed for the single diamond version. It maintains, therefore: exceptionally high standards of cleanliness facilitated by using no relatively-moving parts within the active area; excellent flow patterns; accurate determination of transfer ratio. The key new feature is a sample transport system which enables the sample to travel the comparatively large distances involved below and above the water. The dipping mechanism provides a true vertical movement, with constant insertion and withdrawal rates; only the sample (and not ancillary mechanisms) is passed through the water surface. Moreover, it could readily be adapted to more than two compartments (diamonds).

We would like to thank the SERC for support.

Reference

L S Miller, D E Hookes, P J Travers and A P Murphy (1988): A new type of Langmuir-Blodgett Trough. *J Phys E: Sci. Inst.***21**, 163-167.

AP3

MOLECULAR ORIENTATIONS OF SUBSTITUTED PHTHALOCYANATO-POLYSILOXANES IN LB FILM

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Substituted phthalocyanato-polysiloxane (PcPS) is spread on an aqueous subphase, transferred onto the Langmuir-Blodgett (LB) film of Cd or Ba arachidate, annealed at 150 °C for 2 h and then characterized by a transmission electron microscopy. Electron diffraction pattern of PcPS LB films exhibits two kinds of reflection arcs, which correspond to the intramolecular distance of 0.33 nm and the second-order intermolecular spacing of 1.2 nm, respectively. These arcs extend over an angle of ± 35° with respect to the direction of film transfer. Dark-field images represent domains and high resolution electron micrographs can identify not only single molecules of PcPS but also real structure in polymer LB films.

AP4

SYNTHESIS OF POLYSILOXANE FILMS WITH VARIED MICROSTRUCTURES IN MATRICES OF SYNTHETIC BILAYER MEMBRANES

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Synthetic bilayer membranes can form highly stable molecular aggregates in water and provide a rich variety of well-defined morphologies. Owing to their remarkable self-assembling properties, synthetic bilayer membranes can be thought to be useful as molecular templates for synthesis of polysiloxane network with microstructures controlled on molecular-sized scale. In the present study, polysiloxane films were prepared from alkoxysilanes by the sol-gel method in matrices of synthetic bilayer membranes.

A mixture of synthetic bilayer membrane and $CH_3Si(OCH_3)_3$ was dispersed in water by sonication and spread on a fluorocarbon polymer sheet for casting. The cast film containing synthetic bilayer membrane and $CH_3Si(OCH_3)_3$ was exposed to NH_3 vapor in order to polymerize the alkoxysilyl group to siloxane bridges. By extracting synthetic bilayer membrane from the cast film with solvent, a polysiloxane film was obtained. The microstructure of polysiloxane film was observed with high-resolution SEM.

Polysiloxane films with much different types of microstructures such as multi-layered, fiber-like, small particle-aggregated, spherically-pored, plate-like pored, etc., which were composed of nanometer-order units, were obtained in this method. These molecular-sized microstructures resulted as replicas of a rich morphological variety of synthetic bilayer membranes such as vesicle, lamella, helix, etc. The microstructure of the polysiloxane film also changed with molar ratio of the two components and with the preparative conditions. These microstructures mainly reflected the stability and morphology of the agueous mixed dispersions.

The present methodology is highly valuable for controlling microstructures of the polysiloxane network on molecular scale. It should be generally applicable to preparation of organic and inorganic materials with molecularly defined microstructures.

AP5

ORIENTATION OF POLYIMIDE LB FILMS IN PLANE DIRECTION

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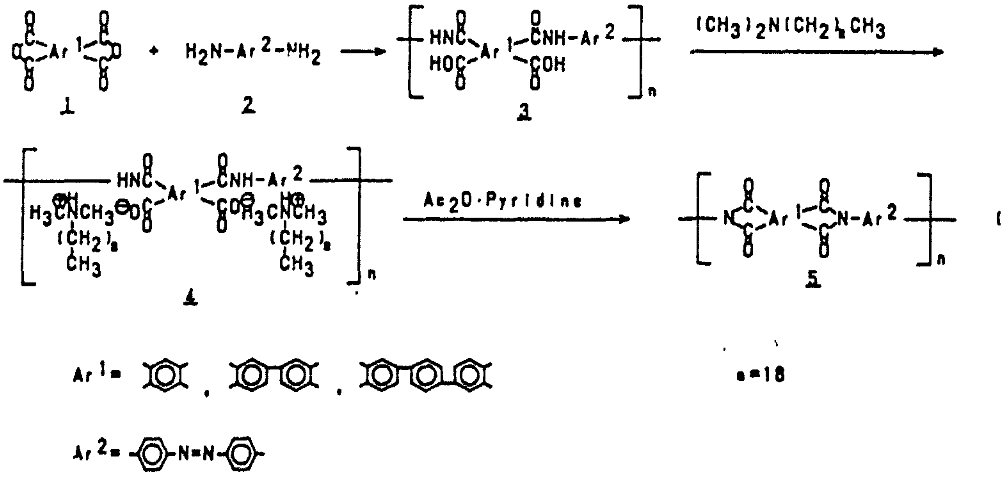
We have developed the precursor method for the preparation of polyimide LB films. As shown in eq. 1, polyamic acids which are the general precursor of polyimides were converted to polyamic acid salts 4 by mixing with long alkylamines. The precursor 4 offered the stable monolayers at air/water interface, and were transferred on to appropriate substrates by the usual LB technique. Polyimide LB films were obtained by treatment of LB films of 4 by the solution of acetic anhydride and pyridine.

Polyamic acids possessing azobenzene unit in the polymer backbone were synthesized to examine the orientation of the polymer chain. It was reported that the polymer chain oriented to the parallel direction of the pressing bar of the LB instrument as the results of measurement of the polarized absorption spectra of the L film, and as far as the monolayer at air/water interface was transferred using the ordinary trough in which the width of the plate was much smaller than that of the monolayer, the orientation direction of the polymer chain was changed by transfer process.[1] This fact can be explained by drawing effect of the polymer chain. On the other hand, the orientation at air/water interface was retained using the moving wall type LB equipment. Factors such as chemical structure of the polyamic acid, surface pressure at the deposition, dipping speed of the plate were examined in detail. It was found that the polyamic acid possessing terphenyl structure tended to highly orient compared with other polyamic acids. Thus, if one can make the polymer chain orient with high degree, highly oriented polyimide LB films should be obtained. These are applied to not only aligning layers of the liquid crystalline cells but also the future molecular devices.

[1] S. Seki, S. Baker, J. Seto, Y. Nishikata, M. Kakimoto, Y. Imai, Extended Abstracts (The 37th Spring Meeting, 1990); The Japan Society of Applied Physics and Related Societies, 1049.



AP6

THEORY OF FLOW ORIENTATION EFFECTS IN LANGMUIR-BLODGETT FILMS

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The Langmuir-Blodgett (LB) technique is based on the manipulation of a monolayer condensed at the air-water interface and the transfer of it by dipping and raising a substrate through the interface (vertical dipping method). Thus, one can hardly miss the dynamic aspects of the technique. We have aimed at a quantitative approach to describe the in-plane anisotropy often seen in LB system in terms of a set of variables characterizing the deposition process.

In previous papers [1-6], we have presented an analytical model of in-plane anisotropy in LB films prepared using the vertical dipping method. The model is an effective medium theory referring to the flow of monolayer during the deposition process. The ideal-fluid approximation is employed for evaluating the velocity potential governing the motion of the monolayer, and the local thermal equilibrium approximation is introduced for examining the rotatory motion of a particle of elongated shape in this field. By these two approximations, the angular distribution is analytically derived [1,2].

The theoretical predictions for the case of one single substrate in a large trough agree well with the experimentally observed in-plane anisotropy of the mixed LB films of a merocyanine and a fatty acid, indicating the possibility of controlling the in-plane anisotropy [2-4]. The model is extended to the more complicated cases such as various types of batch production of LB films [5]. It has been found, however, that the predictions for the batch production are not always adequate for explaining the experimental results, showing that there are certain limitations of the present analytical approach[6].

In this report, we will discuss the prospect of applying the present analytical approach to the more complicated cases together with the theoretical grounds of the ideal fluid and the local equilibrium approximations.

1. N. Minari, K. Ikegami, S. Kuroda, K. Saito, M. Saito and M. Sugi, Solid State Commun. 65 (1988) 1259.
2. N. Minari, K. Ikegami, S. Kuroda, K. Saito, M. Saito and M. Sugi, J. Phys. Soc. Jpn. 58 (1989) 222.
3. S. Kuroda, K. Ikegami, K. Saito, M. Saito, M. Sugi, S. Suga and S. Yasui, Solid State Commun. 71 (1989) 333.
4. S. Kuroda, K. Ikegami, K. Saito, M. Saito and M. Sugi, Thin Solid Films 17
(1989) 555.
5. M. Sugi, N. Minari, K. Ikegami, S. Kuroda, K. Saito and M. Saito, Thin So
Films 178 (1989) 157.
6. Y. Tabe, K. Ikegami, S. Kuroda, K. Saito, M. Saito and M. Sugi, Appl. Phys. Lett. 57 (1990) 1191.

AP7

A NEW, NONDESTRUCTIVE, SIMPLE AND FAST METHOD TO VISUALIZE SUBMICRON DEFECTS IN LANGMUIR-BLODGETT FILMS

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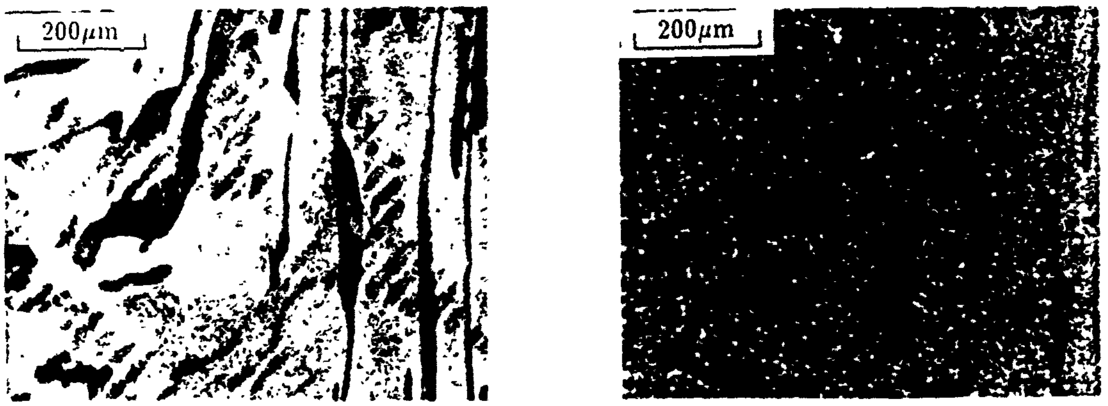
One of the problems with investigating defects in LB-films is, how to make them visible and convert the data into numbers within reasonable time and without introducing artefacts. Many methods give only indirect, averaged results, like cyclic voltammetry, conductivity measurements in metal-LB-metal structures or IR measurements. Some others, like electron microscopy, electroplating or selective etching require the control of many parameters to give meaningful results and are time consuming.

We want to add a new, very simple method to the light microscopy techniques. As is commonly known throughout the semiconductor industry, many defects on wafers can be monitored by looking at them under very bright (ideally short wavelength) illumination. This also is very efficient for LB-films, but gives very qualitative results only. What is surprising at the first glance is that many LB-samples, that look good and almost free of defects, when checked under a light microscope (with different methods), do show varying degrees of 'haze' when inspected by the above method.

We combined this bright illumination method and light microscopy by adding a fiber bundle illumination to the light sources of our microscope. The light from the fiber bundle hits the sample at a low angle under the microscope objective. Thus scattered light only, from this source, enters the microscope.

When this illumination is switched on, many more defects (if a defect is defined as a light scattering center) become visible. This works even while the normal illumination is still on or slightly reduced. In this way the relation of the scattering defects and other structures (*e.g.*, the birefrigent pattern in fatty acid films) can easily be found

Comparing the results qualitatively to electroplating we find that the defects, that are visible in normal illumination seem to be the large defects and the defects, that are added under bright side illumination correspond to the small defects there.



Photographs of the same area of a sample of a fatty acid film in conventional and in our new illumination technique.

AP8

QUASI TWO-DIMENSIONAL ORDER IN LB-FILMS

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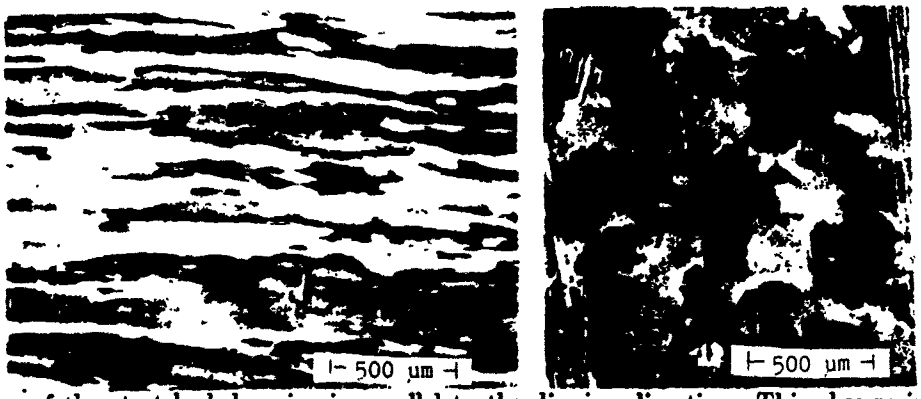
LB-films show, a priory, only a defined long range order in one dimension. For many applications, however, it would be desirable to have long range order in more dimensions. One way to get this is to grow 'single crystals' on the water surface and then trying to deposit these structures without distortion onto substrates, thus obtaining order in 3 dimensions. This last step, to deposit the ordered monolayers without further distortion, however, seems to be quite difficult, if not impossible.

We tried the opposite approach by using the dynamic flow characteristics of the films to order one more dimension. There are several publications about how film flow changes the properties of LB-films during deposition, but to our knowledge so far nobody tried first to orient the films by flow in a defined way and then deposit them.

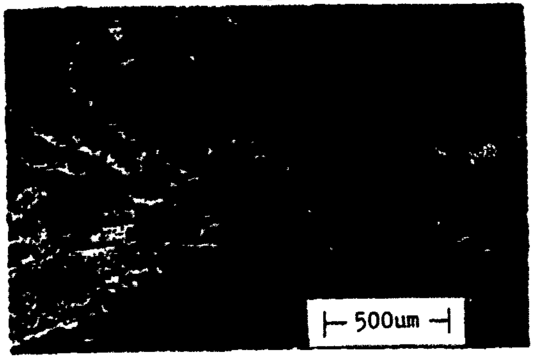
We used the well known technique of visualizing the birefringent domain structures in fatty acid films to see changes when the deposited film was subjected to flow before deposition.

The most simple way to do this is to use a long slide as a substrate, deposit some film on the lower portion of it, thus subjecting the film around the slide to flow and presumably flow orientation, and then depositing the preoriented film on the upper part of the same slide. To our surprise, the domain structure of the higher part looks very much different from the structure of the first part, where the film is not yet affected by flow. A typical structure is shown in the following picture.



Domain structure in a flow oriented(left) and regular fatty acid LB-film.

The long dimension of the stretched domains is parallel to the dipping direction. This change in structure is also reflected in other properties of the film, *e.g.* the light scattering is very unisotropic, as can be seen by naked eye when such a sample is rotated in a microscope while the illumination is on. We will report conditions for depositing such films and compare the properties to non oriented films. One immediate application of the high order in these films allows to visualize intentionally induced, single defects which can be found easily by the change in the otherwhise regular flow pattern. The following picture shows the structure that has been produced by touching the surface a very short time with a thin aspirator tip.



Structure around a defect that has been produced intentionally and allows to identify it under the microscope.

AP9

MONOLAYER STABILITY AND MULTILAYER FORMATION OF INSOLUBLE MONOLAYERS OF IONISING MATERIALS

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Despite much interest in Langmuir-Blodgett (LB) films because of their potential applications in devices, relatively little is understood about the factors controlling the stability of the floating monolayer and their successive transfer to solid substrates. Such factors may include the molecular structure of the film forming material, the nature of the solid substrate, deposition speed etc. Additionally, for ionisable materials such as alkyl carboxylic acids or alkyl amines, the pH and electrolyte content of the subphase solution are important variables. We have investigated the effects of these latter variables on monolayer stability and deposition for a range of ionisable materials. In particular, this talk will cover :

1. The effect of subphase pH on the stability of floating monolayers for a range of novel mono- and di-carboxylic acids, octadecylamine and copolymers of hexadec-1-ene/maleic anhydride containing either a di-acid or an acid-methyl ester in the repeat unit.

2. The composition with respect to ionisation of deposited multilayers of these materials has been determined using infra-red spectroscopy.

3. For one polymer system, the pH dependence of the ionisation in the multilayer will be compared with the pH dependence of the extent of divalent metal ion binding to the floating monolayer as determined using X ray reflectivity.

4. We have used a direct weighing method to determine the dynamic contact angle and the position dependent transfer ratio for the deposition of a range of these materials onto mica substrates. We will discuss these findings in relation to the degree of dissociation in the film and the resulting electrostatic and dispersion forces operating in the zone of contact between the transferring monolayer and the solid substrate.

Reference

R. Aveyard, B.P. Binks, N. Carr and A.W. Cross, Thin Solid Films, 188, 361 (1990).

AP10

MONO- AND MULTILAYERS MADE FROM DISCOTIC LIQUID CRYSTALS

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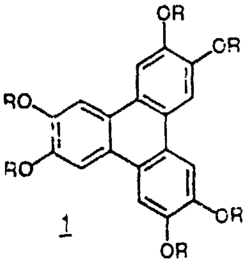
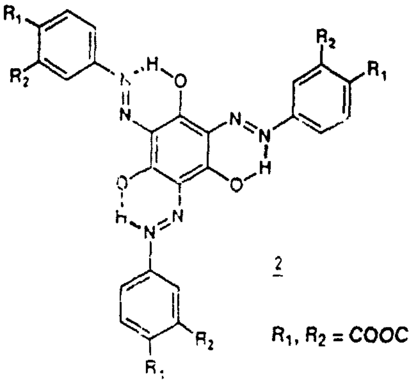
Some discotic liquid crystals (LCs) are known to form stable monolayers at the air water interface$^{1-5)}$. Depending on their chemical structure two different arrangements of the discs are possible, edge-on and side-on, which should crucially influence the mono- and multilayer behaviour$^{5)}$. Hence three different classes of discotic liquid crystals (1-3) bearing rigid cores of different polarity were studied, to examine their influence on mono- and multilayer properties.



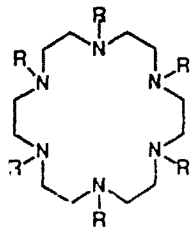
1

1a: $R=R'=R''=C_5H_{11}$
1b: $R=R'=C_5H_{11}$, $R''=(CH_2)_6OH$
1c: $R=C_5H_{11}$, $R'=R''=(CH_2)_6OH$

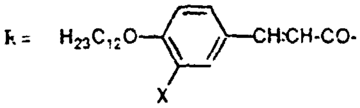


2

$R_1, R_2 = COOC_nH_{2n+1}$



3



It is found, that the rather unpolar triphenylenes 1 prefer monolayers of the edge-on type with rather small collapse pressures^1. Aggregation of the discs seems to result in floating columns of aromatic stacks. Monolayer stability is improved by various methods, the incorporation of hydrophilic groups into the side group region of the molecules (1b, 1c), or alternatively polymer fixation of triphenylene discotic LCs. Interestingly, electron rich triphenylenes such as 1 can be complexed with electron poor compounds such as trinitrofluorenone, to form mono- and multilayers of discotic electron donor-acceptor complexes. Such layers may be useful for photoconductive devices.

In contrast, the more polar classes of disc-like molecules such as azo discs 2 and acylated macrocyclic oligoamines 3 apparently form classical monolayers of side-on type. Due to the multiple, fixed polar groups, such monolayers are suited for selective complexation of various ions (e.g. ATP) from the subphase.

(1) O.Albrecht et al. Colloid&Polymer Sci. 264, 659 (1986)
(2) M.Vandevyver et al., J.chim.phys. 85, 385 (1988)
(3) C.Mertesdorf, H.Ringsdorf, Liquid Crystals 5, 1757 (1989)
(4) J.Malthete et al. J.Chem.Soc.Chem.Commun. 1061 (1989)
(5) A.Laschewsky, Angew.Chem.Adv.Mater. 101, 1606 (1989)

AP11

OPTIMIZING LB-MULTILAYER FILMS OF 2-DOCOSYLAMINO-5-NITROPYRIDINE FOR POTENTIAL APPLICATIONS IN NON-LINEAR AND INTEGRATED OPTICS

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INTRODUCTION

There has been growing interest in materials and thin film devices with second order non-linear optical properties for purposes such as high speed optical computing or optical communication [1,2].

2-Alkylamino-5-nitropyridines have recently been introduced for the preparation of a novel type of non-centrosymmetric Langmuir-Blodgett (LB) multilayer [3,4]. All present data indicate that LB-films of 2-alkylamino-5-nitropyridines are head-to-head and tail-to-tail (Y-type) multi-layers with a rather strong tilt-angle of the alkyl chains. The most effective substance for second order non-linear optical experiments is 2-docosylamino-5-nitropyridine (DCANP), where the square root of SH-intensity increases linearly with the layer thickness up to the micron range [3,4].

We have already demonstrated that the anisotropy with respect to the dipping direction, which is seen in second harmonic generation (SHG) [4] and in UV/Vis-spectroscopy [3,5], can be explained by a structure of the LB-film which consists of relatively small domains, that become preferentially aligned during the dipping process [5]. Recent results on optical waveguiding show that LB-films of DCANP [6,7] are interesting candidates for integrated optics.

RESULTS AND DISCUSSION

In order to understand the deposition process in more detail, we have recently studied the formation of a three-dimensional head-to-head phase of DCANP monolayers at the air/water-interface at surface pressures above 22 mN/m by UV/Vis-spectroscopy [8]. Upon comparison of these spectra with spectra of multilayer films, it was noticed that the multilayer spectra themselves were dependent on the type of film balance used for deposition. Some of the effects are that the spectra were influenced by the angle between the surface of the substrate and the front of the moving barrier. On the other hand spectra are independent of dipping speed only when the samples were deposited with a LAUDA FW1 film balance and not when a NIMA trough was used. Fig. 1 shows preliminary spectra of LB-multilayers of DCANP on quartz substrates, obtained with the NIMA film balance at diffrent deposition speeds. Although the differences in the spectra and therefore the changes in layer structure as well as the molecular mechanism of monolayer transfer leading to them are not yet understood, the present experiments further support that the orientation of the monolayer is induced at the three phase line, where the monolayer contacts the substrate. Currently we try to further optimize the structure of the LB-films by varying the dipping geometry.

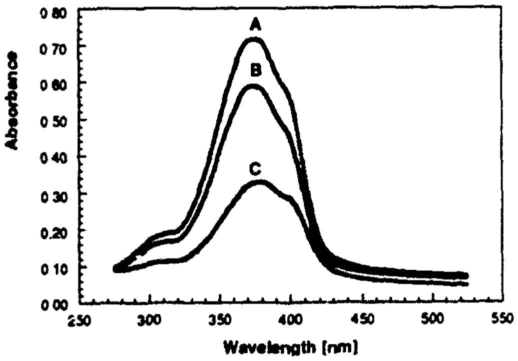

Figure 1. *UV/Vis-spectra of DCANP-multilayers on quartz substrates, deposited with the NIMA trough (A) parallel polarization; (B) perpendicular polarization; (C) parallel = perpendicular polarization; (A) & (B) at high deposition speed; (C) at low deposition speed. Layer numbers are not the same, please note the differences in anisotropy*

REFERENCES

[1] D. J. Williams
Angew. Chem., Int. Edn. Engl. 32 (1984), 690

[2] D. S. Chemla and J. Zyss (eds.)
"Nonlinear Optical Properties of Organic Molecules and Crystals"
Vols. 1 and 2, Academic Press, New York 1987

[3] G. Decher, B. Tieke, C. Bosshard and P. Günter
J. Chem. Soc. Chem. Commun. (1988), 933-934

[4] G. Decher, B. Tieke, C. Bosshard and P. Gü
Ferroelectrics 91 (1989), 193-207

[5] G. Decher et al.
Thin Solid Films178 (1989), 445-4

[6] G. Decher, B. Tieke, C. Bosshard and P. Günter
Eur. Pat. No.: 89 81 01 08 . 4- (1989)

[7] C. Bosshard et al.
Appl. Phys. Lett. 56 (1990), 1204-1206

[8] G. Decher and F. Klinkhammer
Proceedings of the ECOF '90 Conference
Makromolekulare Chemie, in press

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AP12

INTERACTIONS BETWEEN MONOLAYERS AND METAL IONS AT THE WATER/AIR INTERFACE
CONDITIONS FOR THE TRANSFERABILITY AS LB MULTILAYERS

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This work reports the results obtained in the study of the interactions of mono- and multicharged metal ions, introduced in the aqueous subphase, with monolayers of amphiphilic compounds spread at the liquid/air interface. This allows us to define the best conditions for the association or salt formation between monolayers and metal ions at the surface to be transferred and overlapped in order to prepare stable LB films containing metal ions. The following metal ions and amphiphilics are used : K^+, Cu^{2+}, Mn^{2+}, Cr^{3+} ; dihexadecylphosphate (DHP), single-chain fatty acids and their bidimensional mixtures with valinomicin. The last compound is a well known carrier of K^+ ions. The Cu-, Mn- and Cr- containing films are also characterized by ESR for their magnetic properties and the K- containing films for their properties as mimetic membrane selective to ions.

When copper alcanoate films are analyzed, both the spreading isotherms and the ESCA and ESR results ensure on the formation of a monolayer with Cu in dimeric form. However, homogeneous and regularly overlapped LB films can only be prepared when other dipositive ions (e.g. Ba^{2+}) are present in the aqueous subphase. The dimer formation results for the very difficult transferability of the film of the pure copper compound. The dominating factor in determining the LB film formation with Mn alcanoates is the pH of the aqueous subphase.

With DHP, a thorough analysis of the physical phases occuring in the monolayers was carried out by the spreading isotherms as a function of temperature pH and metal ion concentration.

ESCA spectra on mono- and multilayers of pure valinomicin or of its mixtures with stearic acid or with stearic acid methyl ester containing K^+ ions, indicate that a binding exists between K^+ and valinomicin itself when in a bidimensional mixture. This is further proved by FT-IR spectra of the same systems.

AP13

INTERACTION BETWEEN LANGMUIR MONOLAYERS AND HYDROPHILIC SOLID SUBSTRATES

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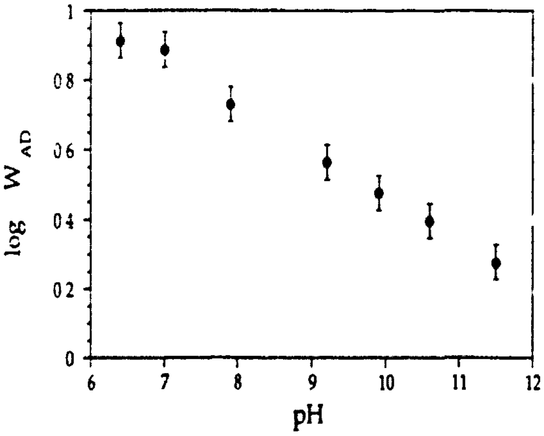
In a series of measurements the dependence of the adhesion energy from the properties of the lipid monolayer and the solid substrate surface has been investigated. In a typical Langmuir-Blodgett transfer configuration for the hydrophilic transfer of the first monolayer the adhesion energy was derived from the contact angle, which is related to the height of the meniscus. This height is measured by transfer fluorescence microscopy through the position of the three phase line, i.e. the line where the monolayer contacts the solid substrate.

The adhesion energy has been determined for a variety of different ions, ionic strengths, pHs in the subphase, and with different substrates. Thus for monolayers of dimyristoylphosphatidylethanolamine (DMPE) and dimyristoylphosphatidic acid (DMPA), the importance of the surface charge density has been evaluated. The negative headgroup charge of both, DMPE and DMPA monolayers increases with increasing subphase pH. This reduces the adhesion energy between DMPE and solid SiO_2-substrates, whereas the interaction between DMPA and the SiO_2-surface is constant in the pH-range investigated (pH6-12). The results can qualitatively be understood in terms of an electrostatic double layer interaction between equally charged surfaces. The experimental differences between DMPE and DMPA are readily predicted when taking into account the different charge densities for DMPE and DMPA. The validity of this interaction model is further tested by studying the adhesion between solid substrates and various lipid mixtures and uncharged monolayers. The adhesion is also affected by the surface roughness and hydration forces. Their influence is investigated by selective variations of the ion type and valence, and different solid surfaces.



log W_{AD} as function of pH for DMPE/SiO_2

AP14

PREPARATION AND MOLECULAR CONFORMATION IN LANGMUIR-BLODGETT FILMS FROM FLUORESCENTLY AMINE LABELED DIACYL PHOSPHATIDYLETHANOLAMINES

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For the first time LB films from dipalmitoyl-nitrobenzoxadiazol-phosphatidylethanolamine (DP-NBD-PE) and dimyristoyl-nitrobenzoxadiazol-phosphatidylethanolamine (DM-NBD-PE) were prepared. These substances were frequently used as staining dyes in fluorescence microscopy investigations of phospholipid films. This work supplies additional information for the interpretation of these data. LB films from these substances could be used for probing d.c. internal fields of similarly oriented molecular dipoles by Stark spectroscopy measurements e.g. in phospholipids.

The surface pressure (P) vs. mean molecular area (A) isotherm at a temperature (T) of 23°C for DM-NBD-PE is shown on Fig. 1 (left). Fluorescence microscopy studies show an ordered structure when deposition is carried out at P = 25 mN/m and T = 6°C. LB films from these compounds have a strong broad absorption band at 464 nm and a weaker ones at 332 nm and about 850 nm.

Small-angle X-ray diffraction at wavelength of 0.154 nm was performed on films from DP-NBD-PE deposited on silicone wafers substrates (Fig. 1, right). Samples were prepared at room temperature and parameters were calculated as follows: sample and curve A - vertical lift, P = 50 mN/m, 21 monolayers, hydrophilic substrate, bilayer distance (D) = 5.45 nm, correlation length in the normal direction (R) = 42 nm; B - horizontal lift without decompression, P = 43 mN/m, 12 touchings of the monolayer, hydrophobic substrate, D = 5.25 nm, R = 12 nm; C - vertical lift, P = 35 mN/m, 21 monolayers, hydrophilic substrate, D = 5.07 nm, R = 9 nm. Stark spectroscopy measurements support the conclusion for great disorder in case C. Molecular conformations with the additional information from molecular space filling models are discussed.

Thanks are due to Prof. A. G. Petrov for many helpful discussions and to Prof. E. Sackmann (TU Munich), Prof. Blinov, Prof. Feigin, Dr. Lvov (Inst. of Crystallography, Moscow), Dr. Savranskii (Inst. of General Physics, Moscow) for the possibility to work in their Laboratories. This project was supported under contract 587 with Bulg. Ministry of Science.

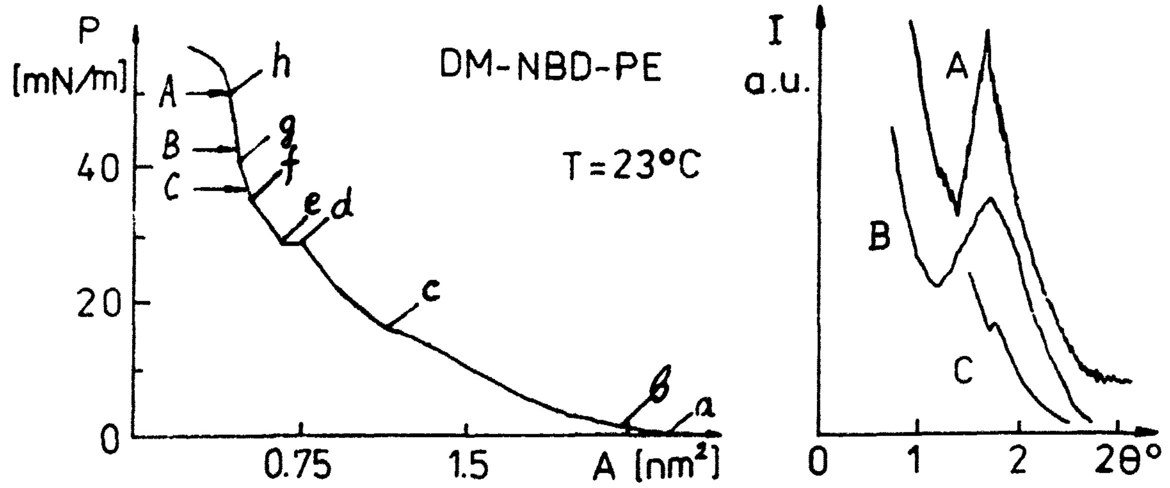

Fig. 1. P-A isotherm of a monolayer from DM-NBD-PE (left) and small-angle X-ray diffraction data of LB films from DP-NBD-PE (right). See the text.

AP15

THE EQUIPMENT FOR PREPARATIONS OF POLAR AND GETEROGENEOUS LB FILMS

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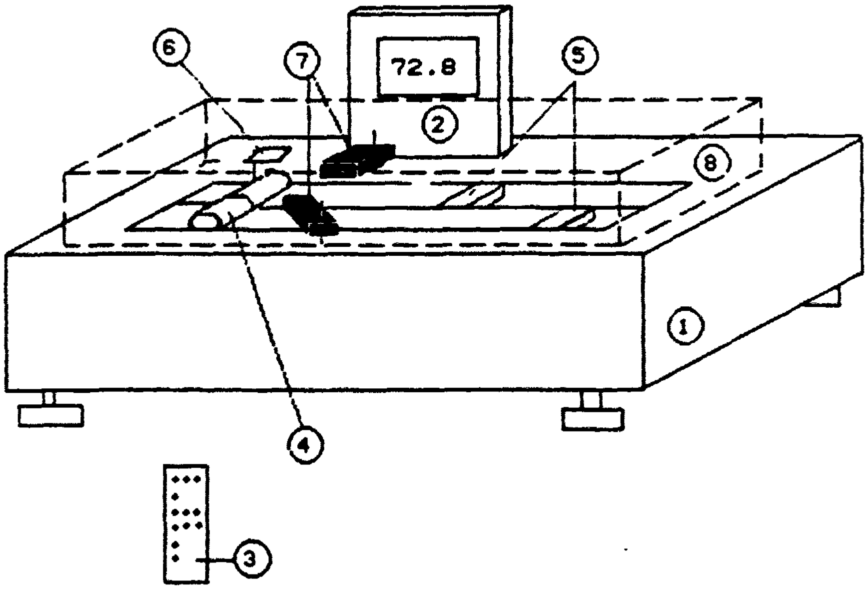
The equipment consists of two troughs and allows to prepare geterogeneous LB structures.

The system hardware offers experimental flexibility. Realy one can get noncentrosymmetric films both X- and Z-type in each of the trough. The two troughs are independent and the subphase in the troughs may be different.

A special mechanism is used to transfer the substrate from one trough to another.This mechanism also devide each of the trough on two sections with a single subphase. One of the section has a pure water surface. It is used to prepare the noncentresymmetric LB films.

The equipment is controlled by a microprocessor system. All proceses of the structure preparation can be monitored by IBM XT/AT computer using RS-232 C interface. The IBM PC-compatible software allows to make traditional invastigations (p-A isotherms) too.



1 - mainframe; 2 - microprocessor system; 3 - keyboard
4 - transfer mechanism; 5 - moving bariers; 6 - substrate;
7 - presure measuring sensors; 8 - box

AP16

TRANSFER RATIO IN LANGMUIR-BLODGETT FILMS: ROLE OF SURFACE CHARGE REGULATION

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A spread fatty acid monolayer at a water-air interface is charged owing to ionization of the carboxylic headgroups. At equilibrium, the dissociation and adsorption can be described by mass action formulas and the Poisson-Boltzmann equation for the electrical field in the adjoining ionic solution. These combine into Grahame's equation for the surface potential as a function of bulk concentrations of the soluble species. From the solution of Grahame's equation we calculate the surface potential, surface charge distribution, and concentrations of the adsorbed species at the monolayer-liquid and liquid-solid interfaces.

We picture monolayer deposition on the upstroke as the approach of two identical surfaces. The energy of interaction at each stage of the deposition process can then be calculated from the double-layer repulsion and estimates of the specific interactions, i.e., H-bonding, between the two surfaces.

The transfer ratio can be calculated on the hypothesis that it depends solely on the composition of the two surfaces, viz. the monolayer-liquid and liquid-solid interfaces, and on the interaction energy, as might be the case in slow depositions. The predictions agree to within 20% of the transfer ratio measured by Honig *et al.* (*J. Colloid Interface Sci.*,**45**, 92, 1973).

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Session BP

Monolayers at liquid-gas interface

BP1

X-RAY DIFFRACTION OF DIACETYLENE MONOLAYERS ON LIOH/WATER SUBSTRATES.

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The in-situ surface crystalline parameters of two diacetylene, 12-8 and 16-8 monolayers on a $LiOH/H_2O$ substrate, were measured by glancing incidence synchrotron x-ray diffraction. The monolayers were formed in an ultra-clean quartz trough by the addition method and further compressed by a pivot barrier. Diffraction scans were measured on non-polymerized and pre-polymerized monolayers. Surface pressure was monitored by Whilhelmy plate, which was then removed before polymerization and exposure to the x-ray beam. The monolayers were illuminated by low-angle (0.098° off of the surface plane) incident x-rays (7600eV, 1.63Å) from the NRL Materials Research Line, X-23B, at NSLS, Brookhaven National Laboratory.

The 12-8 diacetylene monolayer has a single peak corresponding to a d-spacing of 4.10Å for both the monomer and pre-polymerized sample. This is not in agreement with ex-situ electron diffraction results on supported films. The intensity for the pre-polymerized sample was greater than the monomer sample which hints at larger surface crystallites for the pre-polymerized sample. The lack of higher oreder peaks suggest a close packed hexagonal structure, however this is not expected for this sample.

The 16-8 diacetylene monolayer has several peaks for the pre-polymerized sample which correspond to a lattice 4.8Å by 10.3Å which compare favorably, in the direction of polymerization, with electron diffraction results. The cross-polymerization direction represents a stretch from the electron diffraction result of 8.11Å. Two possible explanations for this descrepancy are 1) the in-situ versus ex-situ nature of the two experiments. 2) a molecular tilt of the polymerized sample of 32° from the surface normal. The present resolution of the experiment can not distinguish between the two possible structures.

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3P2

MODELLING THE SURFACE POTENTIAL–AREA DEPENDENCE OF A STEARIC ACID MONOLAYER

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Abstract

Models have been proposed recently [1] for relating quantitatively the experimentally measured surface potential (ΔV) of monolayers at the air–water interface to the group dipole moments of the monolayer–forming molecules. To date, the models have been applied only to condensed monolayers because in the expanded phase of the monolayer, data have tended to be non–reproducible and little information is available on the orientation of molecules during the various stages of compression. Two recent experimental findings now make it possible to attempt a quantitative analysis of the ΔV–A curve:
(i) The fluctuations in ΔV in the expanded phase arise from island formation caused by trace impurities in the water surface [2]. These can be eliminated by adequate water purification.
(ii) The identification of a proton transport mechanism at the monolayer–water interface in monolayers compressed below a critical area per molecule probably indicates the formation of a hydrogen–bonded network between the monolayer headgroups and adjacent water molecules. The formation of such network would lead to a dramatic decrease in the local dielectric constant at the monolayer/water interface. By considering the monolayer as a three–layer capacitor following the Demchak and Fort [3] approach and making reasonable assumptions concerning the local permittivities and allowing for changes in double–layer potential during film compression, it is shown that the main contribution to ΔV for stearic acid is from the headgroup dipoles, all other contributions tending to cancel. The steep rise in the surface potential which is observed experimentally at *ca* 0.39 nm^2 reflects the rapid decrease in the dielectric constant of the water–headgroup interface from 78 in a fully expanded monolayer to 6.4 in a fully condensed monolayer.

References

[1] D.M.Taylor, O.N.Oliveira Jr. and H.Morgan, *J.Coll. and Interface Sci.* in press
[2] D.M.Taylor, O.N.Oliveira Jr. and H.Morgan, *Thin Solid Films*, 173 (1989) L141
[3] R.J Demchak and T.J.Fort Jr., *J.Coll. and Interface Sci.*, 46 (1974) 191

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BP3

The "Time of Observation" of π-A Isotherms III. Studies on the Morphology of Arachidic Acid Monolayers, Observed by Transmission Electron Microscopy of Replica Samples of One-Layer LB Films.

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Insoluble monolayers at the air/water interface are the viscoelastic bodies and it is necessary to consider a characteristic time to measure mechanical properties of them. π-A isotherms of monolayers are not the thermodynamical quantities but the dynamic or time-dependent mechanical properties. In this context, π-A isotherms also require definition of the characteristic time of measurement. This is the "time of observation". The "time of observation" of π-A isotherms is defined by the reciprocal of the strain rate of compression of monolayers.[1] Therefore, a monolayer should be compressed under a constant strain rate to measure a π-A isotherm under a constant time of observation. The shape of a π-A isotherm is governed by the balance of the relaxation times of molecular motions in a monolayer which occur during compression and the time of observation. The surface pressure detected under compression is given by the superposition of a series of partially relaxed pressures up to that instance. We have shown that the shape of π-A isotherms of arachidic acid monolayers changed drastically by changing the time of observation widely and systematically even at a constant temperature as if we change the film material.[1]

Tanaka and his coworkers have reported a novel replica technique for preparing samples of TEM observation using plasma polymerization of a hydrocarbon vapor, such as naphthalene as a monomer under specialized conditions of glow discharge.[2] Iriyama et al. have reported application of this technique to the observation of LB films by TEM and found some new features of LB films of merocyanine dye, micro-pores, local collapse at the pressure under ESP, thermally induced phase separation in mixed monolayers of dye-surfactant and fatty acid.[3]

The object of this paper is to correlate molecular states of film molecules and phase changes estimated from the π-A isotherms of arachidic acid monolayers measured by changing the time of observation widely and systematically with those estimated from the TEM observation of one-layer LB films of arachidic acid deposited at every stage of π-A isotherms using the novel replica technique described above.

1)T.Kato, **Langmuir**, 6(4),870(1990), T.Kato, et al., Langmuir,(submitted,'90.12).
2)A.Tanaka, et al.,**Chem.Lett.**,1989,1219.
3)K.Iriyama, et al.,**Chem.Lett.**,1990, 855, 859, 1189, 1365, 1892.

BP4

Surface Modes on Polymer Solution
by
Surface Light Scattering Techniques

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ABSTRACT

Liquid interfaces are constantly being deformed by thermal motion in the form of waves. For the simple liquids, these waves are typically of small amplitude (~ 10 Å) with wavelength (~ $100 \mu m$) and propagate as capillary waves called ripplons. The propagation of waves is controlled by the surface tension and its temporal damping by the liquid viscosity.

The surface modes on simple pure liquids have been studied by many reseachers and are well understood. The viscosity in this case is a constant and the surface waves are simply the capillary waves. The resonant frequency of the surface waves ω_k is proportional to $k^{3/2}$.

In a polymer solution, in addition to a frequency dependent viscosity, the solution has a nonzero, frequency dependent shear modulus. In such a viscoelastic polymer solution, it has been shown theoretically that several types of surface modes can exist.[1] These surface modes include Reyleigh elastic waves (resonant frequency of the surface waves $\omega_k \propto k$), capillary waves (resonant frequency $\omega_k \propto k^{3/2}$), and overdamped modes depending on the concentrations of polymer solutions and wavenumbers.

In this paper, we present the first direct experimental measurements on the surface modes on the polymer solutions of poly iso-butylene/decane, using the surface heterodyne light scattering techniques. The experimental results is compared with the existing theory.[1]

1. J.L. Harden, H. Pleiner, and P.A. Pincus, *Langmuir* 5(6), 1436 (1989)

BP5

DETECTION OF THE OPTICAL MOLECULAR SWITCHING IN MONOLAYERS BY THE DISPLACEMENT CURRENT MEASUREMENT

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The reversible *cis-trans* photoisomerization of azobenzene offers potential applications such as data storage media. In this work, we firstly succeeded in the detection of the optical molecular switching in monolayers at the air-water interface by using a new experimental system developed on the basis of the displacement current measurement[1-5]. In the measuring system, displacement current was found to flow through the external short circuit only when UV or visible light was applied to the monolayer at the air-water interface; that is, the displacement current was generated due to the *trans*-to-*cis* photoisomerization of the azobenzene derivative by irradiation with UV light, whereas the displacement current was generated in the opposite direction due to the *cis*-to-*trans* photoisomerization by irradiation with visible light. The reversible current generation was found to be sustained by the repeated applications of UV light and of visible light, whereas the current was never generated by the successive irradiation with visible light. Finally, we concluded that the *cis-trans* photoisomerization in monolayers is able to be detected by the displacement current measurement and that the measuring system developed here will be useful as a prototype of detection systems of molecular switching in the field of molecular electronics .

References

1. M.Iwamoto and Y.Majima, Jpn. J. Appl. Phys., *27*(1988)721.
2. M.Iwamoto and Y.Majima, Jpn. J. Appl. Phys., *28*(1989)1922.
3. M.Iwamoto and Y.Majima, Thin Solid Films, *178*(1989)67.
4. Y.Majima and M.Iwamoto, Jpn. J. Appl. Phys., *29*(1990)564.
5. Y.Majima, A.Watanabe and M.Iwamoto, accepted for publication in Jpn. J. Appl. Phys.

BP6

Quantitative Evaluation of the Dynamic Characteristics of Phospholipid Monolayer

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Though there have been many reports on the surface pressure-area isotherms for amphiphile monolayers supported at a liquid-vaper phase, little attention has been paid for the dynamic property of the monolayers. It is well-known that almost all of the monolayers exhibit different pressure-area curves between the processes of compression and expansion.

In the presents paper, we will describe a new strategy to evaluate the dynamic behavior of the monolayer in a quantitative manner. We have constructed a new experimental system to measure the dynamic pressure-area characteristics, which is composed with a trough with couple of moving barriers and with a Wilhelmy plate attached to an electrical balance. The time trace of the movement of the barriers could be controlled to a desired function with a micro-computer. The surface pressure has been continuously stored in the computer. The observed dynamic surface pressure-area curve has been separated into the elastic and viscositic components. These terms have been evaluated using expansion to polynomials. The nonlinear properties of the monolayer was, thus, analyzed in a quantitative manner.

We have performed the measurements and analysis for various phospholipid molecules, such as, dioleoyllecitin(DOPC) and phosphatidylethanolammine(DPPE). It has been found that inorganic salts change the nonlinear viscoelasticity of the monolayer markedly. This results is quite interesting, because it is known that quasistatic pressure-area curve of the monolayer of phospholipids exhibits negligible effects by the inorganic salts in the subphase. These results will be discussed in relation to the oscillatory phenomena of lipid monolayer.

[REFERENCES] (1)J.Am Chem Soc.,106,4423(1984). (2)Langmuir,4,759(1988).
(3)Chem.Phys Lett.,160,623(1989). (4)Biochem.Biophys.Res.Comm.,160,699(1989).
(5)Nippon Kagaku Kaishi, 10,1143(1990) (Japanese).

BP7

A LIVING MONOLAYER OF LIPID SHOWING WELL-REGULATED DISPLACEMENT CURRENT GENERATION

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The structure and function of the mono- and multilayer have been the subject of continuous studies since the discoveries by Langmuir and Blodgett. Excitability is one of the most important properties of cell membranes. To our knowledge, however, there was no appropriate technique used to study the dynamic behavior of amphiphilic molecules in a purposely controlled artificial membrane system. Recently, Iwamoto and Majima developed a new displacement current-measuring technique coupled with a technique originally developed by Langmuir. It was found theoretically and experimentally that displacement current is generated only when the electric flux falling on an electrode suspended in air is changed with respect to time. A monolayer of L-α-dioleoyllecithin (DOL) showed reversible current generation in the so-called gas phase just before the initial rise of its surface pressure by the application of the reversible change of the monolayer-covering area on the surface of distilled water (pH 5.8), although a rigid monolayer of L-α-distearoyllecithin did not show any reversible current generation. These experimental results seem to support our discovery, where the behavior of surface pressure-area isotherm of a DOL monolayer was reversible along with the increase and decrease of the monolayer covering-area. Finally, the surface micro-structure of a DOL monolayer system at various two-dimensional molecular densities was also visualized by using a new replica technique coupled with transmission electron microscopy, which was originally developed by Tanaka et al. From the electron microscopic observation, we concluded that the current generation is ascribed to a gas/liquid phase transition.

As described above, we found for the first time the reversible current generation in the planned artificially prepared molecular film and then concluded that the periodic electric oscillation of a lipid monolayer is able to be controlled under the well-controlled conditions. The reversible displacement current generation was also theoretically analyzed in relation with the dynamic behavior of DOL molecules.

BP8

INVESTIGATION OF MOLECULAR LAYERS ON A LIQUID SURFACE WITH LIGHT SCATTERING

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An experimental installation was constructed for studying monolayer morphology of amphyphilic molecules on the water surface. Integral intensity of light scattered by monolayer inhomogeneities was measured during scanning of the sample surface by a laser beam. One can obtain surface distribution of various defects (dust and aggregated particles, collapse regions) in the molecular layers and also the dynamics of defects creation under surface pressure. Monolayers of stearic acid (HSt) , four-substitutional phtalocyanine (4R-Pc) and bacteriorhodopsin (BR) were investigated.

At low surface pressure for HSt and 4R-Pc monolayers unstable positioned scattering intensity peaks were usually observed; scattered light background was practically absent. The peaks observed were due to light scattering by Brownian moving microparticles (dust, big aggregates etc). Surface pressure increase resulted in fixation of peak positions and in rise of background in their vicinity. It evidences for microparticles being nuclei of monolayer collapse regions. These regions were distributed inhomogeneously over the monolayer surface; in particular there were more of them near the movable barrier.

For BR monolayers consisting of purple membrane (PM) fragments (thickness ~ 50 Å, linear dimensions 0.1 – 0.5 μm) the picture observed was quite different. Presence of scattering centres each less then the wavelength resulted in a background. It should be noted that scattering by BR monolayers of very low surface concentration (1 to 2 orders of magnitude less than that for close packing case) was registered. Study of background intensity vs BR concentration enables one to find out the PM fragments aggregation process. Moreover, when BR concentration increased the regions with low scattering intensity were observed. They emerged when PM fragments were approaching each other forming a continuous BR monolayer.

BP9

MONOLAYERS OF SOME PYRAMIDIC LIQUID CRYSTALS ON WATER SUBPHASE.

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Numerous molecules forming thermotropic liquid crystalline phases compose a less known class of amphiphilic molecules compared to the classical ones. There have been few attempts to spread such molecules at the air-water interface. The first report was made by Dörfler *et al* . [1], in which calamitic molecules, forming nematic mesophase in bulk, have been spread at the air-water interface. Rondelez *et al* . [2] and Albrecht *et al* . [3] studied discotic-like-molecules on water subphase.

We have used a recent class of compounds [4,5] showing mesomorphic phases, synthetized in 1984 and called pyramidic by Zimmermann *et al.* [4]. The studies, in bulk, on some of these compounds have led to the discovery of five columnar mesophases. Our study deals with two pyramidic liquid crystals : Hexa-nonanoyl-oxytribenzo-cyclononene (I-n9) and Hexa-nonyl-oxytribenzo-cyclononene (II-n9). These compounds, present a rigid pyramidical central core and six equal flexible side chains symmetrically bound at the pyramidic base. They were spread at the air-water interface, and their ability to form monomolecular layers has been prooved.

The surface pressure-molecular area isotherms obtained at 21° C and pH = 5.7, show a large plateau then a sharp increase of surface pressure above 66 Å^2 and 61Å^2, for I-n9 and II-n9 respectively, in agreement with the calculated value of the pyramidic base (61 Å^2). Hysterisis diagrams confirm that these compounds form monolayers at the air-water interface. At pH = 13, isotherm shows important changes except for the values at the condensed state areas.

The results indicate that the pyramid base lies at the interface with its top towards the subphase and the aliphatic chains perpendicular to the air-water interface at the condensed state area.

1- H.D. Dörfler, W. Kercher and H. Sackmann, J. Phys. Chem. 251, 314 (1972).
2- F. Rondelez, D. Koppel, J. Physique, 43, 1371 (1982).
3- O. Albrecht, W. Cumming, W. Kreuder, A. Laschewewsky and H. Ringsdorf, Colloid and polymer Science, 264, 659 (1986).
4- H. Zimmermann, R. Poupko, Z. Luz and J. Billard, Z. Naturforsch. 40a, 149 (1985).
5- J. Malthête, A. Collet, Nouv. J. Chimie, 9, 151 (1985)

BP10

CAPILLARY WAVES:
A NEW MONOLAYER CHARACTERIZATION TECHNIQUE USING AN OLD METHOD

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Capillary waves have been used to study the properties of monolayers on water. In all the studies that appeared so far however, none has dealt with the non-uniformity of the monolayer. We have therefore initiated a series of studies aiming at the development of a capillary wave probe as a viable monolayer characterization technique.

We have built and used a capillary wave probe to characterize local as well as anisotropic mechanical properties of monolayers on water. The probe is based on the non-intrusive technique in which capillary waves are generated electrostatically and detected by a laser light[1].

We first demonstrated its utility by showing extreme stress inhomogeneity and anisotropy in stiff monolayers under a uniaxial compression.[2] An example is shown in Fig.1. It clearly demonstrates how the applied pressure at the compression barrier fails to be transmitted to other parts in the monolayer.

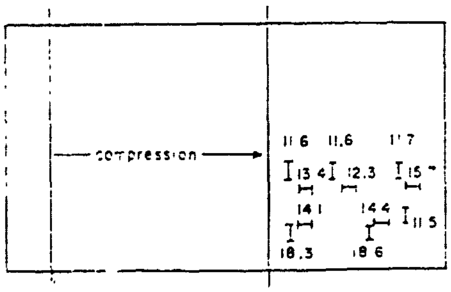

Fig.1: Inhomogeneous and anisotropic surface pressure.

As a first attempt to establish the consequence of the morphological inhomogeneity of the monolayer on the wave propagation, measurements were done simultaneously with a fluorescence microscope observation. In films in the liquid-gas coexistence phase, we found that the effect of the liquid phase on the capillary wave propagation was nearly zero up to the point where the film coverage was 95%, a result not trivial at all. We are currently studying the gas-solid coexisting monolayers.

1) C.H. Sohl, K. Miyano, and J.B. Ketterson; Rev. Sci. Instrum. 49, 1464 (1979).

2) K. Miyano; Langmuir 6, 1254 (1990).

BP11

Effect of Thermal Treatment on Crystal Growth of Surface Monolayer

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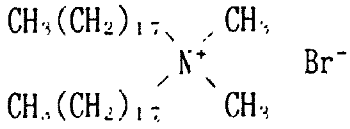
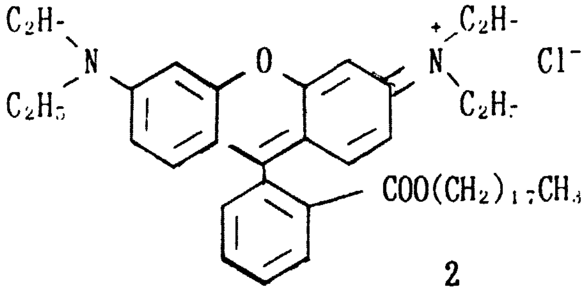
Direct observation of the monomolecular film at the air-water interface is essential to the manipulation of the monolayer and should provide well designed Langmuir-Blodgett films. An *in-situ* observation of the surface monolayer by fluorescence microscopy is a powerful technique as well as reflection spectroscopy of the interface. In this paper, we report construction of a novel fluorescence microscope equipped with a large scale Langmuir trough having a flat panel heater for thermal treatment of the surface monolayer.

In order to survey over a wide area of the water surface, a fluorescence microscope is attached to a microprocessor controlled X-Y-Z stage. Position and moving speeds of the microscope are manipulated by a joy-stick. Focus of the microscope is adjusted by the stepping motor with a resolution of 0.2μm. Excitation light from various light sources at the outside is introduced into an all quartz optics through a quartz fiber. A flat panel heater(15cm x 30cm) for the thermal treatment is placed above water surface. Distance between the heater and the water surface is changeable. Morphological change during thermal treatment is recorded through a small hole in the center of the heater.

Dark crystalline patches in the bright field of the fluid monolayer of double-chain ammonium amphiphile 1 containing 2 mol% of octadecylrhodamine 2 as a fluorescence probe were formed when the monolayer was compressed[1].



1



2

Temperature of the water surface rose up to 45℃ within three minutes when the gap between the heater and the water surface was 5mm. During the thermal treatment at an iso-pressure condition, the crystalline patches disappeared. After cooling down to 20℃, the crystal size grew several times larger than the untreated crystals.

1)M.Shimomura, et al., *Jap. J. Appl. Phys.*, 27, L1761(1988).

BP12

DETECTION OF THE DYNAMIC BEHAVIOR OF MONOLAYERS AT THE AIR-WATER INTERFACE BY THE DEVELOPED DISPLACEMENT CURRENT MEASUREMET

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The structure and function of mono- and multilayer have been the subject of continuous studies since the discoveries by Langmuir and Blodgett. Recently, there has been much interest in the manufacture of the so-called molecular electronic device, where motion of electrons and orientational change of polar molecules in artificial mono- and multilayer systems are assumed to be purposely controlled[1]. Therefore it is required to develop a technique used to detect electron transfer and orientational change of polar molecules in the planned artificially monolayers for a better understanding of the relationship between the structure and function of the monolayers as well as for the manufacture of the molecular electronic device. The technique based on the displacement current measurement seems to satisfy the requirement[2,3], because the dynamic motion of constituent polar molecules in monolayers is able to be detected without destroying the monolayers. In previous reports[4-6], we developed a displacement current-measuring system used for the investigation of monolayers at tne air-water interface. Recently, we have improved the system. At the present stage, we can obtain current-area isotherms with high precision. In this work, we investigated monolayers of fatty acids and of precursor films of polyimide formed on the water subphase, e.g., on the surfaces of pure water and of salt solutions containing Cd^{2+} or Al^{3+} ions, by the displacement current-measuring technique, where displacement current was generated only when the monolayer-covering area was changed. Subsequently, we determined the vertical component of dipole moment of the constituent molecules of monolayers. It was concluded that the dynamic behavior of monolayers formed on the water surface was able to be detected in the entire range from the so-called gaseous phase to the solid phase with high precision. Finally, the mechanism on the current generation observed in the present current measurement was theoretically analyzed.

References

1. E.G.Wilson, Electron. Letter, 19(1983)237.
2. M.Iwamoto and Y.Majima, Jpn. J. Appl. Phys., 28 (1988) 721.
3. M.Iwamoto and T.Sasaki, Jpn. J. Appl. Phys., 29(1990) 536.
4. M.Iwamoto and Y.Majima, Thin Sclid Films, 178(1989)67.
5. Y.Majima and M.Iwamoto, Jpn. J. Appl. Phys., 29(1990) 564.
6. Y.Majima, A.Watanabe and M.Iwamoto, Jpn. J. Appl. Phys., in the press.

BP13

BIDIMENSIONAL MIXTURES OF BIOLOGICAL LIPIDS AT THE AIR-WATER INTERFACE

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As it is known, the monolayer at the air-water interface is the simplest model of biological membranes and its study is very useful because it provides information about the orientation of the molecules and the compatibility of different amphiphilics at the interface.

Spreading monolayers of Ceramide (CER) and Dioleoylphosphatidylcholine (DOPC), as pure compounds and in mixtures, were studied at the air-water interface using two different subphases, containing NaCl 0.1 M (pH 5.6) and a phosphate buffer (pH 7) respectively, in the 15-30 °C range.

These lipids were chosen for their biological interest as components of natural membranes.

We studied the mutual miscibility of these lipids by applying the bidimensional phase rule at the collapse pressure. Furthermore, we determined both the excess free energy of mixing ΔG_{mix}, and the enthalpic and entropic contributions (ΔH_{mix} and ΔS_{mix}) to the interphasal miscibility.

We verified the surface compatibility of DOPC and CER at all the temperatures, either using the Na^+ containing subphase or the buffered subphase.

BP14

THEORETICAL CONTRIBUTION TO ISOTHERM OF SPREAD MONOLAYER

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The study of monolayer on water surface is of significance with regard to assembling technology at molecular level, natural multi-component system researches, etc. The monolayer considered as surface phase in which the water and a monolayer-forming component (solute) form a two-dimensional ideal solution was described by Fowkes[1]. Following this study, the present work is devoted to apply Gibbs-Duhem equation to 2D ideal solutions, give strictly deduced isotherms and calculate the change in free energy for compression process of such system.

For one solute and at constant temperature, the Gibbs-Duhem equation for the surface phase[2] becomes

$$A\,d\gamma + n_1\,d\mu_1 + n_2\,d\mu_2 = 0 \qquad \text{--------(1)}$$

(1 denoting the water and 2 denoting the solute). We may write

$$d\gamma = -\,d\pi\,,\quad d\mu_1 = 0,\quad d\mu_2 = -\,A_2\,d\gamma - RT\,dA \,/\, (A - n_2A_2 + n_2A_1)$$

where A is the total surface area and A_1 and A_2 are the molar areas of water and solute respectively. Substituting these results to Eq. (1) gives

$$d\pi = -\,n_2RT\,dA \,/\, (A - n_2A_2)(A - n_2A_2 + n_2A_1)$$

$$\pi = (RT \,/\, A_1)\ln((A - n_2A_2 + n_2A_1) \,/\, (A - n_2A_2)) \qquad \text{--------(2)}$$

The change in free energy during the compression process is given by

$$\Delta G = -\,W(\text{non-pv}) = -\int_{n_1A_1+n_2A_2}^{n_1'A_1+n_2A_2} \pi\,dA = -\,RT\ln\left(\frac{n_1}{n_1+n_2}\right)^{n_1}\left(\frac{n_1'+n_2}{n_1+n_2}\right)^{n_2}\left(\frac{n_1'+n_2}{n_1'}\right)^{n_1'} \qquad \text{--------(3)}$$

Where n_1' is the molar number of the water remaining in the surface phase during the compression. If the water is squeezed out completely ($n_1' \longrightarrow 0$), $\Delta G = -\,RT(n_1\ln X_1 + n_2\ln X_2)$.

The method described above can be extended to a 2D ideal solution containing more than one solutes. If there exist the water and (n-1) kinds of solutes in the system, the surface pressure can be evaluated from

$$\pi = \frac{RT}{A_1}\ln\frac{A - \sum_{i=2}^{n} n_iA_i + A_1\sum_{i=2}^{n} n_i}{A - \sum_{i=2}^{n} n_iA_i} \qquad \text{--------(4)}$$

The change in free energy associated with compression process is given by

$$\Delta G = -\,RT\ln\left(\frac{n_1}{\sum_{i=1}^{n} n_i}\right)^{n_1}\left(\frac{n_1'+\sum_{i=2}^{n} n_i}{\sum_{i=1}^{n} n_i}\right)^{\sum_{i=2}^{n} n_i}\left(\frac{n_1'+\sum_{i=2}^{n} n_i}{n_1'}\right)^{n_1'} \qquad \text{--------(5)}$$

When $n_1' \longrightarrow 0$, we have

$$\Delta G = -\,RT(n_1\ln X_1 + \sum_{i=2}^{n} n_i \ln \sum_{i=2}^{n} X_i).$$

Reference:

1. F.M.Fowkes, J. Phys. Chem., 66, (1962), 385
2. E.A.Guggenheim, "thermodynamics" 3rd., North Holland Publishing Co., Amsterdam, (1957)

BP15

MONOLAYERS OF BRANCHED CHAIN PHOSPHOLIPIDS

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Phosphatidylcholines containing a branched chain fatty acid at the sn-1 position or at the sn-2 position or at both sn-1 and sn-2 positions of the glycerol backbone were characterized by calorimetric and X-ray diffraction studies with bilayers as well as by thermodynamic studies with monolayers.

The monobranched PCs investigated are mixed-linkage species containing both ester- and ether-linked chains. The replacement of the ester linkage with an ether linkage has only a little effect on the phase transition properties. Branching leads to altered thermal properties which are connected with a modified structural polymorphism. Gel phases with interdigitated chains could be found. Such an arrangement cannot be realized in the monolayer. The question arises of wether how will be the structure of the monolayer in such cases.

All of the branched chain lipids investigated form stable monolayers at the air/water interface with isotherms of qualitatively similar shapes as those of non-branched lipids. The area required by a hydrocarbon chain in the condensed phase was estimated and compared with the area per chain in the corresponding bilayer systems. The pressure-area isotherms were measured over a wide range of temperature. The critical temperatures T_c of the transition between the liquid- expanded and the condensed films were estimated and compared with the main-transition (gel-to-liquid-crystalline) temperatures T_m of the bulk phase. T_c was found to be either lower or higher or equal to T_m. The correlations between T_c and T_m are discussed in terms of chain packing in the two- and three-dimensional systems.

BP16

LB FILMS OF ARCHAEBACTERIAL LIPID MODELS: 1,1'-POLYMETHYLENEBIS(2-ALKYL-sn-GLYCERO-3-PHOSPHOCHOLINE)

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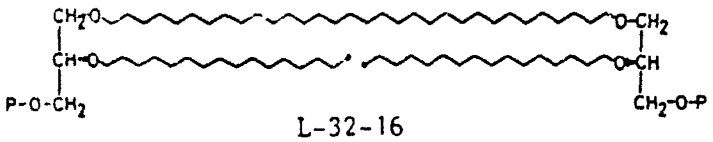
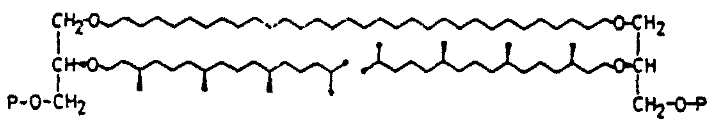
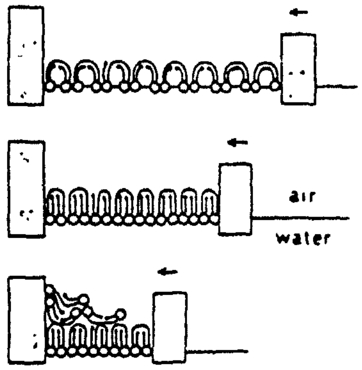
Plasma membrane lipids of archaebacteria are often characterized by their structure, having long isoprenoid chains bound through ether linkages to two polar heads. The bipolar lipids have attracted biotechnological interest as potential materials for thermostable membranes. This paper deals with LB-membranes of archaebacterial lipid models, 1,1'-polymethylenebis(2-alkyl-sn-glycero-3-phosphocholine) (L-32-16, L-32-Phy, etc.).



L-32-16

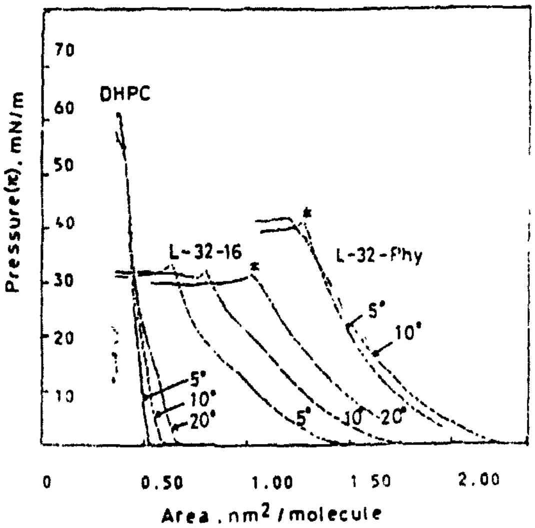


L-32-Phy



The bipolar lipids exhibited peculiar surface pressure(π)-surface area isotherms in comparison with that unipolar 1,2-dihexadecyl-sn-glycero-3-phosphocholine (DHPC). Namely, DHPC formed a stable LB membrane which collapsed only at a lateral pressure as high as 57-63 mN/m. The limiting area occupied by the molecule was about 50 Å^2. By contrast, L-32-16 and L-32-Phy did not show a highly cooperative compression. In addition, it appeared that their LB membranes were compressed, without collapse, maintaining constant pressure as seen from a point * in the π-A curves. The limiting areas and the maximum collapsing pressure were: L-32-16, 90-150 Å^2 and 31-33 mN/m; L-32-Phy, 160-180 Å^2 and 39-42 mN/m.

The results will be discussed in conjunction with a bending structure (U-form) of the bipolar lipids and the bending force for the polymethylene chains.



BP17

A LANGMUIR-BLODGETT MONOLAYER WITH A CONTROLLABLE DEGREE OF POLARITY.

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The main object of this study has been to obtain a molecularly smooth monolayer with a controllable density of carboxylic acid groups, deposited onto muscovite mica. These surfaces could then be used as model surfaces, for example in the Surface Force Apparatus of Israelachvili.

Using three different molecules, docosanedioic acid (DDA; $HOOC-C_{20}H_{40}-COOH$), arachidic acid (AA; $C_{19}H_{39}-COOH$), and eicosylamine (EA; $C_{20}H_{41}-NH_2$), two different series of mixed monolayers have been studied (see figure).

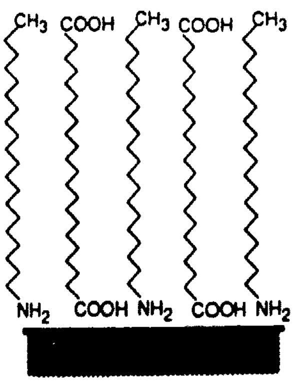
Series #1 consists of monolayers of DDA and EA in different proportions, while in series #2 the monolayers are made up from mixtures of all the three molecules DDA, AA, and EA. In series #2, the ratio (DDA+AA)/(EA) is always unity, and the DDA:AA ratio is varied. In both of these series it is possible to control the carboxylic acid group density on the surface.

The advantage of using mixed monolayers is that the amine and acid molecules fix each other to the water surface by their mutual attraction, thereby stabilizing the spread monolayer. This is evident from relaxation studies of monolayers held at a constant pressure.

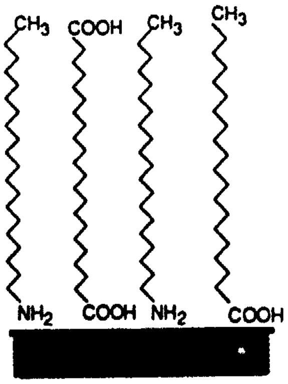
The pressure-area isotherms of series #2 are of the condensed type with a limiting area/molecule of about 20 Å^2. This indicates that the structure on the water surface indeed is the one depicted in the figure. The isotherms of series #1 show a more complex behavior, where the shape depends on the DDA ratio. However, at DDA ratios between about 40 and 70 % the isotherms are of the condensed type. In all cases the transfer ratio is near unity, so the molecular orientation in the deposited layer can be assumed to be the same as in the spread film.

As can be expected, the advancing contact angle decreases with increasing DDA ratio.

An interesting observation is that Z layers can be obtained with the series #1 monolayers, at DDA ratios of about 60-70 %. This is presumably due to the water adsorption onto the polar carboxylic groups, minimizing the deposition on immersion.



Example of a series #1 surface, with a DDA ratio of 40 %.



Example of a series #2 surface, with a DDA ratio of 25 %.

BP18

POLYMERIC GEGENIONS INDUCED VARIABILITY AND MOBILITY OF AMPHIPHILIC SUPRAMOLECULAR STRUCTURES AT THE AIR/WATER-INTERFACE AND ON SOLID SUBSTRATES

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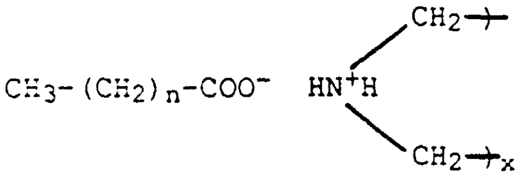
The influence of watersoluble polymers on the micromorphologies of amphiphatic supramolecular structures was examined by fluorescence microscopy at the air/water-interface[1] and on solid substrates. Due to the interaction of polymeric gegenions, the isothermal behaviour of fatty acids at the air/water-interface was altered drastically: The polymer-



n = 12, 14, 16, 18, 20

fatty acid interaction induces the fluid/solid phase transition of different long chain fatty acids at room temperature as was studied by surface pressure/area diagrams. The condensation process of the complexed monolayers at the air/water-interface and the domain formation within the "two-phase" region, was investigated by fluorescence microscopy[2,3]. The dependence of these surface textures on temperature, surface pressure, chain length of the fatty acid and concentration of the polymeric gegenions in the subphase were examined by this method. Due to the stabilisation by the polymeric gegenions, fatty acid monolayers can be transfered by LB-technique to solid supports even from very expanded states without damaging the observed surface texture. Moreover the morphology of these polymer stabilized monolayers on solid supports can be altered, e.g. by annealing This unique variability or mobility of the monolayers at the air/substrate-interface is attributed to the adjacent polymer matrix and was examined by fluorescence microscopy.

References

(1) H. Mohwald, *Thin Solid Films* **159**, 1 (1988)
(2) C. M. Knobler, *Science* **249**, 870 (1990)
(3) L. Chi, R. Johnston, H. Ringsdorf, *Langmuir* submitted

BP19

BULK AND MONOLAYER BEHAVIOR OF A FERROELECTRIC LIQUID CRYSTALLINE MONOMER AND POLYMER

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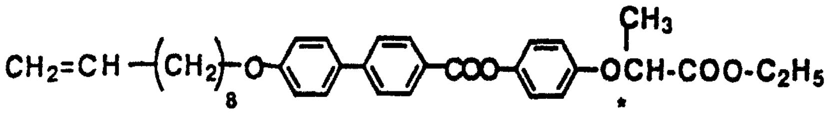
With a view towards studying Ferroelectric liquid crystal behavior on going from the bulk to 2 dimensions, the following chiral monomer was synthesized:



This was reacted with poly(methyl hydroxysiloxane) to form the corresponding side chain polymer. Both compounds showed thermotropic liquid crystalline behavior. On heating in the bulk, both compounds showed the same polymorphism: crystalline-ordered smectic-smectic C^*-smectic A- isotropic melt. The transition temperatures were slightly higher for the polymer. The polarizability and switching times were also measured.

Both substances were also studied at the air/water interface on a KSV 5000 LB trough. From dilute chloroform solutions, isotherm measurements showed that both substances could be spread to form stable monolayers showing little hysteresis upon subsequent barrier expansion. The polymer formed only a condensed phase with a collapse pressure of about 50 mN/m and an area of about 23 $Å^2$. The isotherms of the polymer showed little temperature dependence between 15 to 35 ^{o}C. However, the isotherms of the monomer showed typical polymorphic behavior. Condensed films were only observed at lower temperatures and higher pressures. The collapse pressures of the monomer (about 35 mN/m) were lower than those of the polymer while the collapse areas (about 26 $Å^2$) were somewhat higher than the polymer. Stability measurements at constant applied pressure have indicated that both compounds are suitable to form LB layers on substrates.

BP20

A NEW POSSIBLE APPROACH FOR INTERPRETING SURFACE PRESSURE–AREA ISOTHERMS

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Abstract

Attempts to interpret surface pressure–area characteristics of Langmuir monolayers quantitatively have concentrated either on obtaining phenomenological equations of state using analogies with three–dimensional systems [1] or on thermodynamical analyses which make use of statistical mechanical models and include effects arising from molecular configurations [2]. In this paper we show, based on a purely mechanical model derived from Laplace's theory [3], that surface tension can be defined in terms of a force parallel to the surface, which results from the deficit of attraction in the direction normal to the liquid surface due to the missing liquid above it.

The decrease in surface tension resulting from the presence of a Langmuir monolayer on a liquid surface, termed surface pressure, can be considered as the macroscopic manifestation of the greater attraction between monolayer and water molecules as compared with the attraction between monolayer–monolayer and water–water molecules. In principle then, the surface pressure could be treated according to the approach presented here, and this is something we are working on at the moment.

References

[1] B Stoeckly, *Phys. Rev. A*, 15 (1977) 2558
[2] F A M Leermakers and J.M H.M.Scheutjens, *J.Chem.Phys.*, 89 (1988) 3264
[3] Laplace, *Traité de Mécanique Céleste; Supplément au dixième livre, Sur l'Action Capillaire*, (Courcier, Paris. 1806), and *Supplément à la Thórie del'Action Capillaire* (1807), reprinted in *Oeuvres complétes de Laplace*, (Gauthiers–Villars, Paris, 1880), Vol 4, p 349, 419

BP21

EDGE ENERGY AT THE INTERFACE LIQUID EXPANDED - LIQUID CONDENSED PHASE OF INSOLUBLE MONOLAYERS AND THE SLOPING OF THE PLATEAU OF THE Π-A ISOTHERMS IN THE AREA OF THE TRANSITION BETWEEN THESE PHASES

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At the phase transition from liquid expanded to liquid condensed state of an insoluble monolayer on liquid substratum, the lateral pressure Π may be not constant in the Π-A isotherm of the process (A - mean area per molecule). In the present work one theoretical explanation of this phenomenon is proposed. The reason for the inclined plateau of the dependence $\Pi(A)$ at the area of the phase transition could be the fact that the two phases do not exist as monodomains, separated by the shortest possible interface, but one of them is dispersed in form of little aggregates in the other. The domain of the transition near the liquid expanded phase is considered. The liquid condensed phase is assumed to be the dispersed one. A small number of single molecules with small enough area, that could be treated as nuclei of the condensed phase, can be found in the expanded phase even far from the transition. When decreasing the mean area per molecule this number increases. According to our theory, a threshold A_o exists with the property that for areas less than A_o not only the number of nuclei of the condensed phase increases, but the number of molecules per nucleus increases too (i.e. becomes greater than one). A_o is the "beginning" of the phase transition. The dimensions of the aggregates the slope of the plateau of the phase transition are determined by the edge energy γ of the (one-dimensional) interface between the two phases. The results of the calculations show that the plateau is not horizontal, and the phase transition is strictly speaking of second order, if $\gamma<10^{-6}$dyn, otherwise the phase transition is of first order.

Some experimental data for monolayers of hexadecoxipropanol on water were analyzed. The edge energy obtained for this system is $\gamma\sim10^{-8}\div10^{-7}$dyn. The number of molecules per aggregate of the condensed phase near the midpoint of the phase transition is of the order of 30.

BP22

Bending elastic modulus of monolayers at oil water interfaces

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The thermal fluctuations at a mesoscopic scale of a monolayer at a liquid interface are studied by multiple surface light scattering techniques. The bending elastic modulus K of the monolayer is measured. K is an important parameter in theories of phase diagrammes of oil-water surfactant mixtures. We have measured K as a function of the length of the surfactant molecule and the length of the oil molecule.

BP23

Observation of first order phase transitions in Langmuir monolayers without fluorescent probes

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For the last decade, some first order phase transitions in Langmuir monolayers have been the subject of much experimental work, as a result of the introduction of a new experimental technique, fluorescence microscopy. The drawback of the method is the introduction of fluorescent impurities in monolayers. First, these impurities can change the growth and the shape of coexitence phase domains. Secondly, some first order phase transitions are difficult to study by this method, the fluorescent impurities having a low solubility in the two phases.

We have built a microscope based on the properties of the Brewster angle to visualize the first order phase transitions in Langmuir monolayers without adding any impurities. We present preliminary results obtained with this microscope.

BP24

INVESTIGATION OF THE PHASE TRANSITIONS AND ANISOTROPY OF BEHENIC ACID AT THE AIR-WATER INTERFACE BY ELLIPSOMETRY

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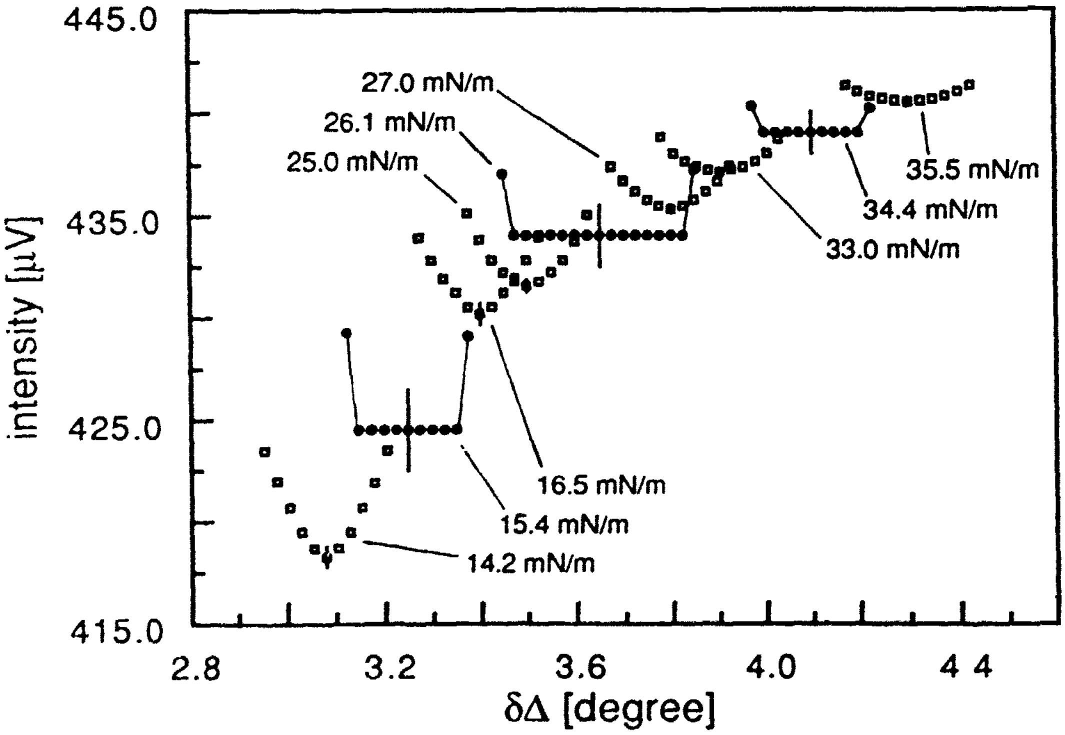
Langmuir monolayers of behenic acid at the air-water interface have been studied by null ellipsometry. In a series of isothermic and isobaric measurements the anisotropy and the phase behaviour of the monolayer have been investigated. The ellipsometric data have been analyzed by using structural data from x-ray measurements to minimize model assumptions. It is shown that behenic acid monolayers are optically anisotropic in the S- and CS-phase and that this anisotropy can be quantified by analyzing data from different phases.

It is also shown that ellipsometry is a formidable instrument to detect and study phase transitions. The intensity minima for the determination of the ellipsometric angles are significantly wider at phase transitions than in adjacent homogeneous phases due to thickness and density variations. Thus temporal and local inhomogeneities can be evaluated.



Shape of the intensity minima for behenic acid at its various phase transitions (T=15.7 °C)

BP25

UV study on the Interaction of Amphiphiles Having Heterocyclic Chromophore

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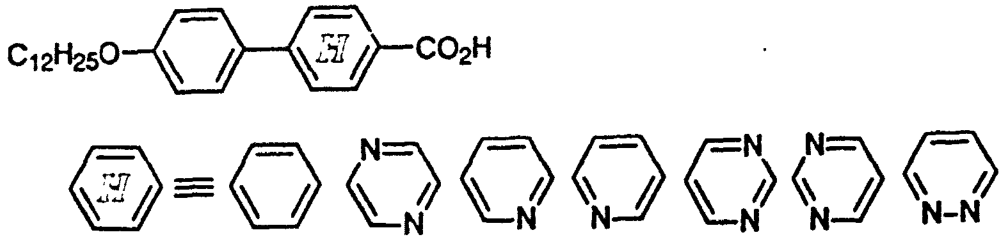
We have synthesized many amphiphilic compounds having various heteroaromatic nuclei, as shown below, which exhibited different aggregation structures in monolayer on water and LB film. The heterocycles are considered to play an important role in determining the structure of aggregation, depending on the attractive and repulsive force of each heterocycle acting as multipole. According to our theoretical study on the electrostatic multipole-multipole interaction using 2-dimensional crystalline model, the most stable structure changes largely depending on the heterocycle incorporated into amphiphile.



1 2 3 4 5 6 7

Here, we report our results aimed to confirm our theoretical study by obtaining informations on the structures of aggregation of monolayers by UV spectroscopy.

Among the amphiphiles studied in this investigation, most intriguing results are UV spectra of the monolayers of pyrimidine derivatives 5, 6, and their 1:1 mixture. The amphiphile 5 formed a expanded monolayer on pure water, whereas the other pyrimidine derivative 6, having reversely directed pyrimidine ring, formed closely packed but very unstable monolayer. However, more closely packed and stable monolayer was formed, when these two amphiphiles were mixed in equimolar ratio. The spectrum of the mixed monolayer did not coincide with the sum of that of each component, and λmax of the mixture was observed at shorter wavelength than those of 5 and 6. These results support our calculation showing stabilization by mixing by more than 30 kJ/mol.

The UV absorption spectra of monolayer of the other compounds and mixing systems will be also discussed in this presentation.

BP26

THERMODYNAMIC STUDY ON PHASE TRANSITION IN MIXED MONOLAYERS OF CHOLESTEROL, LECITHIN AND LITHOCHOLIC ACID

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For mixed monolayers of cholesterol, lecithin and lithocholic acid the surface-pressure has been measured as a function of molecular area at various compositions and temperatures. The liquid-expanded (LE)/liquid-condensed (LC) phase transition takes place over a wide range of monolayer compositions. The cholesterol monolayers are of the condensed type, but they become gradually expanded as the composition of lecithin or lithocholic acid increases. As expected the transition surface-pressure increases as temperature increases. From the temperature dependence of the transition surface-pressure tha apparent molar entropy, enthalpy and internal energy associated with the phase transition have been calculated. The contribution of lecithin and lithocholic acid molecules to the phase transition are not equivalent. The condensing effect of cholesterol on lithocholic acid is more pronounced than that the lecithin on this bile acid.

BP27

2D MOLECULAR ENGINEERING OF AMPHIPHILIC DITHIO TTF DERIVATIVES.

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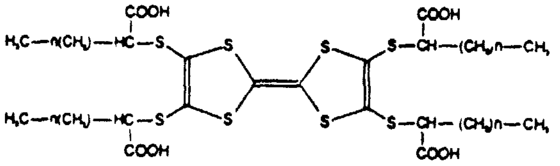
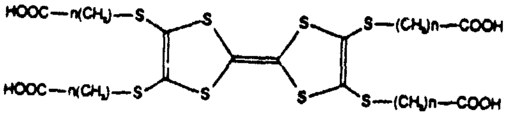
Two dithioTTF derivatives (labelled I and II) have been designed and synthesized in order to organize the macrocycles parallel to the air-water interface and subsequently to the substrate. The ultimate goal is to perform molecular recognition and to create intermolecular chemical bonds through the surrounding functional groups (as for example H bonds and S...S interactions).

Compound I is intended to be ordered as a 2D pavement in the polar planes.

Compound II is intended to make the same 2D arrangement in the hydrophobic plane between two sequential monolayers.



I (n = 19)



II (n = 21)

The synthesis of molecules I and II have been achieved by the condensations of respectively α bromo docosanoic acid, and ω bromo tricosanoic acid on a precursor of bis thio TTF i.e. the zinc complex of 4.5 dimercapto 1.3 dithiol 2 thione (dmit). The amphiphilic thione is then worked up with slight modifications of the solvents as already described for the thione coupling processes.

The two molecules have been studied at the air water interface and transferred onto substrates. The area per molecule is in favour of a macrocycle lying flat on the water.

Visible and infrared spectroscopies are in progress to characterize the molecular organization in the obtained LB films .

BP28

THE INFLUENCE OF CHEMICAL MODIFICATION OF LECITHIN MOLECULES ON THE DIPOLE AND SURFACE COMPONENTS OF BOUNDARY POTENTIAL IN MONOLAYERS

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Lecithin was chemically modified by substitution of CO-group for CH_2-group in one or another or in both hydrocarbon chains. This way 1-palmitoyl-2-hexadecylphosphatidylcholine (PHPC), 1-hexadecyl-2-palmitoylphosphatidylcholine (HPPC) and dihexadecylphosphatidylcholine (DHPC) were prepared. Monolayers of all these substances on subphases of various ionic composition were studied.

The analysis of isochoric curves of boundary potential of PHPC and HPPC monolayers upon the pH of the subphase showed that substitution of one carbonyl oxygen deminishes the boundary potential of the close-packed monolayers at pH 6 by 100-130 mV as compared with that of native lecithin.

When two oxygen atoms are substituted the decrease of the potential is more sufficient and reaches approximately 180--200 mV.

On alkaline subphases the monolayers formed from native lecithin and its derivatives with one substituted oxygen were found to show an anomalous dependence of φ_i upon pH. In these cases on the φ_i-pH curves an extreme at pH 10 exists. The effect was not observed in the case of lipid films in which molecules the both carbonyl groups were substituted.

The effect of variability of the boundary potential of native and modified lecithin monolayers depends upon the package density of lipid molecules and the ionic composition of subphase. The effect may be explained by the change of conformation of the head polar groups of lipid molecules.

The experimental data were analyzed on the base of generalyzed Guy-Stern model. The isoelectric points of the monolayers and the values of pK of ionization of phosphate and choline fragments as well as pK values of adsorption of cations were obtained.

BP29

LANGMUIR MONOLAYERS FORMED BY MESOGENIC MOLECULES AND TRANSLATIONALLY ORDERED MESOPHASES WITH AMPHIPHILIC DOPANTS: A COMPARATIVE STUDY.

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A number of similarities are often noted between Langmuir monolayers and liquid crystals, with molecular ordering in both cases governed by subtle equilibria between anisotropic forces of intermolecular cohesion and steric repulsions determined by geometrical factors.In this report we present two closely related data sets on (a) typical amphiphilic substances in mesophases with layered structures, and (b) typical mesogenic substances forming Langmuir monolayers.

The most interesting result of the first set was a rather unexpected fact that non-mesogenic aliphatic acids (e.g.stearic or undecanoic) did increase the thermal stability of the smectic-A phase of 4-alkoxy-4'-cyanobiphenyls, which could be understood in terms of steric factors.

Using the pressure-area diagrams of the same series of aliphatic acids measured in a parallel set, values of the relative smectic-A to nematic transition temperature increase ΔT_C and of the collapse pressure π_{coll} were plotted versus the fatty acid alkyl chain lenghth n In both cases the curves had strikingly similar behaviour, passing through a maximum at n = 16 - 18. With shorter chains, increase in n led to enhancement of both smectic and Langmuir layer-forming properties; with longer chains, effects of high conformational mobility begins to prevail, mesophase stability decreases, and collapse precedes LC monolayer transition.

Our next focus of attention were π - A diagrams of mixed monolayers comprising 4-alkyl-4'cyanobiphenyls and aliphatic acids. Relative monolayer stabilization regions could be seen on the isotherms, suggesting molecular packing patterns similar to those assumed for the induced smectics formed by the same components.

BP30

Incorporation of Non-amphiphilic Compounds into Host-monolayers

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Monomolecular and Langmuir-Blodgett films normally are built up using compounds that consist of hydrophilic and hydrophobic parts. The lack of a polar headgroup hinders the formation of stable monolayers at the gas-water interface. Substances without a hydrophilic part, like alkanes, alkenes and aromatic compounds, form drops or microcrystallites upon spreading. Such with only little polar parts, like halogenated alkanes or heteroaromatic molecules, upon compression form multilayers of indefined thickness. We have prepared stable and transferrable monolayers with a high fraction of non-amphiphilic compounds.

The molecular arrangement of the mixed monolayers of non-amphiphilic compounds and octadecylmalonic acid as host molecule at the gas-water interface has been studied by measuring surface pressure/area and surface potential/area isotherms, including hysteresis and relaxation measurements at different constant surface pressures in order to examine the stabilty of the mixed monolayers. Halogen alkanes are incorpoated completely into the host matrix. In contrast to terminally substituted fatty acids <1, 2> the halogen atoms are oriented in the direction of the polar headgroups of the host molecules, as deduced from surface potential measurements. From the hysteresis measurements we conclude that the non-amphiphiles are incorporated into the monolayer without any squeezing-out, a behaviour which unsubstituted alkanes for example do not show. The mixed monolayers can easily be transferred to a solid substrate like platinum, which we used to prove complete transfer by surface potential measurements.

1. M.K.Bernett, W.A.Zisman. *J.Phys.Chem.* 67 (1963) 1534

2. M.K.Bernett, N.Jarvis, W.A.Zisman. *J.Phys.Chem.*, **68** (1964) 3520

BP31

ORDERED DOMAINS IN A LANGMUIR MONOLAYER : STRUCTURE, GROWTH AND NUCLEATION

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We investigate the phase transitions and the structure of ordered phases in a Langmuir film made of fluorescent amphiphilic molecules, deposited at the free surface of water. Our Langmuir trough allows simultaneous observation of the film and dynamical measurements of the surface pressure. The optical properties of the ordered domains and their behaviour during growth or at equilibrium give information about the structure of the phase and its anisotropy. In the case of pure NBD-stearic acid, we observe a first order transition between a liquid phase and a solid anisotropic one, organised in bright elongated needles. Their shape is related to the existence of a long-range orientational order of the molecular dipoles, as shown by light absorption experiments. A calculation of the ordered/disordered line energy, based on interactions between electrostatic dipoles, leads to such an elongated shape and agrees with our measurements. In a growth experiment, we simultaneously record the growth of the needles and the relaxation of the surface pressure towards equilibrium. The longitudinal growth velocity of the needles is proportional to the overpressure, like for a rough unidimensional interface. The growth mechanism seems different in the transverse direction. We also measure the nucleation rate of solid domains under a given overpressure, and show that the nucleation is homogeneous. This experiment gives a direct measurement of the average interface energy between the two phases at the transition $\langle\lambda\rangle = 5\ 10^{-7}$ erg/cm. This is in agreement with the value estimated from the dipolar interactions model. We also measure and discuss the influence of the temperature and of controlled impurities on this surface energy.

1 - H. Bercegol, F. Gallet, D. Langevin, J. Meunier, J. de Physique 50, 2277 (1989).
2 - P. Muller, F. Gallet, to appear in J. Phys. Chem. , 15th april 91.

Session CP

Optical properties

CP1

LB-FILMS OF NLO-DYES WITH CHIRAL CENTRES IN MATRICES OF AMYLOSE-ESTERS.

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Langmuir Blodgett films of amylose-esters are used as a matrix for non linear optical active molecules. The structure of the matrix has investigated before (1) and the structure of the mixtures of NLO-active dyes in LB films is investigated now.

A new class of NLO dyes with chiral C-atoms is used to create an interesting NLO-system with molecular asymmetry incorporated in LB layers. Mixtures of the dyes with the polymers with different ratios were spread onto the water surface. The mixtures between the dye and the polymers show stable monolayers whereas the pure dye l[illegible] did not.

From FT-IR- and UV spectroscopy as well as from optical microscopy it was clear that there was no two dimensional mixing on a molecular level. From the known theory of two dimensional mixing this could not be expected (2). By increasing the dye content to a certain ratio crystallites are formed and these can be observed by the afore mentioned techniques. From SHG experiments it turned out that in certain systems the effect of the chiral C-atom can be detected when the system is irradiated with high laser power inputs. The effect of the asymmetric c-atom is estimated to be ± 10% of the effect of the β_{zzz} of the molecule.

References

(1) M.A.Schoondorp, E.J.Vorenkamp, A.J.Schouten Thin Solid Film vol.196 (1990) p?

(2) G.Gabriëlli et al, J.Colloid Int Sci. vol.267 (1989) p 237.

CP2

LANGMUIR-BLODGETT FILMS OF FLUORINATED POLYMERS FOR NONLINEAR OPTICS

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Noncentrosymmetric Langmuir-Blodgett (LB) films are potential media for second-order nonlinear optical (NLO) processes such as second-harmonic generation and linear electro-optic effects. In addition to being amphiphilic, molecules designed for such applications must possess large nonlinear polarizability – usually by including a donor-acceptor-substituted conjugated group. The overall NLO response of a LB film depends on the degree of the polar alignment of the NLO group in the multilayer structure. It is a common problem that the polar orientational ordering tends to deteriorate both with increasing number of deposited monolayers and with time.

From practical viewpoints, polymeric LB films may hold many advantages. However, with few exceptions, previous research activities aimed at the above applications were focused primarily on monomeric materials. Here we report nonlinear optical LB films of a series of polyacrylates and polyoxazolines that contain side groups terminated by hydrophobic perfluorocarbons, either linear [e.g. $CF_3(CF_2)_n$-; n = 5 to 9] or branched [e.g., $[(CF_3)_2CF]_2C{=}C(CF_3)$-]. The polymers are divided into two categories: polymer A containing NLO side groups [e.g., $CF_3(CF_2)_n$-SO_2-Ph-NR-] and polymer B exhibiting only a weak optical nonlinearity. Alternate Y-type deposition of a polymer A and a polymer B yields noncentrosymmetric LB films that exhibit second-order optical nonlinearities. Optical second-harmonic generation (SHG) is used to characterize the optical quality and the temporal stability of the LB films. For films comprising up to 50 AB-bilayers, the SHG intensity displays an expected quadratic increase with the number of bilayers. Excellent in-plane optical uniformity is also seen in all of the LB films in the series. Furthermore, the polar alignment in the films, as revealed by SHG, has remained stable for months.

In the present study, we have demonstrated two possible routes for improving optical quality and stability of nonlinear optical LB films: the exclusive use of polymers, and the incorporation of fluorocarbon groups for hydrophobicity.

CP3

Theoretical Study on the Effect of Heterocycles Reinforcing the Layered Structure

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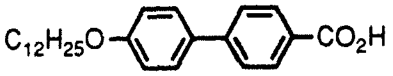
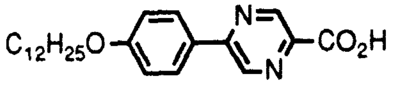
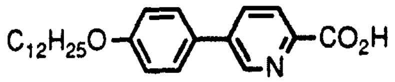
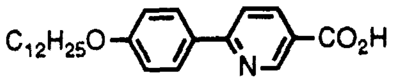
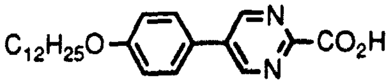
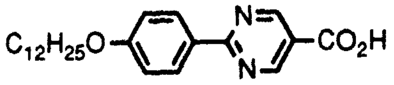
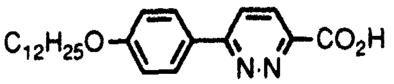
Recently, we found replacement of one benzene ring in 4'-dodecyloxybiphenyl-4-carboxylic acid 1 with pyrazine ring caused remarkable improvement of the stability of monolayer. The monolayer of pyrazine derivative 2 could be alternately deposited with that of arachidic acid to form hetero Y-type LB-film showing strong second harmonic generation.

Comparison of the π-A isotherms of amphiphiles, having pyrazine (2), pyridine (3, 4), pyrimidine (5, 6), and pyridazine (7), suggested the electrostatic multipole-multipole interaction between positive and negative charges on C- and N-atoms, respectively, would play an important role in stabilizing of monolayer. In order to estimate the stabilities of the monolayers, the electrostatic interactions by each molecule surrounding one molecule in all the possible 2-dimensional crystalline models were calculated using the electron density obtained by PPP-SCF method. Summation of the energy contributions from the nearest ca. 500 molecules gave good convergence (0.005 kJ/mol) and the results are shown in the Table. The energies calculated well explained 2 and 7 formed closely packed stable monolayers and 5 and 6 did not.

Table. Stabilization Energies of monolayers at an Area of 0.25 nm^2/molecule.

Compound		kJ/mol
	1	0.0
	2	-14.8
	3	-1.9
	4	-7.4
	5	6.5
	6	-1.4
	7	-31.7

These results demonstrate electrostatic interaction using 2-dimensional model would serve as a guideline for the molecular design of amphiphiles.

CP4

Excitation Energy Transfer between J-aggregates of Cyanine Dyes in LB Films and Liposomes

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Kyoto Institute of Technology, Kyoto 606 (Japan)

Although membrane systems containing J-aggregates of plural kinds of cyanine dyes are interesting for the study of migration of excitation energy among molecular crystals and aggregates, there have been few works on this subject. In this study, we have prepared LB films and liposomes incorporating two J-aggregates at the membrane surface and examined their luminescence properties, i.e., quenching and sensitization of resonance fluorescence (RF).

Four cyanine dyes; 1,1'-diethyl-2,2'-cyanine chloride or iodide (dyeI), 5,6,5',6'-dibenzo-1,1'-diethyl-2,2'-cyanine chloride (dyeII), 5,5'-dichloro-3,3'-diethyl-9-phenylthiacarbocyanine chloride (dyeIII), 3,3'-dimethyl-9-phenyl-4,5,4',5'-naphthothiacarbocyanine chloride (dyeIV) and matrix compounds; arachidic acid (C20), L-α-dimyristoylphosphatidylcholine (DMPC), dicetyl phosphate (DCP) were employed. A chloroform-methanol solution containing C20 and two kinds of dyes were spread at the air-water interface and the monolayer was compressed to π=40 mN/m and then transferred to the quartz plate by vertical deposition method[1]. DMPC:DCP liposomes were prepared in a conventional manner and added to the dilute solution of these dyes to adsorb them at the surface[2].

Fig.1 showed absorption and fluorescence spectra of (dyeII+dyeIII)/C20 layer at the air-water interface and on the quartz plate. Two sharp J-bands due to aggregates of dyeII (λ=602nm) and dyeIII (λ=667nm) were observed, together with RF at λ=606nm (dyeII) and λ=670nm (dyeIII). RF intensity of dyeII aggregate was weak and that of dyeIII aggregate was strong, due to excitation energy transfer from dyeII to dyeIII. Although quenching and sensitization of RF were observed when two J-aggregates were adsorbed at the same liposomal surface, the quenching efficiency of the RF of dyeII aggregate was higher than that in the LB film (Fig.2). Increase in the dyeIII concentration at the liposomal surface as well as in LB films brought about enhancement of the efficiencies of both quenching and sensitization at the beginning. However, the efficiencies seem to attain some saturation values at too large dyeIII concentration. These observations indicate the importance of the excluded volume effect of dye aggregates in the excitation energy transfer.

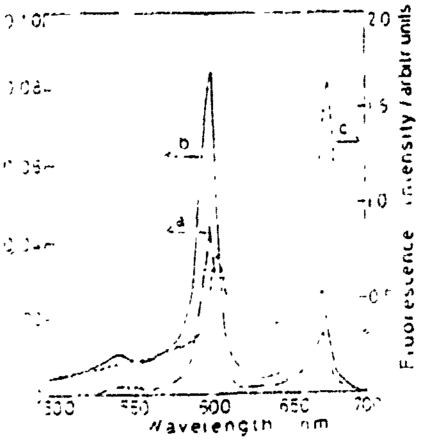
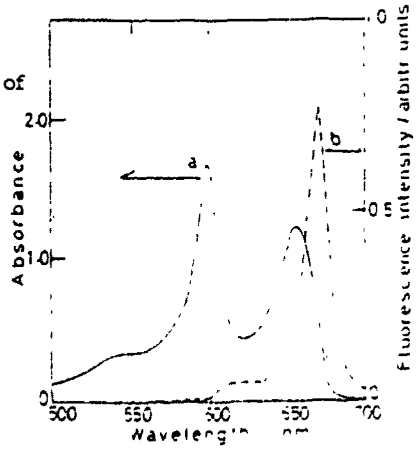


Fig.1
Abs.(a,b) & Flu.(c) spectra of (dyeII+dyeIII)/C20 layers.
dyeII:dyeIII:C20=1:1:10
a:monolayer at air-water interface
b,c:LB film deposited on quartz plate (2x2)
λ_{ex}=400nm

Fig.2
Abs.(a) & Flu.(b) spectra of dyeII:dyeIII:DMPC:DCP liposome solution.
[DMPC]=[DCP]=4.1×10^{-5}M
[dyeII]=[dyeIII]=8.6×10^{-6}M
cell length cm λ_{ex}=450nm



1) Y.Yonezawa, T.Hayashi, T.Sato and H.Hada, Thin Solid Films, 180, 167(1989).
2) T.Sato, Y.Yonezawa and H.Hada, J.Phys.Chem., 93, 14(1989).

CP5

Aggregates of Some Spiropyrans with a Hydrophobic Chain

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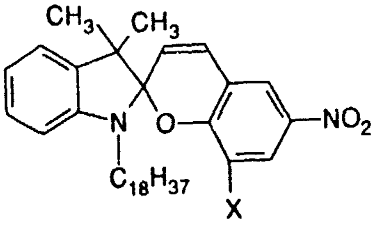
Spiropyran derivatives shown in Fig. 1 were studied on their spectroscopic properties in the states of a monomolecular layer at the air-water interface and of a multilayer as the Langmuir-Blodgett (LB) film. The optical spectra in the LB films of SP18OH and SP147 changed on exposure to UV light or on heat treatment. The UV-Visible and IR spectra suggested the formation of intermolecular hydrogen bond in the J-aggregate (λmax=638nm) for SP18OH and the H-aggregate (λmax=560nm) for SP147, respectively. The half-decay time (560min) of the J-aggregate to the spiropyran (SP) form was found to be longer than that (135min) of the colored monomeric photomerocyane (PMC) form to the SP one. Above results revealed that the intermolecular hydrogen bond between neighoring PMC molecules was formed through thier hydroxyl groups and phenoxide groups in the open-ring form.

SP18Cl with no capability of hydrogen bonding showed the J-aggregate (λmax=652nm) at the monomolecular layers compressed higher than 20mNm^{-1}. On the other hand, the molecule was found to be deposited under UV light irradiation as a H-aggregate (λmax=495nm) in the LB films. Thus, a head-to-tail structure seems to change a side by side structure during deposition. The H-aggregate was disintegrated with life time of 40min, being longer than the half-decay time of 15min from the PMC to the SP form at 25°C in the dark.



	X
SP18OH	CH_2OH
SP147	OH
SP18Cl	CH_2Cl

Figure 1

This work was performed under the management of the FED (the R&D Association for Future Electron Devices) as a part of the R&D of Basic Technology for Future Industries supported by NEDO (New Energy and Industrial Technology Development Organization).

CP6

SECOND HARMONIC GENERATION IN LANGMIUR-BLODGETT MULTILAYERS OF STILBAZIUM SALT POLYSTYRENE

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Abstract

The fabrication of nonlinear optical devices of organic materials using Langmiur-Blodgett(LB) techniques has attracted more and more interest these years. We have studied a stilbazium salt derivative with second order molecular polarizability to the order of magnitude of 10^{-27}e.s.u, which was first reported by D.Lupo et al in 1988. Recently polymers have been widely studied as LB film materials for improving the film stability. We synthesized a stilbazium salt polystyrene as a pre-polymerized material for LB film study.

Surface pressure-molecular area isotherm of the stilbazium salt polystyrene and the stability on water surface were studied, which showed that this material could form stable monolayer on air-water interfaces. The intensity of second-harmonic signal of monolayer on glass substrate was measured in transmission. It was found that this material had relatively high second order molecular polarizability.

Multilayers of the stilbazium salt polystyrene of Z-type and Y-type alternated with arachidic acid were fabricated and the enhancements of the second-harmonic signal with the number of monolayers were studied, which showed that this kind of material might be promising for applications in nonlinear optical devices.

CP7

ELECTRIC FIELD POLING OF COMPOSITION MODULATED POLYMERIC FILMS

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The microstructure of a film can be controlled by depositing alternating monomolecular layers of material of known thickness and composition to form a composition modulated film. In this paper, a NLO polymer layer was alternated with an optically inert glassy polymer. The thickness and composition of the film were then varied systematically to study the effect of film microstructure on the magnitude and stability of the second order NLO properties.

A coumarin dye substituted polymer, poly(methylmethacrylate-co-coumaromethacrylate) [P(MMA-CMA)] was used as a NLO material. The optically inactive spacer material was poly (isobutylmethacrylate)[PIBMA]. Composition modulated films were prepared by the Langmuir-Blodgett technique. Second order nonlinear properties were induced in the films by corona-onset poling at an elevated temperature. Optical properties were measured by UV-VIS spectroscopy and second harmonic generation (SHG).

Composition modulated films were prepared by spacing the NLO monolayers with PIBMA. Each sample had a specific number of spacer layers between each NLO layer. The number of NLO monolayers were held fixed at 5. For comparison, homogeneous films were prepared by depositing LB monolayers of PIBMA/P(MMA-CMA) mixture maintaining constant number of NLO molecules.

Results show that under constant poling conditions, (1) chromophore orientation increases with increasing PIBMA concentration to an upper limit; and (2) at high chromophore concentration the chromophore orientation in modulated films is enhanced over homogeneous films. Stability measurements show that SHG intensity for both composition modulated and homogeneous films stabilize after 10 days at values of 60-80% of the initial values.

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CP8

QUANTUM EFFICIENCIES OF PHOTO-ELECTRIC CONVERSION OF TRIAD MOLECULAR PHOTODIODES

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In previous reports, it was confirmed that a gold optically transparent electrode (Au OTE) modified with an LB monolayer containing the "linear" type A-S-D triad molecule acted as a molecular photodiode and the observed photocurrent efficiency was much higher than that of the "folded" type S-A-D triad molecule.1,2) On the Au OTE, however, the photoexcited state of the pyrene moiety might be partially quenched by energy transfer to the metal substrate3) and the photocurrent efficiency was lowered. It is, therefore, strongly desired to observe the photocurrent of the triads deposited on transparent and nonquenching electrode material for determination of the intrinsic quantum efficiencies.

In this report, we will describe the photocurrent quantum efficiencies, which were calculated from the photocurrents of the monolayer modified SnO_2 OTE and the absorption spectra of LB monolayers on quartz, for triads and the reference compounds shown in Fig. 1. These results indicate that the more preferable spatial arrangement of A, S, and D moieties were attained in "linear" triad than in "folded" triad.

The quantum efficiencies for the systems containing hydroquinone in solution will be also described.

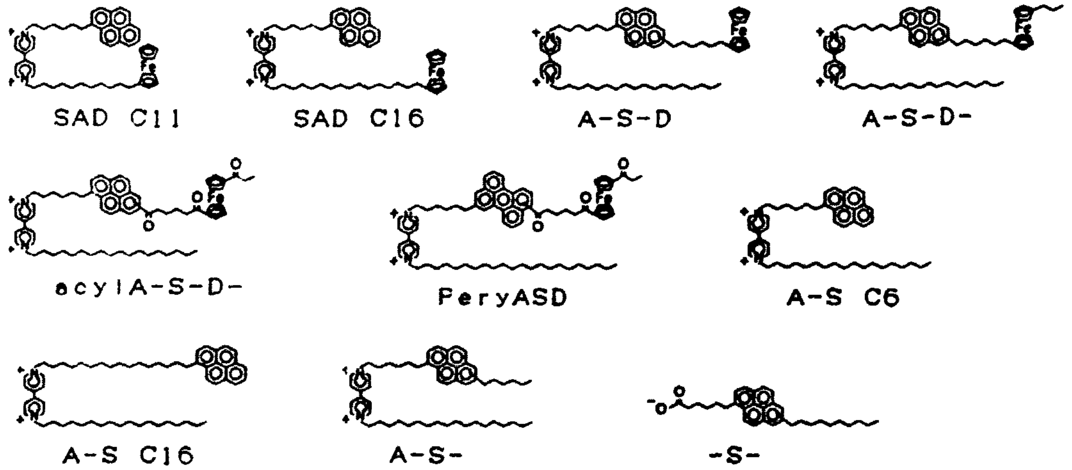

Fig. 1. **The structures of the folded and linear triads and their reference compounds.**

References

1) M. Fujihira and H. Yamada, *Thin Solid Films, 160* (1988) 125.
2) M. Fujihira and M. Sakomura, *Thin Solid Films, 179* (1989) 471.
3) H. Kuhn, D. Möbius, and H. Bücher, in A. Weissberger and B. W. Rossiter eds., *Techniques of Chemistry*, Vol. 1, Part 3B, Wiley, New York, 1973.

CP9

PHOTO-AMPLIFIED STORAGE OPTICAL MEMORY WITH POLYION COMPLEXED PYRENE LB FILMS

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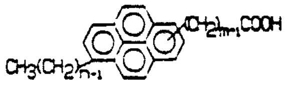
The LB films of photochromic material have been studied recently as possible high density information storage media. In this laboratory, however, the more sensitive information storage LB films have been developed by utilizing rapid quenching of the fluorescent LB films of pyrene derivatives by the photo-oxidative products. Previously$^{1)}$, we reported the monolayer properties of newly synthesized pyrene amphiphilic derivatives, i.e. DPHA and HPDA, in which the pyrene moiety is located not at the end but in the middle of the alkyl chain of fatty acid. The structures of these compounds are shown in Fig. 1. But the homogeneity of the surface concentration of the pyrene moieties in the LB films, i.e. that of the luminescence intensity observed by a fluorescence microscope was not enough for high density information storage.

In this study, we will report the improved properties of the pyrene LB films by polyion complexation with a water soluble cationic polymer, i.e. an ammonium form of polyallylamine (PAA).

The amphiphilic pyrene derivatives were synthesized by the previous method$^{1)}$ and PAA was obtained from Nitto Boseki Co.$^{2)}$

Fig. 2 shows clearly the improved π - A isotherm on PAA compared with that on Ca^{2+}. Fig. 3 shows a fluorescence micrograph of the HPDA-PAA LB film irradiated by N_2 laser through a standard photomask. High homogeneity in the film and high resolution of the photo-oxidatively quenched fluorescent pattern were clearly seen.

Fig. 1



HPDA (n= 6, m=10)
DPHA (n=10, m=6)

Fig. 2

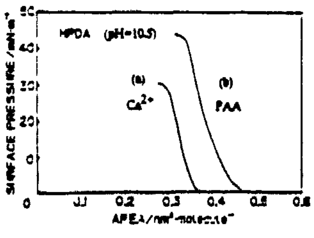


Fig. 3 ⟷ 50 µm

References

1) M. Fujihira, T. Kamei, M. Sakomura, Y. Tatsu, and Y. Kato, *Thin Solid Films*, 179, (1989) 485.
2) K.Nishiyama, M.Kurihara, and M.Fujihira, *ibid.*, 179, (1989) 477.

CP10

SECOND-HARMONIC GENERATION FROM MIXED LANGMUIR-BLODGETT FILMS OF *N*-ACYL-*p*-NITROANILINE AND ITS HOMOLOGOUS AMPHIPHILE

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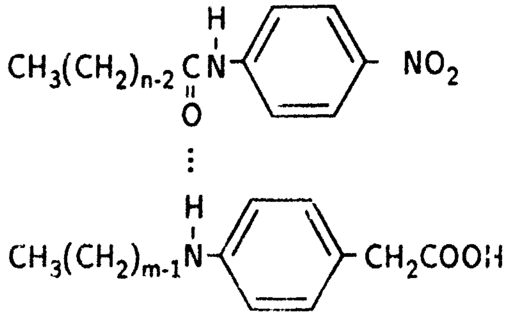
Second-harmonic generation (SHG) has been observed from mixed Langmuir-Blodgett multilayers of *N*-acyl-*p*-nitroaniline (C_nANA) and *p*-alkylaminophenylacetic acid (C_mAPA). The molecule C_nANA is expected to have efficient second-order nonlinearity because of the large molecular polarizability of *p*-nitroaniline, and the homologous amphiphile C_mAPA contributes to homogeneous mixing with C_nANA due to interlayer hydrogen bonding between them. Typical mixtures of $C_{18}ANA$ and $C_{18}APA$ (the molar ratio of 1 : 1) formed stable monolayers on water and were easily transferred onto hydrophobically-treated substrates with a high dipping speed of 10 cm min^{-1} The deposited films up to 300 layers were transparent in the visible-spectrum region without any disturbance.

The SHG has been observed from Y-type films with large anisotropy of the SH intensity to the dipping direction. Further, the SH intensities were strongly affected by the alkyl chain lengths of the mixing components. In order to investigate the mechanism of the SHG from Y-type films, we prepared hetero-structural films of which SHG-active layer(s) are sandwiched between inactive layers such as fatty acids and measured the dependence of the SH intensity on an incident angle of laser light. As a result, a hetero film with one active layer showed a minimum intensity at normal incidence. In contrast, a hetero film with two active layers showed a maximum intensity at normal incidence. This result supports the "herringbone"-like structural model[1] of inclined molecules for a non-centrosymmetric structure in the Y-type film.



C_nANA

C_mAPA

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[1] G. Decher, B. Tieke, C. Bosshard and P. Günter, *J. Chem. Soc., Chem. Commun.*, (1988)933.

CP11

THE ROLE OF THE CENTRAL METAL IN PHTHALOCYANINE LANGMUIR-BLODGETT FILMS STUDIED BY HOLE BURNING

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Persistent spectral hole burning spectroscopy was applied on free base and central metal phthalocyanine Langmuir-Blodgett films (LB Pc) to study the frequencies of normal vibrations (FNV), homogeneous width of optical transitions (Γ_{hom}) and hole burning mechanisms. Γ_{hom} was determined from the hole widths (δ_{HB}) of zero phonon hole (ZPH) measured within the short burn time limit in fluorescence spectra. The observed ZPH was accompanied with a blue shifted antihole and red shifted phonon wing. This phenomenon indicates nonphotochemical hole burning mechanism. Moreover, a set of red shifted off-resonance holes appearing on particular FNV was observed. These FNV were compared with data observed on isolated pigments in solid solutions and polymere foils by means of low temperature fluorescence spectroscopy and Raman scattering. The parameters of ZPH reflect relaxation dynamics of the first excited singlet state in both LB films and isolated molecules. All these effects were studied with respect to the role of the central metal in tetrapyrole ring. Furthermore, the influence of the burning wavelength tuning on ZPH parameters as well as hole burning kinetics provide complete picture of hole burning mechanisms.

CP12

EXCITED ENERGY TRANSFER IN LANGMUIR-BLODGETT FILMS STUDIED BY HOLE BURNING SPECTROSCOPY

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The close contact of neighbouring highly organised dye molecules in Langmuir-Blodgett films (LB) results in strong aggregation effects and fast excited energy transfer (EET) between them. The molecular organisation in LB films can be a model for photosynthetic antenna, where the tight fixation of particular chlorophyll molecules is established in large pigment protein complexes. The fast EET provides significant quenching of the fluorescence together with a deacreasing of the effective dephasing time T_2 of the first excited singlet state. This T_2 value can be directly determined from fluorescence lifetimes τ_F and also from homogeneous width Γ_{hom} of the particular optical transitions. Γ_{hom} can be determined experimentally from the width δ_{HB} of zero phonon hole (ZPH) burned into low temperature fluorescence spectrum. To avoid the broadening of δ_{HB} due to thermal heating and spectral diffussion during burning procedure a set of different fluence experiments was performed. The δ_{HB} observed in isolated phthalocyanines was approx. two orders narrower than that in LB films. This broadening was explained due to fast EET between neighbouring molecules in LB film. Different geometrical arrangements of molecules in LB films, molecular layers (prepared by other techniques) and *in vivo* photosynthetic antennae versus that of isolated molecules in solid solutions (reflected e.g. in various δ_{HB} temperature dependences) provide excelent models for both theoretical and experimental studies of EET.

CP13

LANGMUIR-BLODGETT-MULTILAYERS FROM POLYMERS FOR LOW LOSS PLANAR-WAVEGUIDES

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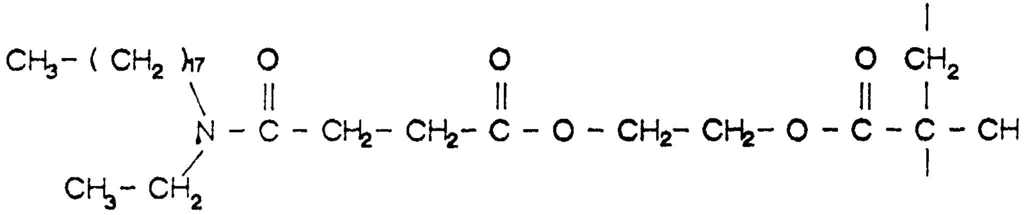
In the field of integrated optics LB materials are of growing interest because of their variable layer architecture, the exact control of thickness and the high nonlinear optical coefficients especially for second order processes (1). For many applications in integrated optics it is necessary to build up multilayers of waveguiding thickness. This means that several hundred monolayers must be transferred to a solid substrate.

Although the optical properties of thick LB-layers are so important for applications very little work has been done on this subject. The main problem for waveguides from LB-films is the high optical loss, typically $\alpha \geq 10$ dB/cm for $\lambda = 633$ nm (2). The aim of our work was to fabricate thick LB multilayers from preformed polymers under reproducible conditions with high optical quality, i. e. low optical loss.

As discussed elsewhere (3), preformed polymers for LB multilayers have interesting properties e. g. high mechanical and thermal stability, low defect density. Therefore it should be possible to prepare thick LB films with high optical quality. For our experiments we used different vinyl polymers with the following monomer unit:



By varying x the conformationally order of the alkyl side chains in the LB film can be influenced (3). Only LB films from polymers with a short alkyl side chain which means low conformationally order are stable and homogenous and therefore the multilayers are interesting candidates for waveguiding.

LB multilayers (500 layers) from the polymers desribed above were prepared on quarz substrates for waveguiding. The anisotropic refractive index was measured using waveguide spectroscopy at $\lambda = 785$ nm, 633 nm and 442 nm. For optical loss measurement a fiber method was used to detect the scattered light which is proportional to the guided intensity in the film. For 0,8 μm thick films the attenuation is quite low: 2 dB/cm ($\lambda = 633$ nm). In addition to the waveguide measurements the samples were characterized by light microscopy to identify the attenuation mechanisms.

(1) D. Lupo et al., J. Opt. Soc. Am. B., Vol. 5, 300 (1988).
(2) R. H. Tredgold et al., Thin Solid Films 151 (1987) 441-449.
(3) F. Embs et al., Adv. Mater. 3 (1991) 1, 25-31

CP14

STRUCTURE AND NONLINEAR OPTICAL PROPERTIES OF LB FILMS FROM p-NITROANILINE DERIVATIVES

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Abstract

Theoretical and experimental contributions are described to a coordinated programme to design, prepare and characterise LB films with high nonlinear optical activity.

The para-nitroaniline derivatives [DAN [1], MAP [2] and NPP [3,4] in single crystalline form have been reported to exhibit encouraging conversion efficiencies for the frequency doubling of laser radiation . Derivatives of these three compounds have been synthesized for the purpose of preparing ordered, homogeneous, non-centrosymmetric thin films using the Langmuir-Blodgett (LB) technique. The resulting materials incorporating the stearyl moiety SDAN, SMAP and SNPP are all crystalline both as the powder and in the LB film form. Moreover, frequency doubling of 1064 nm Nd:YAG radiation to 532 nm has been demonstrated for both powders and LB films of these materials. These results are in marked contrast to those of Tieke et al [5] for other para-nitroaniline compounds since in their case limited LB film-forming capability was demonstrated with no frequency doubling. There are two aspects to the modelling of these films: molecular dynamics simulations and molecular graphics visualizations have been used to investigate their structure, and planewise lattice sums have been used to investigate the collective non-linear optical response of different structures.

Examination of the three dimensional molecular structures reveals that they can be well represented by the combination of a large single interaction site (the aromatic head group) and a set of connected beads (the CH_2 groups on the hydrocarbon tail). We shall report the results of molecular dynamics simulations which are being applied to examine monolayer and bilayer films for these models of the p-nitroaniline derivatives. In preliminary work [1] we have shown that 64 molecules per layer is a large enough sample to obtain accurate tilt angles for a simple hydrocarbon monolayer. Of particular interest is the dependence of tilt angle on the molecular structure and the area per molecule as well as layer separation and extent of interdigitation of hydrocarbon chains in a Y-type bilayer. Such information is of fundamental importance to accurate calculations of nonlinear optical properties and to the interpretation of experimental data. In addition, the nonlinear optical response of ordered films can be calculated from the molecular hyperpolarizabilities, the molecular orientations and the local electric fields in the layers. In turn the local fields depend on the sums of dipole interactions between a molecule in one layer and all the molecules in that or another layer, sums which decrease rapidly with the separation between layers. Calculations of these planewise dipole sums have been performed for a series of close-packed model structures and detailed calculations for tilted model structures will be presented.

References

1. D.S. Bloor et al, *J. Opt. Soc. Am. B.*, 6 (1987) 1013.
2. J.L. Oudar and R. Hierle, *J. Appl. Phys.*, 48 (1977) 2699.
3. J. Zyss et al, *J. Opt. Soc. Am. B.*, 4(6) (1987) 977.
4. J. Zyss et al, *J. Chem. Phys.*, 74 (1981) 4800.
5. B. Tieke et al, Private Communication.
6. M. Hurst and R.W. Munn, *J. Mol Electron.*, 2 (1986) 35.

CP15

SECOND HARMONIC GENERATION IN LB-FILMS OF PREFORMED POLYMERS

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Copolymers of 4-[4-(2-hydroxyethyl)methylamino]phenylazobenzonitrile-methacrylate (HEMAPAN) and dodecylmethacrylate (DMA) were prepared and their monolayers at the air-water interface characterised by π-A isotherms. The polymeric monolayers were transferred to a glass-substrate by the LB-technique ; Z-deposition was observed.

Deposited mono- and multilayers of the HEMAPAN (16 mol%)-DMA copolymer were characterised by dichroic UV-Vis spectroscopy and second harmonic generation (SHG). From results obtained by both techniques the average tilt angle of the NLO-active side groups (NLOphores) was obtained. The SHG-measurements allowed the calculation of the hyperpolarisability of the NLOphores in the copolymer. Compared to solution values of the hyperpolarisability of 4-[4-(N,N-dimethylamino)phenylazo]benzonitrile the hyperpolarisability in the copolymer is strongly decreased presumably due to interactions between the highly polar NLOphores in the polymer. However, favorable orientation effects result in efficient SHG in the polymer films. The SHG-efficiency can be improved by optimalisation of copolymerisation ratios and/or distribution of the NLOphores in the chain. In multilayer films a superquadratic dependence of the SHG-efficiency upon the number of layers was observed.

CP16

POLYMERIC MULTILAYERS FOR NLO-APPLICATIONS

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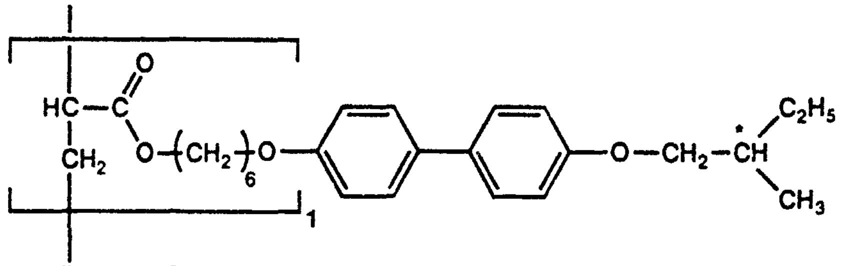
In Langmuir-Blodgett (LB) monolayers and multilayers, amphotropic copolymers$^{1,2)}$ are powerful host systems for functional low molecular weight guest molecules. Such copolymers even enable the transfer of guest compounds not capable to self-organize at the air-water interface by themself. This property is particularly useful for the fabrication of LB-films of highly polarizable NLO dyes like hemicyanins and nitrophenylhydrazones. The later dyes are of special interest since they exhibit high second-order nonlinear optical susceptibility $\chi^{(2)}$ and high molecular hyperpolarizability β values without significantly absorbing light at the second-harmonic wavelength$^{3)}$. To achieve high SHG signals strong donor and acceptor groups have to be incorporated into the dyes. However, such a substitution pattern often results in poor spreading and deposition properties.



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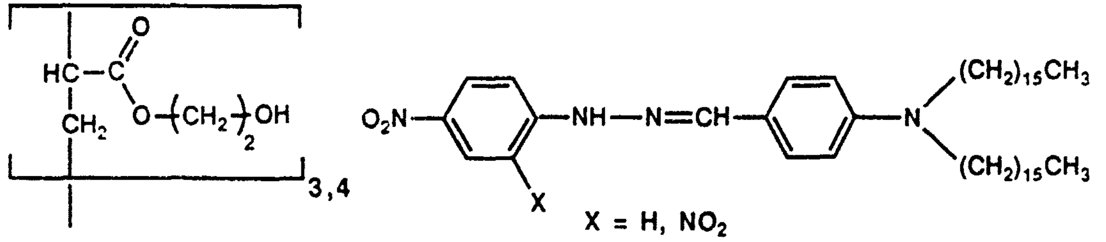

2

In contrast 2:1 molar mixtures of the biphenylcopolymer **1** with the nitrophenylhydrazones **2** form stable monolayers at room temperature although the pure dyes do not. The mixtures can be deposited as multilayers on various substrates, as demonstrated by UV/Vis spectroscopy and by SAXS experiments. The nonlinear optical properties of transfered monolayers of the polymer/dye mixtures were determined by SHG measurements, showing hyperpolarizability values exceeding those measured previously for amphiphilic nitrophenylhydrazones with a less favourable substitution pattern$^{3)}$.

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1) C. Erdelen, A. Laschewsky, H. Ringsdorf, J. Schneider, A. Schuster, Thin Solid Films **180**, 153 (1989)

2) T.L. Penner, J.S. Schildkraut, H. Ringsdorf, A. Schuster, Macromolecules, in press (1991)

3) D. Lupo, W. Prass, U. Scheunemann, A. Laschewsky, H. Ringsdorf, I. Ledoux, J. Opt. Soc. Am. **B5**, 300 (1988)

CP17

Polymerizable Non-linear Optical Langmuir-Blodgett Films based on 2-(21-Docosenyl)amino-5-nitropyridine

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Using the Langmuir-Blodgett (LB) technique, multilayer films of 2-(21'-docosenyl)amino-5-nitropyridine have been made by transferring stable monomolecular films from an air-water interface onto quartz substrates. Such multilayer films can be polymerized by X-ray irradiation. The films exhibit the same enhanced second harmonic generation efficiency before and after polymerization. This is due to the highly ordered Y-type arrangement in the film. No change in the morphology of the films have been observed after polymerization, probably because the vinyl group is at the terminal portion of the hydrocarbon chain.

CP18

ORIENTATIONAL INVESTIGATION OF 2-DOCOSYLAMINO-5-NITROPYRIDINE AND DERIVATIVES BY NONLINEAR OPTICAL TECHNIQUES

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2-docosylamino-5-nitropyridine (DCANP) is a strongly nonlinear optical molecule which forms high optical quality Langmuir-Blodgett (LB) films. Its linear and nonlinear optical properties have been described in [1| and [2]. The DCANP molecules form stable Y-type LB films with its charge-transfer axis in a plane parallel to the dipping direction.

As reported earlier DCANP showed the highest nonlinearity when compared to its derivatives [1]. In order to explain this effect we looked at the orientation of the chromophore of the different derivatives. Using nonlinear optical techniques we observed differences in the orientation when varying the aliphatic chain from $C_{18}H_{37}$ to $C_{26}H_{53}$. We obtained two angles describing the orientation of the charge-transfer axis with respect to the substrate as well as the molecular hyperpolarizability β. The results agree with infrared spectroscopical measurements performed at Ciba-Geigy. The correspondence of β with values obtained from electric field-induced second-harmonic generation (EFISH) measurements is discussed.

[1] G. Decher, B. Tieke, C. Bosshard and P. Günter, Ferroelectrics **91**, 193-207 (1989)
[2] Ch. Bosshard, M. Küpfer, P. Günter, C. Pasquier, S. Zahir and M. Seifert, Appl. Phys. Lett. **56** (13), 1204-1206 (1990)

CP19

The characterization of Langmuir-blodgett films of polymers containing NLO molecules in the side chain

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Abstract

Monolayer film formation has been observed for polymers in which the nonlinear optical (NLO) chromophores are attached in the side chain of polymethacrylate (PMA) backbone. Polymer monolayer were successfully transferred onto a hydrophilic glass substrate using a moving wall type LB trough. Mono- and multilayer were characterized by pressure-area isotherm, polarized UV-visible spectrometer, ellipsometer and SHG technique. The tilt angle calculation from polarized UV-visible spectra indicates NLO chromophores are inclined to the plane of the substrate at a shallow angle. The SH signal from monolayer was observed.

CP20

SYNTHESES AND LANGMUIR-BLODGETT FILMS FORMATION OF DONER-ACCEPTOR ORGANIC COMPOUNDS

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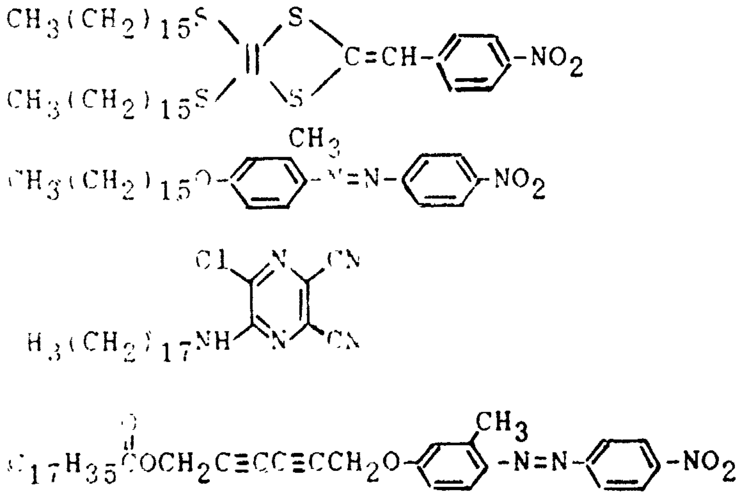
Organic materials have recently been recognized as promising candidates for nonlinear optics (NLO) applications in view of their fast response time and large non-resonant nonlinear effects. Another advantage of organic materials is their relative ease of processing, for example, by using the Langmuir-Blodgett (LB) technique to fabricate into ultra thin films if the organic NLO materials are suitably designed.

4,5-Dihexadecylthio-4'-nitrostyryl-1,3-dithiocyclopentene, 4-hexadecoxy-2-methyl-4'-nitro azobenzene, 2-chloro-5,6-dicyano-3-(N-octadecyl)amino pyrazine and 2-methyl-4-(6-heptadecanoic-2,4-diynoxy)-4'-nitro azobenzene, shown in Figure 1, were designed and synthesized. Their structures were confirmed by elemental analysis, IR, MS and ^{1}H-NMR spectroscopy.



1

2

3

4

Figure 1. Molecular structures of doner-acceptor compounds

The LB films were carried out on a KSV instrument Finland) Although a typical isotherm was obtained for compound 3, during the compression the Wilhelmi plate became itali to the water surface. indicating high viscosity of the Langmuir film.

For the monolayer of compound 1, the molecular hyperpolarizability β value was measured as ca. 10^{-29} esu.

CP21

Studies on Nonlinear Optical Properties of LB Film Formed from Azobenzocrown Ether Derivatives

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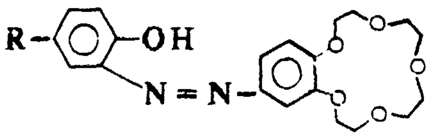
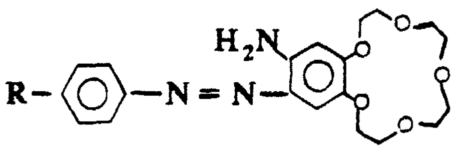
ABSTRACT

A kind of new-type materials of optical film—azobenzocrown ether derivatives have been prepared



$I_aR = C_{12}H_{25}-$
$I_bR = C_{16}H_{33}-$
$I_cR = C_{16}H_{33}O-$



$II_aR = C_{16}H_{33}-$
$II_bR = C_{18}H_{37}-$

The structure and preparing condition of theirs langmuir film have been studied with π-A isotherms. These compounds can well form monolayer on the subphase and transfered to glass base to form multilayer over 100 layer. The film preparation are influenced by the pH, concentration and the kind of ions which subphase contains. The desired structure of LB film can be obtained by varing the method of preparing film. We have also studied the constructure of the LB multilayer with X-ray diffraction and proved that the designed molecule is consistent with CPK molecular model. The X-ray diffraction measurement of same samples after one month showed that the film are quite stable. The second harmonic generation of these compounds were examined, which found to be the order of 10^{-28}—10^{-29}esu.

CP22

SYNTHESIS AND LB FILM DEPOSITION OF SYNDIOREGIC STILBAZOLIUM POLYMERS

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Our laboratory continues to pursue the design, synthesis, characterization and LB film deposition of new polymeric materials specifically engineered for nonlinear optical (NLO) waveguide applications. Our research has focused on NLO polymers as especially attractive candidate materials for applications in optical computing and communications technologies. We are presently investigating a series of main-chain stilbazolium, syndioregic (accordion-like) polymers. These polymers exhibit very interesting LB film formation and deposition characteristics and second-order NLO properties.

The polymers were synthesized by step-growth polymerization of bis-alkylpyridinum and bis-benzaldehyde monomers. The polymers were purified by preparative-scale gel permeation chromatography and characterized by thermal and spectroscopic analysis. Low molecular weight (5,000 to 20,000 g/mol) and intensely colored (absorptivity ~ 100,000 L/cm mol) polymers were obtained. The polymers had glass transition temperatures ranging from 145 to 185°C.

Monolayer films were prepared by spreading chloroform solutions on 18 Mohm water (Waters Milli-Q system) in a dual-compartment NIMA LB trough. Isotherms were generated at room temperature and depositions were performed on fuzed quartz, glass, ZnSe attenuated total reflectance (ATR) crystals and on [100] silicon wafers. Monolayer and multilayer films were characterized spectroscopically for thickness, refractive index and degree of molecular orientation. Second harmonic generation (at 532 nm) was also used to indicate the relative amount of optical nonlinearity present in the films.

Isotherm analysis indicated that collapse pressures for monolayers of these polymers ranged from 40 to 50 mN/m, and that repeat units (each containing 2 stilbazolium chromophores) occupied 0.5 to 0.6 nm^2 at collapse or 0.8 to 0.9 nm^2 when the isotherms slope were extrapolated to zero surface pressure. These areas per chromophore agreed well with those for stilbazolium side-chain polymers reported previously by our laboratory (LB4). Additionally, SHG and other spectrocopic analysis indicated that a high degree of noncentrosymmetric order exists in LB films of these folded main-chain polymers having a syndioregic configuration of chromophores. Multilayer LB film stability and structure will be discussed along with the synthesis of these novel syndioregic chromophoric polymers.

CP23

Dye Fluorescence Kinetics of LB Films.

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Fluorescence decay analysis is one of the most widely used techniques for studying the distribution and mobility of molecules in ordered media [1]. In this paper fluorescence decay is applied to investigations of perylene aggregate formation in ω-tricosonoic acid LB films. The role of temperature in excimer formation is discussed for different concentrations of probe molecules in LB films.

The decay analysis of thiacyanine dye LB films is important for their practical application as a covering for photon and corpuscular detectors to obtain a large Stokes shift. The extremly short lifetime (~500 ps) of the thiacyanine dye LB films is investigated.

The investigation of energy transfer in low-dimensional ordered media by fluorescence decay analysis is also discussed.Detailed analysis of energy migration of LB films with 1.5% concentration of donor molecules (1-pyrenebutanoic acid) and 1.5%;7%,9%concentration of acceptor molecules (16(9-antroyloxy)palmitic acid) is made.

The kinetic fluorescence characteristics were measured by a time-correlated single photon technique. The FWHM of the detection system response function was about 200 ps.

[1]. Vitukhnovsky A.G.,Sluch M.I.,Warren J.,Petty M.,C., Chem.Phys.Letters,1990,173,5-6,425.

CP24

NONLINEAR OPTICAL POLYAMIDE FILMS DERIVED FROM L-AMINO ACIDS

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Thin organic films which contain a permanent alignment of molecular dipoles exhibit nonlinear optical properties that are of great interest in optoelectronic devices. These same films may also exhibit useful piezoelectric and pyroelectric properties. Polymeric films are especially desirable because they are nonvolatile, and can be designed to have high glass transition temperatures. Furthermore, polymeric films can be crosslinked in two or three dimensions to further restrict mobility.

We report here on new polyamides and their nonlinear optical thin film properties. Films were fabricated by the Langmuir-Blodgett (LB) deposition technique. LB deposition was chosen for fabricating multilayer films due to the exquisite control of molecular alignment (pressure-assisted self assembly of polymer chains floating at the air-water interface), and the outstanding control of film thickness. Films were deposited onto transparent solid substrates for further characterization.

Biologically derived amino acids are useful in preparing polyamides because of their singular stereo-configurations. This enables the polypeptides to self assemble into ordered conformations. We have been designing synthetic polypeptides which can easily form ordered monolayers at the air-water interface. We have synthesized novel, chromophore-substituted polypeptides designed for beta-sheet organization at the air-water interface. These polymers are prepared by derivatization of preformed polypeptides, and by polymerization of derivatized amino acids. Molecular ordering by infrared techniques, and the second-order nonlinear optical properties of multilayer films prepared by LB deposition are described.

CP25

ELECTROCHROMISM IN MIXED LB FILMS CONTAINING RARE-EARTH BISPHTHALOCYANINES

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Although good deposition ratios have been obtained for the deposition of rare-earth bisphthalocyanine, notably [Yb(pc)$(\dot{\mathrm{pc}})$], provided suitable Z-type deposition is used, the phthalocyanines have not proved ideal materials for LB deposition as they do not contain a polar head-group. In order to decrease collapse rate and to improve film quality, the bisphthalocyanines have been mixed with stearic acid or cadmium stearate. Presently, rare-earth phthlocyanines are in preparation with alkyl linked side chains to improve the ordering of the LB films. The paper will discuss the structure and electrochromic behaviour of the mixed films, of alternate layer films using different fatty acids plus bisphthalocyanines, the behaviour of the phthalocyanines containing the side chains, and the electrochromic behaviour of films which consist of a mixture of bisphthalocyanines. By these techniques a range of novel voltage-dependent absorption bands are accessible in the visible and near infrared regions of the electromagnetic spectrum.

CP26

THE PHOTOEXCITED STATES OF RHODAMINE AND ANTHRACENE IN MIXED LB-FILMS

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We have studied the photoexited states of octadecyl rhodamine B (Rh) and 2-(9-anthroyloxy)stearic acid (AS) in mixed LB-films by flashphotolysis and picosecond fluorescense decay measurements. The concentration of Rh is kept constant, 20 mol-%, and AS varies from 0 to 10 mol-%. In the samples studied so far AS and Rh compounds are in the same layer in a stearic acid matrice.

In the Rh groundstate spectrum there is a monomer peak in 572 nm and a dimer peak in 535 nm. The Rh monomer absorption maximum at 572 shifts to longer wavelength and the dimer intensity decreases with increasing AS concentration. This indicates that there is a ground state complex between AS and Rh.

Transient absorption spectra were observed at a wavelength range from 405 to 640 nm. The absorption maxima were observed at 425 nm, 450 nm, and 565 nm. It is evident that at least two components are present, a Rh triplet and a Rh anion radical. The Rh cation radical, probably at 495 nm, is observed only when AS concentration is 0. The absorptions at 450 nm and 565 nm increase with increasing AS concentration due to an electron transfer from AS to excited Rh and a Rh anion radical is formed.

In the absence of AS a double exponential decay of the Rh fluorescense is observed with fluorescence lifetimes of 0.2 ns and 1.6 ns. When the concentration of AS was 10 mol-% the lifetimes were 0.4 ns and 2.3 ns. It is well known[1,2,3] that the fluorescence intensity of Rh decreases with an increase of dye concentration. At higher Rh concentrations energy transfer to a nonfluorescent dimer has been suggested as a main quenching mechanism. The increasing lifetime with increasing AS concentration might be due to decreasing self quenching and decreasing dimer proportion.

1 Naoto Tamai, Tomoko Yamazaki and Iwao Yamazaki Chem. Phys. Lett. 147 (1988) 25

2 Nobuaki Nakashima and Keitaro Yoshihara J. Chem Phys 73 (1980) 3553

3. Klaus Kemnitz. Naoto Tamai, Iwao Yamazaki, Nobuaki Nakashima and Keitaro Yoshihara J. Phys. Chem. 90 (1986) 5094

CP27

WAVEGUIDING IN POLYMER/LB FILM SANDWICH STRUCTURES

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The increasing use of optical communications offers many potential applications for switching and modulation devices based on nonlinear optical materials. These devices invariably use waveguides to confine light within a micron scale region, allowing control of the light with small voltages and permitting easy integration with optical fibres and microelectronic circuits.

Langmuir-Blodgett films of certain dye molecules can exhibit significant nonlinear optical properties, particularly for small numbers (≤ 20) of layers[1]. Unfortunately layers of sufficient thickness for waveguiding often exhibit nonlinear effects that are smaller than expected; such structures are also relatively lossy. Thinner LB films have been used as overlays on linear waveguides, but in this geometry the film only transmits the evanescent tail of the waveguide mode, greatly reducing the nonlinear effect. In this work we shall describe a structure in which LB layers are placed close to the field maximum of a polymer waveguide; this combines ease of fabrication with the potential for significant nonlinear properties.

The structure consists of a substrate coated with a passsive polymer layer dipped from solution. LB layers are then applied, followed by a second solution dipped polymer layer. The criteria for choice of the two polymers will be discussed in terms of refractive index and type of solvent. Theoretically calculated guided mode field profiles will be presented showing that the LB film guides a much larger proportion of the energy compared to the overlay device.

The construction of a waveguide of poly(methyl methacrylate) electro-optic LB layers and poly-4-vinyl pyridene is described. The guide was produced on a silicon substrate, allowing cleaving and endfire coupling of light at 632.8 nm.

The electro-optic response of the waveguide is currently under investigation.

Reference

1. S. Allen, Inst. Phys. Conf. Ser. No. 103 (1989) 163.

CP28

STUDIES ON ELECTROLUMINESCENCE OF MULTILAYER LANGMUIR－BLODGETT FILMS＊

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Organic DC electroluminescence (EL) devices are first created by fully using multilay LB films technology, which is different from the method of traditional vacuum evaporation. The film－moleculars possessing regular space arrange and orientation.

This device's basic structure consists of a hole－transport and a electron－transport layer. The hole－transport layer is 15 monolayers of 1, 10－bistearyl－4, 6, 13, 15－tetraene－18－Nitrogencrown－6 (Nc), without fluorescence. The electron－transport layer is 15 monolayers of 8－hydroxyquinoline aluminum (8－Alq), possessing fluorescence. Total is two cycles and 60 layers.

The device's properties of electricity and spectra are analysed. The blue－green emission has been achieved from the cell. Fig. 1 shows the current－voltage characteristics curve for the cell, lower excitation voltage (about 4.0v), and better property of voltage－resistant. Fig. 2 shows the fluorescence spectrum of 8－Alq and EL emission spectrum, in which the peak position shifts a little to red. The emission zone is affirmed in 8－Alq layer through comparing them. So it is proved that the EL mechanism is the recombination of electron and hole coming from the Nc layers in the 8－Alq layers.

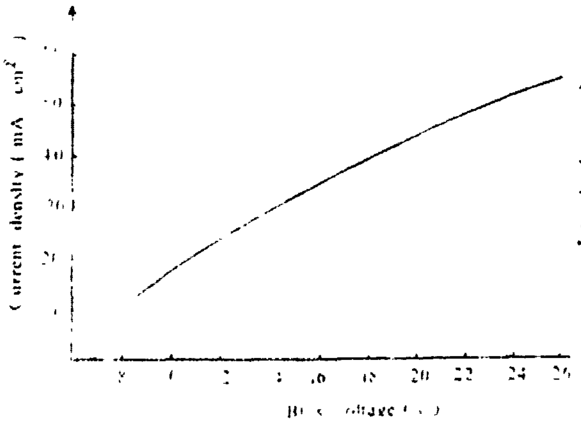

FIG. 1. Current－voltage characteristic for a cell ITO/Nc/Alq/Al

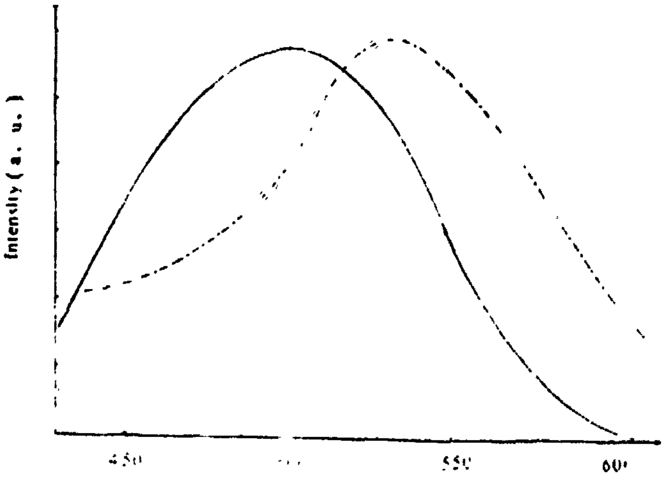

FIG. 2. Dotted line－EL emission spectrum of the cell
Solid line－Fluorescence spectrum of Alq.

＊This subject is suported by the Opening Laboratory of Exciting State Physics, Changchun Institute of Physics, Academia Sinica, China

CP29

PHOTOCHROMISM IN SPIROPYRANS AND SPIROTHIOPYRANS*

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The photochromic properties of spiropyran-containing LB films have been widely studied. In the present paper, we synthesize 5 different spiropyrans and 4 spirothiopyrans. All the compounds form good quality LB films and most of them can form J-aggregates. The J-aggregates formation is very sensitive to the purity of the water subphase since impurities in water can substantially influence the self-assembly process .

The excitation and emission spectra are quite similar for all the compounds, but the time of photoisomerisation is strongly dependent on the molecule. With the Spex F212 Fluorolog Spectrometer, we are only able to detect the photochromism process of two of our compounds, SP1 and SP2. When irradiated with 390nm light, they need ca 30 min at 350 lux to turn from the spiro form to the merocyanine form; the back reactions are even slower.

The photochromism times for the spirothiopyran are much faster while the back isomerisations are very slow.

Once the J-aggregates are formed, they can maintain more then eight months without any protection. It is suggested that the stability of the J-aggregates arise from an energy gain of about 0.2eV during the formation of the J-aggregates. It is estimated from the energy diagram of the spiropyran and its merocyanine form.

After illuminating the LB film with the proper light, J-aggregates are formed. Thus, the orientation of the molecules are changed and then frozen down during the photoisomerisation.

Hence, such LB films may be of potential use in optical memory devices.

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CP30

SECOND HARMONIC GENERATION IN MIXED CAROTENOID-FATTY ACID AND CAROTENOID-CYCLODEXTRIN LANGMUIR-BLODGETT FILMS

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Push-pull carotenoids have recently been found to display efficient optical second harmonic generation (SHG) both in the solid state and in solution [1,2]. Similar results have now been obtained when proper push-pull carotenoids are involved in non-centrosymmetrical structures built by the LB method .

As shown recently [3,4], dissymmetrical carotenoids can be organized in the solid state by the LB method . For instance, the push-pull carotenoid benzodithia-9-polyene-pyridine (BPP9), when diluted with ω-tricosenoic acid (ωC_{23}), gives rise to well-oriented aggregates where the molecular long axis are found perpendicular to the substrate [4]. A similar structure is obtained when the cationic carotenoid benzodithia-9-polyene-methylpyridinium ($BPP9^+$) is diluted with an amphiphilic cyclodextrin (CD), but part of the carotenoid molecules appear in that case as vertically oriented monomers .

These two different mixtures (BPP9 + ωC_{23} , $BPP9^+$ + CD) have been investigated by optical methods as monolayers and non-centrosymmetrical alternated multilayers .SHG experiments performed at $\lambda = 1.064\ \mu m$ [5] allowed us to measure the effective second order susceptibility of the non-linear molecules. By comparison with the second harmonic signal emitted by a single monolayer of $BPP9^+$ + CD , it has been shown that the orientational order of the film increases when monolayers of $BPP9^+$ + CD are built up into alternated active-passive structures with pure CD ($\beta = 396\ 10^{-30}$ esu, tilt angle = 27.5°). On the contrary, the non-linear efficiency of an alternate BPP9 + ωC_{23} / ωC_{23} active-passive film is reduced with respect to the efficiency observed on a single monolayer of BPP9 + ωC_{23}, revealing that non-centrosymmetry is partly broken as the number of layers increases .

Finally, the results suggest that cyclodextrins can be used to help set up a non-centrosymmetrical assembly of dissymmetrically modified carotenoids for use in quadratic non-linear optics. As a next step, we propose to further increase the non-linear optical efficiency by adequate engineering of active-passive mixed carotenoid-cyclodextrin layers .

[1] M. Blanchard-Desce, I. Ledoux, J.M. Lehn, J. Malthête and J. Zyss, *JCS Chem. Commun.*, 1988, 737.

[2] M. Barzoukas, M. Blanchard-Desce, D. Josse, J.M. Lehn and J. Zyss, *Chem. Phys.* , 1989, 133, 323.

[3] A. Wegmann, B. Tieke, J. Pfeiffer and B. Hilti, *JCS Chem. Commun.* , 1989, 586 .

[4] S. Palacin, M. Blanchard-Desce, J.M. Lehn and A. Barraud, *Thin Solid Films*, 1989, 178, 387 .

[5] I. Ledoux et al, *Thin Solid Films*, 1988, 160 , 217 .

CP31

NOVEL ORGANIC LUMINOPHORES FOR LB-MULTISTRUCTURES

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Synthesis of new amphiphilic luminophores in the oxazole, oxadiazole, and pyrazoline series is reported. Langmuir mono- and heterostructures have been obtained, formed by pure luminophores, their compositions and solutions of the luminophores in stearic acid in a broad concentration range. On the basis of P-S diagrams of the systems studied conclusions were made concerning packing of the luminophore molecules in the monolayer.

Spectral-luminescent characteristics of the luminophores were studied in chlorophorm solutions and LB multistructures of up to 100 monolayers. Dependence of luminescence intensity on luminophore concentration in the stearic acid has a maximum in the range of 5-25 mol.% for different luminophores. Highly diluted (10^{-3} -10^{-4} mol.%) luminophore solutions in the low-molecular solvents showed luminescence typical for the isolated molecules. At the same time in LB structures it was observed up to concentrations of 5 mol.%, while higher luminophore content led to luminescence of the associates.

We have obtained luminophore-comprising LB structures where up to 40 mol.% luminescence of both isolated molecules and associates could be observed, which considerably broadens the luminescence range.

CP32

Oxygen induced fluorescence quenching of pyrene labeled phosphatidylcholine in matrix monolayer at the gas/water interface

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We report here on the photophysical properties of pyrene labeled phosphatidylcholine (2,3-bis(1-pyrenedecanoyl)-L-α-phosphatidylcholine ; 2PPPC) embedded in unlabeled phosphatidylcholine matrix monolayer at the gas/water interface. The pyrene chromophore is located at the end of both acyl chains of the phospholipid. Phospholipids with varying acyl chain length such as DLPC, DMPC, DPPC, DSPC and DAPC were used as the matrix molecules. Surface pressure-, reflection-, and fluorescence-area isotherms were used for characterization of the photophysical properties of the pyrene chromophore. The reflection spectrum of the 2PPPC at the air/water interface shows four bands at 278nm, 317nm, 333nm, and 348nm respectively, which are slightly shifted towards longer wavelength as compared to that for monomer and shift further with increasing surface pressure indicating pyrene dimer formation. The reflection-area isotherms at 275nm and 348nm show that the long axis of the pyrene chromophore is not prependicular to the air/water interface. Increasing the acyl chain length of the matrix molecule leads to changes in the shape of the reflection-area isotherms indicating that the pyrene molecular axis becomes more and more parallel to the hydrophobic chains. The fluorescence spectrum of the mixed monolayer (2PPPC:DPPC 1:50) at surface pressure $<$ 0.5mN/m shows both the monomer (378nm 395nm, and 428nm) and excimer (485nm) emission. The fluorescence intensity and the ratio of monomer and excimer bands depends strongly on the surface pressure and the acyl chain length. In accordance with the literature reports, we found that the pyrene fluorescence (both monomer and excimer) is strongly quenched by the prescence of oxygen. However, the degree of quenching is much more pronounced in the the case of monolayer. The effect of oxygen on the fluorescence intensity was found to be reversible The degree and kinetics of quenching of pyrene emission are strongly dependent on the surface pressure and the length of acyl chain of matrix molecule For example in the case of DAPC as matrix molecule hardly any quenching of the pyrene fluorescence was observed. The results are analyzed and discussed in terms of molecuar model.

CP33

SURFACE COVERAGE BY WETTING WITH AMPHIPHILIC DYES BY ADSORPTION OR BY LANGMUIR-BLODGETT TECHNIQUE: A COMPARATIVE STUDY USING SECOND-HARMONIC GENERATION

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Abstract

Symmetry requirements restrict second-harmonic (SH) generation from centrosymmetric media to the interfacial range. Monomolecular adsorbates and near-surface quadrupolar SH-contributions can be the origin of the 2ω-response upon excitation of a surface with a single, monochromatic wave of fundamental frequency ω.

We have covered glass surfaces with both, LB-type monolayers prepared from hemicyanines and alternatively with layers of various coverage densities prepared by simple wetting with chloroform and alcohol solutions of the same chromophores. The wetting technique permits the application of a wide concentration range of the hemicyanines: 10^{-8} - 10^{-2} molar for chloroform solutions.

The adsorbates were analyzed with respect to polarization-dependent SH-signals in terms of s- and p-polarized SH-response and with respect to the average tilt angle ϑ with high angular resolution. This method allowed us to identify two different adsorption characteristics: site-specific adsorption with rather small ϑ-values for low concentrations of the wetting solution and therefore low coverage density of adsorbed molecules. With increasing concentration the molecules are adsorbed at extremely high tilt angles onto the substrate. In comparison at LB-monolayers prepared from hemicyanines at the same (linear-optically monitored) coverage density the SH-signals were approximately two orders of magnitude higher in intensity under favorable conditions, indicating the high degree of organization - in particular their polar ordering - of such films.

CP34

IR-ANALYSIS OF LANGMUIR-BLODGETT FILMS FOR NON-LINEAR OPTICS.

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The state of order of Langmuir-Blodgett (LB) films of 2-docosanyl amino-5-nitropyridine (DCANP) and its N-alkyl homologues with alkyl chain length of 18, 20, 24 and 26 carbons were investigated by polarized IR-spectroscopy. It has been shown that films made from these molecules have high second order optical susceptibilities, provided the structure of the film is non-centrosymmetric. Films of these molecules are therefore promising for applications like second harmonic generation (SHG) of IR-lasers.

In order to quantify the orientation of molecules in films the dichroic ratio is determined with e.g. respect to the dipping direction and the orthogonal direction both lying in the plane of the substrate. Although this ratio accounts only for two spatial directions it allows with some restrictions a comparison of the degree of order among DCANP and its homologues and their alignment on various substrates.

Spectra of films on silanized quartz plates are compared with films on ZnSe and Germanium. From the dichroic ratio one concludes that the alignment of the CH_2-groups in the hydrocarbon chain and of the NH-groups increases with chain length. The absorption intensities show that the number of adsorbed molecules increases in the order: Ge < silanized quartz < ZnSe. The highest SHG efficiency is achieved for DCANP where both the dichroic ratio and the number density are high. For the IR-transparent prism substrates the combination of transmission and attenuated total reflection (ATR) spectroscopy allows to determine the absorption perpendicular to the substrate surface.

The technique to measure the IR-spectra, the analysis and the interpretation are discussed. Geometrical consideration for the mutual arrangement of the molecules to account for a high SHG-efficiency based on the above results will be presented.

CP35

LANGMUIR-BLODGETT FILM FORMATION AND CHARACTERISATION OF A NEW TRIS-CHROMOPHORE NON-LINEAR OPTICAL OLIGOMER

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Some of the problems encountered with LB films are associated with their poor thermal and mechanical stability, though there are reports of polymeric LB films with improved stability and optical properties.(1, 2) However, polymers are rather less tractable than their monomeric counterparts and we report here the properties of an oligomeric structure which appears to possess the good Langmuir film forming properties of monomeric materials.

The structure consists of three chromophores attached to a diamide backbone which forms the hydrophilic end of the molecule. Each chromophore is derivatised with a hydrocarbon chain to provide hydrophobic character. The molecule forms stable Langmuir films over a pure water subphase with a surface pressure/area per molecule isotherm which rises to 50 mNm^{-1} before collapse. The area per molecule obtained by extrapolating to zero pressure can only be modelled by a structure adopting an S configuration of the backbone at the water surface. This appears to be achieved by the amide linkages adopting the cis rather than trans configuration at the air/water interface and in the LB film. LB films are readily deposited onto glass. The efficient transfer seems to result from hydrogen bonding between the headgroups.

FTIR characterisation of the LB film at grazing angle and a neutron scattering study of both the monolayer on the water surface and the LB multilayer gave a detailed description of the behaviour of the molecule and the structure adopted in the LB film.

1. P Hodge et al, Philos. Trans. R. Soc. London, A, 1990, **330**, 153-66
2. W Prass, Hoechst High Chem Magazine, 1989, **7**, 15.

Session DP

Electrical and dielectrical properties

DP1

MEASUREMENTS OF RATE CONSTANTS OF PHOTOINDUCED ELECTRON TRANSFER FROM VARIOUS FERROCENE DERIVATIVES TO AN EXCITED $Ru(bpy)_3^{2+}$ DERIVATIVE IN HETEROGENEOUS LB FILMS

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For the purpose of constructing artificial photosynthetic molecular systems for solar energy conversion, we have studied photoinduced electron transfer kinetics of Langmuir-Blodgett (LB) film molecular assemblies involving organic molecules with spatial regularity[1,2]. In the process of studying these kinetics in solid states, we found that the luminescence decay curves for $Ru(bpy)_3^{2+}$ in LB films could be fitted well as a sum of two exponential functions although those in organic solutions as a single exponential. Previously, we reported the effect of photooxidation of Ru complex, but the other factors giving a fast component have not been clarified yet[3].

On the other hand, in connection with photoelectric conversion in LB films, we have studied the photoinduced electron transfer kinetics in heterogeneous LB films containing the sensitizer (S) and the electron donors (D) with different standard redox potentials, E°'s[1]. Electron transfer quenching was observed even in the S/D LB system in which the electron transfer seemed to be an up-hill reaction based on the energy levels determined by the half-wave potentials, $E_{1/2}$, in acetonitrile. We interpreted this result as the effect of the electrical double layers formed in the LB films. The standard free energy of the electron transfer quenching, ΔG°, based on $E_{1/2}$ should be modified by taking account of the electric potential difference, $\Delta\phi$, generated between the sensitizer and the donor.

In the present work, in order to find out the other origins for the fast component in the decay curves of $Ru(bpy)_3^{2+}$ LB films without D layers, we studied the effects of i) laser power, ii) irradiation time in vacuum, air, H_2O, or N_2 atmosphere, iii) counterions added in the subphase, iv) diluting reagents with various dilution ratios, and v) interaction between $Ru(bpy)_3^{2+}$ and substrate plates. We also reexamined the effect of electrical double layers[4] on photoinduced electron transfer quenching rates from amphiphilic ferrocene derivatives with different charges (+1, 0, -1) at the hydrophilic head groups to an excited $Ru(bpy)_3^{2+}$ amphiphiles in heterogeneous LB S/D systems.

1) T. Kondo, H. Yamada, K. Nishiyama, K. Suga, and M. Fujihira, *Thin Solid Films*, 179 (1989) 463.
2) M. Fujihira and H. Yamada, *Thin Solid Films*, 160 (1988) 125. ;
M. Fujihira, K. Nishiyama, and K. Aoki, 160, (1988) 317.
3) T. Kondo and M. Fujihira, *Kobunshi Ronbunsyu*, 47, (1990) 921.
4) T. Kondo and M. Fujihira, *Chem. Lett.*, 1991, 191.

DP2

DEVICE STRUCTURES FOR THE ELECTRICAL CHARACTERIZATION OF LANGMUIR-BLODGETT FILMS OF CONDUCTING POLYMERS

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Various device structures have been fabricated using Langmuir-Blodgett films of conducting polymers as electrically active elements. Schottky junctions formed to LB films of poly(3-hexylthiophene) exhibit only partially blocking behavior due to a dopant accumulation at the electrode-polymer interface. However, these devices can be utilized in probing the electrical material parameters close to the rectifying contact. With metal-insulator-polymer structures, on the other hand, the depletion layer can be swept through the LB multilayers, and the dopant profile can be examined. Charge carrier mobility was determined by using field-effect-transistor structures. The field-effect was observed even in a monolayer of a conducting polymer. We have also fabricated heterostructures by sandwiching mono- or multilayers of doped polypyrrole between multilayers of undoped poly(3-hexylthiophene). Capacitance measurements with MIS structures and Schottky barrier configurations indicate a modulated dopant profile.

DP3

Photogenerated-Charge-Storage in Hetero Langmuir-Blodgett Films including Steroidal TCNQ, Cu-Phthalocyanine and Steroidal p-Phenylenediamine

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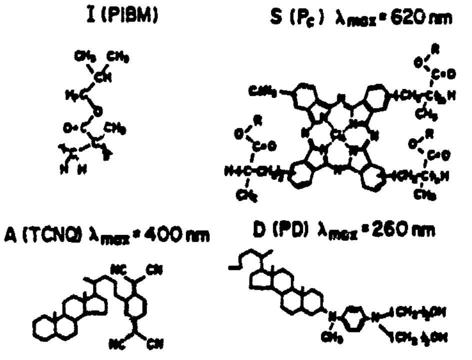
For realizing molecular electronic devices using hetero LB films, electric charge or carrier behaviors in the organic super lattices can be controlled by outer energies such as an electric field. For this purpose, uniform and defect-free dye LB films are indispensable. We have investigated molecular structures producing uniform dye LB films and have synthesized a wide range of dye amphiphiles, substituted by a steroid skeleton.[1] In the present study, we have assembled uniform hetero LB films including donor and acceptor molecules, and have tried to conduct the photogenerated charges with an electric field.

We constructed an MIM-type device by the usual vertical dipping method as shown in Fig. 2: ITO// I, 180 Å/ A, 2 Layers, 36 Å/ S, 2L, 44 Å/ D, 2L, 60 Å / I, 330 Å// Hg (ϕ = 1-2 mm). Electrical measurements were carried out in an ambient atmosphere at rt.

Transient current in accordance with the electron flow from D to A was observed by illumination of red light absorbed by S, as reported by Fujihira et al.[2] In the absence of both A and D, the photocurrent was reduced to 1 %. In the absence of D, it was not reduced very much (92 %). Photovoltage was also observed and was in accordance with the value calculated from the current and the capacitance. The action spectrum indicated that the photoresponses of the hetero film were due to photoexitation of S. The peak height of the transient current was proportional to the 0.75 powers of the light intensity (620 nm). The peak height increased as the applied voltage increased (Hg negative). The open circuit voltage was about 2 V. In the dark, the film was a good insulator (resistivity > $10^{15}\,\Omega$cm at 1 V) and no rectifiable property was observed.

In the film structure including the strong donor and acceptor molecules separated from the electrodes by the insulator layers, the photoinduced electrons and holes can be expected to be stored in separated positions in the dark. The life time of the separated charges was measured by the photovoltage decay and by the photocurrent recovery. Based on the condition of applied voltage of 0 V and 1/8 sec illumination of 610 nm light of 6 mW/cm^2, the time taken for complete photocurrent recovery (Tr) was about 10 min. Tr was controllable by changing the applied voltage: it was extended to 30 min under -0.5 V (Hg electrode), and further extended over 1h under -1 V, on the contrary, shortened to 1 min under 0.5 V. In the absence of D, Tr was extremely shortened to 5 sec under 0 V.



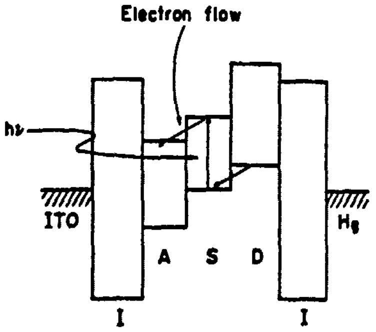


Fig. 1 Molecular structures used here. Fig. 2 Schematic energy diagram.

1) K. Naito, A. Miura, M. Azuma, Langmuir in press.
2) M. Fujihira et al. Thin Solid Films, **132**, 77, **160**, 125, **180**, 43.

DP4

FAST IN-PLANE PHOTOCONDUCTON IN LANGMUIR-BLODGETT MULTILAYERS OF POLYDIACETYLENES

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The motion of charge carriers in Langmuir-Blodgett multilayers of polymerized 10,12 pentacosadiynoic acid has been observed. The carriers, created between surface electrodes by light pulses of 25ps duration from a frequency doubled Nd YAG laser, move along 1-D 'molecular wires', formed by the PDA chains, under the influence of an externally applied electric field. An anisotropy is observed in the magnitude of the photocurrent in the two directions parallel and perpendicular to the dipping direction and indicate a preference of PDA chains to orient parallel to the dipping direction.

The electric field dependence of the measured charge, Q, is found to range from linear to slightly superlinear, and is consistent with 1-D Onsager theory. The dependence of Q on light intensity, I, is sublinear. varying as $Q = I^m$ with $m \cong 2/3$, and is believed to be the result of using surface electrodes. The distance charge carriers move before trapping is found to be between 20μm and 60μm.

DP5

FABRICATION OF ELECTRICALLY CONDUCTIVE LANGMUIR-BLODGETT FILMS COMPRISED OF POLY(3-HEXYL THIOPHENE) AND NICKEL TETRA-TERT-BUTYL PHTHALOCYANINE

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Mixed Langmuir-Blodgett films containing two electroactive components, poly(3-hexyl thiophene) and nickel tetra-tert-butyl phthalocyanine, have been prepared and characterized. In this system, the phthalocyanine molecules act as both a surface active material and as an electroactive material. Mixing the phthalocyanine molecules with a non-surface active conducting polymer results in thin films with novel optical and electrical properties and enhanced thermal and chemical stabilities. Surface pressure-area isotherms suggest that the phthalocyanine molecules are stacked parallel to the air-water interface and are dispersed as a separate phase in a matrix of polythiophene molecules. The structures of the multilayer LB films fabricated from the monolayers of this system were investigated by x-ray diffraction, reflection/transmission FTIR, and optical absorption techniques. Results from these studies indicate that the phthalocyanine rings retain a parallel orientation after monolayer transfer. The conductivities of the LB films doped with oxidizing agents such as $NOPF_6$, $SbCl_5$, and I_2 reached values as high as 0.5 S/cm.

DP6

ELECTRICAL TRANSPORT PROPERTIES OF JOSEPHSON JUNCTIONS WITH A Nb/Au/PI/(Pb-Bi) STRUCTURE

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The LB technique is an important method used to prepare ultrathin films. One of the potential applications of LB films is electrically insulating spacers in the manufacture of Josephson junctions, where it is essential to prepare pinhole-free spacers. Since the preparation of polyimide (PI) LB films[1], having the monolayer thickness of about 0.4 nm, with a small number of conducting defects, much attention has been paid to the PI LB films. In a previous report, we fabricated tunnel junctions having the structure of Au/PI/(Pb-Bi) and observed the tunneling current predicted by the BCS theory[2,3]. However, we were able to fabricate neither Josephson junctions with a Nb/PI/(Pb-Bi) structure[4] nor junctions with a (Pb-Bi)/PI/(Pb-Bi) structure[5]. Because an inherent oxide layer was formed on the base-Nb electrode or the base-(Pb-Bi) electrode was dissolved during the imidization. In this work, we formed base-Nb/Au electrodes and then constructed the Nb/Au/PI/(Pb-Bi) Josephson junctions with neither the presence of native oxide layers formed on the Nb layer nor the dissolution of the base-Nb/Au electrode during the imidization. A typical I-V characteristic of a weakly-coupled superconductor was obtained for junctions having the number of deposited layers of 29, 41 and 51 in the presence or absence of microwave powers with a frequency of 70 GHz, whereas a typical I-V characteristic of an ideal tunnel-type Josephson junction was never obtained. It was concluded that although we were not able to obtain tunnel-type junctions, the junctions were able to detect microwaves with a high frequency, e.g., 0.35 THz. Finally, we fabricated Au/PI/(Pb-Bi) junctions and then measured the IETS spectra of the junctions in order to clarify the electrical conduction mechanism through PI LB films.

References

1. M.Kakimoto et al., Chem.Lett, 823 (1986).
2. M.Iwamoto et al., Thin Solid Films, 180 (1989) 185.
3. M.Iwamoto et al., J.Phys.D, Appl.Phys. 23 (1990) 575.
4. M.Iwamoto et al., Jpn.J.Appl.Phys. 29 (1990) 116.
5. M.Iwamoto et al., Jpn.J.Appl.Phys. 27 (1988) 1224.

DP7

ELECTROOXIDATION OF DIOCTADECYLTHIOETHYLENEDITHIOTETRATHIOFULVALENE LANGMUIR-BLODGETT FILMS

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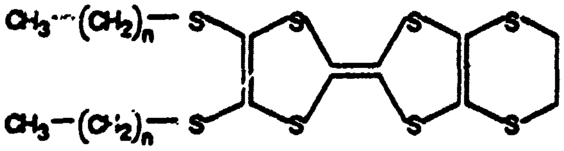
Organic conductors in Langmuir-Blodgett films (LB) can be prepared in two steps i) deposition of the amphiphilic or semiamphiphilic compound onto substrates. ii) chemical oxydation by halogen vapors (mainly iodine gaz) to obtain a mixed valence state responsible for the conductive properties. In some cases as for dialkylthioethylenedithiotetrathiofulvalene derivatives a third thermal step is necessary to achieve the conductive phase. We explore on the diaoctadecylthioethylenedithiotetrathiofulvalene compound (**1**) an electrochemical way to obtain directly the conducting phase.

Experiments have been carried at different constant potentials during the phase deposition onto indium tin oxide glass electrodes with KI and KBr as electrolytes. Chloroform spreading solutions with various molar fractions of **1** and behenic acid mixtures have been used. Amperometry measurements and UV, visible, IR caracterizations have been made.

Two different electrooxidation processes have been found. i) a slow electron transfer from **1** to the electrode at potential higher than 350mV/SCE ii) a complete chemical oxidation of **1** by the oxidized anion produced during the electrolyse at potential values for which the electrolyte can be oxidized (c.a. 450mV/SCE for KI) Conductive material has been obtained only with potassium iodide electrolyte at higher potential than 450 mV/SCE. In this case there are some similitudes with chemical oxidation: i.e. the completely ionized brown phase is obtained directly during the electrolyse and then a thermal treatment leads to the conducting purple mixed valence state associated with the formation of I_3^- chains.



1 : n = 17

DP8

ELECTRONIC AND OPTICAL STUDIES WITH LB TRANSISTORS

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A thin film transistor structure provides an accurate way to measure the charge carrier mobility, their type (p or n type material) and concentration in mono- or multilayer LB films[1]. The transistors used here have channel lengths of 1, 5 and 10 μm. We have characterized LB monolayers of undoped quinquethiophene (QT) and poly(3-alkylthiophenes) (PAT) mixed with arachidic (AA) or stearic acid (SA). QT-PAT heterostructure FETs are also being studied. The mobilities in LB monolayers, $\mu \approx 10^{-9}...10^{-6}$ cm^2/Vs, are typically several orders of magnitude lower than in thicker films, where values up to $\mu \approx 10^{-4}$ cm^2/Vs can be achieved. The reason for this are the increasing hopping distances in the percolation path as the thickness decreases under a certain limit[1]. Another feature which may affect the charge transport is the high ratio of extra holes per monomer unit in monolayers (up to one percent) for large accumulation voltages. - The mobilities are very low compared to the mobilities in crystalline silicon or gallium arsenide ($\mu_{Si,GaAs} \approx 10^3$ cm^2/Vs).

In addition to increasing the conductance of the transistor channel, the extra accumulated holes stored in the polaronic states may act as recombination centers for excitons[2]. The transistor structure here acts as a luminescence quenching device. The films studied were undoped spin-coated poly(3-hexylthiophene) (PHT) films (thickness about 70 nm) and PHT/AA LB films having 3 or 7 layers. Excitons were photoexcited by an argon laser. The luminescence quenching by the gate voltage was clearly seen in LB and spin-coated films. The quenching was a few tens of percents for LB films, considerably less for spin-coated films.

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1. J. Paloheimo et al., Appl. Phys. Lett. 56 (1990) 1157.
2. P. Dyreklev et al., to appear in Proc. International Winterschool on Electronic Properties of Polymers (IWEPP 91), 9.-16.3.1991, Kirchberg, Austria.

DP9

MONOLAYER CHARACTERISATION AND MULTILAYER DEPOSITION OF CONDUCTING LB FILMS

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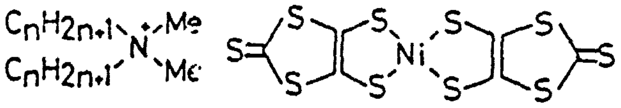
Background and Methods

Conductive LB films of high dimensionality should overcome the problem of stacking defects and the Peierls instability. In a recent report, Nakamura *et al* [1] have reported that the LB technique may be used to deposit films of the mixed-valence complex of $(C_nH_{2n+1})_2Me_2N$-Ni(dmit)$_2$ (Scheme 1) where n = 10, 12, 14, 16, 18 and 22.



Scheme 1

The conductivity of these films is governed by the strong two-dimensional interaction of the sulphur orbitals and on exposure to bromine gas films with conductivity as high as 0.1 S/cm have been prepared.

In related work we have been characterising divalent didodecyldimethylammonium salts of M(dmit)$_2$ and M(mnt)$_2$ where M = Ni, Pd or Pt. Spreading solutions of these salts were prepared in chloroform and monolayers formed on the surface of pure water in a PTFE Langmuir trough located on an antivibration table in a Class 2 semiconductor clean room. Pure water was obtained from a Millipore RO 60 reverse osmosis cartridge feeding a SuperQ system consisting of activated carbon, deioniser and 0.2μm filter cartridges. Surface pressure and surface potential isotherms were obtained for the monolayers at various subphase temperatures.

Figure 1 shows typical π-A isotherms for Ni and Pt dmit$_2$ at 15°C. It is seen that the isotherms obtained for the Ni salt depend on the time which elapses between the spreading of the monolayer and the first compression. After allowing an hour for complete spreading of the layer, the isotherm is similar to those obtained for the Pt and Pd salts. When the subphase temperature is raised to 25°C even the Ni isotherm reaches a steady state within a few minutes of spreading. Similar results were obtained with the mnt$_2$ salts.

Figure 2 shows the surface potential of a deposited monolayer of Nimnt$_2$. The step change in potential as the probe passes over the monolayer is clearly visible. (Each curve represents different scan lines over the

DP10

PHOTO-INDUCED ELECTRON TRANSFER IN MOLECULAR HETEROJUNCTION USING FLAVIN-PORPHYRIN LB MULTILAYERS

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Photo-induced electron transfer in hetero-type Langmuir-Blodgett (LB) multilayers using flavin and porphyrin, which are typical of redox groups for the biological electron transfer system, was investigated in terms of photoconductivity, photovoltaic effect, and transient photocurrent properties.

The photocurrent for aluminium//flavin monolayers/porphyrin monolayers//aluminium structures showed clear rectifying behavior and the quantum efficiency of the photoconduction was found to be extremely high in the range from 5 to 30 % for the transmitted monochromatic light at 450 nm. The rectifying I-V properties and V_{oc} around -0.6 V, which are the characteristics for the single-heterojunction structures, were not observed for the multiple-heterojunction structures (aluminium//(flavin monolayers/porphyrin monolayers)$_n$//aluminium, $n \geq 2$). This result means that internal potential gradient in the MIM (Metal-Insulator-Metal) device is apparently diminished by the formation of the multiple heterojunction. Furthermore, the measurement of the transient photocurrent of the single-heterojunction MIM device showed that three photo-processes are involved in the photo-induced electron transfer. These photo-processes were found to be basically elucidated by a kinetic model of relaxation of the photo-excited flavin.

It is concluded from these results that the photocurrent of the single-heterojunction MIM device originates from the molecular heterojunction between flavin and porphyrin.

DP11

CONTROL OF PHOTOCHEMICAL SWITCHING PHENOMENA BY CHEMICAL MODIFICATION

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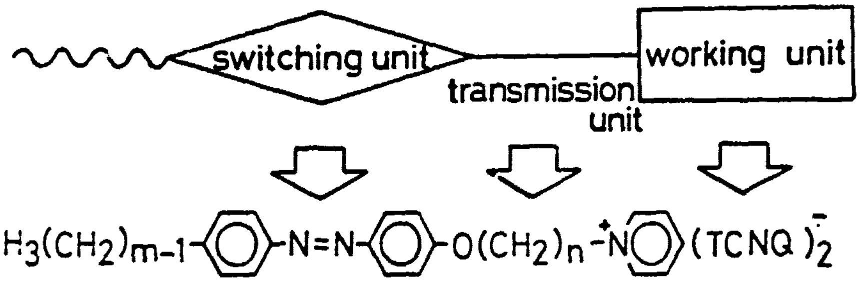
Langmuir-Blodgett (LB) technique is excellent in preparing organic thin films. Various functions of LB films have been developed; nonlinear optical effects, photochromism, electrical conduction etc. A switching device is fabricated by the incorporation of three functional parts into a molecule, consisting of a switching unit, a transmission unit, and a working unit. When the switching unit receives an external stimulus, the signal is conveyed through the transmission unit to the working unit which responds to the signal. For photochemical switching devices, photochromic compounds can be used as the switching unit, taking advantage of the photoresponsiveness.



APT (m - n)

We have used azobenzene as the switching unit, alkyl chain as the transmission unit, and charge transfer complex as the working unit, demonstrating that the conductivity of LB films of APT(8-12) changes reversibly on photoirradiation.[1,2] The conductivity increases with the trans-to-cis photoisomerization of azobenzene and reverts to the initial state with the cis-to-trans photoisomerization.

In this work, we investigate the effect of chemical modification on the photochemical switching phenomena. The length of alkyl chain of the transmission unit is changed in the first step. The photochemical switching phenomena are very sensitive to this chemical modification, that is, the conversion of the trans-to-cis photoisomerization of azobenzene and the simultaneous change in conductivity of the LB film depend largely on the length of the transmission unit. For all the compounds studied, the azobenzene shows reversible photoisomerization with the conversion dependent on the length of the alkyl chain. When the alkyl chain is long enough, the conductivity of the LB film doesn't change reversibly on photoirradiation although the cis-trans photoisomerization of azobenzene is observed.

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1. H.Tachibana, T.Nakamura, M.Matsumoto, H.Komizu, E.Manda, H.Niino, A.Yabe, and Y.Kawabata, J.Am.Chem.Soc., 111, 3080(1989).
2. H.Tachibana, A.Goto, T.Nakamura, M.Matsumoto, E.Manda, H.Niino, A.Yabe, and Y.Kawabata, Thin Solid Films, 179, 207(1989).

DP12

PREPARATION OF POLYIMIDE LB FILMS POSSESSING TRIPHENYLAMINE UNIT AND APPLICATION TO PHOTODIODES

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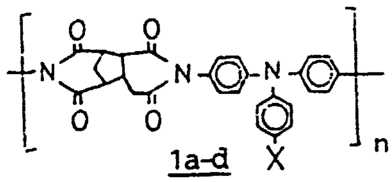
We have reported that preparation and applications of polyimide LB films. The most characteristic point of the polyimide LB films is that they do not have long alkyl chains. Photoconductive devices (photodiodes) were successfully constructed by depositing polyimide LB films which possessed different chemical structure, i.e., electron acceptor (A), sensitizer (s), and electron donor (D) moieties.[1] In this study, a novel photoconductive devices were fabricated by using triphenylamine units as D (1a-d), tetraphenylporphyrin moiety as S (2), and aromatic polyimide (3) as A.

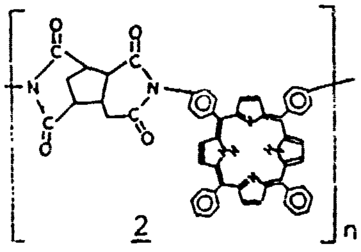
D=



1a-d

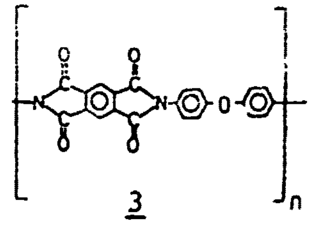
X: a= -H, b= $-CH_3$, c= $-OCH_3$, d= $-N(CH_3)_2$

S=



2

A=



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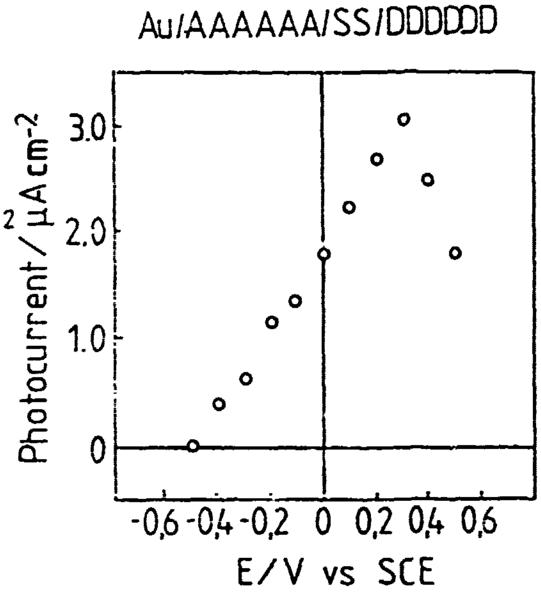

Fig.1. Potential dependence of peak photocurrents in A/S/D system (D: 1c) in constant with 100mM KCl aqueous solution under stepped illumination of visible light of 430nm

Two type of the photoconductive devices having D/S/A and A/S/D structure were prepared on the gold semitransparent electrode. A example of the photocurrents in A/S/D system observed by stepped illumination with the visible light of 430 nm are plotted as the function of the applied electrode potential in Fig. 1. Extremely high photocurrents depending on the chemical structure of D were observed. This phenomena is probably explained because of the absence of the long alkylchain.

[1] Y. Nishikata, A. Morikawa, M. Kakimoto, Y. Imai, Y. Hirata, K. Nishiyama, M. Fujihira, J. Chem. Soc., Chem. Commun., 1989, 1772

DP13

THE SYNTHESIS AND CHARACTERISATION OF NOVEL POLYSILOXANE LANGMUIR-BLODGETT FILMS.

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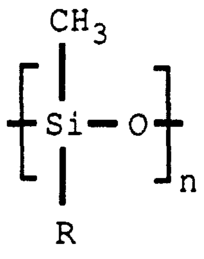
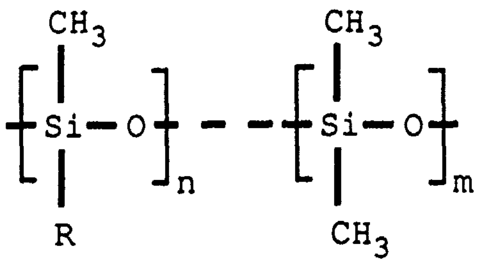
A great deal of effort in previous years has been directed at the study of a wide range of monmeric materials for Langmuir-Blodgett (LB) film deposition. More recently, however, many researchers have directed their attention towards polymeric materials since such compounds offer potentially improved thermal and mechanical stability, and are therefore more attractive to the device engineer. In this work, several polymers, based on a polysiloxane backbone, have been synthesised and characterised.

This work describes the synthesis and characterisation of a poly (hydrogenmethylsiloxane) homopolymer and a poly (hydrogenmethyl-dimethylsiloxane) copolymer both substituted with an aliphatic acid group. Their surface pressure - area isotherms and deposition characteristics have been examined. Excellent agreement has been found between the measured area per polymer unit on the water surface and the modelled value. In addition, a range of optical and electrical characterisation techniques have been used to elucidate some of their thin film properties. For example, dielectric loss tangents and relative permittivies have been measured as well as a study of their pyroelectrical properties. Some structural characterisation has also begun.



$$\left[-\overset{CH_3}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O- \right]_n$$

Homopolymer



$$\left[-\overset{CH_3}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O- \right]_n - - \left[-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{Si}}}}-O- \right]_m$$

Copolymer

$R = CH{=}CH_2(CH_2)_8CO_2H$

DP14

MOLECULAR ORIENTATION IN CONDUCTIVE LANGMUIR-BLODGETT FILMS OF A CHARGE-TRANSFER COMPLEX

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In recent years Langmuir-Blodgett (LB) films of charge-transfer (CT) complexes have attracted increasing attention.[1-4] We have been investigating conductive LB films of a 3:2 CT complex of TMTTF and tetradecylTCNQ by using the electron spin resonance (ESR) technique.[5] Both in-plane and out-of-plane anisotropies in the ESR signal were detected for the films. Anomaly of *g* value, linewidth, and spin susceptibility around 150 K was detected, which suggest the Peierls fluctuations characteristic of 1D metallic domain.

The minimum *g* value at the room temperature (RT) was observed for the external magnetic field parallel to the dipping direction of the substrates.[5] We have found that this in-plane anisotropy of *g* value gradually increased for about 10 days while they were kept in He atmosphere at RT after the deposition. In this period of time the increase in the conductivity of the films was also detected. Moreover, the maximum of the temperature-dependent *g* value around 150 K was more prominent for those aged films than for the as-deposited films. These suggest the lower degree of the misorientation of molecules in the aged films caused by the possible molecular rearrangements.

An inversion of the *g*-value anisotropy was detected at lower temperatures for as-deposited films. A similar phenomenon was reported for EDTTTF$(S\text{-}C_{18})_2$-$TCNQF_4$ films.[6] This inversion can be caused by the domination of signals of the spins trapped at defect sites, where molecules may be misoriented and provide different *g* value from the major part of the system. This interpretation is supported by the fact that the inversion was not observed for the aged films, in which the reduction of the degree of the misorientation is suggested.

1. A. Ruaudel-Texier *et al.*, Mol. Cryst. Liq. Cryst., **120** (1985) 319.
2. A. Barraud *et al.*, Thin Solid Films, **134** (1985) 195.
3. T. Nakamura *et al.*, Chem. Lett., (1986) 709.
4. M. Matsumoto *et al.*, Thin Solid Films, **160** (1988) 61.
5. K. Ikegami *et al.*, Synth. Met., **27** (1988) B587; Thin Solid Films, **179** (1989) 182.
6. J.P. Morand *et al.*, Synth. Met., **27** (1988) B569.

DP15

Electronic transport in Langmuir-Blodgett films of metal-$(dmit)_2$

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The metal-$(dmit)_2$ (H_2dmit =4,5-dimercapto-1,3-dithiol-2-thione) molecules form "more-than-1D" conductors through their close intermolecular S...S contacts, exhibiting metallic states down to low temperatures and superconductivities. By introducing alkylammonium group as a counter cation, the molecules become amphiphilic and suitable for the fabrication of LB films. We have reported conductive LB films based on various kinds of metal-$(dmit)_2$ complexes. One of these systems, tridecylmethylammonium-Au$(dmit)_2$ (Fig.1, 3C10-Au), shows high conductivity of 30-50 S/cm at room temperature.

To investigate the electronic transport properties of the 3C10-Au LB films more precisely, we examine the thermoelectric power together with dc conductivity. The temperature dependence of the conductivity have a broad maximum around 200 K; the conductivity increases with decreasing temperature from room temperature to 200 K, showing a quasi-metallic behavior, and decreases below that temperature down to around 4 K. The thermoelectric power is positive and in the range 10-25 μV/K at room temperature. The temperature dependence of the thermoelectric power exhibits metal-like behavior over the temperature range from 300 to 4 K; the value decreases with decreasing temperature. The small magnitude of the thermoelectric power and the temperature dependence suggest that the LB film is metal-like.

We consider that the broad maximum of the conductivity is not by the transition of Peierls type, but rather due to carrier localization, possibly due to random potentials set up by disorders such as grain boundaries or defects. In fact, the peak of the conductivity is not accompanied by the corresponding transition in thermoelectric power that would be expected if the transition were due to the opening of a gap at the Fermi energy.

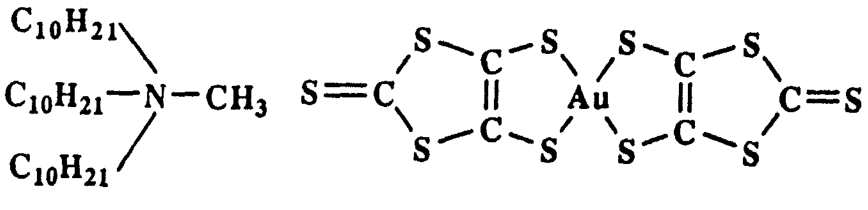

Fig.1 Molecular structure of tridecylmethylammonium-Au$(dmit)_2$

DP16

'SUPERLATTICES' PREPARED FROM DIELECTRIC AND TWO-COMPONENT CONDUCTING LB LAYERS

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Discovery of conductance in LB films gives alluring prospects for creation of new molecular assemblies. The deposition of the films with desired distribution of thin conducting and dielectric layers along the perpendicular to the substrate plane seems to be a substantial step on a way to 'nanoelectronics'. However, experimental evidence of existence of a precise lamellar order in the 'superlattices' containing layers of charge-transfer complexes and salts was absent.

Preparation of the 'superlattices' using these compounds for depositing of conducting areas appeared to be a difficult problem. We tried to prepare the films with different sequences of alternation of dielectric (D) and conducting (C) bilayers. The programs of alternation were the following: DCDCDC...., DDCDDCDDC..., DCCDCCDCC..., DCCCDCCC..., and DDCCDDCC... . Barium behenate and stearate layers were used as dielectrics. Hexadecylbis(ethylenedithio)tetrathiafulvalene (C_{16}-BEDT-TTF) and hexadecylethylenedithiopropylenedithiotetrathiafulvalene (C_{16}-EDT-PDT-TTF) as well as the mixtures of the latters with hexadecyltetracyanoquinodimethane (C_{16}-TCNQ) and 2-heptadecaoxycarbonyltetracyanoanthraquinodimethane (C_{17}-OC-TCNAQ) were deposited to obtain conducting areas. We investigated the films by electron microscopy, X-ray, and electron diffraction techniques. Conductance of the samples was checked also.

One-component C_{16}-BEDT-TTF and C_{16}-EDT-PDT-TTF conducting films possess a crystalline order in the direction normal to the film plane. But no Bragg reflections appear on the X-ray diffraction patterns of 'superlattices' containing these monolayers. Nevertheless, the doped films show high conductivity. These results are explained by poor spreading of conducting monolayers. For this reason the mean thickness of the layer, which is deposited in one dipping process, is more than that of one monolayer, and periodic structure does not arise.

Diffraction patterns of the 'superlattices' produced from the fatty acid salts and two-component mixtures of C_{16}-BEDT-TTF or C_{16}-EDT-PDT-TTF with C_{16}-TCNQ do not show reflections also. This is caused by recrystallization of conducting layer on the substrate when deposition of dielectric is carried out.

Experiments on the preparation of 'superlattices' appeared to be successful when the mixtures of C_{16}-BEDT-TTF or C_{16}-EDT-PDT-TTF with C_{17}-OC-TCNAQ were used to form conducting areas. One crystalline structure arises for any sequence of layer alternation if optimum compositions of components and the best conditions of deposition are used. But additional reflections appear on the diffraction patterns under some variations of these parameters. However, these additional reflections do not correspond to crystalline structures of the components used. Possible variants of structure change are discussed.

DP17

IDENTIFICATION OF THE PROCESS PRODUCING OBSERVED RECTIFYING CHARACTERISTICS OF M/LB/M STRUCTURES

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The Langmuir-Blodgett (LB) technique has been employed in the fabrication of $M_1/C_{16}H_{33}$-Q3CNQ LB film/M_2 structures which have exhibited rectifying properties even when the LB film thickness was a single monolayer by ourselves [1] and using DDOP-C-BHTCNQ by Geddes *et al* [2]. The process responsible for the asymmetric I/V curves has not yet been unambiguously attributed to the intrinsic properties of the LB molecule. There exist several possible explanations which do not require the process to be molecular in origin. It has been suggested that thermal evaporation of the electrode M_2, in this case magnesium, being highly reactive may modify the LB film producing diodic characteristics. The permanent molecular dipole moment or Schottky processes at the electrodes are also possible explanations for the rectification. The results obtained so far with these organic layers, supporting E fields of order $10^9 Vm^{-1}$, are extraordinary and clearly need detailed study.

We are currently performing experiments to help to clarify the rôles of the various possible mechanisms. In particular, we are endeavouring to ascertain whether the observed asymmetric I/V curves are a result of "molecular rectification" or purely due to "bulk" processes arising from device construction. This shall be accomplished using inert LB film spacer layers between each electrode and the active LB layer thus eliminating both chemical interactions with magnesium vapour and interfacial effects at the electrodes. Retaining I/V curve asymmetry in such a device will demonstrate that the rectification is molecular in origin. It may prove possible to reverse the orientation of the active LB film in which case rectification should be observed under opposite polarity.

References

[1]	Ashwell *et al*	1990	J. Chem. Soc.. Chem. Com. **19** 1374
[2]	Geddes *et al*	1989	Thin Solid Films **168** 151

DP18

CONDUCTING LB FILMS OF NEW TETRATHIAFULVALENE DERIVATIVES

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To determine the influence of some molecular structure variations on the properties of conducting Langmuir-Blodgett films we synthesized new surfactant derivatives of tetrathiafulvalene i.e. hexadecylethylenedithiopropylenedithiotetrathiafulvalene (hexadecyl-EDT-PDT-TTF) and hexadecylethylenedithiooxapropylenedithiotetrathiafulvalene (hexadecyl-EDT-OPDT-TTF). In the first place monolayers of these donor molecules at the air-water interface were studied. Then the deposition of multilayers was carried out. To characterize morphology and structure of the films we fulfilled their investigations by electron diffraction and electron microscopy techniques. Conductivity of the films was estimated before and after doping by iodine. The films of hexadecylbis(ethylenedithio)tetrathiafulvalene (hexadecyl-BEDT-TTF) [1] were studied also to understand the tendency of change of the properties.

Characteristics of the monolayers on a water surface and the multilayers deposited on solid substrates are outlined by data presented in the Table.

Compound	Hexadecyl-BEDT-TTF	Hexadecyl-EDT-PDT-TTF	Hexadecyl-EDT-OPDT-TTF
Area per molecule (nm^2)	0.31	0.33	0.32
Collapse pressure (mN/m)	32	24	27
Conductivity ($Ohm^{-1}cm^{-1}$)			
before doping	10^{-3}-$5 \cdot 10^{-3}$	$3 \cdot 10^{-4}$-10^{-3}	$2 \cdot 10^{-4}$-$7 \cdot 10^{-4}$
after doping [x]	0.1-0.5	0.04-0.2	10^{-3}-$5 \cdot 10^{-3}$
Dimensions of crystallites (nm)	100-200	20-30	10-20

[x] Conductivity is attributed only to conducting areas.

The films of hexadecyl-BEDT-TTF possess the best conductivity. But in a day approximately they undergo a recrystallization. On the other hand, the multilayers of hexadecyl-EDT-PDT-TTF have the best morphology, and nothing happens with the films during one month at least. Bad quality of deposition of the hexadecyl-EDT-OPDT-TTF film is explained by high viscosity of the monolayer at the air-water interface.

Our study shows that the values of conductivity depend strongly on the in-plane dimensions of crystallites. This result confirms the conclusion [2] that a contribution of grain boundaries into resistance of the conducting Langmuir-Blodgett films is considerable. Possible reasons of difference of another properties are also discussed.

Patterns in the conducting films were drawn by electron beam. Conductivity disappears under irradiation, but no deterioration of film morphology takes place. The sensitivity of the films to the action of electrons is determined.

REFERENCES

1 C. Lalanne, P. Delhaes, E. Dupart, Ch. Garrigou-Lagrange, J. Amiell, J.P. Morrand and B. Desbat, Thin Solid Films, 179, 171-176(1989)
2. A. Barraud, J.Richard, A. Ruaudel-Teixier and M. Vandevyver Thin Solid Films, 159, 413-419(1988).

DP19

MOLECULAR ORIENTATION-PYROELECTRICITY RELATIONSHIPS IN ALTERNATE LB FILMS

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Relationships between molecular orientation and pyroelectricity in alternate LB films consisting of 5-(p-dodecyloxyphenyl) pyrazine-2-carboxylic acid and deuterated stearic acid were investigated. The same studies were also performed for the corresponding alternate LB films of their barium salts.

Pyroelectricity of the films was measured by a static method in the temperature range from -30 to 60 °C. The maximum values of pyroelectric coefficient due to a decay of the spontaneous polarization were obtained to be 1.2 $\mu C\, m^{-2} K^{-1}$ at 37 °C for the acid alternate film, and 1.8 $\mu C\, m^{-2} K^{-1}$ at 43 °C for the barium salt alternate film. Rapid increases of positive currents due to a depolarization in the films were observed bove 50 °C.

The molecular orientation in the films was evaluated by our new method$^{1)}$ involving FT-IR transmission and reflection-absorption spectroscopy. Temperature dependence of the orientation angles of the hydrocarbon chain axes of the constituent molecules indicates that the depolarization is due to the conformational disorder of the hydrocarbon chains. Temperature dependence of the antisymmetric and symmetric COO^- stretching frequencies of the barium salt film suggests that the spontaneous polarization is ascribed mainly to a structure modification of the carboxylate groups. Furthermore, it is concluded that the alternate films with the more highly oriented molecules give the larger pyroelectricity, and chat if the molecular orientations are in the same order, the acid alternate films have larger pyroelectricity than the corresponding barium salt alternate films. The latter finding may be due to weaker intermolecular interaction in the acid films than in the barium salt films.

1) J. Umemura, T. Kamata, T. Kawai, and T. Takenaka, J. Phys. Chem., 1990, 94, 62.

DP20

PYROELECTRIC BEHAVIOUR OF SYNTHETIC BIOMEMBRANE STRUCTURES

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It is now well established that the spontaneous electrical polarisation of certain alternate-layer Langmuir-Blodgett (LB) films is temperature dependent; the films therefore exhibit pyroelectricity[1-4]. Much of the previous work has concentrated upon acid/amine and acid/aniline systems. We now report preliminary attempts to produce pyroelectric films containing biological molecules.

Initial studies have concentrated upon phosphatidic acid and phosphotidyl serine monolayers alternated with 1-docosylamine. The structure of these films has been investigated using infrared spectroscopy. Pyroelectric coefficients measured by the static technique (-0.9 $\mu Cm^{-2}K^{-1}$) were comparable to those of other LB structures[4]. Relative permittivity and dielectric loss data for these films are typically 3.09 - 3.05 and 0.005 - 0.003, respectively, in the range 10 Hz to 100kHz, see Figure 1. This gives a pyroelectric figure of merit, p/ϵ_r, of 0.29 $\mu Cm^{-2}K^{-1}$. The effect of alternating these phospholipids materials with other phospholipids, e.g. phosphotidyl ethanolamine, instead of 1-docosylamine will also be reported.

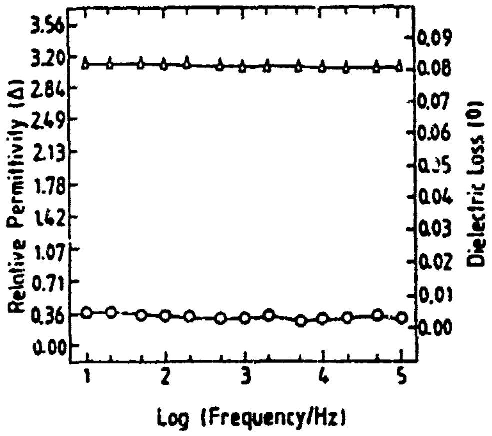

Figure 1. Relative permittivity and dielectric loss data for a phosphatidic acid dipalmitoyl/1-docosylamine film.

References

1. P. Christie, G. G. Roberts and M. C. Petty, Appl. Phys. Lett., 48 (1986) 1101.
2. C. A. Jones, M. C. Petty and G. G. Roberts, Proc. 6th IEEE Int. Symp. on Applications of Ferroelectrics, IEEE, New York, 1986, p.195.
3. G. G. Roberts, Ferroelectrics, 91 (1989) 21.
4. G. W. Smith, M. F. Daniel, J. W. Barton and N. Ratcliffe, Thin Solid Films, 132 (1985) 125.

DP21

THE QTS STUDIES ON METAL / LB FILM / GaAs STRUCTURES

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The metal - insulator - semiconductor (MIS) structure is fundamental for the characterization of the insulating layer and the semiconductor - insulator interface. Incorporation of Langmuir - Blodgett (LB) multilayers in these structures is also interesting from the view point of possible applications based on field effect transistor configuration, especially in the case of semiconductors with no native oxides (e.g. GaAs).

The LB technique was used for the preparation of ultra-thin copper tetra-4-t-butylphtalocyanine (CuTTBPc) films in this work. The phtalocyanines are possibly useful for practical applications because of their high chemical, thermal and optical stability and photoelectric properties. The Au / CuTTBPc LB film / GaAs structure was prepared by evaporating Au top electrodes; as a semiconductive substrate the high doped GaAs ($10^{18}/cm^3$ - Te) was used.

This communication deals with the investigation of these structures by QTS - method (Charge Transient Spectroscopy), which is a modification of Deep Level Transient Spectroscopy originally developed by Lang. QTS response exhibits two broad maxima situated at T_1= 206 K and T_2= 273 K. On the basis of measurements with various values of a time window and subsequent numerical simulation it is shown that the maxima correspond to 2 electron levels distributed around E_{max1}= 0.28 eV and E_{max2}= 0.38 eV, respectively. The experimental results indicate that QTS response of the investigated MIS structure is due to the LB film.

DP22

STRUCTURAL PROPERTIES OF CONDUCTING LANGMUIR-BLODGETT FILMS BASED ON $(NDTA)_2Ni(DMIT)_2$

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Abstract

A very nice horizontal conducting LB films was brought out by Ruaudel et al. who showed that a considerable increase in conductivity (about 0. 1 S per centimeter) could be obtained by means of ID conducting charge transfer systems[1]. Recently, several families of conducting materials of LB films have been found in many laboratories. They are expected to be a basic material for some advance technical applications. A new progress was obtained by Nakamura et al. [2]. That is based on the mixed valence complex of metal$(dmit)_2$ system. It is worth pointing out that the metal$(dmit)_2$ system is an electrical conductor of two dimensionality so that it can suppress some factors of structrual instability.

In this paper, we will describe the structural properties of $(NDTA)_2Ni(dimt)_2$ LB films. The synthesis of $(NDTA)_2Ni(dmit)_2$ was performed by Ruaudel et al. The whole experimental work was accomplished in CEN Saclay. A fresh 5×10^{-4} M (chain concentration) solution of the sample $(NDTA)_2Ni(dmit)_2 + (C_{18})_2NH$ in acetonitrile, benzene and trichloromethane(2 : 1 : 1) is spread onto the water surface, above which dry nitrogen is blown. After evaporation of the solvent, the film is compressed very slowly. The π-A curve is quite reproducible. The monolayers at 28 mN/m were deposited onto a calcium fluoride substrate or on that some gold grid electrodes(gap layers distance, 0. 3mm) were deposited, both substrates have been precoated with six LB layers of behenic acid. Oxidation of the LB films was performed by several chemical atmospheres such as: by iodine, bromine gas with dry nitrogen or with air and so on. We found out a exposure condition suitable for highly conducting LB films of $(NDTA)_2Ni(dmit)_2$ sample. Its conductivity is about 0. 1~0. 4 Scm^{-1}.

REFERENCES

[1] A. Ruaudel-Teixier, M. Vandevyver, A. Barraud, Mol. Cryst. Liq. Cryst., 120, 319(1985)

[2] T. Nakamura, H. Tanaka, K. Kojima, M. Matsumoto, H. Tachibana, [illegible]. Tanak. and Y. Kawabata, Thin Solid Films, **179**, 183(1989)

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DP23

TIME-RESOLVED PHOTOVOLTAGE SPECTROSCOPY OF LIPID-FREE CuTsPc MULTILAYERS ON *p*-Si(111)

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Abstract

Recently, the lipid-free copper tetrasulfonatophthalocyanine (CuTsPc) mutilayers were prepared by LB technique in our laboratory. The films display a photosensitizing effect on *p*-Si(111)[1], and furthermore, the FET modified by CuTsPc films shows good photosensitive characteristics[2]. In this paper, in order to understand their charge transfer and photosensitization mechanism, the interfacial charge transfer processes between CuTsPc film (two layers, 12Å in thickness) and *p*-Si(111) were studied by pulsed laser photovoltaic technique. Comparing Fig. 1(a) with (b), it is obvious that the fast process (I) corresponds to the photovoltaic response of *p*-Si(111), and the slow one (Ⅱ) is associated with the interaction between CuTsPc film and *p*-Si(111). Moreover, We found that the photovoltage signal of process Ⅱ changes with the light intensity. This variation is similar to that obtained from H_2Pc (PVD film)[3]. As the film itself can' t produce signal like that of process Ⅱ, it must have associated with the interfacial charge transfer interaction between CuTsPc film and *p*-Si (111). It is also found that the signal of process Ⅱ becomes very small when a SiO_2 layer (thickness 1450Å) is made on the interface. In this case, the charge transfer between CuTsPc film and *p*-Si(111) is impossible. This indicates that there is another process in process Ⅱ. So for the process Ⅱ, there are two possible mechanisms in it: one is that electrons are injected from the conduct band of *p*-Si(111) into the ground state of CuTsPc(Ⅱ′); the other is that CuTsPc itself can form partial charge transfer complex $CuTsPc^{\delta+}$-$O_2^{\delta-}$[4], and the transition from ground state of $CuTsPc^{\delta+}$-$O_2^{\delta-}$ to the excited state ($CuTsPc^{+}$-O_2^{-}) makes the charge separation of $CuTsPc^{\delta+}$-$O_2^{\delta-}$ complete(Ⅱ″), so the photovoltage is produced. The experimental photovoltage data appear to be adquately interpreted with the model of the interfacial charge transfer in CuTsPc/*p*-Si(111) systems.

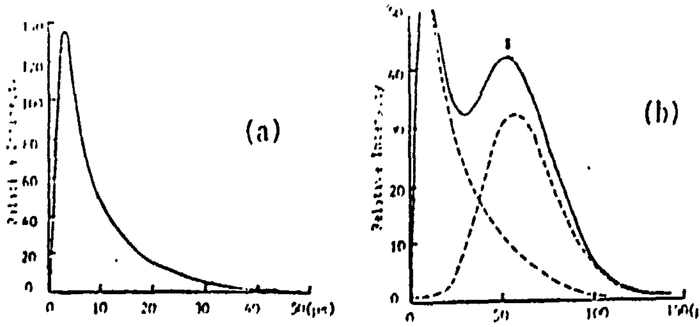

Fig. 1 The time-resolved photovoltage spectrum of *p*-Si(111)(a) and CuTsPc film/*p*-Si(111)(b)

REFERENCE

[1] Wang Liu, Tiejin Li, *et al.*, Thin Solid Films, 179(1989), 309~312

[2] Lei Jiang, Tiejin Li, *et al.*, Chemical Journal of Chinese Universities, (in press)

[3] S. C. Dahlberg and M. E. Musser., J. Chem. Phys., 70(11); 1; Jun. (1979), 5021~5025

[4] S. C. Dahlberg and M. E. Musser., J. Chem. Phys., 72(12); 15 June(1980), 6706-6711

DP24

LANGMUIR-BLOGETT FILMS BASED ON 1,2-DITHIOLIUM-TCNQ RADICAL ANION.

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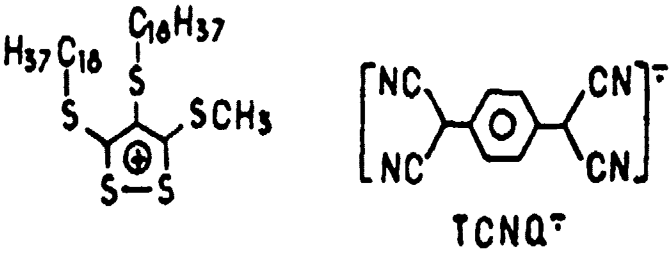
The control of a supramolecular organization in LB films for a designed physical properties is a constant objective. Two main requirements are at least necessary, the presence of an electroactive group which controls an electron transfer and an amphiphilic character which can induce a stable LANGMUIR monolayer. Analyzing the previous results on charge transfer salts its appears that a few series of semi-amphiphilic TCNQ salts furnishes LB films of a remarkable quality.

In the present work, we have developped the synthesis of a new series of 3,4,5-(alkylthio)-1,2-dithiolium salts with iodine, TCNQ (salts 1-1 and 1-2) and other strong acceptor molecules (see scheme 1).



Scheme 1

We have examined the in situ molecular organization on the LANGMUIR trough using the usual compression isotherms but also the surface potential technique and the ellipsometry measurements; these last experiments allow us to distinguish between either a monolayer or a multilayer structure.

After transfer on different substrates we have investigated the physical properties of LB films in particular electronic and vibrational absorption spectroscopy and static and dynamic paramagnetism. In particular the specific behavior found by ESR for the TCNQ compounds will be discussed in relation with the layer type organization evidenced by X-ray diffraction.

DP25

PHOTOELECTRIC PROPERTIES OF LB FILMS CONTAINING AMPHIPATHIC PORPHYRIN AND CARBAZOLE

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A few reports have very recently been made on time-dependent photoelectric responses in LB films. We have reported transient and steady photocurrents in LB films containing photoreaction center porphyrin and alloxazine chromophores.[1,2] We now report the transient and steady photoelectric properties of LB films composed of amphipathic 5-(4'-N-hexadecylpyridinium)-10,15,20-triphenylporphyrin(1) and arachidic acid(2), or 11-(9-carbazolyl)undecanoic acid (3) and palmitic acid(4).

Five monolayers of a mixture of 1 and 2 (1:5, abbreviated to P) were deposited as Y-type films at 20°C and 20 mN · m^{-1} on an ITO substrate. Two monolayers of cadmium palmitate alone, mixtures of 4 and 3 (molar fractions of 3: 2-25%) were further deposited. These LB films are abbreviated to PCUA0, PCUA2, PCUA5 and PCUA25 systems, respectively. Aluminium was vacuum evaporated as sandwich-type electrodes. These LB films were irradiated by a 150 W Xe lamp through a 10 cm water filter, an L-33 filter, and a monochromator. Steady photocurrents were observed by an electrometer. Transient photocurrents upon excitation of porphyrin with a dye laser (Molectron DL-14P pumped by UV24 nitrogen laser, 10 ns) were measured by the use of a high speed current amplifier (Ithaco 1211) and a digital memory.

Positive steady photocurrents observed for these systems with bias voltage larger than about -0.4 V increased with bias voltage. The polarity reversed below -0.4 V. The action spectra well corresponded with the absorption spectrum of 1. Steady photocurrents decreased in the order of PCUA5 > PCUA25 > PCUA2 > PCUA0, which strongly suggested that carbazole derivatives affected the photoelectric properties of these LB films depending on the molar fraction.

Transient photocurrents upon excitation of porphyrin by a dye laser showed a fast rise and a slow exponential decay. No transient photocurrents were observed for monolayers of 2 alone. The action spectrum of transient photocurrents corresponded well with the absorption spectrum (Q-band) of 1. These results indicated that observed transient photocurrents were due to movement of photocarriers generated by the excitation of porphyrin in the monolayer assemblies. The lifetime defined as the slope of a logarithmic plot of transient photosurrents vs. time gradually increased with increasing bias voltage. The lifetime at the same bias voltage decreased in the order of PCUA5 > PCUA25 > PCUA2 ~ PCUA0. These results strongly suggested that carbazolyl chromophores are effective to retard the decay of photocarriers depending on the extent of aggregation in mixed LB films with palmitic acid.

1) T. Nagamura, K. Matano, and T. Ogawa, J. Phys. Chem., 91, 2019 (1987).
2) T. Nagamura, S. Kamata et al., Thin Solid Films, 179, 293 (1989).

DP26

PHOTOINDUCED VARIATIONS OF INTERNAL ELECTRIC FIELD IN LB FILMS WITH AZODYE MONOLAYER.

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This paper deals with utilization of the probing procedure of internal electric fields [1] applied to a new type of polar L-B systems. The investigated L-B films showed a photoinduced optical anizotropy (POA) effect [2,3].

The prepared L-B films consisted of three components: stearic acid (1,4), azodye (2) and anthraquinone dye (3), Fig.1. The active part of the L-B film comprised a monolayer of the azodye and bimolecular layer of antraquinone dye. The azodye molecules show the POA effect in combination with formation of polar L-B films [4]. The anthraquinone bilayer was used as probe of internal electric field in L-B structure [1].

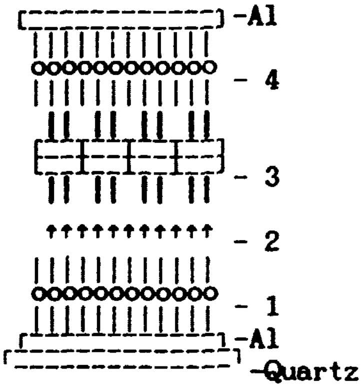

Fig.1

We investigated the variations of d.c. internal field, due to the reorientation of azodye molecules after the light irradiation in its absorption band, using Stark-spectra technique. The electronic bands of the azodye and the anthraquinone compound have a weak overlapping Thus the corresponding contributions of different monolayers in the Stark-spectra can be seen separately. In our case the Stark spectrum $\Delta T/T(\lambda)$ has two various contributions from two monolayers:

$$\Delta T/T(\lambda) = E^{(1)}_{azo} A^{(1)}_{azo}(\lambda) + E^{(1)}_{ant} E^{int}_{loc} A^{(2)}_{ant}(\lambda) \qquad (1)$$

Here $A^{(1)}_{azo}(\lambda), A^{(2)}_{ant}(\lambda), E^{(1)}_{azo}, E^{(1)}_{ant}$ - are spectral dependences of linear and quadratic Stark effect and variable local fields for the azodye and anthraquinone ,respectively. We investigated two contributions in (1) and found the dependence of the values of the internal field E^{int}_{loc} against the conditions of irradiation . The changes of the internal field confirmed the results obtained early in [4]. Using the values of the internal fields we found the macroscopic polarization of azodye monolayer ($P \approx 10^{-7} - 8\cdot 10^{-7}\, C/cm^2$) versus the irradiation conditions. The model of POA is discussed to explain the data obtained here.

References

1 L.M.Blinov, S.P.Palto, S.G.Yudin -J.Mol.Electron., 1989, v.5, p.45-51.

2. V.M. Kozenkov, S.G. Yudin, E.G. Katyshev, S.P. Palto, V.T. Lazareva, V.A. Barachevsky. - Pys'ma Zh.Tekh.Fiz., 1986, 12, 20, p. 1267-1272 (in Russian).

3. M.I.Barnik, V.M.Kozencov, N.M.Shtykov, S.P.Palto and S.G.Yudin. - J.Mol.Electr., 1989, v.5, p.53- 56.

4. M.I.Barnik, S.P.Palto, V.A.Khavrichev, N.M.Shtykov and S.G.Yudin. -- Thin Sol. Films, (1989), 179, p.493 -496.

DP27

Photoinduced electron transfer in monolayers at the air/water interface

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We have investigated the photoinduced electron transfer from the excited donor (oxacyanine OC, incorporated in a matrix monolayer at the air-water interface) to the acceptor (viologen; V^{++}) either present in the matrix monolayer or adsorbed at the monolayer/water interface from the subphase. The kinetics of adsorption of the acceptor at the monolayer/water interface and the steady state surface density was monitored using the surface pressure, surface potential, surface reflection and fluorescence techniques. The adsorption of the acceptor at the DPPA (dipalmitoylphosphatidic acid) monolayer/ water interface leads to the appearance of V^{++} specific band (λ=280 nm) in the reflection spectrum, the magnitude of which increases with increasing acceptor concentration in the subphase ending in saturation at concentrations > 10^{-6} M. The adsorption of the acceptor is largely governed by the interfacial potential, e.g. we did not find any evidence for adsorption of the V^{++} at monolayers of dipalmitoylphosphatidylcholine or arachidic acid (at pH 5.6). The kinetics of adsorption of the acceptor was found to be diffusion controlled and the time to reach steady-state varied between few minutes and hours in the concentration range (10^{-8} - 10^{-5} M). For investigation of the photoinduced electron transfer process, steady-state fluorescence intensity (425nm)-area isotherms were measured simultaneously with the surface pressure-area isotherms. The fluorescence intensity decreased by three orders of magnitude as a result of electron transfer using bulk acceptor concentration in the range 10^{-8} - 10^{-5} M. These results along with the other results obtained by incorporating the long chain derivative of the acceptor in the matrix (DMPC) monolayer are discussed in terms of a two dimensional analog of the three dimensional hard sphere model.

DP28

PIEZOELECTRICITY IN LANGMUIR-BLODGETT FILMS

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The pyroelectric properties exhibited by several types of Langmuir-Blodgett films have generated interest in the piezoelectric properties that these materials should exhibit. For the potential applications of these materials in pyroelectric detectors low levels of piezoelectric activity would be desirable, since large piezoelectric effects introduce problems of acoustic sensitivity. Therefore, the characterization of the level of this activity is important. These materials could also be useful in novel piezoelectric devices. The overall aim of this work is that of establishing a reliable method of determining the piezoelectric properties of thin organic multilayers under the constraints where the active element is supported by a rigid substrate.

The multilayer Langmuir-Blodgett films which were investigated for their piezoelectric effect were comprised of alternate layers of a fatty acid and 1-docosylamine, and an organo-ruthenium complex alternated with a fatty acid. The organic layers, consisting of 21 monolayers, were deposited onto thin (0.8 mm) glass substrates on which aluminium electrodes had been deposited. On top of the organic multilayers an upper aluminium electrode was deposited. A purpose built rig was designed for applying a bending flexure to this composite, producing tensile and compressive stresses in the Langmuir-Blodgett film on its surface. Measurement was made of the force applied perpendicular to the surface of the substrate (the force in bending the substrate) and the resultant charge produced by the flexure. The strain at the surface of the substrate, and that transmitted to the active layer, was determined by applying the theory of bending in a cantilever beam. From the values of the tensile stress in the active layer and the resultant charge, the piezoelectric d_{31} coefficient could be determined. Preliminary results on acid/amine alternate layer films have yielded a d_{31} coefficient of 0.13 pC/N. The accuracy of this experimental set up has been verified by measuring the d_{31} coefficient of a a spuncoat VF/TrFE copolymer as the active layer, giving a coefficient which is in excellent agreement with published values.

Session EP

Chemistry in mono and multilayers

EP1

SUMMARY

ISOMERIZATION OF (α-NAPHTYL)(n-CHLORPHENYL)ETHYLENE SOLUTION BY THE RUTHENIUM COMPLEX LANGMUIR-BLODGETT FILM.

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Our paper is concerned with the investigation of the photocatalized properties of the Langmuir-Blodgett(LB) films of synthesized surface-active diperchlorate bis(2,2'-bipyridine) (4,4'-diheptadecyl-2,2'-bipyridine) ruthenium(2+) complex.

Trans to cis isomerization of (α-naphtyl)(n-chlorphenyl) ethylene(NCE) in hexadecane solution photosensitized by the LB multilayer was investigated.In addition to this, luminescent quenching of the LB films by a $CuSO_4$ water solution was studied to determine the effectiveness of such a heterogeneous catalytic reaction.

It was shown that the effectiveness of the trans to cis NCE isomerization photosensitized by the ruthenium complex LB film is 100 times less than the effectiveness of an analogos reaction in a homogeneous solution.Each layer of the LB film contribute the equally to the rate of the isomerization.This can be explained by penetration of the NCE solution deep into the multilayer or by efficient migration of energy to the surface of the film followed by isomerization on the surface.To determine the mechanism of this process an additional luminescent quenching of the LB film by the $CuSO_4$ water solution was carried out.With increasing quencher concentration in the solution the efficiency of the quenching reached a limit.This demonstrated the absence of efficient energy transport in the LB multilayer and also that $CuSO_4$ solution only penetrates wearly into the film.Thus the efficient contribution of all monolayers of the ruthenium complex LB films results from good penetration of non polar hexadecane solution of NCE into the depth of the LB multilayers.

EP2

PENETRATION KINETICS OF CIS-DIAMMINEDICHLOROPLATINUM II LOADED NANOPARTICLES IN LIPID MONOLAYERS AS MEMBRANE MODEL OF RETICULOENDOTHELIAL SYSTEM

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In the last years various attempts have been made in order to minimize the toxic effects of citostatic drugs and improve their penetration into the cellular membranes.In this way, different kind of drug delivery systems, such as liposomes, nanocapsules and nanoparticles, were used.

Cis-diamminedichloroplatinum II (Cisplatin) is a higly effective drug in the treatment of several neoplastic diseases but its use must be limited by severe systemic toxicity as nephrotoxicity or neurotoxicity.In an attempt to modify the therapeutic index this drug has been previously encapsulated in liposomes but with a very low encapsulation efficiency and poor stability.

Biodegradable polymers such as polyalkylcyanoacrylates (PACA) are of special interest in the desing and fabrication of nanoparticles, as prolonged-acting dosage forms. Conjugation of citotoxic drugs to this polymers could reduce side effects by altering pharmacokinetic disposition of the drug.

Monolayer measurements at liquid-gas interfaces can give valuable information about the interfacial behaviour of membrane compounds and also on interactions at interfaces, which can be well correlated with phenomena at biological membranes.

The present study was undertaken in order to know the nature of the interaction between cis-diamminedichloroplatinum II loaded or unloaded polyalkylcyanoacrilate nanoparticles, with the same components as lipids present in cellular membranes of reticuloendothelial system spreaded as monolayer at liquid-gas interface. This lipid composition of monolayers has been chosen because a major limiting factor to the systemic use of particulate drug delivery systems is the rapid clearance of the carrier from the circulation by the reticuloendothelial system. The possible interactions of the surfactant used in the nanoparticle formulation with the lipids above mentioned were also investigated.

The surface pressure increases produced in lipid monolayers spread at several initial pressures when different amounts of cis-diamminedichloroplatinum II loaded or unloaded nanoparticless or free nanoparticless were added to the aqueous subphase showed a maximum value for the drug loaded nanoparticles.

EP3

AN IN SITU INVESTIGATION OF THE PHOTOPOLYMERIZATION OF DIACETYLENE LB FILMS.

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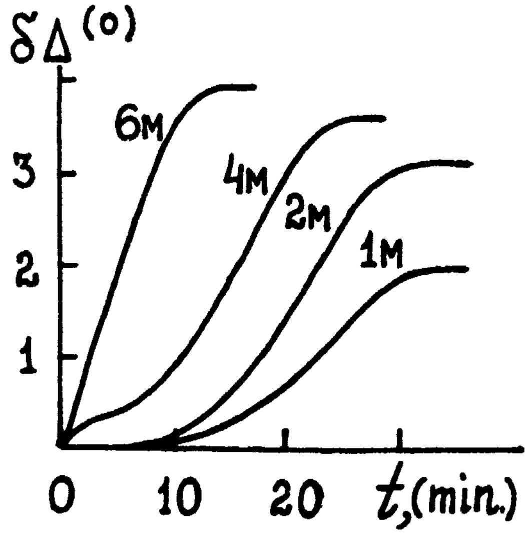
The aim of the present work was to study the polymerization of mono - and multilayers LB films of the amphiphilic derivative (DA 11-8)

$$[CH_3(CH_2)_{11}-C{\equiv}C-C{\equiv}C-(CH_2)_8COO]_2Cd$$

by means of high-speed ellipsometry.

DA 11-8 was dissolved in hexane at a concentration of about 0.1 - 0.15 mg/ml and spread on water containing about $3x10^{-4}$ mol/l $CdCl_2$ at pH=7.0-7.1. The monolayers were transferred onto silicon substrate at a surface pressure of 30 mN/m. Photopolymerization was achieved by UV irradiation of the sample using Hg - lamp and registered by ellipsometry with the fast action about 50 ms. The kinetic dependences of the polymerization of DA 11-8 (1, 2, 4 and 6 monolayers) are presented in Figure. After the short period of initiation (3-5 min) the spontaneous polymerization was observed in a case of film thickness less then or equel 4 monolayers. The films of PDA 11-8 absorbes light with the maximums of absorption at 570 and 640 nm. The values of refractive index 1.64-1.65 and absorption constant 0.1 were observed for these films at 632.8 nm. Mechanism of the processes of polymerization, photochromic transition and photolysis was discussed.



EP4

LB FILMS OF HEXADECYLVINYLDIMETHYLAMMONIUM CHLORIDE AND THEIR OZONE SENSITIVITY

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ABSTRACT

A 77.8 MHz Surface Acoustic Wave (SAW) device (1) and a 158 MHz dual SAW device has been used to measure the ozone sensitivity of Langmuir-Blodgett films of hexadecylvinyldimethylammonium chloride (CVDAC). The 77.8 MHz SAW device was also used to characterize the deposition of monolayers as a linear decrease in the resonant frequency of the device indicates a homogeneous deposition (1,2).

CVDAC forms a liquid expanded monolayer on a pure water subphase because of the ionic repulsion between the polar head groups and monolayers can not be deposited onto a solid substrate. However in a mixture with arachidic acid at a molar ratio of 1/6 a monolayer similar to that of pure fatty acids is formed. Y-type films were deposited onto solid substrates and characterized by UV-visible absorption spectra. Furthermore deposition onto the SAW device indicates a homogeneous deposition as the resonant frequency of the device decreases linearily with number of layers.

Charged monolayers can be stabilized by complexation with polyelectrolytes (3). A stable monolayer of CVDAC was formed by polyion complexation with polystyrenesulphonate. Deposition was succeeded only on the upward movement of the substrate, giving Z-type films. UV-visible absorption spectra of the transferred films indicates a successful complexation and a reproducible monolayer transfer.

The resonant frequency of a SAW device coated with CVDAC layers decreases with time when exposed to ozone. The decrease in frequency is irreversible and the rate of the decrease depends on the number of layers deposited onto the device. This indicates a penetration of ozone into the layers as the response rate increases with film thickness. Ozone would adsorb only near to the surface if the response did not depend on the film thickness. The decrease in frequency of the SAW device is linearily dependent on the ozone concentration.

REFERENCES

1. Vikholm, I. and Helle, H., Progr. Colloid Polym. Sci. 82 (1990) 163.
2. Vikholm, I. and Helle, H., Thin Solid Films 178 (1989) 197.
3. Shimomura,M., Kunitake,T., Thin Solid Films 152 (1985) 243.

EP5

THE POLYMERIZATION OF MONOLAYERS AND LB-MULTILAYERS OF SOME UNSATURATED FATTY ACIDS

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ABSTRACT

The polymerization of several unsaturated fatty acid Langmuir-monolayers (cis-9-oleic acid (C18:c9), cis-6-petroselinic acid (C18:c6), cis-9,12-linoleic acid (C18:c912) and trans-9,12-linolelaidic acid (C18:t912)) has been successfully carried out under a 30W low pressure mercury lamp UV-irradiation.

The polymerization was monitored as a change in barrier speed under a constant surface pressure of 15 mN/m for monolayers on a 0.1mM $TbCl_3$ subphase and 25 mN/m for 0.1mM $CdCl_2$ subphases, respectively. All the measurements were done under a constant temperature of 20°C.

The unsaturated fatty acids with two double bonds ((C18:c912) and C18:t912)) where more reactive than those with a single bouble bond ((C18:c6) and C18:c9)). Also, the cis-type double bonds were observed to be more easily polymerized than those of trans-type.

More detailed study was focused on C18:c912. The indication that a polymer was indeed produced came from the following facts: The speed of the barrier increased to a clear maximum when the monolayer was irradiated with UV-light. After 100 min. UV-irradiation the collapse pressure of the monolayer (22.3 mN/m) was higher than that of a unreacted monomer (18.0 mN/m). As well, after a 100 min. polymerization, by sweeping the surface of the Langmuir trough, a resin-like surface residue was obserbed by microscopy. However, the monomer cis-9,12-linoleic acid is a liquid with melting point between -1°C and -5°C.

The reactivity of the monolayers was studied also under an argon atmosphere but no significant differences were observed compared with those measurements done under normal air conditions. This indicates that the oxidation and degradation of the monomer in air atmosphere during a 100 min. UV-polymerization were not the dominant effects in our experiments.

The polymerization tests for the corresponding LB-multilayer structures under a 100W high pressure mercury lamp as well as using electron beam will be characterized by x-ray diffraction measurements.

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EP6

Electrochemistry of Viologen-containing Langmuir-Blodgett Film Prepared by Polyion Complex Technique.

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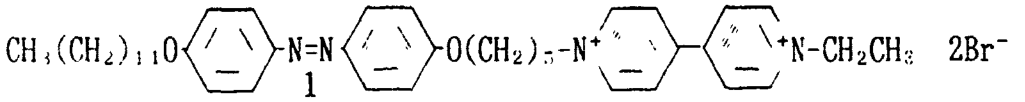
We describe in this article electrochemical property of an amphiphilic viologen in the Langmuir-Blodgett(LB) multilayers prepared by the polyion complex technique.

Shimomura and Kunitake succeeded to immobilize the bilayer membranes as the LB multilayers by the polyion complex technique. As the result of the electrostatic interaction at the air-water interface, a stable monolayer of the bilayer-forming charged amphiphile was prepared on an aqueous solution of the counter charged polyelectrolyte. The polyion-complexed monolayers could be transferred on the solid substrates as the multilayer films by the normal LB technique[1]. Molecular orientation in the polyion-complexed monolayers should be strongly affected by the chemical structure of the polyelectrolytes.

The azobenzene amphiphile having the violoqen group as a hydrophilic head forms the bilayer assembly in water.



1

Due to high water solubility, however, amphiphile 1 could not form a stable monolayer on pure water subphase at 20℃. Addition of an anionic polyelectrolyte into the water subphase could stabilize the monolayer. A condensed monolayer with a limiting molecular area of ca. 0.6 nm^2/molecule was formed on dilute solution of potassium poly(vinyl sulfate). Carboxymethylcellulose (degree of substitution of carboxymethyl group per glucose unit ;d = 1.41) in the subphase made the monolayer more expanding. Shape of the pressure-area isotherms(π-A curves) on the aqueous carboxymethylcellulose was strongly dependent on the degree of substitution. Condensed monolayer was found on the solution of higher substituted carboxymethilcellulose (d = 2.81). Molecular orientation in the polyion-complexed monolayer is strongly affected by the charge density of the polyelectrolyte.

Reversible reduction-oxidation reaction of the viologen group by the electrochemical process was found in the polyion complexed LB film. The formal redox potential($E^{0'}$) of the LB film was found to be strongly affected by the chemical structure of the anionic polymer. The complex film with carboxymethylcellulose(d = 1.41, $E^{0'}$ = -473mV vs. SCE) was more easily reduced than the film complexed with poly(vinyl sulfate)($E^{0'}$ = -577 mV). Positive shift in the redox potential was found for the complex film having expanding nature of the monolayer.

As was expected, the π-A curve on poly(acrylic acid) solution showed a large pH-dependence. Lowering the pH value of the subphase, the π-A curve of the monolayer was found to be extremely expanding. A large pH dependence of the redox potential was also found in the LB film.

1) M.Shimomura, T.Kunitake, *Thin Solid Films*, 132,243(1985)

EP7

PHOTOINDUCED PROTON TRANSFER IN LB FILMS

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In nature, photosynthesis is the major process which converts solar energy to chemical energy. That process starts with a photoinduced electron transfer, and results in the hydrogen ion concentration gradient across a membrane. The concentration gradient can be a driving force to synthesize ATP from ADP. Several polypeptide units are concerned with that process.

On the other hand, some kind of halophilic bacteria have a quite different energy conversion process. A polypeptide unit which named bacteriorhodopsin pumps hydrogen ion directly as a result of photoisomerization of retinal. That proton pumping mechanism is much simpler than that of photosynthesis. The process does not link with electron transfer and needs no other polypeptide unit. This molecular process suggests us a novel molecular device for solar energy conversion other than the previous molecular photodiode.1)

In this study, we intended to assemble a photoinduced intermolecular proton transfer system with LB films. This is the first report which aims to control the direction of proton transfer in artificial aggregates.

We used 2-naphthoic acid (2-NpA) as a photofunctional compound. Some aromatic compounds with acid-base functional groups have different pKa's in the ground state and in the excited state. In the case of 2-NpA, pKa in the ground state is 4.1, while in the excited state pKa(S1) was reported as 10-12.2) We incorporated 2-NpA$^-$ ion as a proton acceptor into appropriate proton donating amphiphiles such as imidazole and amines with long alkyl chains. Regularity of LB films should control the direction of proton transfer.

References

1) M. Fujihira, K.Nishiyama and H.Yamada, *Thin Solid Films*, 132, 77 (1989)
2) G.Jackson, G.Poter, *Proc.Roy.Soc.(London)*, A260,13,(1961)

EP8

CONTROL OF PHOTOCHROMISM OF DIACETYLENE LB FILMS BY POLYION COMPLEXATION

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It is important to control molecular orientations and intermolecular distances in mono- and multilayered LB films. In this respect, we have found that, for the monolayer which consists of an amphiphilic aliphatic acid and a polycation used as the counter ion, the molecular area could be controlled by the pH of the subphase, the size of monomer unit of polycations, and the chain length. We have also reported that the photoisomerization of the azobenzene amphiphiles in LB films, which had so far been irreversible, became reversible due to the increase in the free volume by polyion complexation.[1,2]

In general, the topochemical reactions depend upon the molecular arrangements and the intermolecular distances. Diacetylene derivatives are representative compounds which show the topochemical reaction. Therefore, in this paper, we will discuss how the photopolymerization of diacetylene, is affected when the molecular area of photoreactive moieties is controlled by the polyion complexation.

The cross sectional area of the diacetylene moieties of the monolayers was controlled by the pH of the subphase and by the chain length. The photopolymerization of the moieties was largely influenced by the area. By controlling the area, the LB films which display new types of spectra of photochroma were obtained. The difference in absorption spectra and polymerization behavior between the monolayers at the air-water interface and the corresponding multilayered LB films was observed.

References

1) K. Nishiyama and M. Fujihira, Chem. Lett., 1988, 1257.
2) K. Nishiyama, M. Kurihara, and M. Fujihira, Thin Solid Films, 179, 477 (1989).

EP9

ELECTROCATALYTIC REDUCTION OF CO_2 ON MODIFIED ELECTRODE WITH LB FILMS OF LONG ALKYL SUBSTITUTED NICKEL CYCLAM COMPLEXES

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In biological systems, various kinds of metal complexes such as hemes, iron sulfur clusters, and manganese centers act as active sites of enzymes. Several recent papers reported that carbon dioxide could be electrocatalytically reduced by metal complexes$^{1-3)}$. The metal electrodes in contact with an aqueous solution of Ni-cyclam complex (cyclam:1,4,8,11-tetraazacyclotetradecane) can reduce carbon dioxide to carbon monoxide selectively in more preferable potentials than the same metal electrode without the complex.

To immobilize the metal complex catalyst on an electrode, we first investigated the position of Ni-cyclam to which we substituted alkyl chains without lack of the activity, and reported that nickel complexes of N-alkylated cyclams are more stable than Ni-cyclam in an aqueous solution. Then we synthesized a Ni-cyclam derivative with an N-substituted long alkyl chain, i.e. Ni-N-docosylcyclam. We examined the electrochemical properties of its monolayer and the catalytic activity for reduction of carbon dioxide.

The monolayer of the Ni-cyclam derivative was spread from the chloroform solution onto a 0.5 mM $NaClO_4$ aqueous solution at 15 °C. The limiting area of Ni-N-docosylcyclam was 0.88 nm^2. The monolayer of the complex was deposited on a glassy carbon (GC) disk electrode.

The cyclic voltammograms on the electrode were recorded in a 0.1 M $NaClO_4$ aqueous solution under nitrogen or carbon dioxide atmosphere. Under nitrogen, the cyclic voltammogram of the monolayer of Ni-N-docosylcyclam showed a redox peak at ca. -1.4 V vs. SCE, and it was almost the same as the redox potentials of nickel N-short alkylated cyclams in an aqueous solution. Under carbon dioxide, the increase in cathodic current was observed at -1.3 V vs. SCE. These results indicate that the LB films of the complex possess sufficient electrocatalytic activity to reduce carbon dioxide.

References
(1) J.P.Sauvage, et.al., J. Am. Chem. Soc. 108, 7461 (1986).
(2) M.Fujihira, Y.Hirata, and K.Suga, J. Electroanal. Chem. 292, 199(1990).
(3) B.Fisher, R.Eisenberg, J. Am. Chem. Soc. 102, 7361 (1980)

EP10

PHOTOCHEMICAL SWITCHING OF ELECTROCHEMICAL PROCESSES ON MODIFIED ELECTRODE WITH IONIC SPIROPYRAN LB FILMS

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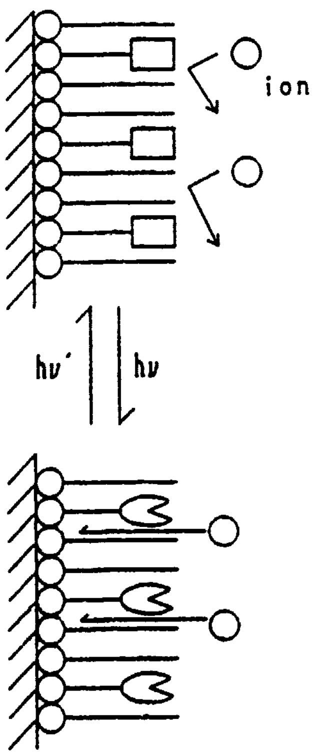
In relation to the human visual system we reported that the spiropyran LB film can control the electrochemical reaction of Fe^{3+}/Fe^{2+} by UV and visible light irradiation$^{1)}$. In the present study, we will report photochemical switching of electrochemical processes by using ionic spiropyran derivatives. This device is composed of a gold optically semi-transparent electrode (Au OTE) modified with LB films containing photoresponsive moieties in contact with a redox solution in a photoelectrochemical cell.

In general, the rate of electrochemical reaction greatly depends on the state of electrode surface, LB films or adsorbed monolayers on the electrode surface inhibit the electrochemical reaction. If the film blocks the electrochemical reaction perfectly, no faradic current is observed.

If this photoresponsive film changes its inactive structure by light irradiation with one frequency (v) into active structure and the coated electrode with this new structure allow the electrochemical reaction in solution, the large faradic current should be observed. If the initial blocking state can be recovered by irradiating light with the other frequency (v'), only charging current is observed again.

In this way, photochemical reactions in the film caused by weak photoirradiation trigger a large electrochemical current in a reversible manner as in the visual system.



Reference

1) K. Nishiyama and M. Fujihira Chem. Lett., 1987, 1443.

EP11

PHOTOPOLYMERIZATION OF ω-TRICOSENOYL DERIVATIVE OF β-CYCLODEXTRIN IN LANGMUIR-BLODGETT FILMS

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LB films of long-chain derivatives of cyclodextrins (CDs) will provide new molecular systems owing to the unique environment in the cavity.[1] A variety of functional molecules can be incorporated into the LB films of CDs giving a well organized layered system with specific functions.[2] On the other hand, polymerization in the LB films is expected to enhance the mechanical strength, thermal stability and solvent resistance of the LB films.[3][4]

In this paper, a ω-tricosenoyl derivative of β-CD (Vinyl-β-CD)(Fig.1) was synthesized (mp 74.5°C) and the photopolymerizations in the built-up multilayers and the monolayer on water have been studied. Vinyl-β-CD can form stable monolayer at the air-water interface. From the π-A isotherm the limiting area was 230 Å^2/molecule, indicating that Vinyl-β-CD molecules are aligned in the closest hexagonal packing of the cylindrical bases in the monolayer and long chains stand vertically (Fig.2). In the equimolar mixed monolayer with ω-tricosenoic acid (TA), TA molecules filled blank space between Vinyl-β-CD molecules in the hexagonal packing without any increase of the area, although additional molecules of TA contribute to the area increase in proportion to the molar ratio of TA. The monolayer of Vinyl-β-CD can be deposited onto phydrophobic solid substrates by the LB method. The polarized IR spectra for the LB films of Vinyl-β-CD revealed that the hydrocarbon chains stand nearly vertically and the CD rings are oriented pararell to the film plane.

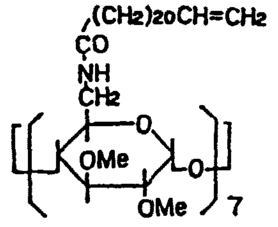

Fig.1 Vinyl-β-CD

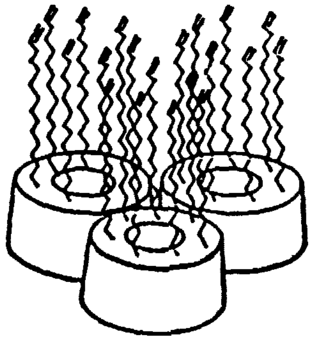

Fig.2

In order to obtain the thermally and mechanically stable ultra thin films of β-CD, homopolymerization of Vinyl-β-CD and copolymerization with TA in the LB films were examined by UV irradiation under nitrogen atmosphere. Polymerization process was followed by the decrease of C-H deformation band of terminal vinyl group at 910 cm^{-1} in the IR spectra. Homopolymerization of Vinyl-β-CD was rather slow, while copolymerization with TA proceeded faster and reached high conversion. Further, the polymerizability of Vinyl-β-CD in the multilayers prepared by the horizontal lifting method was higher than that by the convensional LB method, probably because the monolayer on water surface should be transfered on the plate without disturbing the molecular arrangement. It was found that solvent resistivity of the LB film of Vinyl-β-CD was improved after the polymerization.

1) Y.Kawabata, W.Tagaki, H.Nakahara and K.Fukuda, etal., Thin Solid Films, 159(1988)353.
2) A.Yabe, Y.Kawabata, W.Tagaki, H.Nakahara and K.Fukuda, etal., Thin Solid Films, 160(1988)33.
3) K.Fukuda, Y.Shibasaki and H.Nakahara, Thin Solid Films, 99(1983)87, 133(1985)39, 160(1988)43, 179(1989)103.
4) H.Niino, Y.Kawabata, A.Yabe, W.Tagaki, H.Nakahara and K.Fukuda, etal.,179(1989)53.

EP12

PREPARATION AND PROPERTIES OF POLYAMINE LB FILMS

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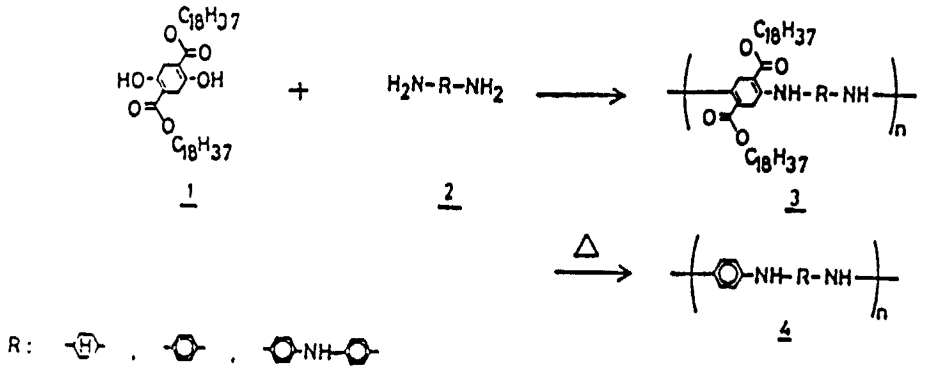
We have prepared polyimide and poly(p-phenylene vinylene) LB films using "Precursor method". In this paper, we report the first preparation of polyamine LB films containing no long alkyl chains.

The amphiphilic precursor polymers 3 of polyamines 4 were synthesized by the condensation reaction between dioctadecyl succinylsuccinate 1 and various diamines 2 as shown in eq. (1). Polymer 3 synthesized from tans-1,4-diaminocyclohexane was fairly stable in air and soluble in chloroform.



(1)

The stable L film of 3 was obtained, and could be deposited onto solid substrates as Y-type films using the usual LB technique. Fig.1 shows the relationship between absorbance at λmax (245 nm) of absorption spectra and the number of deposited layers onto quartz plate. The linear plots indicates that the monolayers of 3 are reproducibly and uniformly transferred onto the substrate.

Subsequently, the long alkyl chain was removed away by heat treatment. In order to observe a chemical change of the LB film of polymer 3, the films were heated at different temperature under reduced pressure. The UV-visible absorption spectra and IR spectra indicated that the remarkable change of chemical structure occurred at 300°C.

Although in the case that the diamines were aromatic amines such as p-phenylenediamine and 4,4'-diaminodiphenylamine the polymer 3 were easily oxidized in air, preparation of LB films of polyamine 4 (polyaniline) from these aromatic precursor LB films is also discussed.

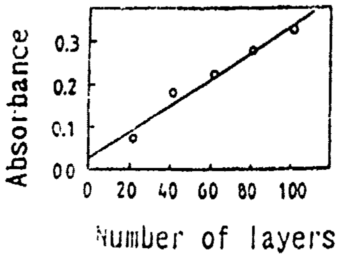


Fig.1 Absorbance at λmax of absorption spectra vs the number of layers

EP13

ORIENTED POLYPEPTIDE MONOLAYERS BY RAPID SPONTANEOUS CONDENSATION OF AMPHIPHILIC AMINO ACID ESTERS AT THE AIR-WATER INTERFACE

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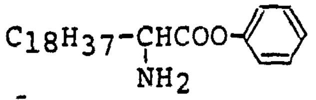
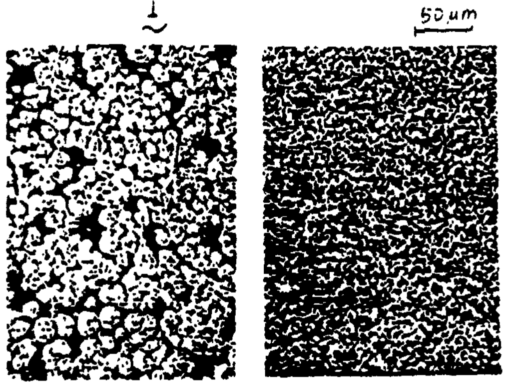
Amphiphilic derivatives of amino acid esters undergo topologically accelated self-condensation when brought into a monolayer orientation.1) However their reaction rates are still far lower than a practical synthesis level due to lacking in reactivity of the ester groups so far employed. A new monolayer-forming amphiphile phenyl ester of amino acid derivative **I**, enables rapid self-condensation forming peptide bonds in ambient conditions.

Polycondensation of **I** spontaneously took place on a neutral aqueous subphase at room temperature and was completed in 2 hours. Progress of polycondensation was visualized by scanning electron microscope on a Si wafer, which revealed morphology of laterally growing polymer domains. IR absorption measurement enabled estimation of the rate constant of condensation based on a band peak analysis. **I** achieved a rate constant of $7 \times 10^{-4} s^{-1}$, which is 70 times larger than that shown by a methyl ester derivative. Topological effect on the condensation rate was investigated for fluid monolayers on an aqueous subphase, LB films on an substrate, and non-oriented cast films, indicating that orientation and fluidity are essential requisite to drive this reaction. Surface pressure of the monolayer accordingly affected the reaction rate. Of stereochemical importance is that a L-serine derived enantiomer of **I** yielded a much more homogeneous film than its racemic mixtures (see figure), reflecting a better packing of molecules occurring in **I** as detected in F-A curves. The polypeptide LB films thus prepared are insoluble in most organic solvents and showed high permeation resistance on an electrochemical analysis by cyclic voltammetry.



I



racemate serine deriv.
polypeptide monolayers

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1) for example, T. Folda et.al., Macromol.Chem.Rapid.Commun., 3, 167(1982).

EP14

DIFFUSION PROCESSES IN LB-MULTILAYERS OF HAIRY ROD MOLECULES

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A new type of non amphiphilic LB-materials consists of rigid rod like polymers with covalently attached flexible alkyl chains.

Substituted Polyglutamates, Phthalocyaninatopolysiloxanes and Cellulose derivatives are some examples for these new hairy rod molecules, which can be used to build up LB-multilayers with improved thermal and chemical stability.

The ability to incorporate guest molecules in the alkyl skin of the stiff polymers may be useful for the design of optical waveguides or sensor devices.

In order to investigate the mobility and diffusion processes of guest molecules in multilayers and to determine the structure and stability of alternating bilayer superlattices of different rod , the X-ray reflexion technique was applied. This method can be used to analyse the electron density profile in multilayers perpendicular to the substrate.

Diffusion processes of guest compounds and of polymer rods as well as chemical reactions in multilayer systems which are correlated with a change of the electron density profile were investigated in this way.

EP15

X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF MONOMOLECULAR FILMS OF Q-STATE NON-STOICHIOMETRIC LEAD SULFIDE IN LB FILMS

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Abstract

The investigation on the insertion of inorganic compounds in organized assemblies has been payed more and more attentions to due to their fantasting solid state chemistry and potential applications as semiconducting, photoelectric and quantum confinement materials[1~3]. Following our work to prepare non-stoichiometric copper sulfide layers in the polar planes of LB monolayers[4], lead sulfide was synthesized with the same method. X-ray diffraction, IR and UV-visible spectroscopy revealed that it has a monomolecular film structure with Q-state absorption. These results will be published elsewhere.

X-ray photoelectron spectroscopy (XPS) shows that the S : Pb ratio of the lead sulfide monomolecular films is about 1.5 : 1. The S_2, binding energy peak of this non-stoichiometric product is at 161.7±0.2 eV which is higher than that of bulk PbS (S_2, binding energy peak at 160.6 eV). In the air, the lead sulfide monomolecular films decomposed to lead stearate (LB films), H_2S, S(element). The decomposition process was studed in detail. 77 days after its exposure to air, about 90% lead sulfide decomposed. This property is different from that of the surface of PbS bulk and Q-state PbS small particles(in ethylene-15% methacrylic acid copolymer). This difference was considered due to the structure of the polar planes of the LB films, the metastable phase(orthorhombic crystal form) of stearic acid LB films and the structure of lead sulfide.

REFERENCES

[1] A. Ruaudel-Teixter. J. Leloup, A. Barraud, Mol. Cryst. Liq. Cryst. , **134**(1986). 347

[2] E. S. Smotkin, Chongmok Lee, A. J. Bard, A. Campion, M. A. Fox, T. E. Mallouk, S. E. Webber and J. M. White, Chem. Phys. Lett. **152**(1988), 265

[3] Kyunghee C. Yi and Janos H. Fendler, Langmuir, **6**(1990), 1519

[4] H. J. Chen, X. D. Chai. Q. Wei, Y. S. Jian and T. J. Li, Thin Solid Films, **178**(1989), 535

EP16

A STUDY OF PROPERTIES OF 10,12-TRICOSADIYNOIC ACID LB FILM

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Abstract

The structure and properties of the diacetylene compounds LB films have widly been researched[1~3]. 10,12-Tricosadiynoic acid has been synthesized by ourselves. Using LB film trough, the monolayers are spread on the water and $CdCl_2$ subphase. Its pressure-area isotherms are recorded. The collapse pressures are 14 and 38 mN/m on the subphase of pure water and $CdCl_2$, respectively. This is due to that cadmium diynoate is obtained, the film is more stable. In a general $CdCl_2$ subphase, the monolayer is transferred onto quartz, CaF_2 and silicon substrate.

From the linear dichroism IR-spectra of cadmium diynate LB films we found that ν_{CO} of the acid is shifted near 1550 cm^{-1}. This further illustrates that the cadmium salt LB films have been formed. The molecular orientation in the cadmium salt LB films have been gained through an analysis of the dichroic behavior of infrared absorption spectra. The results were shown in Table 1. After irradiation using UV light, the molecular orientation was changed into slight straight(also see Table 1).

We have made a systematic study on photo-polymeric characteristic of the cadmium salt LB films. Using 30W low pressure mercury light, the sample is put at a distance of 15 cm from the light. After irradiation for 5 sec., a weaker absorption peaks appears in about 650 nm. After irradiation going beyond 20 min, the blue colour is not continuously deepened and the absorption is not increased, this shows that the polymerization is not increased and the polymerization has been finished. If a multilayer in its bule form is treated by ethanol or chloroform, an immediate and irreversible color change to bright red is induced, absorption peaks are shifted to about 550 nm.

Table 1 The orientation angles of major transition bands in the cadmium diynoate salt LB films

Wovelength(cm^{-1})	Assignment	Befor irradiation	After irradiation
2919	$\nu_a(CH_2)$	65.7 $\nu = 33.5$	70.4 $\nu = 26.6$
2851	$\nu_s(CH_2)$	68.5	72.7
1540~1529	$\nu_a(COO^-)$	62.6	82.5
1407	$\nu_s(COO^-)$	85.2	66.1

REFERENCES

[1] B. Tieke, G. Lieser and G. Wenger, J. Polym. Sci. Polym. Chem. Ed., 17(1979), 1631
[2] B. Tieke, G. Liser and K. Weiss, Thin Solid Films, 99(1983), 95
[3] F. Kajzar, J. Messier, Thin Solid Films, 99(1983), 109

EP17

THE PREPARATION AND PROPERTIES OF COLLOIDAL CdS LB FILMS §

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Quantum size particles exhibit many novel properties. In the present paper, we use the semiamphiphilic method to confine colloidal CdS particles into LB films and study their properties by fluorescence spectroscopy.

The colloidal CdS is prepared as following : 300 ml of $CdCl_2$ 10^{-4}M in 18MΩ deionized water are placed in a 500 ml flask. Pure H_2S gas is bubbled into the solution, which is stirred at high speed. When the solution turns yellow, the H_2S injection is stopped. The stirring is carried on 30 mn further . The solution is then filtered through a high speed filter paper. The resulting filtrate is the desired colloidal solution.

A freshly prepared colloidal solution, diluted with deionized water, is used as a subphase in an ATEMETA LB 105 trough. A chloroform solution of 4-n-octadecacyloxy benzene trifluoro acetone is spread onto the colloidal CdS subphase and compressed in one hour. This particular amphiphilic molecule has been chosen because it prevents the growth of large clusters of CdS, which is induced by ionic forces. It is believed that the colloidal CdS particles can only be adsorbed on the LB monolayer through Van der Waals interaction. The colloidal solution and the resulting LB film exhibit similar excitation spectra, but the emission behaviour appear slightly different. The colloidal CdS solution exhibits a unique sharp fluorescence peak at 436 nm, and a broad shoulder which extends to 600 nm. The CdS containing LB film exhibits three peaks at 418, 436 and 464 nm respectively. The first is the strongest one, which indicates that the CdS particles are actually confined by the LB matrix. This is confirmed by the peak at 464 nm. Besides, the emission band appears narrower than the one of the colloidal solution, which means that large particles are not easily adsorbed on the LB film.

All the results show that the LB matrix is a good medium to confine colloidal particles. It appears hardy possible to modify the size of the confined particles by this method.

§ The Project is supported by Wang Kuan Cheng Education Fundation

EP18

ELECTRICAL PROPERTIES OF COPPER SULFIDE SEMICONDUCTORS INSERTED IN LANGMUIR-BLODGETT (LB). FILMS

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We report electrical and physical properties of copper sulfides built in situ by chemical reactions in the polar planes of behenic acid multilayers obtained by the LB method.

By this way conducting samples can be obtained in the range 10^8-10^{11} Ω ($\sigma \sim 10^{-3}$ - 10^{-6} S. cm^{-1}) for twenty layers films. Samples of inserted copper sulfides exhibit also photoconduction. A study of the current versus the applied potential have shown almost linear variation for about four order of magnitude (from 10^{-3} V to 10 V).

When keeped in air, samples do not remain conducting after several days. But under high vacuum (10^{-6} torr) (or under static vacuum after pumping under high vacuum), samples can remain conducting during several years.

Sometime under this last condition, uncontrolled doping can occur ; the resistance then drops by about four orders of magnitude in a few months. Typically, samples of resistance less than 10^5 Ω have been obtained whose resistivity is estimated to be less than 1 Ω cm.

Studies of resistance versus temperature have shown a degenerate semiconducting behaviour for a sample of resistance less than 10^5 Ω and a semiconducting one with a shallow level of impurity or defect (at about 50 meV) for a sample of resistance 4.10^5 Ω at 300 K.

Some other properties and problems of fabrication will be discussed.

EP19

INORGANIC MONOLAYERS INSERTED IN AN L.B. MATRIX.

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This paper describes the first attempts and results regarding the synthesis of monolayers of metallic thiohypodiphosphates $M_2P_2S_6$ ($M^{2+}, P_2S_6{}^{4-}$), inserted in a LB matrix. Three synthetic routes are investigated with that aim.

1. The synthesis of an amphiphilic compound containing a protonated form of the $P_2S_6{}^{4-}$ anion associated with an organic cation (namely N-docosyl trimethyl ammonium:NDTA) is achieved. The corresponding Langmuir film is transferred onto silicon substrates. Then the diffusion of an aqueous solution of $CdCl_2$ in the LB matrix produces the precipitation of $Cd_2P_2S_6$ in the polar planes. But the poor quality of the transfert associated to the slight chemical instability of the film, does not give highly satisfactory results regarding the purity and the amount of the inorganic compound inserted.

2. The same amphiphilic compound used in the first route is synthesized by ionic exchange, at the air/water interface of the Langmuir trough. The reaction takes place between a monolayer of NDTA bromide and $Na_4P_2S_6,6H_2O$ dissolved in the aqueous solution of Na_2HPO_4 used as subphase. The resulting film is stable and transferred onto silicon slides. Aqueous diffusion of $CdCl_2$ produced $Cd_2P_2S_6$ inserted as monolayers in the polar planes. X-Ray and XPS analysis confirm this result.

3. LB films of cadmium behenate are prepared on silicon substrates. The diffusion of aqueous solution of $Na_4P_2S_6,6H_2O$ in the polar planes precipitates mixtures of $Cd_2P_2S_6$ and CdS .The side reaction is attributed to traces of S^{2-} species provided by the chemical attack of the $P_2S_6{}^{4-}$ anion.

From the three experiments worked out in this study the second route proved to give the best results.

EP20

SCANNING TUNNELING MICROSCOPIC, OPTICAL, AND SCANNING TUNNELING SPECTROSCOPIC CHARACTERIZATION OF SIZE-QUANTIZED CADMIUM SELENIDE PARTICULATE FILMS *IN SITU* GENERATED AT MONOLAYER INTERFACES.

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Cadmium selenide (CdSe) particulate semiconductor films were *in situ* generated at positively charged, dioctadecyldimethylammonium bromide (DODAB) monolayers floating on an aqueous subphase which contained appropriate concentrations of sodium selenosulfate and cadmium nitrilotriacetate. DODAB-monolayer-supported, 300-400 Å thick, CdSe particulate films were quantitatively transferred to solid supports by horizontal lifting. Absorption spectra showed shoulders at 605 nm and absorption edges at 646 nm, which led to the assessment of a direct band-gap of 1.92 eV and 65 ± 10 Å for the diameter of the particles in the CdSe particulate film. Heating at 280°C for five minutes shifted the absorption edge to a longer wavelength and the direct band-gap to that corresponding to bulk crystalline CdSe (1.73 eV). Dark resistivities of a glass-supported CdSe particulate film were also observed to decrease from 10^7-10^8 Ωcm to 1-10 Ωcm upon heating. The increased conductance accompanying annealing, along with the recovery of the bulk band-gap, substantiates the proposed size quantization in CdSe particulate films prepared at DODAB interfaces. Scanning tunneling microscopic images indicated the presence of interconnected CdSe particles with 50-60 Å mean diameters. Current-voltage (I-V) and differential conductance *vs.* voltage (dI/dV *vs.* V) tunneling spectra of CdSe particulate films were determined in air. The obtained data indicated n-type Schottky behavior, sample- and tip-distance-dependent band bending, and around 2.0 eV band-gap energies.

Support of this research by grants from the National Science Foundation and the United States Army Research Office is gratefully acknowledged.

EP21

TWO-DIMENSIONAL STRUCTURES IN POLYMERIZED MONOMOLECULAR FILMS

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Fluorescence microscopy images of UV irradiated monomolecular Langmuir-Blodgett films of the styrene-functionalized surfactants, bis[2-(n-hexadecanoyloxy)ethyl]methyl (p-vinylbenzyl)ammonium chloride and di-n-octadecylmethyl(p-vinylbenzyl)ammonium chloride, show structural domains of polymerized molecules.

The shapes and sizes of the domains have been studied by an image analysis system.

If the photopolymerization is performed at constant surface pressure, the mean area of the domains depend on the irradiation time and the rate of the domain increase is correlated to the polymerization kinetics.

The polymerization surface pressure effects the domain shape.

The dependence of the film viscosity on the domain sizes was also studied.

Session FP

Short and long term applications

FP1

QUALITATIVE CHARACTERIZATION OF ENZYME ADSORBED TO L-FILM, AND ITS APPLICATION TO AN UREA SENSOR

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Various kinds of biosensors have been developed and some of them are now commercialized. Almost all studies to date, however, are mainly concentrated on the practical aspects and the structure of films on biosensors constructed by the LB technique is not fully understood. To clarify the relationship between the structure of the film adsorbing enzyme and its characteristics as a sensor, the following experiments were performed in this paper:

1. The amount of enzyme adsorbed to L film was measured as a function of the concentration of enzyme dissolved in a subphase. The concentrations of urease and glucose oxidase adsorbed to stearylamine and cetylamine monolayer at the air-water interface were measured.
2. The density of pinholes existing in the cadmium stearate LB films was estimated by the copper decoration method.
3. An urea sensor was constructed by immobilizing urease on an ISFET and the characteristics was evaluated.

The results are summarized as follows:

The Langmuir's adsorption isotherm was used to evaluate the quantity of the adsorbed enzymes. The equation which treats the monolayer case of BET's adsorption isotherm can be written as follows:

$$Na/O=(Ns/O)p/((Ns/O)(2mkT)^{1/2}\exp(-\phi/kT)+p), \qquad (1)$$

where Na number of adsorbed molecules, Ns number of adsorption sites, O area of the adsorption surface, p pressure of gas, m molecular weight of adsorbent, and ϕ activation energy, respectively. We have modified the eq. (1) to apply it to the problem of adsorption of enzyme to a Langmuir monolayer. Pressure p was replaced by akT where a is the activity of enzyme and further, substituted by concentration c. Then the eq. (1) can be simply rewritten as

$$O/Na=O/Ns+A/C, \qquad (2)$$

where A is a constant at a fixed temperature. The density of adsorption sites can be obtained from the eq. (2) as Ns/O.

Density of pinholes in the cadmium stearate LB films measured by the copper decoration method was interpreted based on a simple model of pinholes. The depression of pinholes was realized by annealing.

The Langmuir's adsorption isotherm did not hold only for the cetylamine- glucoseoxidase case. It is shown that in the other three cases, the quantity of adsorbed enzyme to LB films obeys to the Langmuir's adsorption isotherm, and that the average area of adsorption site corresponds to the cross section of urease. Thus we can conclude that the L-film adsorbs only monomolecular film in these cases. The sensitivity and response of the urea sensor were measured. It is shown that these factors can be controlled by changing the number of covering layers of cadmium stearate LB films. The characteristics of the sensor was improved by depositing covering layers of cadmium stearate, which is concerned with the density of pinholes in cadmium stearate LB films.

REFERENCES

1 S.Miyauchi, S.Arisawa, T.Arise, and R.Yamamoto,
Thin Solid Films, 180(1989)293
2 I.R.Peterson, J. Mol. Electron. 2(1986)95

FP2

RELATIONSHIP BETWEEN STRUCTURE AND FUNCTION OF A BUILT-UP FILM OF AMPHIPHILIC NI-PHTHALOCYANINE RESPONSIBLE FOR NO_2

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It has generally been recognized that an appropriate morphological regulation of a Langmuir-Blodgett (LB) film system should allow the optimization of film properties for their practical use. To our knowledge, however, there has been no report that the morphological regulation of the film structure could allow the practical use of an LB-film. Recently, we added a new replica method for transmission electron microscopy (TEM) in order to visualize the surface micro-structure of an LB-film[1]. The replica technique have allowed us to study the surface micro-structure of an LB-film system on the nanometer scale.

In addition, we developed a family of amphiphilic Ni-phthalocyanines. They are responsible for NO_2 and tend to form their monolayer on the surface of distilled water (pH 5.8-6.0) to be deposited onto a solid substrate such as glass and gold. Chemical structure of one of them (Pc4) is shown in Fig. 1.

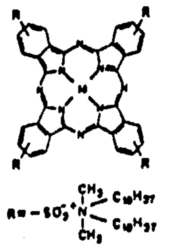

Fig. 1

We found that the response of the LB-film system for NO_2 was strongly dependent on the surface film-structure on the electron microscopic scale. Fig. 2 (a) shows a replica image of a gap cell, whose surface was covered with three Pc4 monolayers according to the vertical dipping technique. Numerous domain-like patterns were visualized. Electron microscopic examinations revealed that the LB-film system having its smooth surface tended to increase its response for NO_2. Fig 2 (b) shows a replica image of a gap cell, on which a single Pc4 monolayer was deposited according to the subphase-lowring technique[2]. The gap cell, whose replica image is shown in Fig. 2 (b), could be electrically responsible for NO_2.

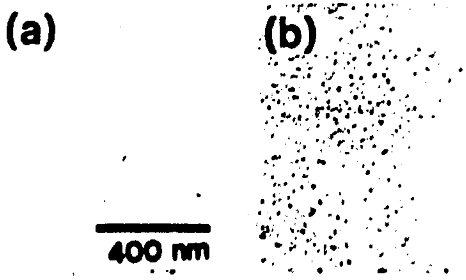

Fig. 2

The morphological regulation of the film structure on the electron microscopic scale could allow the optimization of the film function.

1) Chem Lett., (1989) 1219. 2) Chem. Lett., (1990) 855.

PATTERN FORMATION AND PHOTOPHYSICAL APPLICATIONS OF LB-MULTILAYERS BASED ON POLYGLUTAMATES

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Poly[(methyl-L-glutamate)-co-(octadecyl-L-glutamate)] with an amount of the long chain component of 30 to 60 % is an excellent material to form highly ordered LB-multilayers. The side chains are in a fluid phase which prevents formation of grain boundaries and, thus, multilayers with a thickness in the range of the wavelength of light are low loss optical waveguides.

The introduction of functional groups into the "side chain matrix" allows for specific interactions and/or reactions between the parallel oriented α-helices in the layers.

Side chains with photoactive cinnamoyl groups lead to crosslinkable mono- and multilayers. The reaction was monitored at the air/water interphase following the effect of irradiation by UV-light on surface pressure and area. UV- and FTIR- spectroscopy and X-ray reflection was applied to investigate the crosslinking of the multilayers.

Waveguide-mode loss measurements of multilayers up to 700 layers gave values in the range of 2 - 12 dB/cm depending on various parameters.

Pattern formation can be achieved by UV- or electron beam irradiation. The chloroform developed structures have been characterized by optical and scanning electron microscopy.

FP4

POLYDIACETYLENE MONO- AND MULTILAYER LB FILMS AS E-BEAM RESISTS: SEM AND RAMAN IMAGES

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Mono- and multilayer films of 10,12-pentacosadyinoic acid (PCDA) diacetylene have been prepared by the Langmuir-Blodgett technique. Patterns with sub-micron dimensions have been written on the films using an electron-beam lithography system. The quality of the patterns has been verified by scanning electron microscopy and Raman microscopy[1]. The latter images were formed on a CCD camera by light which had been Raman scattered by polydiacetylene molecules. Polymerization of the diacetylene monomer had been induced by the electron beam or subsequent UV polymerization. The 1455 cm^{-1} Raman band producing the image was resonantly enhanced as the incident HeNe laser beam was within the optical absorption band of the polymer.

The ability of the polymerized films to act as a resist has been demonstrated by depositing them onto slides which were coated with an evaporated aluminium layer. When the specimens were etched with alcoholic sodium hydroxide solution, the aluminium layers were unaffected in areas which were protected by a polydiacetylene film.

1. D.N. Batchelder, B.J.E. Smith and C. Cheng, Proc. XII Intern. Conf. of Raman Spectroscopy, edited by J.R. Durig and J.F. Sullivan, 1990, pp. 836-837.

THE BIOMIMETIC PROPERTY OF GAS-SENSITIVE FILMS FOR ODORANTS CONSTRUCTED BY THE LB TECHNIQUE

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The smell of odor gas is sensed by the adsorption of odor molecules onto the cytoplasmic membrane of olfactory cells(1). An LB film bears a multi-layer structure of a surface monolayer, and is similar to the cytoplasmic membrane.

As a gas-sensitive film, an LB film is ultra-thin. So, it was considered that the amount of adsorbed odor gas would be very small, and that it would be difficult to measure this weight. Thus, a surface acoustic wave(SAW) device was used. The weight change on the surface of an SAW device in an oscillator can be determined by the frequency change(2). The SAW device covered with an LB film detected the adsorption of odor molecules of nano-gram order per one square centimeter.

The Hansch-Fujita equation of the quantitative structure-activity relationship is widely used in drug-design(3). This equation uses physicochemical parameters such as hydrophobic, electronic, or steric as structural parameters, and the sum of these parameters determines the physiological or pharmacological activity. Many kinds of activities related to the cytoplasmic membrane are described by this equation.

Thus, LB films possessing various values of structural parameters were deposited onto SAW devices, and the property of the adsorption of odor gases was studied. It was investigated whether the Hansch-Fujita equation would be applicable to not only the cytoplasmic membrane but also to the LB film. One of the structural parameters was varied, and the change in amount of adsorption was determined. The amount of adsorption was linearly related to each parameter. And the amount of adsorption could be described by the hydrophobic and electronic parameter. When a linear multiple regression analysis was applied to the relation between the amount of adsorption and the parameters, the multiple correlation coefficient was nearly 1.00. This result shows the amount of adsorption can be described by the structural parameters of the Hansch-Fujita equation.

This result demonstrates that a biomimetic gas-sensitive film, possessing properties similar to the cytoplasmic membrane, could be realized by the LB technique.

(1) Kashiwayanagi,M.and K.Kurihara,Brain Res.,359:97,(1985).
(2) Snow,A.W.et al.,Langmuir,513,(1986).
(3) Hansch,C.and T.Fujita,J.Am.Chem.Soc.,86,1616(1964).

FP6

PROPERTIES OF LIQUID-CRYSTAL CELLS OF PYROLIZED POLYIMIDE LB FILMS

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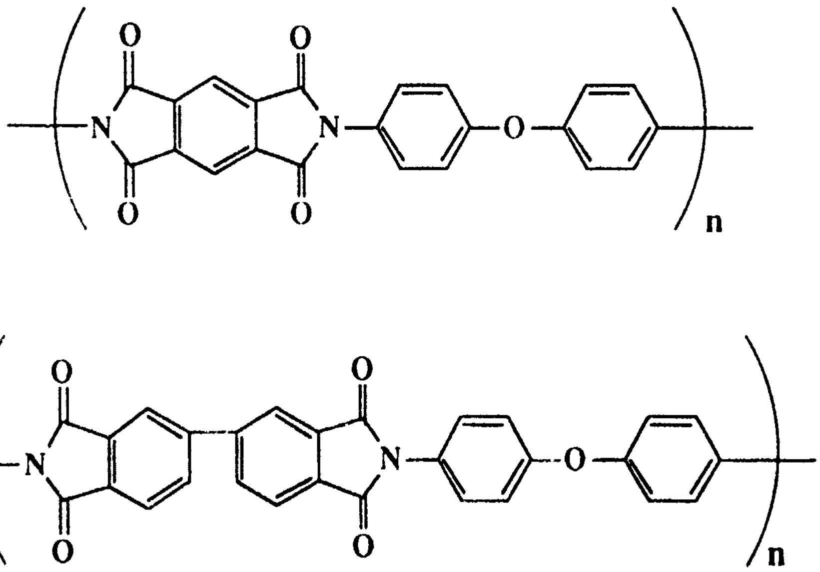
The conductive Langmuir-Blodgett (LB) films are interesting from the viewpoint of ultrathin organic conductors. For the application of LB films to electronic devices, it is necessary to construct highly conductive LB films with stability. We have recently reported the pyrolysis of LB films of aromatic polymers [1,2]. The highly conductive LB films were obtained by the pyrolysis of polyimide LB films at 1000℃ in vacuum or under nitrogen atmosphere for 60 min. The films showed the conductivity of as high as 300 S/cm, depending on the thickness of the precursor films. The surface of the film was smooth and uniform revealed by SEM. The films were stable under ambient conditions over months.

In this paper, we describe the properties of liquid crystal cells using the pyrolitic polyimide LB films as orientation films and electrodes. The nematic liquid crystal, Merck E-7 (Merck Japan Inc.) was used to fill the gap between the inner surfaces of quartz plates coated with pyrolitic polyimide. The thickness of the LC layers was 9 µm. The electrooptic performance of the LC cells will be reported by examining the effect of the layer number of the LB film and the temperature of pyrolysis.



Chemical structure of polyimide.

1) T. Akatsuka, H. Tanaka, J. Toyama, T. Nakamura and Y. Kawabata, Chem. Lett., (1990) 975.
2) T. Akatsuka, H. Tanaka, J. Toyama, T. Nakamura and Y. Kawabata, Synth. Met., in press.

FP7

Fabrication of Fine Patterns by Positive-working Resists Using a Polyimide Langmuir-Blodgett Film System

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It is expected that a high resolution will be achieved by preparing thermally stable ultrathin organic films without pinholes on the substrate in a microlithographic technique. For microstructure fabrication, it is desirable for ultrathin films themselves to be photosensitive, which allow fine patterns to be easily fabricated with them. In this work, multilayer films of polyimide containing disilane unit were prepared on substrates by the novel technique coupled with the conventional LB technique, which was originally developed by Kakimoto et al.[1,2], and then applied to KrF excimer resists. The films were found to be nearly pinhole-free and the monolayer thickness was about 0.5 nm. The multilayer films prepared on both CaF_2 substrates and Si substrates were exposed by the radiation of deep UV light with a wave length of 248 nm at an interval of 5 msec using a KrF excimer pulse laser, whose irradiation energy was 0.18 mJ/cm^2. It was concluded from the IR and UV-visible spectra that the photochemical reaction has occurred in the PI LB films, due to the scission of disilane bonds in the back bone of PI molecular unit. After the exposure, the films were developed by soaking the substrate in a 1:1 DMAc:ethanol solution. It was found that no PI LB films with deep UV irradiation remain after the development, whereas PI LB films without the UV irradiation remain as deposited. Finally, Si substrates covered with a 21-layered PI LB film were exposed through a photomask using a deep UV laser stepper for the fabrication of fine patterns. We concluded that positive fine patterns with a resolution of 0.25μm lines and spaces were able to be fabricated.

[1]M.Suzuki et al., Chem. Lett. (1986)395.

[2]M.Kakimoto et al., Chem. Lett. (1986)823.

FP8

Transduction of Chemical Signals to Optical Signals by using Multibilayer-Deposited Optical Fiber

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We have found for the first time that the water-insoluble multibilayer (polyion complex)-deposited plastic optical fiber (POF) provides remarkable phase transition temperature dependence of the optical signal, resulting from the change of refractive indexes of the bilayer phase.[1]

It is well known that the conformation of poly(methacrylic acid)(PMAA) changes drastically by varying pH based on protonation or deprotonation of the carboxyl groups. Thus, we designed a triblock polyanion containing PMAA segment and prepared the polyion complex ($S_{10}M_{49}S_{10}/1$) of this triblock polyanion and the cationic amphiphile, which was then immobilized on POF as schematically depicted in Fig. 1. The optical signal through the modified POF thus obtained showed a marked phase transition temperature (42°C) dependence which was also observed in the refractive index of the multibilayer. The modified POF provided reversible optical signal changes, responding to pH. The extent of such a pH-response was controlled by the phase transition temperature of the matrix membrane. These phenomena were attained due to a combination of the conformational property of polymer and the change of the membrane physical state (refractive index), which was induced by the conformational transition of the polymer. Influences of the other chemical additives for the optical responses are also discussed.

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[1] M. Niwa, T. Yamamoto, N. Higashi, *Chem. Lett.*, **1990**, 1603.

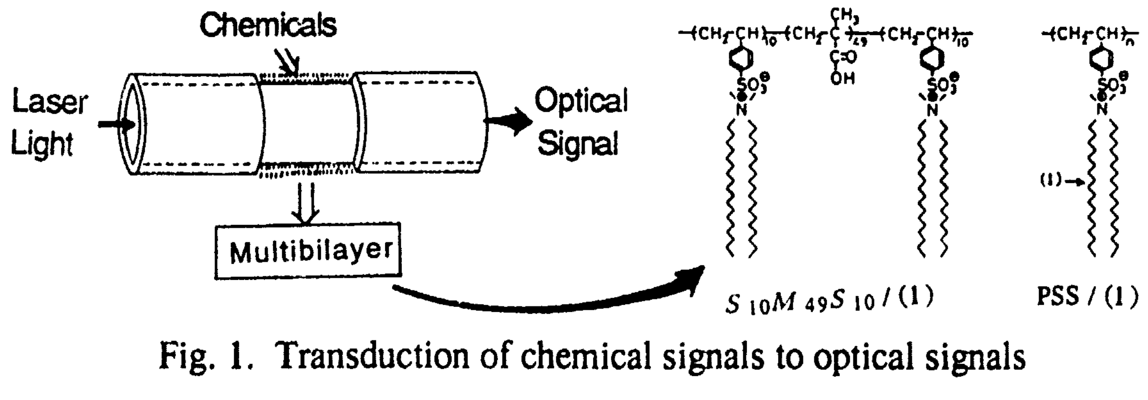

Fig. 1. Transduction of chemical signals to optical signals

FP9

ORGANIC ELECTROLUMINESCENT DEVICE WITH CYANINE DYE LANGMUIR-BLODGETT FILM AS AN EMITTER

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Using the Langmuir-Blodgett (LB) technique, we fabricated a electroluminescence (EL) cell with a molecular-size emitting layer.

The EL cells consisted of indium tin oxide (ITO) electrode, diamine (TAD) hole transport layer (HTL), cyanine dye (OCD) LB film as an emitting layer (EML), oxadiazole (PBD) electron transport layer (ETL) and MgAg electrode (Fig.1). Firstly, TAD layer was vacuum-deposited on ITO substrate. Then, OCD monolayers were deposited on the substrate by the LB technique. At last, PBD layer and cathode MgAg layer were successively vacuum-deposited. Thickness of TAD and PBD layers was 50 nm.

OCD formed J-aggregate in LB film. Absorption peak (550 nm) of OCD LB film is 50 nm longer than that of OCD in chloroform. Further, intense fluorescence with very small Stoks-shift was observed in the LB film.

Efficient EL was attained even in the EL cell with OCD bimolecular layer as an emitting layer owing to the confinement of charge carriers and excitones within the very thin emitting layer.1) Yellow emission was observed with naked eyes under a usual illumination when more than DC 20 V was applied to the EL cell. Luminance in the EL cell was about 30 cd m^{-2} at injection current density of 100 mA cm^{-2}. The EL spectrum well corresponded to fluorescence of the J-aggregated OCD (Fig.2).

1) C. Adachi et. al, Appl. Phys. Lett., 57, 531 (1990).

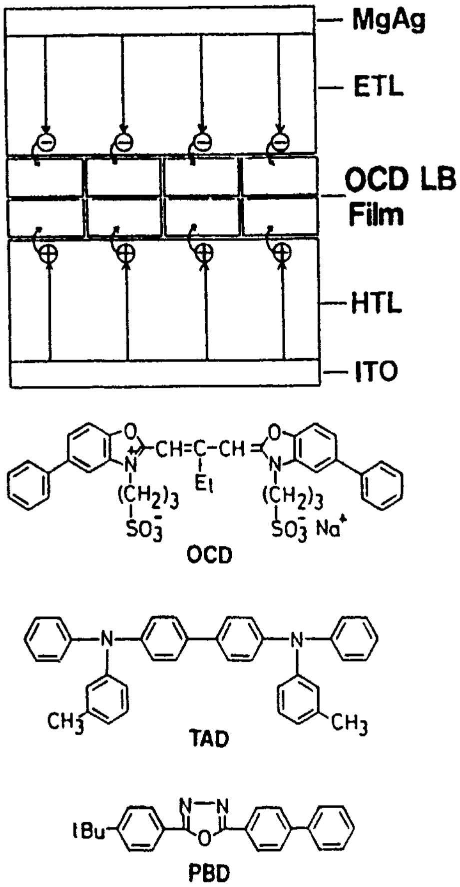

Fig.1. Structure of an EL cell and chemical structure of organic compounds used in this study.

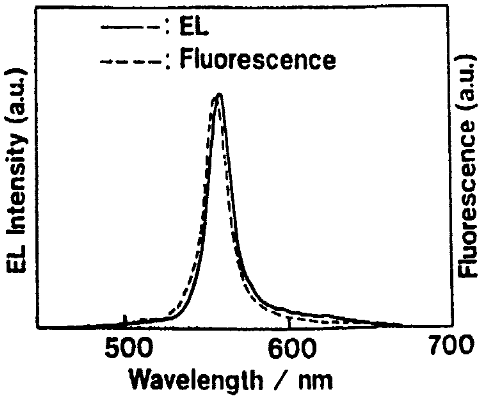

Fig.2. EL spectrum of an EL cell with OCD bimoleuclar layer (solid line). Broken line is fulorescence spectrum of J-aggregated OCD.

FP10

HYBRID GAS DETECTOR OF SQUARYLIUM DYE LANGMUIR-BLODGETT FILM DEPOSITED ON A QUARTZ OSCILLATOR.

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At the 4th International Conference on LB-Films, Tsukuba, we reported about highly sensitive optical NO_2 gas detector of squarylium dye LB-film containing J-aggregate.

At this conference, we'll present hybrid gas detector coupled optical NO_2 detector with a weighing system of adsorbed gas by squarylium dye LB film deposited on a quartz oscillator. A piezoelectric quartz oscillator has been known to be a very sensitive weighing device. We make a hybrid gas detector by building up LB-film of squarylium dye mixed with Cd-arachidate on this quartz oscillator. Responses with this detector for NO_2, trichloroethylene and NH_3 were evaluated. Oscillating frequencies of this detector under these gases were measured with fluorescence intensity simultaneously.

On exposure to 0.8ppm NO_2 gas, most of fluorescence was quenched and estimated ratio of adsorbed NO_2 molecules to squarylium dye molecules from shift of oscillating frequency was about 0.2. For a vapor of organic solvent such as trichloroethylene, decrement of oscillation frequency was observed without quenching of fluorescence. On the other hand, a slightly increment of fluorescence was observed with decrement of oscillation frequency for NH_3.

It was confirmed that the remarkable quenching of fluorescence from squarylium dye J-aggregate was caused by highly concentrated adsorption of NO_2 molecules in LB-film, both optically and quantitatively. This gas detector also shows a possibility to develop an intelligent sensing system which could recognize type and concentration of gases by integration of each responses.

FP11

GAS DETECTION IN THE PPB-RANGE WITH A NEW HIGH FREQUENCY, HIGH SENSITIVITY SAW DEVICE

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A high frequency SAW gas sensing device has been developed for an operating frequency of 600 MHz. It contains three separate SAW delay lines which are the frequency determining elements of oscillator circuits. They can be coated with different thin organic films as adsorbants for gas detection measurements. The mass of the film increases due to the adsorption process, causing a decrease of the surface wave velocity. This leads to a downward shift of the oscillation frequency.

First measurements were made with two classes of NO_2 sensitive films: evaporated lead phthalocyanine layers from 1 to 15 nm in thickness and Langmuir Blodgett (LB-) films with molecules consisting of a soluble iron-phthalocyanine derivate. The dependence of sensitivity with the thickness of the sublimated films and the type of interaction of NO_2 with these coatings are discussed.

In addition to the experiments performed in air and special gas-flow chambers, experiments have been performed under UHV-condtions.

Substrate cleaning procedures and electrical connections of the SAW device with the oscillators were designed for UHV conditions. The gas-sensitive organic layers were deposited through masks on one of the three delay lines. Substrate cleaning, film deposition and measurements were done in a single vacuum cycle. For gas detection, the vacuum chamber was purged with controlled amounts of test gases. The purpose of these experiments was to investigate the adsorption behaviour of the gas sensitive adsorption films under well defined conditions without the presence of contaminants, e.g. from ambient air. Under these conditions, a novel anomalous damping behaviour was observed.

FP12

PREPARATION OF CYANOACRYLATE LB FILMS AND THEIR UV AND ELECTRON RESIST APPLICATIONS

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Monomolecular layers of polycyanoacrylates at the air-water interface as well as multilayers on solid substrates were studied. Cyanoacrylates with the hydrocarbon chains containing from two to ten carbon atoms (C2-C10) were used . Surface pressure-area isotherms show that monolayers of polycyanoacrylates C2-C5 are not stable. Slow collapse of monolayers and dissolution of molecules take place under compression.

On the other hand, isotherms of C6-C10 monolayers show a distinct region of collapse and precise value of area per molecule. The collapse pressure is equal to 22 mN/m,and the area per molecule varies from 0.19 nm^2 (C6) to 0.30 nm^2(C10).

Molecular weights of polycyanoacrylates were determined by measuring the surface pressure-area isotherms of monolayers in a gaseous state i.e. at the beginning of the curve. The influence of temperature on the properties of monolayers was studied also. Then the conditions of multilayer deposition were worked out. Thin films of C6-C10 containing from 10 to 100 monolayers were deposited for investigation. The thicknesses of the monolayers appear to be equal to 0.8-1.3 nm.

New method of production of negative Langmuir-Blodgett deep UV-sensitive resist is proposed. The multilayer of sensitizer is deposited over LB resist film for this purpose. The resolution obtained was equal to 0.3 µm. The sensitivity is found to be equal to 0.5 J/cm^2.

High resolution electron beam resist based on polycyanoacrylate LB films was prepared too. The measured values of sensitivity (D50) are in the interval between 2×10^{-5} and 3×10^{-7} C/cm^2 for various compounds. Irradiated LB films are resistant to plasma etching. The rate of etching is ten times lower than that of silicon crystal.

Properties of polycyanoacrylate LB resists give us the possibility for application of these films in microelectronics.

FP13

AN OPTICAL BIOSENSOR PRINCIPLE BASED ON FLUORESCENCE ENERGY TRANSFER

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Radiationless fluorescence energy transfer (Förster energy transfer) has been used for various studies. With LB films, sophisticated multilayer systems have been developed for theoretical analyses of various phenomena [H. Kuhn, D. Möbius, H. Bücher in: Physical Methods of Chemistry, Vol. 1, Pt. 3B, pp. 577, John Wiley, New York 1972]. On the other hand, the technique has been used in biosciences, in particular in genetics and immunology, as a "spectroscopic ruler" to determine molecular distances [L. Stryer, Annu. Rev. Biochem. 47, 819-846 (1978)].

The idea is to use this technique for the detection of an analyte molecule that binds to a biological receptor attached to or integrated into an LB film. This receptor molecule can be "anchored" into the film by means of a hydrophobic chain, or one can covalently bind the biomolecule to the film by techniques similar to the conventional immobilization methods.

The LB films are built up from amphiphilic polymethacrylates that contain a donor dye for the fluorescence energy transfer and reactive groups to which protein receptors can bind. Dyes can be attached covalently to the polymers or can be co-spread with them before film transfer. The prepared films show a stability that is high enough to survive the bioassay conditions.

To evaluate the potency of the systems, the principle of a distance dependency of the energy transfer was demonstrated with a lectin labeled with an acceptor dye. Other experiments, where the concentration of an acceptor dye in an LB film was varied, showed that the sensitivity is enhanced by at least one to two orders of magnitute compared with direct fluorescence detection.

Mannoside ligand molecules labeled with the acceptor dye (TRITC) were then bound to the LB surface covered with concanavalin A as a receptor molecule. A specific binding of the ligand was found.

These experiments show that the combination of the technique of Förster energy transfer and Langmuir-Blodgett films can result in a functioning sensing principle.

FP14

GRAVIMETRICAL BIOSENSORS BASED ON LANGMUIR-BLODGETT FILMS OF IMMUNOGLOBULIN

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An event of antibody - antigen binding can be studied by the microgravimetric method, using a mass- sensitive quartz resonator to detect and measure the amount of antibody in a test solution. The basic frequency of oscilation of the crystal (F) is changed due to adsorption of an immunogen on the modified surface.

The relationship between the surface mass change (Δm) and the frequency shift (ΔF) is given by the Sauerbray equation: $F = -k\Delta m$. LB films of antibody or antigen were immobilized onto the resonator surface for a direct record of the specific binding to be made. 9 MHz quartz crystals with silver-plated electrodes were used.

The piezoelectric resonators were modified by γ-aminopropyltriethoxysilane vapour at a temperature of 220°C. The initial silane layer is polymerized with other silane derivatives to form a siloxane polymer having a high reactivity to proteins and the antigen or antibody is bound to this polymer. The shift in resonant frequency due to water penetration was only 20 to 50 Hz over the experimental period of about 30-40 minutes.

LB films of the human IgG (fraction II, Fluka) were prepared in a Langmuir trough (Joyce-Loebl) under a surface pressure of 20 dyn/cm, at room temperature.

Glutaraldehyde coupling IgG film was then deposited onto a piezoelectric resonator modified with γ-aminopropyltriethoxysilane and used as a sensing element by dipping into solution of sheeps anti-IgG serum.

Specific adsorption between the immobilized antibody and test solution has been measured. One sensor serves as a reference sensor and the other as an indicating sensor. Frequency shifts associated with the corresponding base pairs were 300 - 900 Hz depending on concentration of test solution.

FP15

LB RESISTS OF DIAZONAPHTHOQUINONE NOVOLAC RESIN MADE BY A NEW HORIZANTAL DEPOSIT METHOD

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LB multilayered resists for fine line lithography have been well studied by several groups.(1,2) We intended to use electron beam sensitive polymeric materials to make the LB resists in order to increase its etch resistance and decrease the pinhole density .

Diazonaphthoquinone novolac resin (DQN) has been used to form the monolayer on the air-water interface. The monolayer was stable until the surface pressure up to 35 mN/m at the temperature around 20°C. A moving wall trough was built to transfer monolayers to chromium surface at the surface pressure of 15 mN/m by a new continuous horizontal deposition method ,which can transfer y-type films of DQN on Cr substrate. The thickness measurement showed that this new deposit process could fabricate homogenuous and oriented LB film for polymeric materials. The 10 layered resist had good adhesion and high etch resistance in ordinary Cr etch solution.

The exposure tests to the 10-layered resist of DQN were made under 80 w UV lamp for 5 seconds through a photomask with the pattern of the line-width of 1μm. Following the developing process the samples were immersed to Cr etch solution for 1 min to transfer the resist pattern to Cr film. The pattern with 1μm line-width resolution on 1000Å thick Cr film has been obtained.

Reference:

1.A.Barrand, C.Rosilio and A.Ruandel-Teixier,Thin Solid Films, 68(1980)91-98.

2.A Barrand, Thin Solid Films, 99(1983)317-321.

A GAS SENSOR FABRICATED WITH FET AND L-B FILM OF PORPHYRIN

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The prophyrin used in this study was deposited using the L-B transfer technique.In order to make the prophyrin molecule compatible with the L-B method,a peripherally substituted prophyrin compound was synthesised. Using the cobalt acetate, gave the Co complex, this prophyrins had satisfactory IR and UV spectra.

Two FET were made on the same silicon substrate, both are N-channel enhancement mode. One is MOSFET, the other is OSFET which is similar to ISFET sensor in structure.The characteristics of FET will be measured with MOSFET,gas sensitive will be measured with OSFET covered by L-B film of prophyrin on its gate area.

Isotherms of spread monolayer of the porphyrin used showed that they were stable up to a surface pressure of 50mN/m with an acceptable collapse rate.At room temperature,PH 6.8-7.2,with the spread film compressed to 30mN/m ,porphyrin films were tranferred to the gate area of OSFET substrate. We named this device: LB-OSFET sensor. Contact was made to the sample electrodes using aluminium line spot weld to IC pedestal.

The drain currents of porphyrin LB-OSFET were measured when they were in air. The sample was then either exposed to NO_2, CO, NH_3,C_2H_5O. The respondses of various film thicknesses to various partial pressures of gas have been monitored,only NO_2 affects the drain currents clearly.

When the sample was exposed to 5-250 PPm of NO_2,the change of I_{DS} was measured in 3V drain-source bias.When exposed to 5 PPm,the I_{DS} in 39-layer film changes from $1*10^{-8}$-$1.5*10^{-7}$after 60 minutes,exposed to 250PPm, change to $1*10^{-5}$after 20 minutes.These results show that response time and signal magnitude were related to thickness and partial pressure of gas with thinner films providing faster response times but weaker responses,high partial pressures providing faster response time and stronger resposes. When the partial pressures of gas were constant,the changes of I_{DS} were measured in various drain-source bias,the results come close to output characteristics of MOSFET.

We consider that the change of I_{DS} in various partial pressures of NO_2 is because of NO_2 accepting a electron from porphyrin molecule,then inducing a hole in the surface of SiO_2, this result correspond to has a bias on the semiconductor surface of gate areas,so the I_{DS} changes with the partial pressures of NO_2.

FP17

PROTOTYPE OF GAS SENSOR BASED ON LB CONDUCTING FILMS.

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Abstract:

We have studied the feasibility of a gas sensor based on LB conducting films (1). The doping process (applied to the LB films to make them conducting) is quite easy to be performed and the films exhibit good stability (2).

When exposed to oxidizing or reducing gases, the d.c. conductivity of the film changes significantly. So a conducting film of (N-octadecyl-pyridinium$^+$, TCNQ$^-$)$_{1,4}$TCNQ^0 doped with iodine vapours has been exposed to phosphine. Its useful sensitivity to phosphine in dry air ranges from 1ppm to 100 ppm (3). To run tests in real conditions, a prototype has been designed and realized in view of an industrial development.

The present paper describes the encapsulation of the sensing films, the gas circulation circuit and the signal processing electronics. The prototype is designed for differential measurements. Thus the limiting factors (steep temperature change, moisture and interfering gases) are reasonably compensated although some problems have not been solved (film reproducibility, selective absorption of humidity and phosphine). The main material studied with this prototype is a LB film of (N-ODPyr$^+$, TCNQ$^-$)$_{1,4}$TCNQ^0. The early performances of the cell were found slightly worse than those obtained with the experimental hand made laboratory cell, although the flow rate had been optimised to 3 lh^{-1}. This is discussed in terms of flow mechanics and gas /film contact time. The optimization of others parameters have restored performances quite comparable to those of the experimental laboratory set.

The prototype appears as an efficient tool which can be used either as a dose accumulator in its simplest form or as a differential integrated sensor in its final form.

References:

(1) : L.Henrion, G.Derost, A.Ruaudel-Teixier, A.Barraud.
Sensors and actuactors 14 (1988) 251-257.
(2) : M.Vandevyver, A.Barraud, P.Lesieur, J.Richard, A.Ruaudel-Teixier
Journal de Chimie-Physique, 1986, 83, n° 9, 599-602
(3) : L.Henrion, G.Derost, A.Barraud, A.Ruaudel-Teixier.
Sensors and actuators 17 (1989) 493-498.

ELABORATION OF A GLUCOSE BIOSENSOR BASED ON LANGMUIR-BLODGETT TECHNOLOGY.

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We report here on the development of a glucose biosensor based on Langmuir-Blodgett technology. This approach consists in elaborating well ordered structures in which an enzyme is immobilized. The first step corresponds to the formation of a mixture of a fatty acid and an enzyme on the surface of an aqueous phase in a LB trough. This mixture is then transferred onto a gold-coated matrix by the classical method; this matrix is used as an electrode in order to detect the product of the enzymatic reaction.

The enzyme used for measuring glucose concentration is a glucose oxidase (*Aspergillus niger*). This enzyme catalyses the oxidation of glucose into gluconic acid which is accompanied by a production of hydrogen peroxide; this species is detected at the surface of the gold electrode by measuring its oxidation current at a fixed potential (600 mV versus SCE electrode). A calibration is necessary to relate the current measured to the glucose concentration.

The first results are promising:
- short response times are obtained (a few seconds for obtaining 99% of the steady state signal), as expected from the geometry of the system: nanoscopic scale ensuring very short characteristic times for the diffusion processes involved.
- very good linearity of the relationship between the current measured and the glucose concentration in the range corresponding to biomedical applications (1-10 mM).

Our current work consists in improving the reproducibility of the measurements by adequate treatments of the gold electrode surface, and in testing the durability of these treatments.

The next step will be an optimization in order to perform measurements in complex biological fluids such as plasma and blood. It will be necessary, in particular, to develop differential measurements.

FP19

LANGMUIR-BLODGETT FILMS AS RADIATION SENSITIVE LAYERS FOR THE USE OF MICROLITHOGRAPHY

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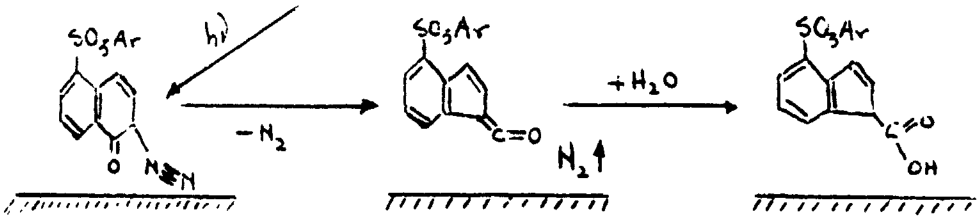
The continuous decrease of the features required by semiconductor technology compels the microlithography to obtain more planar images. Using diazo-naphto-quinone DNQ based Langmuir--Blodgett (LB) films as an imaging layer one can obtain planar images at the interface, Y/N (treshold) behaviour, single expose-develop step, and possible high resolution, steep profile in the etched layer.

Deposition.

The deposition of a diazo-naphto-quinone (DNQ) based substance (with cvasi-linear structure and with hydrophilic and hydrophobic extremities) on hydrophilic substrates (metal: Cr, Al, Si, etc. i.e. first mode) or on hydrophobic ones (i.e. second mode). The hydrophobic extremity must be the diazo-quinone group and the hydrophylic one can be either a sulphonic-ester group, or other polar group. The deposition of DNQ on hydrophobic substrates is of extreme importance.

Exposure.

Using DNQ based LB films as imaging layer, one can obtain perfect planar latent image either at the top, or at the bottom of the layer. The latent image is planar because it is obtained through photochemical reaction at the interface. The transformation of the hydrophobic group into a hydrophilic one, through photochemical reaction, can be summarized in the reaction:



The pop-off effect (development).

When someone build a LB DNQ based film with the hydrophobic extremity on the substrate, it is believable that the layer in the irradiated region will be poped-off from the film mainly because (i) the hydrophobic group is destroyed during photochemical reaction and is replaced by a hydrophilic group, and (ii) the gas, N2, is generated in this reaction. In this way one can obtain a self developable resist, or at least the exposed region can be easyly removed from the substrate.

LB films as a Y/N imaging layer.

It is expectable to obtain sharp concentration profiles of the photolized DNQ in the LB film (even in multilayer mode), when transferring the intensity profile of the aerial image into the imaging layer . Also it is expectable that the / value (chemical contrast) to be very high, if not infinite. The very organized structure of the LB film can minimize the scattering effects.
It is also possible to use the upside latent image, when bulding the LB films with the hydrophilic group on the substrate, silvlating the exposed region. The concept is analogue with the DESIRE process, but here the diffusion step is replaced by a chemical reaction on the top surface of the LB film, obtaining a perfect masl for the anisotropic etch step.

Session GP

Characterization

(structural and other)

GP1

CELLULAR AUTOMATA FORMALISM AS A METHOD IN MEMBRANOLOGY

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Computer simulation based on the cellular automata method proved to be a useful tool for describing macroscopic systems such as gases and fluids. In our previous paper we suggested to use this method to study the properties of lipid membranes. Now, we would like to show how to use the cellular automata method to study some structural changes in lipid membranes modified with some amphiphilic modifiers with various chain lengths. By taking into account trans-gauche conformation changes of the modifier and lipid alkyl chains we obtained optimum lengths of chains of the modifiers which cause greatest structural changes in the lipid membrane. Comparison of the obtained results with experimental results allowed us to conclude that the mechanism of intermolecular interaction we proposed seems to be probable. In further work we are going to test the possibilities of some mechanisms of the effect of two-component amphiphilic modifiers on membrane and compare them with our experimental data.

GP2

DIFFERENTIAL X-RAY REFLECTOMETRY OF IMPERFECT LB FILMS

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The conventional small-angle X-ray diffraction scheme for the investigation of large-scale (supermolecular) LB film structure probes the average periodic component of the film electron density distribution with depth. In this report we describe two new versions of the low-angle X-ray scattering method, designed to study the real LB film structure imperfections, and the results of their practical testing. The first method is the analogue of the well-known triple crystal diffractometry for crystal structure investigation. In our case, due to the generally lower perfection of LB film structure, there is no urgent need to use two additional single crystals as the collimator and the analyzer. Their functions can be actually performed by the entrance and detector slits, which greatly simplifies the technique. The experiments, carried out with the modified DRAM-2.0 diffractometer on LB films of lead stearate (100 layers) and barium behenate (30 layers) deposited on glass and silicon substrates at different surface pressures, showed that angle distribution of the reflected intensity near the first Bragg reflection contained 3 components, which depended on the sample inclination angle α with respect to the symmetrical orientation.Their correspondence with the main Bragg peak, pseudo peak and diffuse intensity maximum in the triple crystal diffractometry was identified. Theoretical treatment leads to the conclusion that the most unambiguous and complete information about the film structure imperfections can be extracted from the orientation dependence of the magnitude and position of the diffuse intensity maximum, which corresponds, in fact, to the Bragg reflection from the deformed (tilted and compressed) LB layers near film structure defects. The simple relations are deduced that enables one to obtain the full deformation distribution around the "average" defect. This is done for the investigated samples, and the results agree well with the independent SEM data for same samples. Two other peaks contain the information about the average periodic structure and small-scale irregular deviations from it. The connection between the parameters of the latter and the peak characteristics is less straightforward and can be established within a semiempirical approach supported by a large amount of experimental data. The second method originates, in fact, from the same idea but applied to the total external, rather than Bragg, X-ray reflection, which leads to the so-called Ioneda, or anomalous reflection, effect. The diffuse maximum is poorly seen now but the main peak (mirror reflection) and especially the pseudo peak (anomalous reflection) are very sensitive to the film structure irregularities. This conclusion is supported by experimental results for LB films of lead stearate with varied characteristics and the corresponding theoretical analysis. In conclusion we note that these two techniques are rather simple in experimental realization and suitably complement each other.

GP3

ELECTRONIC STRUCTURE OF NITROGEN SQUARE PLANAR COPPER COMPLEXES IN LB FILMS

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Specific substituted phtalocyanine compounds called CuS18 are ideally suited to form LB films (1). The molecule is basically a copper phtalocyanine with 4 pyridine rings in the outskirts of the macrocycle, each pyridinic nitrogen atom being quaternized to attach a carbon chain. The main difference of such films with the same compound in an amorphous phase is that the molecule is built-in in a reduced form ($CuS18^{2-}_{LB}$). Surprisingly, this reduced form keeps the copper atom in the same CuII redox state, as for the amorphous phase and any compound of the same family.

In order to clarify this problem, we have performed X-ray photoelectron spectroscopy in the region of C1s, N1s and Cu2p lines. The Cu2p spectra show major differences on the redox state of copper. This is because the main line energy and satellite intensity are quite different for CuI compared to CuII. We observe that amorphous CuS18 has a CuII central atom, but upon irradiation, the compound is easily reduced and we see a clear CuI signal appearing in the spectrum. For $CuS18^{2-}_{LB}$, we observe only a dominant CuII contribution, in agreement with the results reported by other methods (1). Consequently, it seems that one of the additional electrons is added to copper for the reduced form of amorphous CuS18, whereas in $CuS18^{2-}_{LB}$, the two electrons attach themselves to the macrocycle. We have tried to investigate the C1s and N1s spectra to detect such effect but we could not observe any significant differences from reduced amorphous CuS18 to $CuS18^{2-}_{LB}$, probably because the X-ray spectra provide a mean information on the many carbon and nitrogen atoms.

Using semi-empirical calculations, we show that the outer valence shells of CuS18 is composed of two close-by orbitals, one, b_{1g}, located mainly on the copper atom, another, e_{2g}, fully localized on the macrocycle. We offer to interpret the surprising electronic structure of the LB film as the result of the reduction on the macrocycle alone, perhaps due to a small distortion of the nitrogen square plane around copper, which removes the degeneracy of the outermost orbital e_{2g} of the macrocycle, one component being shifted down with respect to the b_{1g} copper one.

(1) S. Palacin, A. Ruaudel-Texier, and A. Barraud, J. Phys. Chem. (1986), **90**, 6237

GP4

OPTICAL PROPERTIES OF LANGMUIR-BLODGETT FILMS: A MULTIPLE-ANGLE REFLECTOMETRIC INVESTIGATION

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Multiple angle reflectometry has been used to investigate the optical properties of Langmuir-Blodgett (LB) films of a variety of materials. The technique (Travers et al 1988) allows the simultaneous determination of refractive indices and film thickness. In treating the data the multilayer is modelled as a uniaxial crystal with the optic axis perpendicular to the substrate. The optical properties of the LB film can thus be described in terms of two principal refractive indices, $N_\perp (= n_\perp - ik_\perp)$ and $N_\parallel (= n_\parallel - ik_\parallel)$. By using purely s or p-polarised light the analysis is simplified relative to ellipsometry.

Multilayers of pure 22-tricosenoic acid (22TA) and mixed 22-tricosenoic acid/cadmium tricosenoate films (obtained by introducing Cd^{2+} into the subphase) have been studied. The analysis for these samples was simplified by assuming that absorption was negligible (i.e. $k_\perp = k_\parallel = 0$) in the wavelength range considered. Values obtained for monolayer thicknesses are in reasonable agreement with published data (Barnes and Sambles, 1987). Dispersion curves ($n_\perp$ against λ) have been determined for pure 22TA films and for mixed films deposited at a pH of 5.2 and 5.8. The incorporation of Cd^{2+} into the deposited multilayers results in an increased polarisability. Auger analysis was carried out on the mixed samples to determine the cation concentration and hence the degree of salt conversion.

Reflectivity data from LB films of absorbing materials has also been analysed. Dispersion ($n_\perp$ against λ) and absorption ($k_\perp$ against λ) curves have been calculated for a phenylazonaphthylamine dye which show approximate Lorentz-Lorenz type band shapes.

W. L. Barnes and J. R. Sambles (1987):
Surf.Sci., **187**, 144.

P. J. Travers and L. S. Miller (1990):
Submitted for publication to *Thin Solid Films* December 1990

GP5

SECONDARY ION MASS SPECTROMETRY STUDIES OF MIXED ARACHIDIC ACID AND BARIUM ARACHIDATE LANGMUIR-BLODGETT FILMS.

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Since the pioneering work of Benninghoven in 1976, secondary ion mass spectrometry (SIMS) has been widely used for the characterization of organic solids (1). The nature and the intensity of the secondary ions have been found to depend on the nature of the molecules and also on the intermolecular interactions. New informations concerning the influence of these processes can be obtained with well organized Langmuir-Blodgett films.

In this communication, we report results concerning the influence of the Ba^{2+} concentration in a LB bilayer of arachidic acid on the nature and the intensity of molecular secondary ions. The LB films were transferred onto hydrophobic Au substrates from a subphase containing Ba^{2+}; the pH of the subphase was adjusted in the range 5-10. Cs^+ 5 keV primary ions bombarded the sample (flux:2×10^9 $Cs^+ cm^{-2}.s^{-1}$) and the secondary ions were analyzed with a quadrupolar mass filter. The Ba concentration in the bilayer was determined by ESCA, from the ratio of intensities of Ba(3d5/2) to C(1s).

The stricking features of the SIMS spectra were mainly the deprotonated molecule $(M\text{-}H)^-$ of arachidic acid, the protonated molecule $(M+H)^+$ and the cationized ion $(M\text{-}H+Ba)^+$. By increasing the pH from 5 to 10, the Ba concentration linearly increases, when the intensity of $(M\text{-}H)^-$ and $(M+H)^+$ strongly decreases in a similar manner. The intensity of $(M\text{-}H+Ba)^+$ slightly increases with the pH . Thus the presence of Ba in the bilayer drastically influences the SIMS spectra. These results will be discussed in terms of intermolecular interactions in the bilayer.

(1)A. Benninghoven, F.G. Rudenauer and H. Werner in "Secondary Ion Mass Spectrometry ", Vol 86 in Chemical Analysis, Wiley Interscience (1987).

GP6

Langmuir-Blodgett Film Assembly of Cu-Phthalocyanine derivatives Substituted by Methacrylate Oligomer Chains

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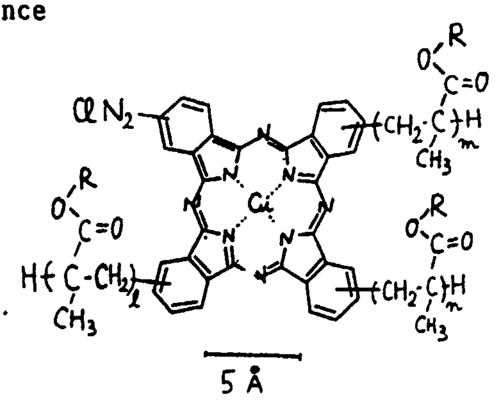
Many Phthalocyanine (Pc) derivatives have been applied in LB film formation due to their unique electrical and optical properties. Unfortunately, a considerable part of the Pc derivatives produced very rigid and fragile films on a water surface, resulting in inhomogeneous LB films. For smaller dye skeletons, introducing bulky hydrophobic tails such as plural long alkyl chains or steroid skeletons is effective in producing stable and condensed monomolecular films.[1] The Pc moiety, however, is too large to apply the method. On the other hand, we have revealed that one of the poly(methacrylate esters), polyisobutylmethacrylate (PIBM), produced a fluid monomolecular film on a water surface and yielded a homogeneous LB film.[2] In this study, we have investigated Cu-Pc derivatives substituted by plural oligomer chains of methacrylate esters as candidates for producing homogeneous LB films.

A Cu-Pc derivative (1) was kindly supplied by Dainichi Seika Co. Ltd. The oligomer chain of methacrylate esters was introduced to the Pc moiety by oligomerization of the methacrylate esters using a tetra-diazonium Cu-Pc compound as a radical initiator. From the results of the elemental analysis, 1 possessed 16-17 monomer units of ethyl- and n-butyl-methacylate (16:3 molar ratio).

The surface pressure of the 1 film spread on a water surface began to rise at 350 Å^2/molecule and gradually increased to show an inflection at 230 Å^2/molecule at 18 dyn/cm (collapse point). The film was stable at constant surface pressures before the inflection. The shape of the F-A curve was similar to that of PIBM.[2] The observed area suggested that the oligomer chains formed not a monolayer but a bilayer film, as shown later. The VIS spectrum changes of the film during compression indicated that an aggregation of the Pc rings increased as the surface pressure rose. The surface viscosity of the 1 film measured with a canal viscometer was 0.015 g/s and small enough to reduce the surface-pressure-drop and the pressure distribution, that caused the inhomogeneities of the LB film.[3]

The monomolecular film was transferred by the vertical dipping method (dipping speed: 5 mm/min) at 12.5 dyn/cm onto a hydrophobic substrate, yielding a Y-type multilayer film. The surface of the built-up films, when observed with a differential interference contrast microscope, appeared smooth. The monolayer thickness was determined to be 22 Å by low angle X-ray diffraction in accordance with the bilayer thickness of the oligomer chains. The polarized VIS spectra indicated that the Pc ring declined at about 45° from the film surface. The stacking axis of the Pc rings was almost perpendicular to the dipping direction.



Film-forming properties of other Pc derivatives with different oligomer chains will be discussed.

1) K. Naito, A. Miura, M. Azuma, another presentation in this conference.
2) K. Naito, J. Colloid Interface Sci., 1989, 131, 218.
3) K. Naito, T. Iwakiri, A. Miura, M. Azuma, Langmuir, 1990, 6, 1309.

GP7

INFRARED AND INELASTIC ELECTRON TUNNELING SPECTROSCOPY OF ADSORPTION LANGMUIR-BLODGETT FILMS

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The Adsorption Langmuir-Blodgett(LB) technique1) enables us to fabricate the LB films containing many kinds of water-soluble functional materials. We have been applying this technique to fabricate the adsorption LB films2,3) containing two dyes and investigated the interaction between these dyes.

In this report, we describe the experimental results of infrared(IR) and inelastic electron tunneling spectroscopy(IETS) of adsorbed LB films and the molecular interaction concerned with the adsorption mechanism. Merocyanine dye(MC) was used as a spreading material. Four kinds of triphenyl methane (TPM) derivatives(BG,EVG,CV,FBD: Fig.1 (a)) were used as adsorption dyes. From the experimental results, it was found that carboxyl group and benzothiazole ring in the MC molecule and nitrogen atom in TPM molecules are strongly concerned with the adsorption mechanism. Figure 1(b) shows the IR and IETS of adsorbed LB films. The IETS of an MC/BG sample shows new peaks which could not appear in MC or BG sample. These results demonstrate that IETS is a powerful means to investigate LB films.

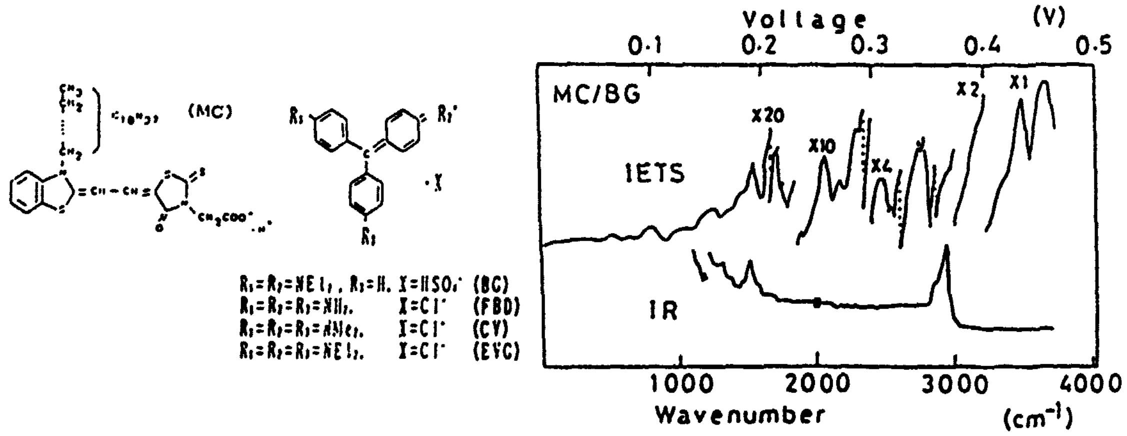

Fig.1 (a)Chemical structures of materials (b)IR and IETS of MC/BG samples

1) D.den Engelesen, J.Collid Interface Sci.,45(1973)1.
2) C.Okazaki et al., Thin Solid Films, 179(1989)503.
3) C.Okazaki et al., Jpn.J.Appl.Phys., 29(1990)2506.

GP8

INFLUENCE OF SUBSTITUENTS ON IN-PLANE DICHROISM IN LANGMUIR-BLODGETT FILMS OF PHTHALOCYANINE DERIVATIVES

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We have already reported that Langmuir-Blodgett (LB) films of copper tetrakis(n-butoxycarbonyl)phthalocyanine exhibit an extraordinarily high in-plane dichroism, which is caused by the highly preferential orientation of the stacking axis of phthalocyanine assemblies parallel to the dipping direction[1,2]. The role of the peripheral substituents seems to be important for this phenomenon, since their flexibility may prevent the monolayer being too rigid and enable it to flow smoothly during the dipping process. In this paper, we report on the property of the monolayers and the LB films of copper tetrakis(n-alkoxycarbonyl)phthalocyanines (CnPc; n denotes the number of carbon atoms per alkyl chain), especially on their in-plane dichroism, varying n from 6 to 18.

Surface pressure(π)-area(A) isotherms for these samples are shown in Fig.1. The numbers beside each line correspond to n. Although the monolayers collapse at rather low surface pressures, most of them were fairly stable below the surface pressures of the plateau-like region of the isotherms. LB films could be prepared on hydrophobic glass plates by vertical dipping method at the surface pressures of 13-16 mN/m and the subphase temperature of 20°C, for C6Pc-C16Pc. The deposition of C18Pc was difficult, but achieved when the temperature of the subphase was 35°C.

In-plane dichroism was observed in all these LB films. The dichroic ratios (R; defined here as R=A(90)/A(0), where A(90) and A(0) represent the absorbance in the spectra polarized perpendicular and parallel respectively to the dipping direction at the wavelength of Q band maximum) of the films (20 layers per side, as-deposited films) are plotted against n (Fig.2). Highly anisotropic LB films were obtained for the samples which have relatively short alkyl chains. The molecules for this type of highly ordered LB films may be designed, even besides the phthalocyanines, as combinations of planar cores which may form aggregates, and relatively short side chains equipped peripherally.

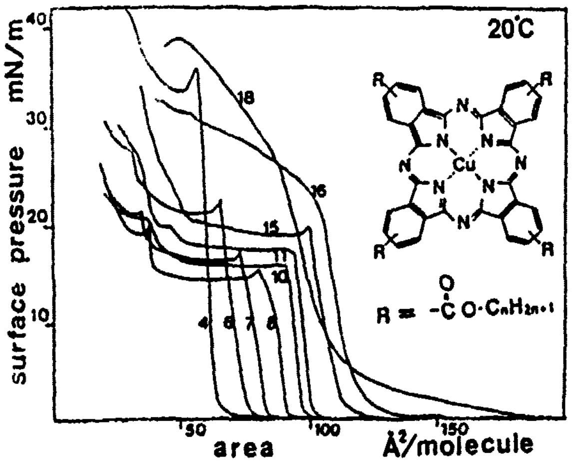

Fig.1. Structural formula of the samples and π-A isotherms.

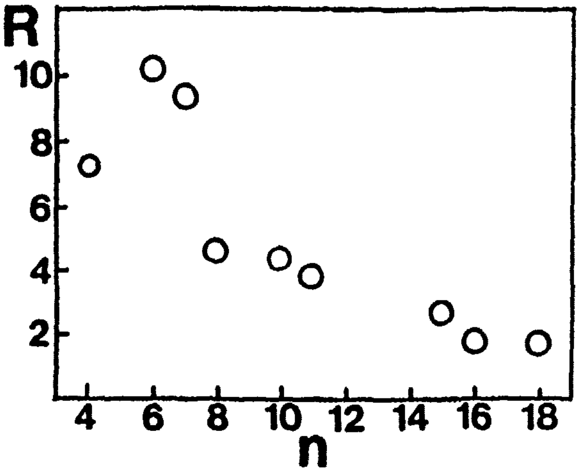

Fig.2. Number of carbon atoms (n) vs. dichroic ratio (R).

1) K. Ogawa et al., J. Chem. Soc., Chem. Commun., (1989) 477.
2) K. Ogawa et al., Thin Solid Films, 178 (1989) 439.

GP9

2D ORDERED LANGMUIR-BLODGETT FILMS OF STEARIC ACID ON SEMICONDUCTOR SUBSTRATES

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Stearic acid (HSt) Y-type Langmuir-Blodgett films (LBF) transferred onto semiconductor (Si, GaAs and $Cd_xHg_{1-x}Te$) substrates with different physical-chemical states of surface were studied. The methods used were ellipsometry, X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and work function measurements.

Ellipsometry gives ~ 4 nm as a thickness value for each bilayer of HSt molecules. It may be due to inclination ~ 30° of molecular axes to the surface normal. One cannot obtain LEED patterns from a bilayer of HSt molecules on the Si (111) and GaAs (110) surfaces having native oxide. But taking as a substrate $Cd_xHg_{1-x}Te$ (111) surface, ordered and chemically passive after ion etching, leads to quite a different situation. In this case LEED pattern was obtained, typical for 2D hexagonal lattice with 0.5 nm as a lattice constant. The above value corresponds to close packed structure of HSt bilayer and differs from that for proper $Cd_xHg_{1-x}Te$ (111) hexagonal lattice (0.26 nm). Side by side with LEED the work function measurements were taken in vacuum with Anderson method for the HSt bilayer - $Cd_xHg_{1-x}Te$ (111) system. A work function increase of ~ 1 eV was found after transferring HSt bilayer. Correspondence of this value to a potential jump due to HSt molecules having longitudinal dipole momentum [1] evidences for high degree of film ordering. This conclusion is supported also by XPS measurements of photoelectron free path length for the same object.

A model for forming 2D ordered HSt molecular bilayer on the $Cd_xHg_{1-x}Te$ (111) was proposed. According to it such an ordering may be due to atomic steps on the $Cd_xHg_{1-x}Te$ (111) surface oriented preferentially along $[11\bar{2}]$ (in line with [2]).

References:

1. V.Vogel, D.Möbius, Thin Solid Films. 159 (1988), 73-81.
2. V.Vogel. C.Völl, J. Chem. Phys.. 84 (1987). 5200-5204.

GP10

TEM STUDIES ON LB FILM OF COPOLYMER OF PHENYL P-NITROAZO ACRYLATE

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In this work, polymeric LB film is based on the use of amphiphiles which have already been copolymerized. The copolymer compositions were confirmed by IR, NMR and elemental analysis. The phase transition was characterized by DSC, optical microscope and X-ray diffraction. It exhibited that copolymer can form both smectic and Nematic phase.

LB multilayers of preformed copolymers were prepared and diposited using a langmuir trough. A typical surface pressure area isotherm of copolymer was obtained.

The morphology and thickness of copolymer LB films were inspected with an H-500 transmission electron microscope. The thickness of built-up films of copolymer was measured by using the folding method of electron microscopy.

The dependence of morphology and properties on film-forming conditions is discribed for the copolymer LB films. The effects of LB flim-forming condition (such as the surface pressure, PH value and the concentrations of spreading solutions) on film quality were studied in detail.

* This work was supported by Academia Sinica Selected Research Program and National Nature Science Foundation China.

GP11

STRUCTURAL EVALUATION OF LB FILMS OF SOME AMPHIPHILIC PHTHALOCYANINES USING INFRA-RED SPECTROSCOPY

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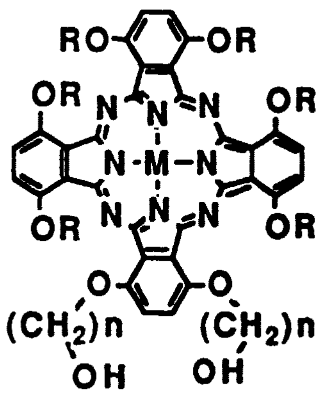
A number of metal free and metalated amphiphilic phthalocyanine derivatives, eg 1,2 & 3, have been deposited as LB films. These have different degrees of molecular order as judged by low angle x-ray reflectivity measurements. The present research explores the potential of IR techniques for investigating in closer detail the molecular assemblies within the films.



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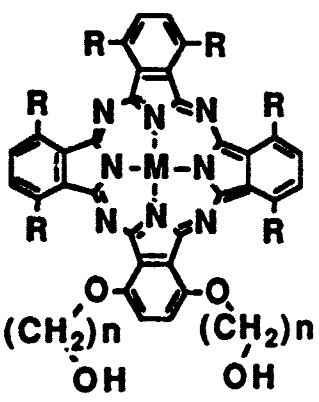

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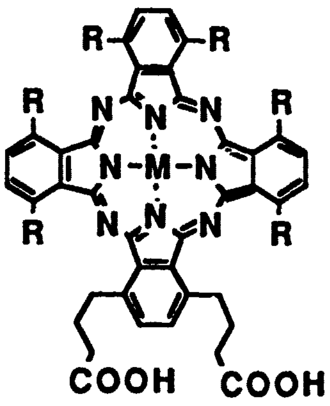

3

R= ALKYL

M=H, H Cu Ni

Normal and grazing angle transmission FTIR and reflection absorption infra-red spectroscopy (RAIRS) of films deposited on silicon and gold substrates are described. Differences in intensity of in-plane vibrations, eg of the ring and the N-H bonds (of metal free derivatives), are observed in the two types of transmission spectra and are interpreted in terms of the orientation of the phthalocyanine ring system with respect to the substrate surface.

Absorption spectra of films differing in the number of dips provides a probe for monitoring the packing registration as a function of film thickness; polarisation experiments monitor the extent of ordering along the dipping direction.

GP12

SOLITON MECHANISM OF OPTICAL ANISOTROPY PHOTOINDUCTION IN LANGMUIR-BLODGETT FILMS

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Nonlinear excitations (kinks and vortices) in layered molecular structures are investigated. A great attention is paid to the role of interaction between orientational and translational degrees of freedom and its influence on the character of the system ordering. Dynamics of orientation and translation solitons and their interaction is discussed.

A theoretical interpretation is given of the influence of linearly polarized light on molecular ordering in Langmuir-Blodgett films. It is shown that changes in the energy of the orientation interaction between molecules in the excited states with respect to the ground one cause their rearrangement in the layer. The intermolecular orientational and translational interactions provide a coherent and cooperative soliton character of the rearrangement. The radiation from a comparatively low-intensity light results in changes in the orientation and translation order in macroscopic regions of the layer. An expression for the "rearrangement" velocity of ordering regions is obtained. The relevance of the results to recent experiments on the photoinduced optical anisotropy in Langmuir-Blodgett films is discussed.

GP13

THE PROPERTIES AND STRUCTURAL CHARACTERISTICS OF L-B FILMS FORMED FROM METALLOPORPHYRIN COMPLEXES WITH DIFFERENTIAL ALKYL CHAINS *

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Abstract

(Fax.1331)

In this paper, the properties and structural characteristics of L-B films built up of metalloporphyrin complexes were reported.

5 -(p-hydroxylphenyl)-10, 15, 20-tri(p-methoxyphenyl) porphyrin and it's nickel complex [NiTPP(OH)], 5, 10, 15, 20-tetra-4-oxy(2-stearic acid) phyenyl porphyrin and it's copper complex [Cu (II) TPP (-COOH) have been synthesized.

The physical properties of monolayers of NiTPP(OH) and Cu (II) TPP(-COOH) on ultrawater were studied and π-A curves were given. The pH of subphase were selected carefully. So that the pH >6.2 for NiTPP(OH) and pH<4.0 for Cu (II) TPP(COOH) was decided. From π-A curve a molecular area of 134 sq.A for NiTPP(OH) and 240 sq.A for TPP(COOH) and Cu (II) TPP(COOH). The molecular orientation on water surface was independent of complexed matal ion.

The good quality L-B film of NiTPP(OH) were only deposited on hydrophilic ITO glass. The stable monolayers formed from Cu (II) TPP(-COOH) could be easily transferred to various solid substrates. The properties and composition of NiTPP(OH) L-B films was investigated by xps and resolved xps spectra. The results determined by angular resolved xps showed that the L-B films were even and dense as a whole. The UV-visible spectra measured for L-B films of NiTPP(OH) showed a distinct red shift but no changes for that of Cu (II) TPP(-COOH) relative to that of chloroform solution. The linear dependence of absorbance of number of layers for L-B films of Cu (II) TPP(COOH) with the result of SEM confirmed the uniformity of the L-B films. The results measured by polarized-light absorbance showed that the macrocycles of Cu(II)TPP(COOH) in the L-B film was arranged parallel to substrates. This conclusion is coincident with the result deduced from the π-A curve.

An X-ray diffraction of L-B film of NiTPP(OH), and Cu(II)TPP(-COOH) were performed. There was no Bragg reflection peaks for L-B film of NiTPP(-OH). Only one order of Bragg peak occured in even number of layer of Cu(II)TPP(-COOH) and several subcidiary maxima can be distinguished from the diffraction pattern. The lattece spacig was 31 A. This particularty low d value for Y type deposition indicated that the alkyl chains were non fully extended.

The electric conductivity measurements showed that the electrical conductivity in the plane of the film of NiTPP(OH) is larger than that of films of Cu(II)TPP(COOH) by several orders of magnitude. Such a reletively high electrical conductivity was ascribed to the absence of long alkyl chains and face to face packing of porpgyrin ring with well orderd structure in the films.

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* The project supported by National Natural Foundation of China (NSFC)

GP14

ABSORPTION PROPERTIES AND STRUCTURE CHANGES CAUSED BY PRE-ANNEALING IN POLYDIACETYLENE LB FILMS

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The reversible color phase transitions between the blue phase and the red phase caused by annealing have been reported for polydiacetylene (PDA) Langmuir-Blodgett (LB) films. An application of the PDA LB films to an optical switching device has been proposed using the reversible color phase transition. The absorption properties of the PDA LB films strongly depend upon lengths of the alkyl side chains of the molecules, the deposition conditions and treatments.

In this report, absorption properties and structures are investigated as a function of pre-annealing temperature for the PDA LB films having different lengths of the alkyl side chains: 10-8, 12-8 and 14-8. After diacetylene monomer LB films are deposited and pre-annealed at various temperatures, the LB films are polymerized using UV exposure and the PDA LB films are obtained. The spectra of the pre-annealed LB films strongly depend upon the side chain lengths, the deposition conditions and the pre-annealing temperature. Absorption spectra of typical PDA LB films without the pre-annealing treatment have main peaks at 640nm, while the pre-annealed 10-8 and 12-8 PDA LB films exhibit new absorption peaks at 704nm, that is, a red-shifted blue phase, instead of the peaks at 640nm. The spectra of the pre-annealed 14-8 PDA LB films do not exhibit the peak at 704nm, but the main peaks at 640nm only decrease by the pre-annealing.

X-ray (001) diffraction measurements show that the pre-annealed films have extremely ordered layer structures without changes of the layer spacing and the improvement in the structures is closely related to the increase in the new absorption peaks at 704nm for the 10-8 and 12-8 PDA LB films. The pre-annealed 14-8 LB films have ordered layer structures too, but the layer spacing of the 14-8 LB films increases with the pre-annealing. It is estimated that the increase of the spacing hinders the polymerization of the 14-8 LB films. The reversible color phase transition of the new peaks at 704nm is measured. The peaks at 704nm exhibit stronger reversibility than the peaks at 640nm. Pre-annealing is thought to be an important technique for improving characteristics of LB films.

GP15

STRUCTURAL STUDIES OF LANGMUIR - BLODGETT POLY-3-BCMU FILMS

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The soluble polydiacetylene (poly-3-BCMU) has been extensively studied in the solid state and in solution and particular attention has been devoted to the transition from coil to rod conformations [1,2]. Recently the deposition on a solid substrate by the L.B. technique has been attracting attention, since it has potential ability to control thickness, orientation and packing density at the molecular level. We have prepared L.B. films of poly-3-BCMU in view of obtaining material with non linear optic properties to be used for the engineering of wave guides. The structure of the monolayer and the packing of the multi-layers deposited on a Ge crystal have been investigated by FTIR-ATR technique. The infrared spectra of films deposited from the expanded form reveal the presence in the monolayer of a mixed structure consisting of both rod and coil conformations. In the successive layers the rod conformation becomes predominant. On the contrary, in the films deposited from the condensed phase only the rod conformation is present. We are also carrying out experiments on L.B. films of the polymer deposited on a wave guide using the resonance Raman spectroscopy. This tecnique should provide a sufficient Raman signal also in the presence of a monolayer together with a good monitoring of the building up of the wave guide.

REFERENCES

1 - G.N.Patel, R.R.Chance, J.D.Witt,
J. Chem. Phys., 70, 4387 (1979)
2 - J.E.Biegajski, R.Burzynski, D.A.Cadenhead, P.N.Prasad,
Macromolecules, 23, 816 (1990)

GP16

LANGMUIR-BLODGETT FILMS OF POLYHETEROCYCLIC COMPOUNDS WITH LONG ALKYL CHAINS.

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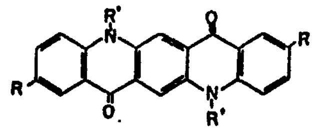
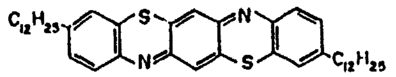
Polyheterocyclic compounds which are interesting as functional pigments are almost insoluble in organic solvents. By introducing long alkyl chains to chromophores the soluble pigments can be obtained and spread as monolayers on water surface. In this work, long-chain derivatives of quinacridone, triphenodithiazine and carbazoledioxadine were newly synthesized and used for the LB films to control the arrangements of the chromophores.

Surface pressure — area isotherms of the quinacridone derivatives (1) were strongly dependent on the length of alkyl-chains and the temperature of aqueous subphase. In the cases of R or R' = $C_6 - C_8$, the phase transition from expanded to condensed monolayers was observed. The multilayers can be prepared by the horizontal lifting method, although the deposition by the conventional LB method was unsuccessful. Polarized electronic absorption spectra of the multilayers together with fluorescence microscopy indicated that the orientation and packing of the chromophores were changed with the compression through the transition region in the monolayers. From the results of X-ray diffraction of the multilayers, the derivatives with the same chain length of R and R' were found to give more homogeneous layered structures than those with the hetero-length of the chains. Polarized IR spectra of the films revealed that the short-axis of the chromophore was oriented nearly vertical and the long-axis horizontal in the former, while the chromophore took almost flat orientation in the latter. Different orientations of the quinone moiety seem to have an influence on the electron acceptabilities in the layered systems.



$R, R' = C_6H_{13} \sim C_{18}H_{37}$

(1)



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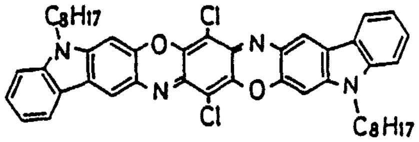

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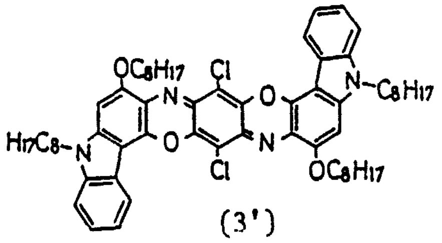

(3')

The equimolar mixture of the triphenodithiazine derivative (2) and stearic acid gave the stable monolayer. The polarized electronic absorption spectra and the film thickness indicated that the chromophore was oriented with the long-axis nearly vertical in the LB films. The visible band at 510 nm in the films changed to the broad band around 600 nm immediately after exposure to hydrogenchloride gas. The reversible colour change from blue to violet was observed by ammonia gas. This chromism is expected for applications such as optical devices and sensors.

For the carbazoledioxadine derivatives (3 and 3') with linear and angular-shape structures, the monolayer behaviours on water as well as the thickness and polarized electronic absorption spectra of the built-up multilayers reflected clearly the difference of the molecular geometries.

LB films with well-defined orientation and packing of these π-electron systems are of particular interests for electrical and optical functions.

GP17

GRAZING INCIDENCE X-RAY DIFFRACTION STUDY OF LANGMUIR AND LANGMUIR-BLODGETT MONOLAYERS OF ARACHIDIC ACID

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Using grazing incidence diffraction technique with synchrotron X-rays(λ=1.488Å), we studied structures of Langmuir monolayers of arachidic acid on three types of subphases(pure water, 10^{-4}M Cd^{2+} solution and 10^{-4}M cyanine dye solution) at 20°C, and compared these with structures of 1, 3 and 13 Langmuir-Blogett monolayers (arachidic acid prepared at 30 mN/m, cadmium arachidate prepared at 25 mN/m and complex of arachidic acid and cyanine dye prepared at 40 mN/m) on glass substrates. Information on tilt of molecules was obtained by measuring the intensity distribution along the Bragg rod with 1D position sensitive proportional counter.

In the case of an arachidic acid monolayer on the surface of pure water, our experimental data indicates that a chain molecule tilts toward a nearest neighbor in a hexagonal lattice at lower surface pressures and stands upright at higher pressures. This result agrees with the observations reported by Kjaer et al(1988,1989). In the case of a monolayer on the surface of 10^{-4}M Cd^{2+} solution, the peak position of overlapping (1,0), (0,1) and (1,-1) reflections stayed constant (2θ=20.85°, d=4.11Å) in the pressure range from almost zero(A=50Å^2) to 25 mN/m. The diffracted X-rays were mostly directed into the low q_z region along the Bragg rod indicating that molecules stand upright even at a very low pressure, where q_z is the component of scattering vector along the surface normal. For a monolayer on the surface of 10^{-4}M cyanine dye solution, we observed two peaks in 2θ scan at lower pressures with respective intensity peaks at medium and high q_z along the Bragg rod. This result cannot be explained by the model in which a chain molecule tilts toward a nearest neighbor, but can be explained by a model in which a molecule tilts toward a next nearest neighbor. At higher pressures(>35 mN/m), molecules seem to be standing upright judging from the intensity distribution along the Bragg rod.

Diffraction curves for single LB monolayers on glass substrates were similar to those for corresponding Langmuir monolayers. For 3 and 13 monolayers, broadening and distortion of diffraction curves were observed. This can be explained by distortion of inplane structures or by formation of 3D crystals. For 13 monolayers of cadmium arachidate, the intensity of diffraction peak was strongly dependent on the sample orientation.

GP18

STRUCTURAL CHARACTERIZATION OF POLYION COMPLEX LB FILMS OF PERFLUOROUNDECANOIC ACID-POLYETHYLENEIMINE

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In recent years,Langmuir-Blodgett(LB) films possessing fluorocarbon chain have been attracting much attention because of characteristic properties such as low friction, excellent insulation, excellent durability, and so on. Since the fluorocarbon chain has weak interaction between them, it is very difficult to deposit organic molecule possessing fluorocarbon chain on solid substrate in multilayer form. A few papers[1-3] have been reported for a preparation of LB film possessing fluorocarbon chain.

In the present work, we have studied another example for the preparation of LB film of perfluoroundecanoic acid(PFUA), using polyethyleneimine(PEI) as polycations and also the structure of the LB films by using X-ray diffraction, polarized Fourier transform infrared spectroscopy(FTIR-RAS) and X-ray photoelectron spectroscopy(XPS).

The surface pressure-area isotherm shows that the molecule of the PFUA doesn't form stable monolayer on pure water,but forms stable monolayer on aqueous PEI solution. The monolayer of PFUA on aqueous PEI solution can be readily transferred on a solid substrate as Y-type multilayers. It is confirmed from FTIR-RAS and XPS measurements that the LB films are deposited uniformly and regularly. From the measurements of X-ray diffraction, it was found that the monolayer's thickness in the LB film was 12.2A and this value is good agreement with that of ellipsometry. These data suggest that the fluorocarbon chains in LB film are laid on the surface. Also, the depth profile of PFUA LB films was determined by XPS. The angular dependence of F/N peak ratio indicates that the fluorocarbon chains are located close to the surface and that the head groups are located close to the solid substrate. The values of critical surface tension of these LB films obtained from Zisman plot were 14.2 for monolayer and 14.0 for 3 and 5 layer LB films. From this result,it is evident that most of CF_3 group (the end of fluorocarbon chain) exists on the surface of LB films.

References

1) N. Higashi and T. Kunitake, Chem. Lett., 1986, 105.
2) H. Nakahama, S. Miyata, T. T. Wang and S. Takasaka, Thin Solid Films, 141, 165 (1986).
3) Y. Goto and M. Fugihira, 56the Annual meeting of The Chemical Society of Japan, Tokyo , 2IIH 37, 1986.

GP19

AGGREGATION CONTROL OF PHOTOCHROMIC SPIROPYRANS IN LANGMUIR-BLODGETT FILMS

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The control of photochromic reactions has been investigated in Langmuir-Blodgett(LB) films. It has been shown that spiropyran(SP1822) having two long alkyl chains forms J-aggregate(head-to-tail interaction) in LB films[1]. In this work, we show that novel spiropyran(MSP1822) having methoxy group at 5' position of SP1822 forms both H-aggregate(side-by-side interaction) and J-aggregate in LB films.

MSP1822 forms stable monolayers at the air-water interface in the dark and the most stable monolayer is formed on being mixed with octadecane in molar ratio of 1:2. The assemblies of these monolayers under UV irradiation at temperatures above 40°C exhibit a sharp and intense absorption band at the shorter wavelength(490nm) than a monomeric merocyanine band(560nm) which is assigned to the formation of H-aggregate.

Furthermore MSP1822 forms stable monolayers on being mixed with methyl stearate. The assemblies of this film form monomeric merocyanine under UV irradiation, but by rubbing with cloth, they form another aggregate, which has two sharp and intense bands located at 550nm which is near the monomeric band and at 595nm. The absorption band at 595nm could be assigned to the formation of J-aggregate, judging from short Stokes shift(34nm). Detailed characteristics on these bands are now under investigation.

A part of this work was performed under the management of Japan High Polymer Center as a part of the R & D of Basic Technology for Future Industries sponsored by NEDO(New Energy and Industrial Technology Development Organization).

Reference

1. E. Ando et al., Thin solid films, 133, 21(1985).

GP20

LANGMUIR-BLODGETT FILMS OF POLYMERS WITH CHROMOPHORIC SIDE CHAINS

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Langmuir-Blodgett (LB) multilayer films have been fabricated from amphiphilic preformed polymers with chromophore-containing side chains. Depending on the particular chromophore and the film structure, these materials show a variety of physical properties, ranging from liquid crystal-like thermal phase transitions to nonlinear optical behavior. We have investigated these ultrathin films by spectroscopic and optical techniques such as transmission linear dichroism at ultraviolet-visible and infrared wavelengths, FTIR at grazing incidence, ellipsometry, and second harmonic generation. From such experiments we have been able to characterize order and orientation of molecular segments including the chromophores, as well as film quality and structure. We conclude that such materials can form LB films with a high degree of order and stability in the presence of the bulky chromophoric groups.

GP21

ORIENTATION OF PORPHYRINS WITHOUT LONG ALKYL CHAINS IN MIXED LB FILMS WITH CADMIUM ICOSANOATE

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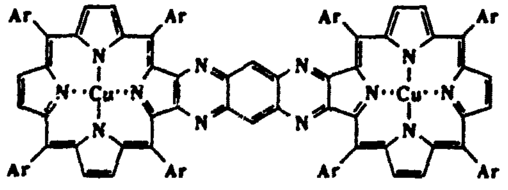
Porphyrins and their metal complexes are extensively studied from the viewpoint of modeling electron transfer processes in biological systems. It is of interest to incorporate porphyrins into thin films by using the LB technique, to fix the position and orientation of the dyes.

In this work we obtained LB films of new types of porphyrin derivatives without long alkyl chains, PD and PM, by using cadmium icosanoate as a matrix, to determine their orientation in the films.

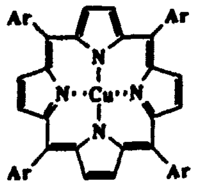
The area per molecule of PD for the monolayer with the mixing ratio r=1/15 at a surface pressure of 25 mN/m is ca. 2.2 nm^2 whereas it is ca. 1.1 nm^2 for the monolayer with r=1/3, indicating different structures for the two monolayers. In the case of PM, these values are ca. 1.4 nm^2 and 0.9 nm^2 for the corresponding ratios.

Polarized absorption spectra at normal and 45° incidence for the LB films of PD indicate that the long axis of PD molecule is parallel to the surface for both films. The anisotropic hyperfine structure of ESR spectra due to the coupling of the electronic spin and Cu nucleus indicates that the macrocycle plane of PD is rather perpendicular to the film surface for both films, with a lesser distribution of orientations evident from the spectrum for PD with the smaller mixing ratio.

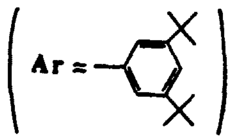
In the case of PM, the hyperfine component, perpendicular to the macrocycle plane, is only weakly observed in the spectrum when the external magnetic field is parallel to the film surface, suggesting that the macrocycle plane of PM is rather parallel to the film surface. These results are consistent with those obtained from polarized absorption spectra.



PD



PM



GP22

ANALYTICAL SURFACE SPECTROSCOPY OF PHOSPHOLIPID LB FILMS

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The interactions of biomolecules such as hormones, antibodies, or neurotransmitters with cell membranes are important in various biological processes including cell growth, immune cell recognition, and neuromuscular function. Biomimetic surfaces of phospholipid/protein mixtures, deposited as planar membranes using a Langmuir trough, are used widely to investigate such molecule-membrane interactions. This research centers on the evaluation of various high vacuum surface analytical techniques for the characterization of LB films containing phospholipids. Of special significance are the techniques of X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (static SIMS). These spectroscopies complement more traditional characterization tools by providing new information on membrane structural properties such as substrate coverage, film thickness, film orientation, and chemical composition. Concomitantly, the LB films provide surface layers with controlled spatial and chemical characteristics that enable fundamental studies of processes controlling analytical signal generation. Examples include the relationship of ion beam sputtered secondary ions observed in static SIMS to molecular surface structures, and the influences of LB film stability, orientation, composition, and thickness on XPS data obtained as a function of photoelectron emission angle.

Initial applications involve mixed LB phospholipid monolayers and multilayers composed of dipalmitoylphosphatidylcholine (DPPC), and dinitrophenyldiphosphatidylethanolamine (DNP-cap-DPPE). The DNP group serves as an antigenic site for subsequent antibody binding studies. Surface modification and characterization studies of various substrates (e.g., silver, silicon, glass, oxidized graphite, mica) also are necessary to optimize sample characteristics for correlative surface analysis and microscopy measurements.

GP23

A NOVEL RANGE OF POTENTIALLY ELECTROLUMINESCENT MATERIALS FOR LANGMUIR-BLODGETT DEPOSITION

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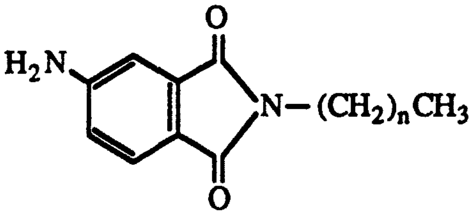
A range of amphiphiles has been synthesised with fluorescent polycyclic aromatic headgroups and long-chain hydrocarbon tails. For example, compound (I) has been prepared with n=1,7,17.



(I)

The molecules all fluoresce strongly in solution, with emission bands in the range 425nm to 510nm.

Preliminary characterisation work with the long chain analogues has led to reproducible films on the water surface. Molecular areas, which are largely independent of the subphase pH, indicate a slight tilting (between 15 and 20°) of the chromophore from the normal.

Such films have been successfully deposited onto a range of substrates. The best transfer ratios have occured when the materials were deposited in alternate layer structures with behenic acid. Optical and electrical characterisation of these films is now in progress.

Quenching of the fluorescence in LB films, due to molecular interactions, has been observed. The aggregation effects in mixed films are currently being investigated using scanning optical microscopy. Further structural assessment is being carried out using X-ray diffraction.

The materials will soon be tested in an electroluminescent device structure.

GP24

FOURIER TRANSFORM INFRARED SPECTROSCOPY STUDIES ON MODEL BIOLOGICAL MEMBRANES DEPOSITED BY THE LB TECHNIQUE

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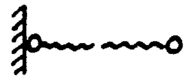
Abstract

Vibrational spectroscopic studies have been used to study the ordering and molecular interactions of lipid bilayers of 1,2-dipalmitoyl-sn-glycero-3-phosphatidic (DPPA) engineered by the LB technique onto metal or semiconductor surfaces. Current work is aimed at the characterisation of a 'biologically' relevant bilayer,  and we report our attempts to deposit and understand such molecular assemblies using both external and totally attenuated reflection infrared techniques. The degree of lipid chain ordering and conformation, and the extent of head group interactions have been studied using infrared linear dichroism – both directly and using subtraction techniques. We have studied the effect on the structure and interactions of adding Ca^{2+} cations to the subphase and of bathing the model membrane in a suitable (but variable) aqueous environment in a novel micro ATR infrared cell. 'In situ' infrared measurements have enabled studies of the head group hydration or ionisation, and have allowed an exploration of molecular rearrangements at the multilayer/water interface. These new data have been compared with our recent data on DPPA multilayers [1] in order to highlight the special features of a single bilayer, especially in the context of the likely molecular behaviour in real membrane structures.

1. V.A. Howarth, D.F. Cui, M.C. Petty, H. Ancelin and J. Yarwood, Thin Solid Films, 180 (1989) 111; ibid. 192 (1990) 391.

GP25

STUDIES OF ALTERNATING LB FILMS PREPARED FROM PREFORMED POLYMERS

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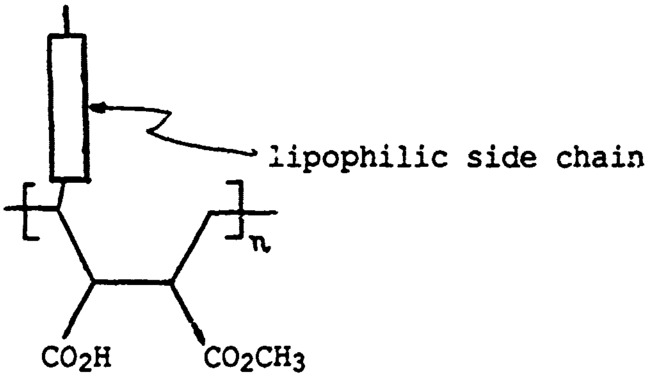
Many micro- and opto-electronic devices can in principle be fabricated from LB films. Unfortunately, many of the films prepared from low-molecular-weight (LMW) compounds are too fragile to be used commercially. Polymeric LB films are, however much more stable and in appropriate cases they still have significant order. We have been interested in polymeric LB films for several years and have concentrated on the design, synthesis and study of polymers which form good polymeric LB films directly, i.e. no polymerisation on the water surface or of the films is required. We have shown that polymers of the type (1) form particularly good LB films and they are sufficiently ordered to show upto 3 Bragg peaks in X-ray studies.[1]

Many devices require alternating (AB) LB films. We wish to report our studies of alternating multilayers prepared using preformed polymers. In one type every alternate layer is a polymer and every alternate layer a LMW amphiphile. In a second type the alternating layers are two different polymers. Many of these films are still ordered as evidenced by the appearance of Bragg peaks in X-ray studies. We are now developing these AB films to produce stable devices.

Certain multilayers can be rendered even more stable by UV-initiated crosslinking. In this way it is possible to draw patterns in the films.



(1)

Reference

1. P. Hodge, F. Davis and R.H. Tredgold, *Phil. Trans. R. Soc. London,* **330**, 153-166 (1990).

GP26

Thermally induced phase transitions in multilayers of Cd arachidate

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Monolayers and multilayers of Cd arachidate on SiO_2 support have been studied by X-ray diffraction and reflection (see Fig.1).

The monolayer exhibits a hexagonal lattice with vertical aliphatic tail orientation and lattice spacing as previously measured for the monolayer on water.

The multilayer, however, independent of thickness, at room temperature exhibits two diffraction peaks attributed to the (1,1) and the (0,2) spacings of an orthorhombic lattice spanned by the hydrocarbon chains. This corresponds to unit cell dimensions of a=4.85Å and b=7.50Å. Measurements along the Bragg rods, i.e. for a fixed in plane angle corresponding to the maxima but varying the out of plane diffraction angle, then yield the tilt angle of the tails with respect to the plane normal. One derives a uniform tilt angle of 7±1° towards the a axis and no tilt towards b. This tilt angle is independent of temperature up to 100°C. Raising the temperature above 60°C the most pronounced change is the shift and the intensity reduction of the (0,2) peak revealing an increase of the b dimension. Approaching 100°C this peak broadens and merges into the (1,1) peak which itself shifts to smaller angles. The lattice spacing then corresponds to the one measured for the hexagonal phase of arachidic acid monolayers on water and on silica support. Reducing the temperature again basically the original orthorhombic structure can be restored. X-ray reflection in addition shows that neither the interlayer spacing nor the overall thickness change during heating up to 100 °C.

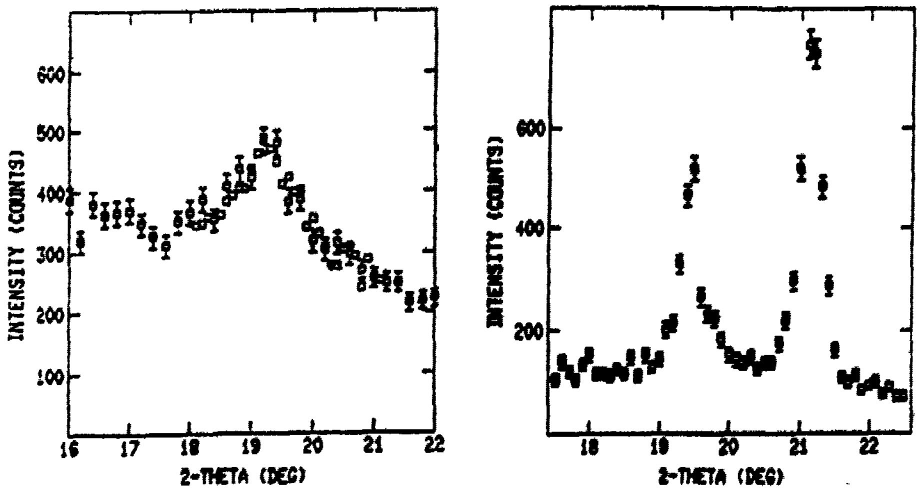

Fig.1: X-ray diffraction intensity versus in plane diffraction angle for a monolayer (left) and for a multilayer existing of 3 monolayers (right) of Cd arachidate.

GP27

FT-IR METAL OVERLAYER ATR SPECTRA OF LB FILMS OF 12-HYDROXYSTEARIC ACID AND ITS CADMIUM SALT

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Hydroxystearic acids are known to exhibit wide plateau regions in their π-A isotherms. From various view points including the result of the surface dipole moment measurement, this plateau region has been attributed to the structural transition from an initial contact of both hydroxyl and carboxyl groups with the aqueous subphase to a contact only of the carboxyl group, where the hydroxyl group is forced out of the interface during surface compression. Spectroscopic examination of structural changes during this process has not been performed. Therefore, we tried to make these points clear by preparing their LB films transferred at various stages of surface compression to a flat metal surface and measuring FT-IR metal overlayer ATR spectra which has been recently proposed by Ishida et al. as a high-sensitivity tool for studying the molecular structure and orientation in ultrathin organic films.

By combining both vertical and horizontal lifting methods, 7-monolayer LB films of *dl*-12-hydroxystearic acid (12HSA) were fabricated on silver-coated slide glasses from monolayers on the water subphase controlled to pH 4.5 at various stages of surface compression including the plateau region. 7-Monolayer LB films of cadmium salt of 12HSA were also made from monolayers on the water subphases at pH 6.0 with 3×10^{-4} M $CdCl_2$ and 3×10^{-4} M $NaHCO_3$. These samples were tightly attached to a flat surface of a hemicyrindrical germanium prism, and subjected to FT-IR ATR measurements with the angle of incidence of 75° by a Nicolet Model 6000C spectrophotometer equipped with a Harrick Model AHC-15P variable angle ATR attachement.

The intensity ratio of the symmetric CH_3 stretching band to the symmetric CH_2 stretching band was almost unchanged in the plateau region, while it increased drastically at the solid condensed state. This ratio is a measure of the orientation of hydrocarbon chains, because the vertical alighment of the hydrocarbon chain to the film plane diminishes the intensity of the symmetric CH_2 stretching band, but keeps that of the symmetric CH_3 stretching band practically unchanged, by the surface selection rule of the metal overlayer ATR spectroscopy. Therefore, the above experimental results indicate that the average orientation of the hydrocarbon chain (methylene segments) does not change during the transition although the chains are gradually forced out of the water surface. The average orientation are improved only in the solid condensed state. The low frequency shift of the symmetric CH_2 stretching band was also observed only at the solid condensed state, indicating that the straight trans-zigzag conformation of the hydrocarbon chains prevails only at this state.

In the case of cadmium salt of 12HSA, there was no plateau region in its π-A isotherm as in cadmium stearate. Metal overlayer ATR spectra of these LB films showed only the high intensity ratio of the symmetric CH_3 stretching band to the symmetric CH_2 stretching band irrespective of the surface areas, indicating the presence of islands at large surface areas.

GP28

IN-PLANE ORIENTATION OF A DODECYLOXY SUBSTITUED TRIARYL PYRYLIUM SALT BY THE LANGMUIR-BLODGETT METHOD

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The triaryl pyrylium salts presented in Fig.1 display columnar liquid crystalline phases which are strongly fluorescent. Moreover, it has been reported recently that discogenic molecules can form stable monolayers in the air/water interface.

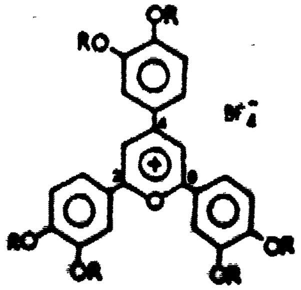

Fig. 1: The 2,4,6 triaryl pylylium fluoroborates C_nPy, $R=C_nH_{2n+1}$

In the present communication, LB films formed by the short chain triaryl pyrylium salt $C_{12}Py$ are investigated. A monolayer of pure $C_{12}Py$ is stable at the air/water interface up to 37mN/m. Multilayers can be very easily built up. Those films are optically perfect and free of any light diffusing defects. They exhibit a strong birefringence the optical axes of which are parallel and perpendicular to the dipping direction. Such a strong anisotropy is also found in the polarized infra-red absorption spectra. In particular, the lines at 1633cm^{-1} and 1520 cm^{-1} assigned to in-plane skeletal vibrations of the pyrylium and the phenyl groups respectively are highly anisotropic: the absorption intensity observed when the light electric vector is parallel to the dipping direction is six times higher than the one obtained for the perpendicular orientation.
Such a behaviour rules out a molecular arrangement in which the aromatic cores lay flat on the substrate and strongly suggests a side-on packing. This is in reasonable agreement with the molecular area determined from the compression isotherms, 105Å^2, instead of 190Å^2 for flat cores. These results show that the LB technique appears to be an attractive method for the orientation of discogenic compounds over extended surfaces.
The question arises if the molecular disks, oriented in the LB films, form a columnar structure or a possible interaction with the substrate give rise to a nematic discotic order whithin each layer. A comparative study of the luminescence properties, which are sensitive to the local environment of the chromophore, indicate that the second type of molecular arrangement is more probable.

FTIR STUDIES OF CONDUCTING LANGMUIR-BLODGETT FILMS OF *O*-HEXADECYLTHIOCARBOXYTETRATHIAFULVALENE (HDTTTF)

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Abstract

Highly conducting ($\sigma \cong 1$ S cm^{-1}) thin films of HDTTTF have been prepared by LB deposition followed by iodine doping. Fourier Transform Infrared Spectroscopic (FTIR) characterisation of the LB films is presented in this work. Upon iodine doping, significant changes in the infrared spectra are observed. These include the appearance of the vibronically enhanced TTF$^{\bullet+}$ band at 1344 cm^{-1}, the disappearance of the ν(C=C) TTF band at 1524 cm^{-1}, the shifting of the ν(C=S) stretching band at 793 cm^{-1} and the out-of-plane deformation band at 645 cm^{-1}, and the intensity enhancement of the ν(CH) and the out-of-plane deformation bands. All these changes in the spectra can be attributed to the ionisation of the TTF molecule and the delocalisation of the valence electrons in TTF$^{\bullet+}$ radical. From the comparison of FTIR ATR (Attenuated Total Reflection) and RAIRS (Reflection Absorption Infrared) spectra, structural information such as orientations of the alkyl chains and the individual dipoles have also been obtained. We demonstrate how FTIR can be employed to correlate changes in the microscopic ordering of the individual molecules (e.g. orientation of alkyl chains and individual transition dipoles) with the electronic rearrangement (e.g. ionisation and delocalisation of valence electrons) important for the conduction process.

GP30

The structure and stability of metal surfaces modified by silane LB-films

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Very frequently, organic polymers are used to protect reactive metals like Fe, Cr, Ni against corrosion. The stability of the polymer film depends strongly on the chemical interaction between the molecules of the polymer and the metal substrate. Therefore, it is expected that the stability of the interface is increased significantly, if chemical bonds are formed between reactive groups of the polymer and the substrate surface.

Silanes are wellknown as primers and coupling agents and should react in exactly the manner as described above, forming stable Si-O-metal bonds. In order to study such interfaces, polymeric and monomeric silane LB-films (n-Hexa-, n- Octadecyltrichlorosilane, Chlorodimethyloctadecylsilane) have been formed on substrates like Fe or Ni and analyzed as well in an UHV-enviroment by surface sensitive methods as in a humid atmosphere by a Scanning Kelvin Microprobe.

During preparation of LB-films, the trichlorosilanes form polysiloxanes on top of the water surface. Because of geometrical reasons a twodimensional polymer will be formed with a high stability an a low elastisty which results in domain formation and cracks within the LB-film during transfer. The degree of coverage of such modified metallic substrates was tested by SEM and/or SAM. It could be recognized that the metallic substrates modified with polysiloxanes exhibited more or less an island structure. The surface analytical experiments also allow to define the orientation of the molecules within the LB-film and their interaction with the substrate surface.

Besides ex situ UHV studies the lateral order of LB-film on top of the metal substrate and its stability has been studied in a humid atmosphere with a Scanning Kelvin Microprobe.

GP31

RESONANCE RAMAN AND INFRARED STUDIES ON LB FILMS OF SOME CYANINE DYES

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Resonance Raman and infrared spectra have been measured for LB films of 3-octadecyl-2-[3-(3-octadecyl-2-benzothiazolinylidene)-1-propenyl]benzothiazolium iodide (NK-2560) and some other cyanine dyes in order to provide new insight into their molecular orientation and structure in the films.

Resonance Raman spectra of the LB films including one monolayer films have been obtained with high signal to noise ratio. The 488.0-nm excited resonance Raman spectrum of one monolayer LB film of NK 2560 is almost identical with the spectra of its 2- and 3-monolayer LB films, indicating that the structure of the dye does not depend upon the number of monolayers and the interaction between the dye and the substrate (CaF_2) is very weak.

Vibrational assignments of the above spectra are not straightforward, but it may be possible to assign bands at 1557, 1465, and 1422 cm^{-1} to stretching modes of the central conjugated system. Vibrational frequencies of the three bands are almost identical with those of the corresponding bands of NK-2560 in solutions. Since NMR study of NK-2560 showed that it takes conformer A, in which the central conjugated system assumes all-trans configuration and the bond order of each bond in the system is one and half, the close similarities in the band frequencies between the LB films and solutions suggest that NK-2560 also takes conformer A in the LB films. Although the band frequencies of the three stretching modes are very similar to each other, the relative intensity of the 1557 band is much stronger in the LB film spectra, compared with those in the cast film and solution spectra. The 488.0-nm excitation of the LB film spectra gives the spectra of H-aggregate of the cyanine dye while the same excitation of cast film and solution spectra provides the spectra of its dimer. Therefore, it seems that the marked intensity increase in the 1557 cm^{-1} band is characteristic of the H-aggregate. Probably, the structure of NK-2560 alters slightly upon the formation of the H-aggregate.

A comparison of infrared transmission and reflection-absorption (RA) spectra of the 6-monolayer LB film of NK-2560 shows that the intensities of bands due to CH_2 antisymmetric and symmetric stretching modes and those of bands arising from stretching modes of the central conjugated system do not exhibit large changes between the two spectra. This observation indicates that both the chains and the conjugated system are neither perpendicular nor parallel to the surface, being tilted considerably from the surface normal.

Bands due to the CH_2 antisymmetric and symmetric stretching modes appear at 2918 and 2850 cm^{-1}, respectively, in the NK-2560 LB film spectra while they are identified at 2922 and 2852 cm^{-1}, respectively, in the infrared spectra of LB films of NK-2861 (3-octadecyl-2-[7-(3-octadecyl-2-benzothiazolinylidene)-1,3,5-heptatrienyl]benzothiazolium perchlorate), which has larger chromophoric group. These results suggest that the hydrocarbon chains of NK-2560 are highly ordered (trans-zigzag) in the LB films but those of NK-2861 are slightly less ordered there. Probably, the larger chromophore of NK-2861 produces less ordered structure in the hydrocarbon chains of the LB films.

GP32

CHARACTERIZATION OF LANGMUIR-BLODGETT OVERLAYERS BY TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY (TOF-SIMS)

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Thin films prepared by the Langmuir-Blodgett (LB) technique have turned out to be suitable model systems for various applications. On the one hand films consisting of components from one substance class (e.g. fatty acids) can be used to get insight into basic processes of the used surface analysis technique (here Secondary Ion Mass Spectrometry (SIMS)). On the other hand more complex systems (e.g. binary mixtures of a polymeric amphiphile and a peptide or a saccharide) offer the possibility to gain a better understanding of the principles of operation of biological membranes or biosensors. Especially for the latter application a surface analysis technique of high sensitivity supplying molecular informations with high mass resolution is required.

We have therefore applied high mass resolution TOF-SIMS to the analysis and characterization of different LB systems ranging from fatty acids to binary mixtures containing polymeric amphiphiles. Noble metals (Ag, Au) evaporated onto polycarbonate have been used as substrate materials. The influence of primary ion dose density, substrate material and film thickness on the secondary ion formation will shortly be discussed. The more application oriented investigations have included the comparison of monomeric and polymeric amphiphiles concerning the film quality, the detection of contaminations, the monitoring of decomposition effects and long-term stability, the influence of additional components like lipides, saccharides and peptides as well as the monitoring of vertical diffusion in binary mixtures.

Additionally results obtained by the application of imaging TOF-SIMS and laser postionization mass spectrometry will be reported.

GP33

THE CHARACTERIZATION OF TWO COPPER PHTHALOCYANINE LANGMUIR-BLODGETT FILMS AND THEIR GAS-SENSITIVE PROPERTIES*

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The monolayer and deposition behaviour of a symmetrically substituted [tetra-4- (2.4-ditert-amylphenoxy)](tapCuPc) and an asymmetrically substituted [tri-4- (2.4-ditert--amylphenoxy)-mono-4-(2-methoxyethoxy)] (AsyCuPc) copper phthalocyanine wereinvestigated. Surface pressure vs. area isotherms for both compounds showed reduced hysteresis and better monolayer stability. The area per molecule, obtained by extrapolating the steeply rising part of the curve to zero pressure, is less than that of Pc macrocycle. This implies that the molecular overlaps with different degrees can be occured. The linear dichroic IR spectra and UV-visible absorption spectra of tapCuPc and AsyCuPc LB films transferred on CaF$_2$ substrates showed primarily that the orientations of both tapCuPc and AsyCuPc molecules are different. The molecule of AsyCuPc is more flat, the tilted angle of Pc ring on substrate surface is relative small. This represented that interaction mechanism between symmetrically substituteed group and water molecule was different from that of asymmetrically substituted group with water molecule.

In order to obtain well-ordered bilayer assemblies by y-type deposition, the stable mixed monolayers composed of AsyCuPc and Stearic Acid (SA) with the various molar ratio were formed on an aqueous subphase. The experimental results showed that the molecules of stearic acid have a certain effect on ordering structure of AsyCuPc molecules. The structure of the mixed LB films in the ratio range of AsyCuPc:SA(mol) from 0.25:1 to 1:0.25 was studied by x-ray diffraction. The low angle x-ray diffraction patterns showed that the mixed LB films have a well-defined layer structure. From the experiment result. It can be considered that the mixed LB films contain partly a double-molecule structure, i. e. some of the AsyCuPc molecules can be superimposed beneath stearic acid molecules and the other of the AsyCuPc molecules can be squeezed among the stearic acid molecules.

The measurements of conductivity of LB films in the presence of different gas mixtures (20ppm of NH$_3$, 200ppm of NO$_2$ in air and 200ppm of SO$_2$ in air etc.) reveals that both AsyCuPc and tapcuPc LB films are only sensitive to the presence of NH$_3$. The response and recovery processes of both tapCuPc and AsyCuPc LB film gas sensors on exposure to 20, 40, 60, 80 100ppm of NH$_3$ in air was given out. The response and recovery time exposed to 20ppm of NH$_3$ in air were less than 30 seconds and 3 minutes respectively. Compared with the results reported by previous works,[1,2,3] it is presented that the excellent selectivity of the two CuPc material may be attributed to the interaction between peripheral substituent of Pc ring and tested gas molecule.

[1] S.Baker G.G.Roberts and M.C.Petty, IEE Proceedings, Vol.130, No.5(1983)260
[2] H.Wohltjen, W.R.Barger, A.W.Snow and N.L.Jarvis, IEEE Trans.Electron. Devices, 32(1985)1170
[3] W.H.Ko, C.W.Fu, H.Y.Wang, D.A.Batzet, M.E.Kenney and J.B.Lando, Sensors and Materials, 2, 1(1990)39

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GP34

STEREOREGULARITY EFFECTS OF PMMA ON THE MONOLAYER CHARACTERISTICS AT THE AIR-WATER INTERFACE AND ON THE LANGMIUR-BLODGETT FILMS

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The stereoregularity effects of poly(methyl methacrylate) (PMMA) on the pressure-area (π-A) isotherm, transfer ratio and film homogeneity have been investigated. The π-A isotherm of atactic and syndiotactic PMMA's were similar in shapes but larger specific area for atactic PMMA. However, that of isotactic PMMA was different from the other's showing two inflection points at the pressure of 8 and 15 dyn/cm and long tail at low surface pressure. Hysteresis upon compression and release was found for all PMMA's when the floating monolayers were compressed above approximately 20 dyn/cm. The hysteresis increased as the compression speed increased. On the contrary, when they were compressed below 15 dyn/cm and released, little hysteresis was noticed. Collapse pressure increased in the order of atactic, isotactic and syndiotactic PMMA's.

Transfer ratio indicated that all the PMMA films were Y-type when they were transfered onto Cr coated slide glass at 15 dyn/cm, but the transfer ratios for the upstrokes were higher than for the down strokes. Film homogeneity was examined by etching the LB film deposited samples by Cr etchant. Micrographs on the syndiotactic and atactic PMMA's were featureless, suggesting that the films are rather homogeneous. However, that of the isotactic PMMA shows streaks parallel to the dipping direction. This difference may reflect the difference of the floating monolayers at the air-water interface. The differences in π-A isoterms and the film morphology will be discussed in relation to the polymer interfacial conformation and molecular arrangement based on surface potential measurements.

GP35

Studies on Synthesis of PMACME-AN-1 and Character of LB Films

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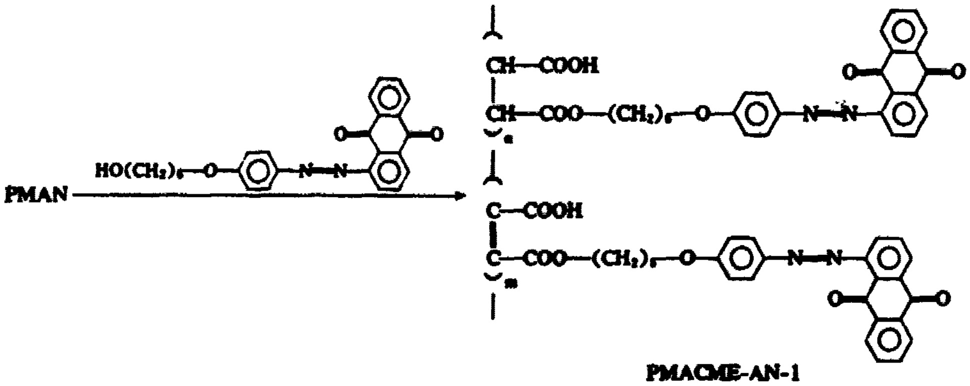
Abstract

We have reported that a new kind of polymer is synthesised and its LB films is studied[1]. That is about the mono-[6-(4,1′-azonaphthalene)oxy]hexyl ester of polymaleic acid (PMACME). In this paper we report that the mono-[6-(4-anthraquinone-1-azo-phenoxy)]hexyl ester of polymaleic acid (PMACME-AN-1) was synthesised by the reaction of 6-(anthraquinone-1-azo-4′-phenyloxy) hexanol and polymaleic anhydride (PMAN) which was prepared by free radical polymerization with BPO as the initiator at 90～95℃. Schematic synthesis route is as follows:



PMACME-AN-1

The title compound was charactorized by FT-IR, ^{1}H NMR, Elementary analysis and MO.

It was determind that the $\overline{M}_n$ of PMAN equals to 1.1×10^3, its correponding D.P(n+m) equals to 11. But the $\overline{M}_n$ of PMACME-AN-1 equals to 3.2×10^3.

The π-A curve was drawn on the surface of water. This curve has a good linear relationship area. We have prepared some good LB films on the substrate of quartz or CaF_2. We could see that 6-anthraquinone-1-azo-4′-phenyloxy side chain has asymmetrical structure, this is meaningful for the study on nonlinear optics and photochromism. In addition, we studied the effect of the interaction among the functional groups for eletronic excited processes. We also prepared the same kind of polymer in which the number of methylene equals 2. From the UV absorption spectrum, we found that the former and the latter are different in UV absorption, so that there are a different interaction among the two kinds of molecules. At the same time, we prepared the similar polymer with 6-(or 2-)anthraquinone-2-azo-4′-phenyloxy side chain and found that the effect of different substituted positions for the interaction of different groups.

Four kinds of PMACME-AN have been studied by conventional and laser spectroscopy and their characters of LB films were contrasted with corresponding compounds in solution. With the aid of the linear dichroism infrared and UV spectrum, it has been investigated that the molecular orientation of LB films deposited on a CaF_2 substrate with multilayers. We found that the intensity of the characteristic absorption frequencies depends on the change of molecular radical orientation. The results mentioned above show that the arrangement of the polymer on the CaF_2 substrate is regular. The fundamental chain of the polymer may be run parallel and the side chain retains an angle with the substrate, and the carboxy groups between the layers are linked by hydrogen bonds.

RERERENCE

[1] Yingying Zhao, *et al.*, In "CJBSLB" (Beijing), 1990

GP36

SPECTRAL CHARACTERIZATION OF THE LB FILMS OF COPPER PHTHALOCYANINE DERIVATIVES

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The excellent chemical and thermal stability of phthalocyanine compounds and their diverse functions with the potential application of semiconductors, photoconductors and sensors have led to extensive interest for chemists and physists. The symmetric and asymmetric substituted copper phthalocyanine derivatives ($CuPc(Dt\text{-}PP)_4$ and $CuPc(Dt\text{-}PP)_3(p\text{-}CP)$) and their various types of LB films have been studied.

The π-A isotherms, polarized UV-vis spectra, polarized IR transmission spectra, ATR and SERS of the LB films of the different compounds were observed and compared.

The area per molecule obtained with asymmetric compound is smaller than that with symmtric one at the same transferred pressure of 30mN/M.

The polarized UV-vis spectra of the LB films of asymmetric derivative show obveous difference with the electric vectors of incident radiation from parallel to vertical to the dipping direction, but no dichroism effect was observed for the LB film of symmetric compound. This indicates that the phthalocyanine rings in the LB film of the asymmetric substituents are tilted to substrate, instead of the parallel orientation of the macrocycles on substrate like the symmetric one.

The same result was obtained from observation of their IR and Raman spectra.

In addition electric conductivities of the LB films were measured, The relationships between conductivity and deposited type of the LB film, as well as between the substituents and orientation of the rings are discussed.

GP37

Stabilization of Layered Structure of Poly(vinyl octal) LB Films Studied by Interlayer Energy Transfer Method

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The Langmuir-Blodgett technique is an elegant procedure for making an ultrathin film with a thickness of a few nanometers. The deposition on a substrate one by one enables us to design spatial arrangements of each layer. The layered structure in molecular dimension yields various specific functions of the LB films. From the application standpoints, it is a critical point whether LB films have a mechanical and thermal stability of the layered structure.

We have applied energy transfer method as a probing technique for the structural relaxation and stability of polymer LB films. Excitation energy transfer from a donor-labeled layer to an acceptor-labeled layer was measured by fluorescence spectroscopy which enabled quantitative evaluation of the disordering of the layered structure. In the case of poly(vinyl octal) (PVO), the samples are shown in Figure 1. Phenanthrene (P) and anthracene (A) were used as a donor and an acceptor probe, respectively. Several layers of PVO were sandwiched by the chromophoric layers containing P or A units. The fluorescence spectra of the LB films show sensitized A emission, then the energy transfer efficiency varies with the structural relaxation of the LB films. Figure 2 shows the plot of transfer efficiency given by I_A/I_P vs. the observed temperature. The rapid increase of I_A/I_P (○) with the rise of temperature indicates that an irreversible disordering starts at ca. 40 °C. Once the samples are heated up to 100 °C, the value stays constant in successive heating-cooling cycles.

The layered structure of LB films, however, can be easily stabilized on exposure to a mixed gas of hydrogen chloride and formaldehyde for a few hours, without any detectable disordering. The plot (●) in Figure 2 shows merely a slight increase of the efficiency with the rise of temperature. This result indicates that the PVO LB films are conveniently cross-linked by formalization of hydroxyl groups and that the heat-stability is much improved.

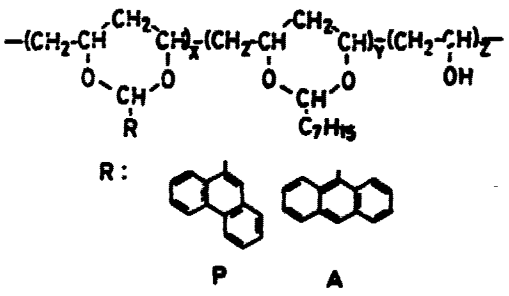

Figure 1

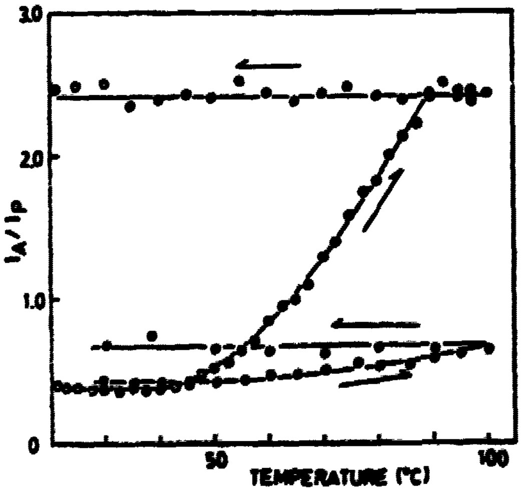

Figure 2

GP38

MOLECULAR ORIENTATION OF PHOTOGENERATED RADICALS IN NOVEL PHOTOELECTROCHROMIC LANGMUIR-BLODGETT FILMS

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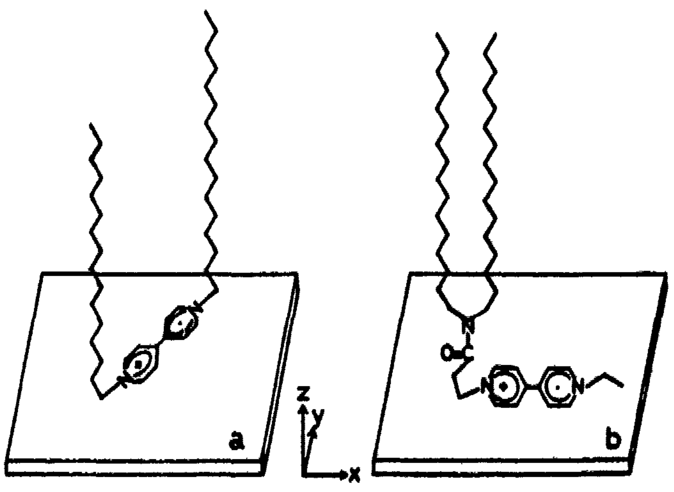
Recently we found the persistent and reversible reduction of 4,4'-bipyridinium ions in their salts with tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate anion (abbrebiated to TFPB$^-$) in the solid state or in organic solutions in inert atmospheres upon excitation of an ion-pair CT band. We now report the control of molecular orientation of 4,4'-bipyridinium cation radicals photogenerated in LB films by the substituents.[1]

N,N'-dihexadecyl-4,4'-bipyridinium(TFPB$^-$)$_2$ (abbreviated to HV) and N-ethyl-N'-(2-ethylamide)-N",N"-dihexadecyl-4,4'-bipyridinium (TFPB$^-$)$_2$ (abbreviated to AV) were prepared. A 1:4 mixture of HV or AV and arachidic acid(abbreviated to AA) was deposited at 18°C and 20 mN・m^{-1}. These samples were irradiated in vacuo by a Hamamatsu 150 W Xe-Hg lamp equipped with an L-39 cut-off filter (λ >365 nm) and a 10 cm water filter to excite their CT absorption band alone. The incident angle dependences of both s- and p-polarized absorption for 4,4'-bipyridinium cation radicals were measured in vacuo together with the polarization angle dependence at normal incidence.

Upon irradiation the colour of both LB films (HV/AA and AV/AA) changed from pale yellow to blue. The UV/vis absorption spectrum characteristic to 4,4'-bipyridinium cation radical monomer was observed together with a broad single line ESR spectrum. Coloured species photogenerated in mixed LB films of AV/AA and HV/AA in vacuo decayed almost exponentially in the dark. Such photochemical colouring and thermal fading was repeated reversibly. No polarization angle dependences were observed at normal incidence. The p-polarized absorptions of 4,4'-bipyridinium cation radicals corrected for the decay and the optical path length showed a minimum in a HV/AA system and a maximum in a AV/AA system at normal incidence. From these results and the simulation of angular dependences by taking the distribution of transition dipole moments with respect to the surface normal into accounts, it was shown that both long and short axes of 4,4'-bipyridinium cation radicals almost lie flat in AV/AA LB films and oblique by about 46° in HV/AA LB films to the substrate surface as schematically shown.



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[1] T. Nagamura et al. J. Chem. Soc., Chem. Commun., 703 (1990).

GP39

STRUCTURE OF THE LANGMUIR FILMS FROM AMPHIPHILIC POLYIMIDES

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The set of amphiphilic polymers of the polyimide type with various chemical structure of the rigid backbones and the long flexible side methylene chains have been studied in the form of common cast films and in the form of thin Langmuir films. The set of polymers consists of a systems with and without fluorocontaining phenyl rings and with one or two flexible side chains.

The pressure-area diagrams and corresponding LB films with the number of layers from 5 to 10 have been obtained by the conventional Langmuir method. For ellucidation of the possible arrangement of the backbones onto the interphase boundary we have determined the most favourable conformation and the charge distribution along the backbones by means of the quantomechanical (MNDO) calculations. To study the structural ordering for films the conventional X-ray diffraction method in reflection and transmition modes has been used. The thermal properties of the polymeric films have been studied by DSC method.

From the analysis of pressure-area diagrams we have determined the area per monomeric unit in expanded and condensed states. It has been demonstrated, that the corresponding value (varied from 1 to 2 nm^2) is determined by the features of the conformation of the monomeric units and it depends on the chemical structure of the backbones and the type of the attachment of the side chains. From X-ray data for cast films one can conclude the realization of perfect layered ordering of the macromolecules (period is equal to 1.8 nm) with overlapping the side chains. In the corresponding LB films the one-dimensional order has been observed with the translation correlations, propagated on the whole thickness of films. The type of ordering is determined by the type of attachment of the flexible side chains to the backbones. The conformation and, especially, charge distribution depends on the presence of the fluor atoms into the backbones. After chemical and thermal treatment to remove the side chains the LB films are stable up to the high temperatures (250-300°C).

The possible models of the layered packing with taking into account the favourable conformation of the backbones, the correlation of structure of the cast films and LB ones and the changes of structural ordering after removing the side chains by the chemical and thermal treatments have been discussed also.

GP40

A NEW KIND OF AMPHIPHILIC POLYMERS---"DUCKWEED" AND "REVERSED DUCKWEED" TYPES OF LANGMUIR-BLODGETT FILMS

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In our previous work, we reported a new kind of microgel amphiphilic polymer synthesized through radical initiation polymerization and grafting, its hydrophobic and hydrophilic parts were St-DVB microgel core, polymethylacrylic acid or other hydrophilic polymer chains respectively. Some properties for monolayer and multilayer of this kind of polymer were studied. In this paper, we further confirmed that the amphiphilic molecules rearranged to the structure of Duckweed at air/water interface, and its LB films had good laminar structure by TEM and X-ray diffraction.

In contrast with Duckweed LB film, we synthesized another kind of amphiphilic polymer which formed stable monolayers of Reversed Duckweed type. The hydrophilic microgel was prepared with radical polymerization of N-vinyl-2-pyrrolidone with β-hydroxyethyl methacrylate, whereas PETA acted as crosslinking agent. And the hydrophobic part was polystyrene chains.

Comparing Duckweed with Reversed Duckweed type LB films, we could draw the following conclusions:

(1) The shape of surface pressure-area isotherms is largely dependent on the ratio of hydrophilic/hydrophobic groups. Both Duckweed and Reversed Duckweed types of amphiphilic polymer form stable and condensed monolayer at air/water interface, but show different molecular-weight dependence.

(2) The ratio of hydrophilic/hydrophobic groups makes great effects on the relaxation behavior of monolayers after compression, though monolayers of Duckweed and Reversed Duckweed type show different features due to their different structure and composition.

(3) Using monolayer-coated glass carbon (GC) electrodes, it was found that the blocking effect provided by monolayer of Duckweed type is better than that by Reversed Duckweed type. This result may be caused by their different Duckweed structures.

(4) The layer structures of Langmuir-Blodgett films for Duckweed and Reversed Duckweed types were confirmed by X-ray diffraction patterns, and interlayer spacings were calculated.

(5) Corresponding to Duckweed type monolayer, the monolayer of Reversed Duckweed type was easily compressed to higher density monolayer. Maybe this is responsible for its larger blue shift in UV-Visible absorption spectra (from 254 nm in solution to 198 nm in solid LB film).

GP41

LANGMUIR-BLODGETT FILMS OF CROWN ETHER CONTAINING BIPHENYL MESOGNIC GROUPS

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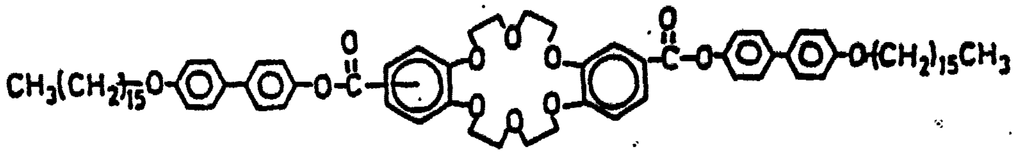
Combination of Host-Guest chemistry with LB techniques will be promising for applications in chemical sensors, molecular recognition and specific electrocatalytic oxidation-reduction. In this paper, we report a new kind of Langmuir-Blodgett film of crown ether containing biphenyl mesognic groups in the side chains.

The compound of Bis(-p-hexadecyloxy-p'-biphenyl-)-dicarboxybenzo-18-crown-6(CEBB in brief) was synthesized. Its chemical formula is



DSC measurement and studies with a polarizing microscope reveal that the compound is well-ordered semctic liquid crystalline.

CEBB amphiphiles form stable monolayers in the condensed phase at air/water interface. The molecular area is estimated to be 0.8 nm^2/molecule from the isotherms, it is nearly the accordance with the calculated result from CPK model. The fluorescence spectra of CEBB LB films which peak at 400 nm are almost identical to that of a dense solution in chloroform(392 nm), but different from the fluorescence spectra of dilute solution(normally, monomer fluorescence peak 340 nm). The results mean that all the molecules in solid LB films or dense solution exist in the "eximer" state. A linear behavior of the fluorescence intensity of CEBB LB films as a function of the number of monolayers indicates that CEBB gives a good Y type multilayers.

The structure of CEBB LB films is further investigated by X-ray diffraction analysis. Two sharp Bragg peaks were observed in the range of 2θ angle 1-10° when we use weaker Cr target(K 2.29 Å), and the sharpness of these peaks indicates highly ordered structure in LB films. According to the Bragg equation, a layer spacing 66 Å was calculated from the first reflection peak. Using stronger Cu target(K 1.54 Å), two peaks were also observed, one was sharper and stronger, the other much smaller and weaker. It was found that the intensity of the first reflection peak decayed to a constant level within 30 min, and its corresponding layer spacing also decreased several angstroms, whereas the small peak had no any change in period of radiation time. This maybe means that CEBB multilayer exist in metastable state.

Molecular orientation of CEBB films deposited on CaF_2 substrates was investigated by polarized IR spectroscopy. The difference of molecular packings (Y or Z-type assemblies) was discussed, and the orientation of the mesogenic units within a multilayer arrangement was studied.

GP42

THE FORMATION AND CHARACTERIZATION OF AGGREGATES OF LANGMUIR - BLODGETT CYANINE DYE FILMS.

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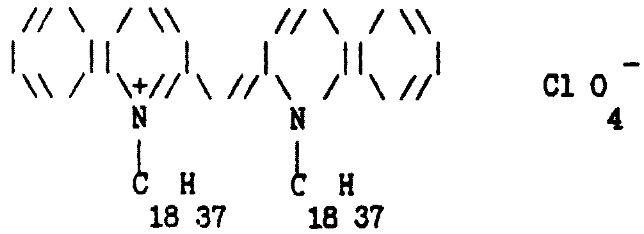
The conditions of the formation of aggregates in Langmuir -Blodgett (L-B) films of pseudocyanine dye



and deaggregation by thermal treatment and laser irradiation were investigated.L-B films of the dye mixed of behenic acid,octadecyl alcohol (OdOH), methyl and ethyl stearate (MeSt,EtSt) were deposited to quartz plates. In absorption spectra of pure dye was observed two maximum with 500 and 535 nm, which correspond to dimeric and monomeric forms. In the films of the dye - OdOH was observed H-aggregates with characteristic band at 492-495 nm. The films of dye - MeSt, EtSt show the intense narrow band at 575-578 nm, which can be attributed to J-aggregates. The maximum of absoption spectra dependend upon the molar ratio components of the mixed films.

The temperature dependence of deaggregation was established. The rate of the dissociation of J-aggregates by thermal treatment and laser irradiation was more higher than H-aggregates. H-aggregates dissociate into J-aggregate, while J-aggregate to monomeric form.

GP43

POLAR MULTILAYER LB-FILMS OF P-OCTADECYLOXYAZOBENZENE-P'-SULPHAMIDE

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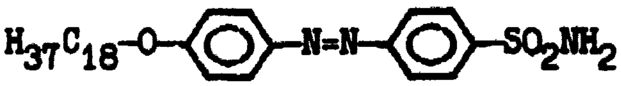
Polar LB-films may be produced by several methods: by the deposition of two alternate layers of different materials or by the deposition of a single material under special conditions, for example, as in the Langmuir-Schaefer method .

We have studied the temperature dependence of the pyroelectric coefficient, dielectric constant and structural period of polar LB-films built by the Langmuir-Schaefer method from the molecules of p-octadecyloxyazobenzene- p'-sulphamide (18-OABS),with the chemical formula:



The significant pyroelectric effect in the films proved them to be polar.The periodicity of structure of the films investigated was approximately equal to the lengths of the molecules used.

An irrevesible transition from polar to non-polar state has been observed in 18-OABS films at 95+100 °C. At this transition the pyroelectric coefficient decreases from 0.7nC/cm^{2}K to 0 and the structural period of the films changes from D_1=39Å to D_2=69Å. This transition does not relate to melting of the film, the temperature of the melting point lies far higher (at 150°C).

The films were found not to have the single solid-to-liquid transition but the liquid-crystal state. A strong frequency dependence of the dielectric constant was obseved at T>120°C.In this temperature range the frequency dependence of the complex dielectric constant is written by a Cole-Cole expression.In the liquid-crystal state the films have several smectic mesophases. Phase transitions take place at 126°C (69Å $\leftrightarrow$ 63Å) and 135°C (63Å $\leftrightarrow$ 41Å). During the transitions the structural periods of the films and the value of the dielectric constant are subject to change.

GP44

PHONON CONDUCTION PROCESS IN LANGMUIR-BLODGETT FILMS

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The conduction of phonons in oriented organic materials is one of the most interesting subjects in materials science. An experimental and a computational study have been made by the present authors in order to obtain the microscopic understanding of the thermal diffusion process through stackings of monolayers of organic chain molecules.

By using the usual technique, the Y-type Langmuir-Blodgett films of arachidic acid $CH_3(CH_2)_{18}COOH$ are prepared; the stacked layer thickness = 2.7 nm, the number of stacked layers = 1000 - 2000. The thermal diffusivity D of the specimen in the stacking direction is measured by a pulse heating method. The observed high value of the thermal diffusivity ($D = 0.40$ cm^2/sec for the 2000-layer specimen at $T = 300$ K) suggests that strong phonon conduction along the aligned carbon chains of the material is occurring.

The thermal transport processes through anisotropic media are also studied by computer experiments. A mass-spring model (one dimensional array of point mass coupled by springs) is used to simulate the LB-film system. An end point of the mass-spring system is vibrated randomly during a certain period, and the process of kinetic energy transport is investigated by the molecular dynamic calculation. It can be concluded from these computer experiments that the strong coupling between the carbon atoms in the molecular chains and the weak coupling between the chains are possible reasons for the high thermal diffusivity observed experimentally.

GP45

CHARACTERIZATION OF POLYALKYLTHIOPHENE BASED L.B. FILMS

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We have extensively investigated the conditions of obtaining stable L.B. films starting from poly(3-alkylthiophenes), which are soluble. We have varied the alkyl chain length (eptyl. decyl. unde-cyl). the molar ratio between the PAT and Cd arachidate (from 1/20 to 3/1).PAT alone are not able to give stable monolayers at the air-water interface. thus preventing their transfer on suitable substrates.On the contrary by mixing arachidic acid and PAT. usual pressure-area isotherms are obtained, hence L.B. films are formed. The monolayers can be transferred.at 20 mN/m. on quartz or silicon substrate.

X-ray diffraction studies on L.B. mixed films have shown no appreciable differences as compared with patterns of pure Cd arachidate indicating a strong phase segregration between the components. From UV visible spectroscopy. carried out on both LB and cast films. it is evident that the absorption maximum of LB mixed film is shifted towards lower energy with respect to PAT cast films . suggesting that the polymer chains assume a more extended conformation.

In order to obtain more insights on the molecular organization of PAT chains we have performed a detailed fluorescence microscopy analysis. as the polymer present emission effect near to 670 nm. The microphotographs, performed on a single layer. evidence the presence of PAT aggregates with different size well separated from Cd arachidate domains.

GP46

ON THE STRUCTURE OF MIXED LANGMUIR-BLODGETT FILMS OF TWO DIFFERENT FATTY ACID SALTS

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ABSTRACT

It seems to be important to study the structure of Langmuir-Blodgett films formed by mixing of two different compounds. The main question is: do the compounds really mix or they form unmixed domains? In order to answer this question Langmuir-Blodgett films of mixed behenic and stearic acid salts of cadmium were deposited and investigated by small-angle X-ray scattering. The ratio of compounds was varied from 1:4 to 4:1. It was found that for 1:1 ratio X-ray pattern contained a single system of reflection with a lattice spacing equal to 54.0 Å.

For any other ratio, X-ray patterns contained two systems of reflections, each of them corresponding to one of the pure fatty acid salts (49.0 Å and 58.5 Å respectively) .

When the ratio is different from 1:1, the molecules of the two acids form domains not mixing with each other; these domains grow as monolayers are deposited, like in an epitaxy process.

Session HP

Modern investigation methods

VISCO-ELASTIC PROPERTIES OF THIN FILMS PROBED WITH A QUARTZ CRYSTAL RESONATOR

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Abstract

We report on the application of quartz crystal resonators to the characterization of visco-elastic thin organic layers.

A passiv measurement of the quartz crystals electrical impedance allows for the measurement of it's resonant frequencies als well as the damping in a number of vibration modes, spanning in frequency from about 3 MHz to about 40 MHz. A parallel ellipsometer setup is used for simultaneous optical characterization.

The shift in resonant frequency and damping induced by an organic film deposited on one quartz surface can be used to measure the effective acoustic impedance $\hat{F}/\partial_t\hat{u}$ of the film ($\hat{F}(\omega)$ the complex force per cm^2 and $\hat{u}(\omega)$ the amplitude of the oscillation). For "hard" materials the effective acoustic impedance is equivalent to the films mass. For "soft" and viscous materials the shear modulus $\hat{G} = G' + iG''$ enters the formulae and can sometimes be measured.

The glass transition of a 350 nm film of low molecular weight polystyrol can be followed. Resonances in frequency shift and damping occur, when the wavelength of transverse sound in the film equals $(2n + 1)/4$ times its thickness. At these resonances quantitative analysis with respect to G' and G" is possible.

During the UV-induced desorption of poly[(bis)-m-butoxy-phenyl]silane under oxygen atmosphere a strong increace in viscous damping and a strong decrease of frequency occur. At the same time there is little change in optical thickness. Possibly the desorption takes place via an oily phase of medium size oligomers.

When LB-Films of poly-glutamates carrying cinnamate ester side groups are irradiated with $\lambda = 254$nm, the processes of bondbreaking in the main chain, cross linking of cinnamate esters and desorption can be followed.

HP2

INTERFACIAL RECOGNTION REACTIONS AS SEEN BY FLUORESCENCE–, SURFACE PLASMON– AND ATOMIC FORCE MICROSCOPY

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We investigated site specific recognition reactions at the gas/fluid and solid/fluid interface. As a modell system we used the highly specific and strong interaction between Biotin and Streptavidin ($K_{\blacksquare} = 10^{-15}$ m). This well known system is in many ways comparable to biological receptors and ligands and can be chemically modified in various ways, e. g. Biotin bound to a lipid. With a binary mixture of such a Biotin functionalized lipid with a "nonreactive" lipid, monolayers can be build up at the air–water interface (in a filmbalance) and the binding properties to Streptavidin can be studied by fluorescence microscopy.

After transfer of such an reactive lipid–monolayer to a solid support, which is capable of carrying surface–plasmon modes one can also apply these novel technique, without the need for labeling the molecules of interest. Surface–Plasmon microscopy combines high lateral resolution (~ 5μm) with extremly high thickness sensitivity (~ 0.1 nm). The used flow–cuvette set–up allows for the online exchange of the subphase, e. g. against a Streptavidin containing solution.

Analoge experiments from the monolayer–electrolyt interface were carried out with the Atomic–Force–Microscope (AFM), which yields too qualitative pictures of the sample, but this time with "sub–optical" resolution, some times even molecular resolution. The obtained micrographs can be processed to get quantitative information about height distribution, force spectroscopy and layer compressibility. It is also possible to online monitor the thickness changes due to the adsorption of molecules to the interface.

HP3

ELECTRO-OPTICAL SPECTROSCOPY ON AGGREGATED CHROMOPHORE SYSTEMS IN LANGMUIR-BLODGETT FILMS

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The linear and the quadratic Stark effects have been employed to characterize aggregate formation of a cyanine dye mixed with a fatty acid in various concentrations within LB multilayers. Two different electrode configurations have been used to test the responses of the electronic spectra to external electric fields: in films assembled into a sandwich arrangement, dipole moment changes perpendicular to the plane of the molecular films are observed; in films deposited onto an interdigitated microelectrode structure, the charge redistribution parallel to the interface is accessed.

The observations have been used to quantify the induced and static dipole moment changes on excitation of the chromophores. As expected from theory, it is found that the experimental observations reflect the symmetries of (i) the dye molecule, (ii) the molecular aggregates, and (iii) the layer structure as defined by the preparation process. Hence they can serve to assess the local arrangement of the molecules within the superstructure. Comparison of the results obtained from different multilayer arrangements are indicative of inter-layer coupling for the case of a head-to-head configuration of the amphiphilic chromophores. This coupling occurs only between dye aggregates and is not detected for the monomer species. An asymmetric charge distribution due to different electrode materials is thought to be responsible for breaking of the symmetry and results in the visualization of this phenomenon in the linear Stark effect.

Mixing studies (variations of the dye concentration between 2 to 100 mol%) reveal the evolution of *two different* aggregated species, i.e. of hypsochromically shifted H-aggregates dominating the absorptions spectra at moderate dye concentrations and of bathochromically shifted J-aggregates that become prominent at the highest concentrations. At low concentration, the Stark spectra are dominated by strong inhomogeneous local electric fields due Cd^{2+} incorporated as counter-ions to the prevailing fatty acid in the deposition process.

At external field application parallel to the film surface the Stark spectra reflect the molecular symmetry of the chromophore and confirm a model that the molecules stand on edge on the substrate with their symmetry axis close to the surface normal. Extraordinarily large polarizability values parallel to the surface are observed.

HP4

LANGMUIR MONOLAYERS OF PERFLUOROALKYL-TERMINATED AMPHIPHILES STUDIED BY OPTICAL SECOND-HARMONIC GENERATION

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As a hydrophobic group in amphiphiles, a perfluoroalkyl chain is more rigid and has a larger cross-sectional area than its hydrocarbon counterpart. Using optical second-harmonic generation (SHG) and ellipsometry, we have studied Langmuir monolayers of a series of amphiphiles with a perfluoroalkyl tail: (para) $CF_3(CF_2)_9\text{-}SO_2\text{-}Ph\text{-}X$, where X is (a) $-N(CH_2CH_2OH)_2$, (b) $-N(CH_3)(CH_2CH_2OH)$, and (c) N-substituted L-prolinol. The long axes of the tail and the phenylene core are at an angle estimated to be ~ 45 deg. Two parameters of the monolayer film are obtained — an average tilt angle of the molecules at the air-water interface deduced from polarization dependence of the SHG signal, and an effective monolayer thickness deduced from ellipsometry.

Langmuir monolayers of all three compounds exhibit an extended pressure-area (Π-A) isotherm (at 25 °C) with the surface pressure increasing monotonically over a wide area range as the monolayers are compressed. The "collapse" of the monolayer film is marked by a sharp kink in the Π-A isotherm followed by a plateau region. Our optical measurements indicate that in the plateau region multilayers start to form and the Langmuir film is no longer uniform. The average molecular area at the pressure kink (i.e., maximum monolayer packing) depends on the head group X; it is 41 Å^2, 47 Å^2 and 54 Å^2, respectively for compounds (a), (b) and (c). The values are significantly larger than the cross-sectional area of the perfluoroalkyl tail (~ 30 Å^2), presumably due to the bending between the tail and the phenylene core. We find the increase of Π upon the monolayer compression is correlated with a change in the average molecular orientation as well as an increase of the monolayer thickness. At the maximum monolayer packing, while the phenylene core is still tilted at a large angle (~ 50 deg.), the perfluoroalkyl tail is roughly normal to the water surface.

HP5

IMAGING OF THE LATERAL STRUCTURE OF LB FILMS BY METAL DECORATION AND POLARIZATION MICROSCOPY

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Recently a new method was described that is able to image the lateral surface structure of LB films by metal decoration and polarization microscopy /1/. The principle of the method is based on the high surface sensitivity of the growth of metal films on organic surfaces. In the initial stage, the metal atoms nucleate to metal islands. In the case of a lateral anisotropy in the orientation of transferred monolayers, this leads to a distinct anisotropy of the mobility of the metal atoms, the distribution of nucleation sites and finally to an anisotropic distribution and coalescence of metal islands.

The pleochroism of such evaporated gold or silver islands on LB films is used to see the morphology of the uppermost monolayers in the polarization microscope. A multitude of new information about the lateral structure of LB films is available by this method that was not accessible before. This will be elucidated by several examples.

By means of polydiacetylene LB films it is demonstrated that the same domain structure and morphology is imaged by metal decoration that can be seen already without metal decoration due to the intrinsic and large dichroism of oriented polydiacetylene chains.

However, most of the LB films are prepared with materials that do not show an intrinsic birefringence large enough for such a direct image to be obtained by polarization microscopy. By means of the metal decoration technique, their morphology can be made visible as will be shown with fatty acid salts such as Cd-arachidate and preformed polymers for example polyglutamate or other rigid rod polymer systems.

The influences of film preparation conditions, monolayer flow on the Langmuir trough, shear forces during the film transfer can be seen clearly. This visibility of the real lateral structure of LB films is viewed as a major step forward to control and improve their structural quality.

Reference

/1/ C. Bubeck, Adv. Mater. 2 (1990) 537.

HP6

ANGLE-RESOLVED PHOTOEMISSION FROM LANGMUIR-BLODGETT FILMS OF COPPER TETRAKIS(n-BUTOXYCARBONYL)PHTHALOCYANINE

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The interest in studying angle resolved ultraviolet photoelectron spectroscopy (ARUPS) is due to its capability for obtaining information on the angular parts of wave functions of valence electrons as well as their ionization energies. This in turn means that the molecular orientation in ultrathin films or in the surface layer of the film of organic molecules can be probed by investigating the valence band with a definite orbital symmetry using this technique.

Langmuir-Blodgett (LB) films of phthalocyanine (Pc) derivatives can be considered as one of the most useful films for organic devices due to their thermal stability and the existence of Pc rings. Among these, a recent study of thick LB films (40 layers) of copper tetrakis(n-butoxycarbonyl) phthalocyanine [$(BuOCO)_4CuPc$] with polarized UV-visible absorption spectra [1] revealed that the molecular planes (Pc rings) are nearly perpendicular both to the surface and the dipping direction.

We measured ARUPS spectra of ultrathin LB films (8 layers) of $(BuOCO)_4CuPc$ deposited on metal substrates with synchrotron radiation in order to study the molecular orientation of the CuPc rings in the films. The incidence angle of photons (α) and take-off angle (θ) of the photoelectrons were fixed at 0 and 45, respectively.

The photoelectron intensity from the top π-band showed a pronounced azimuthal angle (ϕ) dependence with a maximum at $\phi \simeq 0$, where ϕ is the angle between the component of photoelectron momentum parallel to the surface and the electric vector of the incident photon. This result indicates that the CuPc rings in the films are well oriented with the molecular planes perpendicular to the dipping direction.

Reference
[1] K.Ogawa, S.Kinoshita, H.Yonehara, H.Nakahara and K.Fukuda, J.Chem.Soc., Chem.Commun. 478 (1989).

HP7

DIRECT MEASUREMENTS OF SURFACE FORCES BETWEEN MONOLAYERS OF POLY(METHACRYLIC ACID) AMPHIPHILES

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Importance of accurate, direct measurements of interactions between various surfaces has been widely acknowledged since introduction of Surface Forces Apparatus (SFA) designed by Israelachivili. Study of synthetic polyelectrolytes is useful in many industrial applications, and also from their relevance to natural polyelectrolytes. Poly(methacrylic acid) (PMA) shows a marked pH-induced conformational change from a rodlike form to a hyper-coiled form when pH decreases beyond a critical pH of 4-6. The interlayer interaction of monolayers containing poly(methacrylic acid) segments as a head group is studied. The surface pressure - area (π - A) isotherms is measured to monitor the intralayer forces.

Amphiphile **1** formed a stable monolayer at the air-water interface. Figure 1 shows pH dependence of the π-A isotherms. The isotherm changes slightly except at large molecular areas where the pressure increases at higher pH's. The monolayer of **1** was transferred to hydrophobized mica surfaces at a pressure of 35 mN/m in the down-stroke mode. Repulsion extends longer than 3000 Å in pure water (pH ~ 6), and increases significantly at pH 8.1 (Figure 2). At lower pH of 3.5, observable repulsion exists only in the surface separation range smaller than 600 Å. The separations showing repulsion of 20 mN/m are ca. 700 Å at pH 8.1, 0 Å in pure water (set as a reference position), and - 100 Å at pH 3.5. The conformatinal change of the polyelectrolyte head group of **1** causes this pH dependence of forces. Interlayer and intralayer interactions will be discussed.

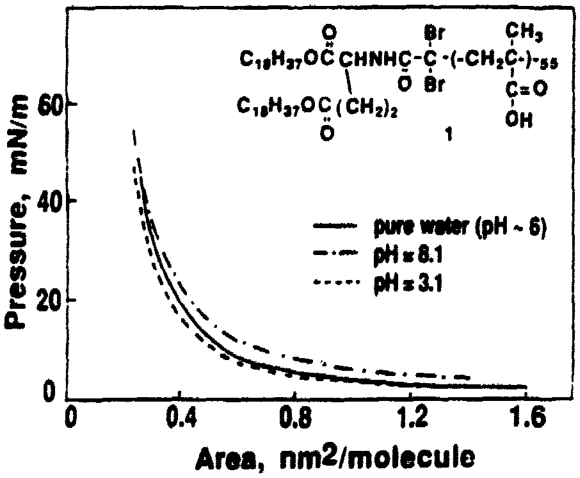

Fig. 1. The π-A isotherms of **1** at various pH's.

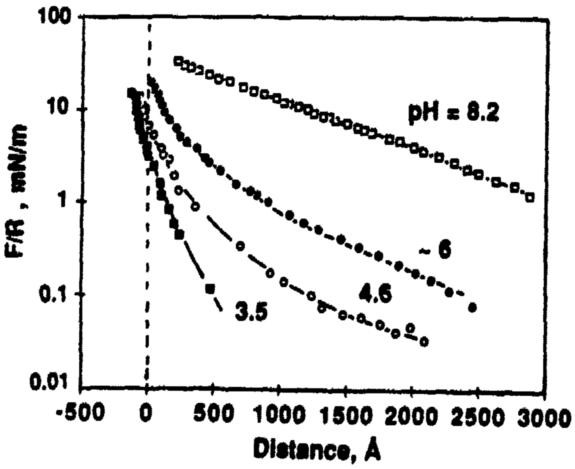

Fig. 2. Repulsive forces between monolayers of **1**.

HP8

PERFECTNESS AND BLOCKING PROPERTY OF LB FILMS ON PLATINUM ELECTRODE INVESTIGATED BY CYCLIC VOLTAMMETRY AND SCANNING TUNNELING MICROSCOPY

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The perfectness and blocking properties of LB films have been studied by cyclic voltammetry and scanning tunneling microscope. A trielectrode electrolysis cell composed of working platinum electrode,saturated calomel electrode (SCE),and platinum counter electrode have been used. Arachidic acid (C_{20}) was deposited on the platinum working electrode. Cyclic voltammograms showed that in solutions of 3N H_2SO_4 and 1N KCl the LB film of arachidic acid acted as an insulation layer on the platinum surface,and the insulation ability increased as the number of deposited layer became more. However,STM showed that there were defects still existed in the LB film. Although rough and inhomogeneous surface of Pt substrate, individual domain of monolayer with a certain order structure were first imaged on practicable polycrystal platinum surface.The domain of C_{20} monolayer imaged by STM was becoming larger as the number of deposited layer increasing, which may provided a new thinking of multilayer structure.

HP9

MONOLAYER AND MULTILAYER FILM CHARACTERISATION USING SURFACE PLASMON RESONANCE

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Surface Plasmon Resonance (SPR) is a technique ideally suited to the analysis of mono-molecular films, produced using the Langmuir-Blodgett (LB) method. The coupling of laser light to a tightly confined propagating plasmon mode at a silver surface is greatly influenced by a dielectric film at this surface. Internal reflectometry of a dielectric-coated thin silver film on glass may be analysed to deduce film thickness and permittivity information.

The reflectometer apparatus has been developed with an emphasis on high accuracy (<0.1% error). The entire instrument has been modelled and characterised, and systematic losses compensated to permit a reliable fit to theory. A fast Laurent-Marquardt fitting procedure has been applied, using the exact Fresnel reflectance formulae over a wide range of angles, allowing all 6 pertinent thickness and (complex) permittivity parameters to be simultaneously determined.

The technique has initially been applied to LB films of behenic acid, a well characterised simple fatty acid system. Excellent agreement of film refractive index and thickness per layer was obtained between measurements, even for a single monolayer. Using a molecular model, a tilt angle of 25° was predicted in accord with infra-red spectroscopy data.

The systematic study of an extensive class of Organo-Ruthenium complex surfactant molecules is in progress to determine the dependence of film structure on molecular structure. Consistent film deposition is obtained through the use of a single, stable, hydrophilic head-group. Measured pyro-electric response from these molecules is related to film structure.

The potentially promising electro-optic properties of the class, due to incorporated donor-acceptor molecular moieties, will be investigated. High film quality is particularly relevant for optical applications, but has only been obtained for simple systems.

HP10

SCANNING OPTICAL MICROSCOPY OF LANGMUIR-BLODGETT FILMS

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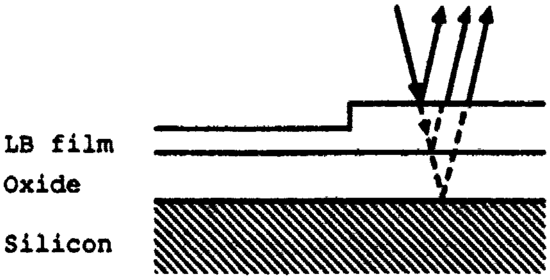
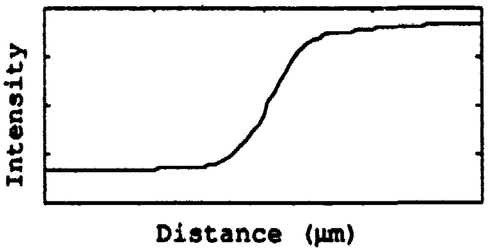
Many optical techniques are available in order to characterise the structure of Langmuir-Blodgett (LB) films. Confocal imaging, using a scanning optical microscope (SOM), offers improved resolution over conventional microscopy, as well as offering great flexibility in image processing.

High quality images have been produced by depositing the films as step structures on silanised silicon wafers.





The intensity produced is modelled by considering the interference effects caused by multiple reflections from the various interfaces in the system. Using a range of different laser wavelengths and known oxide thicknesses (measured using ellipsometry) film parameters such as thickness or complex permittivity can be determined. The technique thus provides quantative data while simultaneously allowing high quality images to be displayed.

This work is complementary to the many forms of imaging which display only phase information. Differential phase contrast and Nomarski microscopy have also been used in these studies to yield additional information about film quality.

The system has been fully characterised using simple materials such as behenic acid and is now being used to assess the structure of pyroelectric LB films. Altering the polarisation of the incident beam will allow the orientation of dye chromophores to be determined and aggregation effects, particularly within mixed films, to be studied.

HP11

OPTICAL CHARACTERISATION OF HIGHLY ABSORBING LANGMUIR-BLODGETT FILMS USING ATR TECHNIQUES

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There is substantial interest in the fabrication of non-centrosymmetric thin film or waveguide structures in the form of Langmuir-Blodgett multilayers. These have potential in non-linear optics for use as optical switches and in second harmonic generation applications. However to have high non-linear coefficients there is often the need for a strong resonance in the wavelength region of interest. This then means that the structures are optically strongly absorbing, which therefore makes them difficult to characterise using conventional waveguide-coupling techniques. An alternative procedure is to use the excitation of surface plasmons in a structure comprised of a prism/metal/LB film. This allows, provided the thickness of the film is known, a reasonable characterisation of the optical properties. However, unlike the guided mode technique, which allows full optical dielectric tensor characterisation, the surface plasmon approach leads to an assumed-isotropic refractive index.

There is a second approach, for highly absorbing films, which may be better than the surface plasmon technique. This is simply a study of the reflectivity of a thin film deposited on a prism of high index, measured with light incident from inside the prism. for angles of incidence close to the critical angle. Using this procedure with both p and s polarised radiation, the s remember not being available with the surface plasmon, it is possible to obtain more complete information on the optical properties of the film, particularly at wavelengths close to the resonance. In this study we have used both techniques to characterise the optical properties of LB films composed of Zwitterion complexes. The results obtained are compared with the direct absorption measurements using more conventional spectroscopic techniques, which only provides a very limited optical characterisation of the layers.

HP12

TWO-DIMENSIONAL ORGANIC CRYSTALLINE FILMS STUDIED BY TUNNELING MICOSCOPY

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The two dimensional ordering of small organic molecules on the surface of graphite and molybdenum has been investigated with nearly atomic resolution by scanning tunnelling microscopy (STM). We will discuss the structure, the registry, the adsorption and imaging mechanism as well as lattice defects and dynamical aspects of the interfacial layer. We will concentrate on DNA bases and show some additional examples of liquid crystals and a dye molecule.We prepared monomolecular films which are homogeneous over many micrometers, although they sometimes show lattice defects. Molecular orbital calculations allow for the comparison of predicted electron densities with the observed STM contrast and are a valuable help for the interpretation of the observed experimental results.

Lit. D.P.E. Smith and W.M. Heckl, Nature, Vol. 346, No. 6285, pp.616 - 617, 1990

HP13

DIRECT MEASUREMENT OF THE FORCES BETWEEN GANGLIOSIDE BILAYERS DEPOSITED ON MICA SUBSTRATES

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ABSTRACT

Glycosphingolipids are ubiquitous membrane components and have been implicated in cellular interactions, oncogenesis and differentiation. The forces between mica surfaces coated with a bilayer of the gangliosides GM_1 and GT_{1b}, as a function of surface separation have been measured using the mica surface forces apparatus. The results show that at long distances the data can be rationalised in terms of electrical double layer theory, whilst at shorter range, steric forces dominate and prevent any adhesion between the bilayers occurring Ganglioside/phospholipid mixtures, show similar results although at sufficient dilution the normal adhesion observed with phospholipid bilayers returns. P-A isotherms and surface potential measurements for the same system will also be reported.

HP14

Symmetry and Orientational Structure in Hemicyanine Monolayer by Surface SHG and Absorption Spectrum

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Symmetry and orientational structure of the hemicyanine dye (fig.1) monolayer were studied by surface second-harmonic generation (SHG) and absorption spectra. It was found that the formation of the H-aggregates in the monolayer of higher dye fraction strongly depends on the compression process; the conventional compression by moving the barrier does not bring about the formation of the H-aggregates, while the compression by spreading the dye solution does cause the formation. Moreover, the formation of H-aggregates breaks the homogeneous orientation ($C_{\infty v}$ symmetry) of the hemicyanine molecule in the monolayer on water. By the deposition of the H-aggregated molecules onto a substrate, the monolayer obviously changes its symmetry into homogeneous $C_{\infty v}$ structure, where H-aggregated oligomer and monomer coexist. On the contrary, mixed hemicyanine monolayers with arachidic acid maintain their structure of the homogeneous orientation after the deposition in spite of a slight change in average tilt angle of the molecule. We infer that the electrostatic interaction between the anion (arachidic acid) and the cation (hemicyanine) makes them rigidly packed. In the compression of the mixed monolayer and pure hemicyanine monolayer on water by the conventional compression by moving the barrier, they maintain their symmetry and orientational structure.

From a view point of nonlinear optics in L and LB film, we found some important results. In evaluating these structures, previous workers neglected the frequency dispersions of the dielectric constant of the monolayer, $\varepsilon_m(\Omega)$ at frequency W. By comparing the computer simulation and the SHG measurement, we found that $\varepsilon_m(2\omega) \neq \varepsilon_m(\omega)$ should be taken into account. We could determine $\varepsilon_m(2\omega)/\varepsilon_m(\omega)$ of various kinds of monolayer by measuring the SH light intensity with parallel and perpendicular polarizers as a function of the polarization direction. If we have data of $\varepsilon_m(2\omega)$ and $\varepsilon_m(\omega)$, we can even determine the ratios of the susceptibility tensor elements without neglecting the contribution of the local field factors.

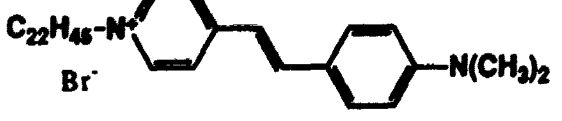

Fig. 1 Hemicyanine dye

HP15

MOLECULAR GRAPHICS IN THE STUDY OF THE STRUCTURE OF LB FILMS

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ABSTRACT

Molecular graphics has found wild applications in many aspects of chemistry such as drug design and protein engineering. However, seldom efforts have been put on the study of the structure of LB films. This paper describes some molecular graphics methods which have been used in our laboratory in the study of the structure of LB films and the structure of J-aggregates.

The arrangement of molecules in the LB films and the structure of J-aggregates are interesting aspects of the study of LB films. They are also important in the study of molecular electronics. Molecular graphics has not only been used to show the structure of LB films, but also to measure the molecular area in the LB films.

Molecular graphics cooperated with molecular mechanics and molecular dynamics can be used to study and even predicate the structure of the LB films. Thus, the experimental results can be explained. Molecular graphics can also predicate the property of the LB films.

A molecular graphics program run on IBM PC has been developed to study the LB films. The program can build the 3-dimensional molecular model, and measure the molecular area. Molecular mechanics study has found the most probable structure of a kind of cyanine LB film, and the calculation process and the result was shown by molecular graphics.

Molecular graphics is helpful in the research of LB films, and computers can be used to simulate the LB films.

HP16

EVALUATION OF HORIZONTAL LIFTING METHOD OF LB FILMS BY USING A QUARTZ CRYSTAL MICROBALANCE

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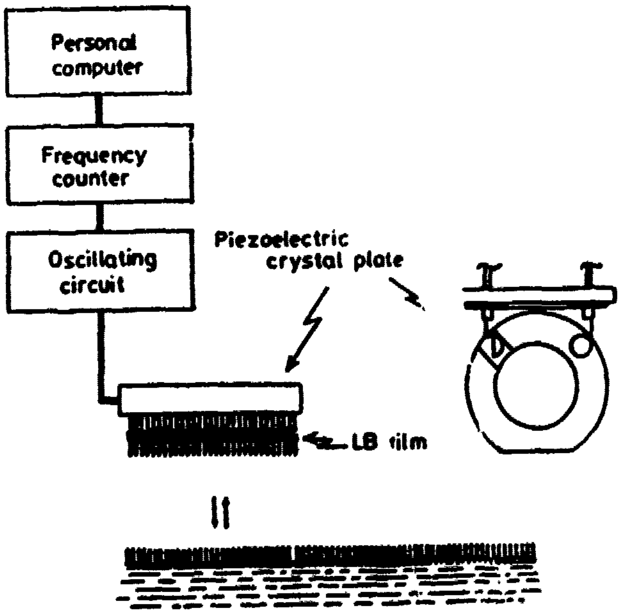
The characterization of Langmuir-Blodgett (LB) films has been widely studied in the dry state by various methods. However, the *in situ* evaluation of LB films during the dipping process has not been fully explored.

In this paper, we report evaluations of horizontal lifting methods of LB films by using a quartz crystal microbalance. Although the horizontal lifting method of LB films is known as one of techniques for transferring monolayers onto a substrate, quantitative characterizations of a transfer ratio of monolayers and transferring mechanism because of difficulties of studying those parameters quantitatively. We observed the transfer ratio and transfer mechanism of horizontal lifting method of LB films by using a quartz crystal microbalance (QCM) as a substrate. QCM is well known to detect a mass on the plate from frequency changes in a nanogram revel. Thus, the transferred weight on the QCM substrate can be determined directly in a ng level from frequency changes of the QCM plate.

In the case of vertical dipping methods, monolayers having hydrophilic head groups were not transferred with a good transfer ratio. On the contrary, most monolayers were able to be prepared by the horizontal lifting method with a transfer ratio of 2 and their LB films showed well oriented structures from X-ray analyses.



Session IP

Biological and biomimetic aspects,
BLM

IP1

PULMONARY SURFACTANT PROTEIN SP-C AND PHOSPHATIDYLCHOLINES IN BILAYERS AND MONOLAYERS

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Pulmonary surfactant is material which lowers surface tension in the lung alveoli, so that it reduces the work of breathing and prevents alveolar collapse or atelectasis at low lung volumes. The material consists of about 90% lipids, of which dipalmitoylphosphatidylcholine, DPPC, is the major component, and at least four proteins, SP-A, SP-B, SP-C, and SP-D. Two of these proteins, SP-B and SP-C, are very hydrophobic and are considered to help in the process of transferring the lipid from bilayers, the form in which it is secreted by lung cells, into a monolayer at the air-water interface.

The interaction of the protein SP-C with saturated phosphatidylcholines in bilayers and monolayers has been studied by ^{2}H-nuclear magnetic resonance spectroscopy, high sensitivity differential scanning calorimetry, and epifluorescence of monolayers under compression.

It has been observed that SP-C produces a perturbation in the packing of the saturated PC. The gel to liquid-crystalline phase transition was broadened by SP-C as seen both by calorimetric scans and in the first moments of ^{2}H-nmr spectra from perdeuterated chains in the lipids. The T_1 relaxation times of the acyl chains was essentially unaffected by the protein. The T_{2e} of the chains was decreased in the liquid crystal and its temperature dependence was altered in the gel. Initial studies indicate that the first moments of the spectra ^{2}H-nmr of the head group of DPPC were not substantially affected by SP-C. SP-C affected the distribution of condensed and fluid domains in monolayers in the liquid expanded/liquid condensed region by producing more, smaller, condensed domains in the two phase region than seen for pure lipid monolayers. SP-C appeared to provide nucleation sites for condensation during the LE/LC transition.

These results are consistent with SP-C being embedded, at least in part, in the acyl chains of the lipid, and there being a relatively good matching of the packing of the protein with the lipid so that severe packing dislocations in PC bilayers are not produced by the proteins. (Supported by the Medical Research Council and the Natural Sciences and Engineering Research Council of Canada.)

IP2

SIMULTANEOUS ELECTRICAL AND OPTICAL INTERFEROMETRIC MEASUREMENTS OF PRESSURE AND APPLIED POTENTIAL INDUCED BILAYER LIPID MEMBRANE DEFORMATION

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Hydrostatic-pressure- and transmembrane-potential-induced deformations of glyceryl monooleate (GMO) and bovine-brain phosphatidylserine (PS) bilayer lipid membranes (BLMs) were investigated by simultaneous optical and electrical measurements. The investigation of a large number of samples established subtle variations in the observable parameters (appearance of concentric optical interference fringes, capacitance, voltage-dependent capacitance, resistivity and voltage-dependent resistivity changes as a function of hydrostatic pressure and applied potential) of separately formed, but otherwise identical, BLMs. Simultaneous optical and electrical measurements were performed on given BLM preparations, each of which had relatively small Plateau-Gibbs borders and "survived" for six hours or longer. Application of (4-21) mNm^{-2} hydrostatic pressure (P_{hp}) resulted in the appearance of concentric optical interference fringes (some of which were transient) which allowed the calculation of translational (lateral) displacements (F_t) and curvature changes (F_c). Plots of F_c values against P_{hp} gave good straight lines from which interfacial tensions (γ) of GMO and PS BLMs were calculated to be 0.22±0.02 mN/m and 0.29±0.03 mN/m, respectively.

Support of this work by a grant from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

DESIGN AND PROPERTIES OF LANGMUIR FILMS OF PHOTOSENSITIVE PROTEINS

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Design of Langmuir films employing biocomponents is a field of much research in recent years [1]. Photosensitive membrane proteins (bacteriorhodopsin or bacterial reaction centers) in which effective directional light-dependent electron (or proton) transport take place [1-3] are not only unique systems for investigation of molecular mechanism of photoreception but also promising as potential sensor materials in molecular electronics. A problem of fundamental importance is the design of highly ordered Langmuir films incorporating such proteins to provide vectorial charge transfer.

The optimal conditions for stable mono- and multilayer preparations of reaction centers from Chl. aurantiacus, Rb. sphaeroides, Rps. viridis and bacteriorhodopsin were determined [2,3]. It was shown that optical and photoelectrical properties of the obtained Langmuir films were similar to those of the native proteins. The sign of photopotential provides evidence that the H-subunit of Rb. sphaeroides is oriented preferentially to the water at the air/water interface. In contrast to this, the H-subunit of Rps. viridis orients to the air, because of the presence of a more hydrophilic cytochrome-subunit in these reaction centers. The ratio 20:80 was obtained for oppositely oriented protein molecules [2].

The possibility was shown [3] for regulation of the orientation and the lifetime of the intermediates in the bacteriorhodopsin photocycle by using Langmuir techniques combined with immobilization of the protein in a polymer matrix.

1. Yu.M.Lvov, V.V.Erokhin, S.Yu.Zaitsev Biol.Membranes 9 (1990) 917
2. N.A.Kalabina, S.Yu.Zaitsev, M.A.Kutusov et al. Biol.Membranes 7 (1990) 1086
3. S.Yu.Zaitsev, S.V.Dzekhtser, V.P.Zubov Studia Biophysica 132 (1989) 105

IP4

INTERFACIAL THERMODYNAMICS and ACTIVITY OF IgG MONOLAYERS

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Isotherms of antibody films have been examined to determine the behaviour and conformation of IgG molecules at the gas water interface. Films of polyclonal IgG, monoclonal IgG and $F(ab)_2$ fragments were examined over a temperature range of 15-40°C. These were compared with those of human serum albumin which is one of the proteins commonly used for preparing Langmuir films.

All the isotherms exhibited an isopiestic point, that is a point on the π-A diagram that is common to all temperatures. The isopiestic point suggests that the monolayer exsists in two or more phases. In particular, the isopiestic point of films of whole IgG and of fragments occurs at around the same pressure, (between 29 and 31 mN/m), and all these isotherms have similar shapes. It can thus be concluded that the crystallizable fragment of the antibody plays a negligible role in determining its behaviour at the gas-water interface.

From the isotherms, we have calculated the surface compressional modulus, entropy and the free energy of desorption of the molecules at the interface. A simple physical model is proposed which explains the curves in terms of the flexibility of the hinge region of IgG molecules and $F(ab)_2$ fragments.

The immunological activity of films of whole IgG and fragments upon transfer to a glass slide were determined by enzyme linked immunoassay. Films were deposited by both dipping and touching. The activities were similar in both cases, and over 3 times greater than that of adsorbed films, indicating that the L.B. method can furnish high surface densities, but in the case of antibodies, with little control over their orientation.

IP5

SURFACTIN : INTERFACIAL PROPERTIES AND INTERACTIONS WITH MEMBRANE LIPIDS IN MIXED MONOLAYERS

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Surfactin, which is produced by several strains of *Bacillus subilis* is the most efficient biosurfactant so far known. Moreover this compound possesses an antibacterial activity and inhibits the fibrin clot formation. It is a cyclic lipopeptide consisting of a heptapeptide and a lipid portion which is a mixture of β-hydroxy fatty acids (C_{14} and C_{15}) :

$$\begin{tikzcd}
\text{L-Glu} \arrow[r] & \text{D-Leu} \arrow[r] & \text{D-Leu} \arrow[d] \\
\beta\text{-OH-}C_{14\text{-}15} \arrow[u] & & \text{L-Val} \arrow[d] \\
\text{L-Leu} \arrow[u] \arrow[r] & \text{D-Leu} \arrow[r] & \text{L-Asp}
\end{tikzcd}$$

We have studied the interfacial properties of surfactin as a function of temperature and subphase composition (pH and nature of the ions). From the compression isotherms we have determined the pK of the surfactin at the interface (pKs) that is 2 units above the pK in solution.

Because the biological properties of surfactin seem related to its interactions with membrane cells we have studied the interactions of surfactin with membrane lipids. In mixed monolayers spread on an acid subphase, surfactin is miscible with dimyristoyl phosphatidylcholine (DMPC). The mixture behave ideally as indicated by the examination of the mean molecular areas (no deviation from the additivity rule) and transition pressures. Isotherms of mixed surfactin-cholesterol monolayers show that surfactin interacts non ideally with cholesterol (positive deviation of the mean molecular areas).

IP6

Interfacial Films of The Membrane Protein: Photoreaction Unit

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Recently, thin films of proteins attract much attention of researchers in both fields of biological science and material science. Most of these works are concerned with soluble proteins. We show an example of the Langmuir-Blodgett films of a membrane protein with high molecular weight in this report. Photoreaction unit (PRU) is an integral membrane protein with molecular weight of 368,000 daltons. It is a pigment protein complex consisting of a photoshynthetic reaction center and light-harvesting chlorophyll proteins. The shape of PRU has a hexagonal symmetry.1) Top and bottom faces of PRU are hydrophilic while side faces are extremely hydrophobic.

We purified PRU from photosynthetic bacterium Rhodopseudomonas viridis by electrophoresis in the presence of a detergent 3-[(3-cholamidoproryl)dimethyl ammonio]-1-propanesulfonate (CHAPS).2) The purified PRU is soluble in low ionic condition but insoluble in high ionic condition. It could be spread on the surface of the solution containing 3 M ammonium sulfate and 100 mM Tris HCl (pH 8.2) to be a thin layer film. We estimated the area of the thin layer by the suminagashi method with sumi-suspension (Japanese traditional ink).3) The area of the thin layer was almost proportional to the amount of added PRU. The absorption spectrum of the thin layer was similar to that of native PRU solution. It suggested that PRU was not denatured by the surface tension while spreading on the air-water interface. Densely packed PRU in the thin layer was observed by electron microscopy with negative staining. Surface pressure of PRU could be also measured by a LB trough in the absence of sumi-suspension.

Above results showed that the monolayer film of PRU was formed on the air-water interface.

References

1) Miller, K.R. (1982) Nature 300, 53-55.
2) Hara, M., Namba, K., Hirata, Y., Majima, T., Kawamura, S., Asada, Y. and Miyake J. (1990) Plant. Cell. Physiol. 31, 951-960.
3) Ishii, T., Muro, J., Yamakoshi, Y. and Shimizu, M. (1987) Nihonkagakukaishi (in Japanese) 11, 2064-2069.

IP7

Preparation of Langmuir-Blodgett Films of the Photosynthetic Proteins

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Thin films of proteins have a great possibility of constructing new biological devices with interesting functions. Many works on protein films have been reported with respect to soluble proteins, but the examples with membrane-bound ones are not so much. Reaction center(RC) from a photosynthetic bacterium Rhodopseudomonas viridis is a typical membrane protein with a molecular weight of 137,000, and exhibits sequential functions of charge separation and electron transfer following light absorption. Its structure has been revealed by X-ray crystallography, and RC consists of the hydrophilic H- and C-subunits and the hydrophobic L- and M- subunits1). Here, we have fabricated a Langmuir-Blodgett film of RC and studied the properties of the film.

We purified the RC by gel filtration chromatography in the presence of a detergent lauryldimethylamine N-oxide (LDAO). LB films were prepared with a homemade and computer-controlled film balance. The purified RC could be spread on the subphase containing 2 mM $BaCl_2$ and 2 mM PIPES(pH 7.0) by means of the glass rod method. With the decrease in surface area per RC, the surface pressure-area isotherm showed an abrupt transition and a steep increase in the surface pressure. This suggested the formation of a densely packed monolayer. Then, the monolayer was transferred to a solid substrate at the surface pressure of 25-35 mN/m by the vertical lifting method. The absorption spectrum of the LB film was similar to that of the native RC solution, suggesting that RC was not denatured during the LB film fabrication. Furthermore, we have sandwiched the LB film with a pair of electrodes, and detected the electrical responses of the device upon light-excitation.

These results showed that the LB film of RC was still retained the activity to convert light energy to electric energy.

Reference

1) Deisenhofer,J.,Epp,O.,Miki,K.,Huber,R. and Michel,H.: Nature, 318,618-624 (1985)

ADSORPTION OF PROTEIN AT THE AIR/BUFFER INTERFACE: EVIDENCE FOR LATERAL INTERFACIAL DIFFUSION

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Adsorption of protein at interfaces plays a key role in foaming and emulsifying processes of the food industry. Surface tension lowering and stability of the interfacial film are determined by its molecular structure and dynamics. Recent data (Coke et al., 1990) show that the mobility of β-lactoglobulin adsorbed at the air/buffer interface is very low

In this communication, we present evidences for the very fast diffusion of Rubisco molecules at the air/buffer interface. Rubisco was adsorbed either by local deposition in the subphase or by spreading, using a capillary glass rod. The rise of surface presure, measured 19 cm away, was immediate in the spreading experiment, and accompanied by a burst of surface fluorescence. When Rubisco was adsorbed by local deposition in the subphase, surface pressure rise was not so fast, but surface pressure was significant before any protein could be detected in the subphase below the Wilhelmy plate. In both cases, surface pressure rise could be impeded by interposition of a surface barrier between the deposition point and the surface pressure measurement device. Removal of the surface barrier results in an immediate rise of the surface pressure 10 cm away.

Our qualitative results and those of Coke et al. could be reconciled by hypothesizing that protein interfacial diffusion is strongly dependent on surface pressure. Their results were obtained at a surface pressure of 20 - 30 mN/m. In our experiments, surface pressure was hardly detectable at the beginning of diffusion.

IP9

INCORPORATION OF MEMBRANE PROTEINS INTO LIPID SURFACE MONOLAYERS: CHARACTERIZATION BY MEASUREMENTS OF ISOTHERMS AND BY ELECTRON MICROSCOPY

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The development of complex functionalized surfaces is a prominent goal of organic thin film technology. Proteins are particularly interesting objects to incorporate into such systems since they embody specialized machineries dedicated for specific tasks and optimized by the principles of evolution. We have examined techniques to insert detergent solubilized membrane proteins into lipid surface monolayers and have transferred these systems onto solid substrates for further characterization.

On a Langmuir film balance we have optimized the conditions that lead to the insertion of photosynthetic reaction centers from *R. rubrum* into monolayer films of behenic acid as judged from pressure-area isotherms. For the incorporation we spread protein solutions at extremely low detergent concentrations onto the pre-spread lipid monolayer.

Subsequently, we have optimized the transfer of these structures to solid substrates. After deposition of the lipid/protein films and Carbon-Platinum shadowing, we have assessed the topology of the replicas and found essentially two types of particles that are tentatively attributed to (mostly linear) protein aggregates and larger inclusions of detergent micelles.

IP10

PHOTOELECTRIC RESPONSE OF BLACK LIPID MEMBRANES INCORPORATING AMPHIPHILIC AZOBENZENE DERIVATIVE

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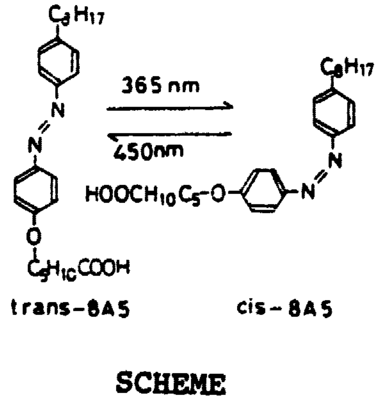
The lipid membrane system containing dye molecules capable of photoisomerization, e.g., retinal, azobenzene, spiropyran, is of great importance as a model of biomimetic visual systems. In this study, we have fabricated the black lipid membrane(BLM) of egg lecithin modified by an amphiphilic 4-octyl-4'-(5-carboxypentamethyleneoxy)azobenzene(8A5).

The BLM cell was of conventional type having a quartz window for illumination. In the Teflon septum which separated two cell compartments, there was a hole of 1.5–2 mm diameter, in which the BLM was formed by "brush technique"[1]. The membrane-forming solution consisted of egg lecithin(Sigma)(50 mg)(unmodified BLM) or of 8A5(Dojin)(4.5 mg)+egg lecithin(50 mg)(modified BLM) in a 0.65 ml n-decane–chloroform solution(10:3 by volume). The DC voltage, V_{app}=0–50 mV, was applied to the cell and the photoelectric response was monitored by an electronic picoammeter.

The BLM was subjected to 60 min irradiation with 450 nm light followed by about 10 min irradiation with 365 nm light at V_{app}=10 mV, and then the photoelectric response was examined. A sharp current signal in the negative direction was observed when visible light was thrown over the modified BLM, which decayed to the original value with a time constant of about 50 s (Fig. 1). A successive irradiation with UV light gave rise to weak current signal in the positive direction. The unmodified BLM did not show any photoresponse. A comparison of the action spectrum of the negative photocurrent with the absorption spectrum of 8A5 in solutions suggests that photoresponse is initiated by excitation of the cis form of 8A5.



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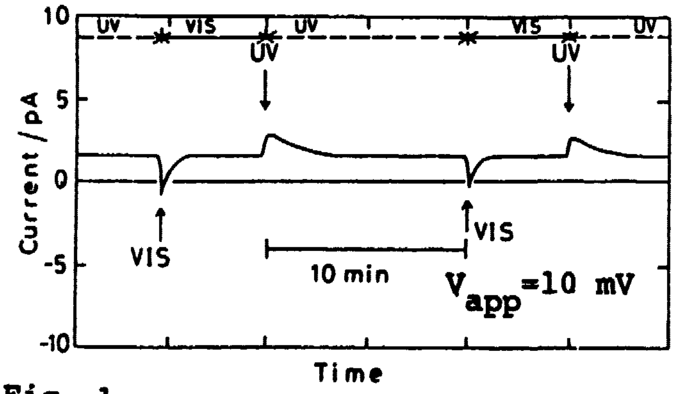

Fig. 1. Time dependence of the change of current upon continuous illumination of the modified BLM with UV(λ=365 nm) and visible (λ=450 nm) light. The arrows indicate onset of UV and visible light.

[1] P. Mueller, D.O. Rudin, H.T. Tien and W.C. Wescott, Nature 194, 979(1962) ; J. Phys. Chem., 67, 534(1963)

IP11

CHARACTERIZATION OF MONOLAYERS AND LANGMUIR-BLODGETT FILM OF DRY AND WET CHLOROPHYLL *a*.

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The π-A and $\Delta\sqrt{}$-A isotherms of dry and wet chlorophyll *a* at the gas-water interface were measured. It was observed that the properties of chlorophyll *a* from dry non-polar organic solvents differed from that of wet non-polar organic solvents. This is probably due to the state of chlorophyll *a* molecules which can exists as non-hydrated or hydrated monomers, dimers and/or oligomers.

A variation in the collapse region is observed for dry chlorophyll *a* when we change the relative humidity and the speed of compression, moving from ~ 28 mN/m to ~ 48 mN/m. By the photophysical studies such as absorption, circular dichroïsm, fluorescence and infrared of LB films, we concluded that the wet chlorophyll *a* forms self-organized molecular assemblies consisting of at least 5-6 chlorophyll *a* molecules and some bonded water molecules.

IP12

INTERACTION OF CYTOCHROME C AND RIBONUCLEASE WITH PHOSPHOLIPID MONOLAYERS .

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Abstract : Protein / phospholipid interactions were investigated with the pressure - area technics in monolayer . Ribonuclease and cytochrome C,water soluble and positively charged proteins , were shown to be attracted by opposite charged phospholipids spread at the interface air-water . This attraction is weaker with ribonuclease than with cytochrome C . With zwitterionic phospholipids the insertion of the protein depends essentially of the fluidity of the phospholipid monolayer . The possible change of conformation of these proteins would allow their insertion into the hydrophobic part of the phospholipids. Cytochrome C and ribonuclease would not only interact with phospholipids but form aggregates at the interface .

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IP13

A FOURIER TRANSFORM INFRARED SPECTROSCOPIC INVESTIGATION OF HYDROPHOBIC PEPTIDES IN LIPID ENVIRONMENT : A MONOLAYER STUDY

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The properties of the tripeptide Ala-Ala-Tyr and those of Leu-Leu-Tyr were investigated in monolayers by resolution enhanced Fourier-transform infrared spectroscopy. Interaction with an acidic phospholipid(DPPA) in the mixed monolayer results in changes in the backbone amide groups, whereas neutral phospholipid has no effect on the peptides. The conformations adopted by the two peptides in the lipid environment are different from each other. From the position of the amide I bands of the peptides, it can be inferred that the groups are in non-ordered conformation. These observations have important implications for the mechanisms of peptide hormone-receptor interactions and particularly for the role of membrane lipid phase as a biologically important modifier of the hormone conformation.

IP14

DRUGS IN BIOMEMBRANE MODELS. A MONOLAYER STUDY OF THE INTERACTION BETWEEN A PHOSPHOLIPID AND TWO ANTIBIOTICS, LASALOCID AND MONENSINE.

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Phospholipid membranes with low electric resistance and high ion selectivity can be produced by the addition of small amounts of a variety of compounds referred to as ion-carriers or ionophores, most of which exhibit antibiotic activity.

Our study deals with two such antibiotics, lasalocid and monensin (Na salts) belonging to the family of monocarboxylic polyethers, and their effect on Langmuir films of dipalmitoylphosphatidylcholine. This system provides a model for one half of the biomembrane.

Investigations on bilayer systems of these compounds report that the antibiotics are implanted in the lipophilic part in a large ring configuration [1,2], the ether oxygens and the carboxylic groups are directed inwards and the periphery is covered with non polar groups, in such a way that they constitute the lining of a pore through which ions are allowed to pass.

The usual penetration experiments of drugs into the monolayer could not be performed due to insolubility of the antibiotics in the aqueous subphase. However, important modifications in the lipid organization took place when small quantities of the compounds were introduced into the spreading solution, as shown from the π-A isotherms.

We can summarize the results as follows:

- the characteristic phase transition at 6 $mN.m^{-1}$ disappeared as a consequence of local area expansion
- the area expansion was concentration dependent in the domain studied, molar ratio antibiotic/lipid: 1/240, 1/120 and 1/60

The film area occupied by the antibiotics alone have been estimated from the π-A curves of the pure antibiotics at various concentrations of the spreading solution.

Their molecular area observed at the pressure of maximum lipid layer expansion had consistent values. The areas occupied at $\pi = 0$ were also determined.

The results indicate a very strong interaction between many lipid molecules and one molecule of the antibiotics leading to higher rigidity of the film in the transition region.

1. H.H.Mollenhauer, D.J. Morré and L.D.Rowe,
Biochim. Biophys. Acta, 1031 (1990) 225

2. F.M.Menger, Bol. Soc. Chil. Quim., 35 (1990) 33

IP15

APPLICATION OF TWO-DIMENSIONAL CRYSTALLIZATION OF PROTEINS ON PLANAR LIPID FILMS TO STRUCTURE DETERMINATION BY ELECTRON CRYSTALLOGRAPHY

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Electron image analysis of thin two-dimensional (2-D) crystals allows high-resolution structure determination of biological macromolecules (Henderson et al., *J. Mol. Biol.*, 1990, 213, 899-929). The obtention of 2-D crystalline assemblies of macromolecules constitutes one of the main limiting steps for such studies. A general method of crystallization has recently been developed for soluble proteins (Uzgiris & Kornberg, *Nature*, 1983, 301, 125-129). This method is based on specific interaction between soluble proteins and ligands coupled to lipid molecules and incorporated in a lipid film at an air-water interface.

In order to understand the process of crystal formation involved in this technique, we have carried out a systematic analysis of parameters involved in the formation of cholera toxin B-subunit 2-D crystals on GM1-containing lipid films. The influence of concentrations of protein and of lipid components, as well as of the surface pressure have been analyzed.

These results have been used to obtain 2-D crystals of annexin V, a Ca^{2+}-dependent phospholipid binding protein. The projected structure of annexin V at 20 Å resolution allows to resolve four domains of 70 amino acids per molecule. The implication of these results will be discussed.

IP16

Physicochemical properties of hepatitis B peptide fragments at an air/water and lipid/water interface.

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The development of the immunogenic response is a complex phenomenum in which the interactions between peptide epitopes and the lipid components of the membrane play an important role, at least in the first steps of the recognition process.

In the present paper we describe the interaction of four lipopeptides derived from the Pre S (120-145) sequence of the HBV with DPPC, PC, PE, PA, PS, PI, DCP, Sulphatides and Sphingomyelin.

Parent Peptide Structure: MQWNSTALHQALQDPRVRGLYLPAGG .

Peptide derivatives contained a residue of Pam_3CSS-, Cholanoyl- and stearoyl- residues attached to their amino terminal end. These chemical modifications were carried out in order to modify the hydrophobicity of the peptides and improve their potential antigenicity.

The interactions have been studied by using compression isotherms of monolayers and penetration kinetics. All the peptides showed surface activity and formed stable monolayers. The monolayers were in different ordered states, throughout the compression process, depending on the peptide derivative. The area/molecule, the surface pressure corresponding to the phase changes and the maximum pressure achieved had been determined and were indicative of the existence of different conformations (alfa helix or beta structure) depending on the chemical structure of the peptide derivatives. No collapse pressures in the working conditions were observed.

The presence of these peptides under a monolayer of DPPC caused an expansion in the area occupied per molecule and modified the phase change of the DPPC. The shift in the pressure-area curve of the phospholipid gave the area occupied by the peptide present at the interface. Nevertheless , as there was only a small shift in the pressure-area curve at high surface pressures, one can asume that the peptides were squeezed out during compression.

IP17

TWO-DIMENSIONAL CRYSTALLIZATION OF MUSCLE PROTEIN ACTIN BY ADSORPTION TO CHARGED LIPID MONOLAYER

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Two-dimensional crystal of muscle protein actin was formed by adsorption to charged lipid monolayer[1]. Keys to the procedure are: (1)that this method is suitable for making two-dimensional crystal because it utilizes the air/water interface, and (2)that the protein preserves its physiological activity because it remains within water during the whole process. Those two features are essential for constructing a biochip.

First 100 µl of a buffer solution (containing 10 mM of KH_2PO_4/K_2HPO_4 (pH 7.4), 100 mM KCl, 50 mM $MgCl_2$, 0.2 mM $CaCl_2$, 1 mM ATP, and 1 mM β-mercaptoethanol.) was put into each well (6 mm diameter, 2 mm deep) in a Teflon plate. A slightly excessive amount of phosphatidylcholine + stearylamine solubilized in chloroform and hexane (50:50 in vol/vol) was placed on the surface of the buffer solution to form the lipid monolayer. F-actin solution (10 µl) was subsequently injected into the buffer solution using a micro-syringe. Adsorption was facilitated by electrostatic attraction between the negative surface charge of actin and the positive charge of stearylamine incorporated into the lipid monolayer. The plate was placed in a sealed Petri dish containing water to keep the water level of buffer solution in the well constant. Crystallization was promoted by use of highly fluid egg-yolk phosphatidylcholine and by incubating the specimen at room temperature for half an hour. The protein-stearylamine complexes are expected to migrate within the two-dimensional water surface, colliding more frequently to grow crystal than they would in solution.

Electron microscopy showed that larger paracrystals were obtained more rapidly (30 min) than those (several days) obtained in solution[1], indicating the usefulness of this adsorption method.

REFERENCES

[1] A.TOMIOKA, H.O.RIBI, T.FURUNO, H.SASABE, K.MIYANO and T.WAKABAYASHI, Adv. Biophys., accepted.

THE PROTEIN CONCENTRATION OF IGG MIXED FILMS DEPOSITED ON WAVEGUIDES

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ABSTRACT

The human immunoglobulin G (IgG) is a protein antigen which reacts with antibody to form an antigen-antibody compound. We can produce a fluoro-immunosensor by immobilizing the IgG on the surface of an optical waveguide[1], and the LB method has been expected to be one of useful immobilizing methods[2]. In this paper, we incoporated the IgG in subphase into the DPPC monolayer on the subphase surface and measured the relative amount of IgG in the mixed film by depositing the film onto quartz waveguide, and the results show that the relation betweem the amount of IgG penetrated into monolayer and the concentration of protein in subphase conforms to Langmuir's adsorption isotherm.

The IgG solution is injected into the subphase underneath the DPPC monolayer , and the change in surface pressure at constant film area is monitored. The surface pressure change of the mixed monolayer shows a good linearity with the IgG concentration in subphase (Cp) in lower Cp, while Cp>2ug/ml, the slope increases gently and finally attains its maximum point (17mN/m at 10ug IgG per ml). After the fixed film is deposited on the waveguide, a dye (FITC) is coupled to the protein surface. From the fluorescence observation, we know that the protein in the mixed film on waveguide surface can be devided into at least two components, one is the protein penetrated into the film, and the other is the adsorbed protein on the polar head of phospholipid. When Cp<10ug/ml, there may exist a adsorbed monolayer formation, while Cp>10ug/ml, there exists a multilayer protein adsorbed in the film. But the number of penetrated protein is limited by the energy barrier that the protein should overcome when they penetrate into the film. The relationship between the amount of penetated protein and the concentration of protein in subphase conforms to the Langmuir's adorption isotherm. The mixed film on the waveguide surface seems have good stability during the experiment time. These results show the feasibility of using the IgG immobilized LB films as sensing membranes for biosensors.

[1]. Bin Lu, Yu Wei, J. Transduction Tech., 2(4),p28(1989)
[2]. M.Sriyudthsak,et al, Thin Solid Films, 160,p463(1988)

IP19

FACTORS DETERMINING STABILITY OF BACTERIOCHLOROPHYLL MONOLAYERS

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Study of bacteriochlorophyll **a** (called BChl here) in monolayer form requires exact knowledge of the factors which may affect the chemical stability of this compound. Because BChl is more reduced than the more commonly studied chlorophyll-a, potential problems arising from oxidative reactions must be more closely apprehended. Although early studies of BChl monolayers by Brody indicated that BChl was readily oxidized to e. g. a desvinyl chlorophyll derivative, no systematic study of the important factors governing BChl has yet appeared.

Spread monolayers, on buffered, monolayer grade water, were subjected to a variety of conditions thought important for the chemical integrity of BChl. The effects of the following factors were studied: Subphase pH, oxygen content of the atmosphere over the monolayer, temperature, light (fluorescent, incandescent actinic and safety green) and the influence of antioxidants both dissolved in the subphase and present as a second component of the monolayer (ascorbyl palmitate). BChl monolayers were formed by spreading from chloroform solution and compressed to a surface pressure of 20 mN m^{-1}. All variables were held constant except for the specific one being studied. At the termination of an experiment the monolayer was collapsed by compression of Teflon barriers, the monolayer collected and subjected to high performance liquid chromatography (HPLC).

Under conditions in which maximum decomposition was noted, HPLC indicated five major decomposition products, the most important of which was 2'-desvinyl chlorophyll-a. Separated decomposition products were produced in sufficient quantities to allow spectral characterization by Raman spectroscopy, which provides a more characteristic identification than does adsorption spectroscopy.

It was found that decomposition increased progressively with increasing temperatures (12° to 40°). Low pH conditions favored formation of bacteriopheophytin through magnesium removal. Decomposition was maximal in a pure oxygen atmosphere, minimal in a nitrogen atmosphere. Highest stability was attained in complete darkness, and maximum decomposition occurred with irradiation with fluorescent light and oxygen. Greatly decreased decomposition took place with irradiation with green safety light. The presence of antioxidant greatly decreased decomposition rates when present either dissolved in the subphase or present as a monolayer component.

Results of this study provide an accurate experimental basis for future monolayer studies using bacteriochlorophylls.

IP20

CHEMICALLY DRIVEN PHASE SEPARATION IN BLACK LIPID MEMBRANES AND ITS COUPLING TO MEMBRANE FUNCTIONS

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The understanding of order–function–relations in membranes is still a major challenge in membrane research. One particular aspect concerns the coupling of the function of integral proteins to the transversal and lateral organization of the lipids in a bimolecular matrix composed of many components.

We adress this question by studying the coupling of a membrane function (the transport of Cs^+–ions by the ionophore gramicidin) to chemically driven phase changes in black lipid membranes of binary lipid mixtures.

Lateral phase separation in the membrane could be induced isothermally by synthetic polyelectrolytes, as peripheral model proteins. This was shown clearly by a bimodal distribution of gramicidin pores with different conductivities and mean lifetimes.

Another effect of the polymers was a blocking of the gramicidine pores through recharging the membrane positivly. This depended on the concentration, structure, chain length and charge density of the polyelectrolytes.

Using a polymer with functional groups which can be titrated, one can switch between a homogeneous mixed membrane and a phase separated state also by changing the pH.

Finally we investigated the specific binding of avidin to biotinylated lipids in a BLM. Our results gave a first indication, that under certain conditions in connection with calcium ions, the specific binding of avidin may trigger phase separations.

IP21

Immobilisation of Enzyme on Electrode Modified by an Hydrophobic Self-organized Structure: Mediation of the Catalytic Activity of an Hydrogenase via Lateral Diffusion of an Electroactive Amphiphile.

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Growing interest in electrodes modified by immobilized enzymes has been generated by their importance as highly selective surfaces for analytical, electrosynthesis or bioelectronic applications. Recently, we have described a new way to produce modified electrodes supporting active enzyme molecules immobilized in a self-organized structure (1). Glucose oxidase was immobilized on a bilayer self-assembled on a porous template of aluminium oxide coated at a gold electrode. The outer monolayer of the assembly was an electroactive amphiphile able to carry the electron between the enzyme catalytic site and the electrode surface.

To increase our knowledge of the nature of interactions between the enzymes and this artificial bilayer we use, in the present communication, a different oxido-reductase known as relatively hydrophobic (but water soluble), the periplasmic hydrogenase from *Desulfovibrio Gigas*. Compared to an hydrophilic enzyme like glucose oxidase, we found the enzyme molecules incorporated inside the hydrophobic part of the bilayer. This situation represents an interesting step before the immobilization of membrane-bound enzymes, a class of hydrophobic enzymes, unusable at this time for analytical devices.

The main objective of this communication is to describe the structure of the bilayer modified by incorporation of a relatively hydrophobic protein.

A second goal is to demonstrate, both by potentiometric and amperometric methods, the high efficiency of the lateral diffusion of the amphiphilic mediator leading to a kinetic coupling between the catalytic activity of hydrogenase and the electrochemical reaction.

(1) C. BOURDILLON and M. MAJDA. J. Am. Chem. Soc.1990, **112**, 1795.

IP22

IMPROVEMENT OF ENZYMATIC ACTIVITY AND LIFETIME OF LB FILMS BY USING SUBMICRON SIO_2 PARTICLES

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A common problem often being tackled in work on chemical sensor preparation,especially in the case of biosensors, is the lifetime. We have reported the application of Langmuir-Blodgett technique for biosensor preparation which could extend the response region of glucose concentration and improve the life time of biosensor [1][2].

Inspite of numerous work on biosensor[3][4], improvement in the sensitivity and the lifetime of biosensors continues to be a main goal of investigation. In this paper it has been reported that the activity and lifetime of glucose oxidase membrane has been improved by introduction of submicron SiO_2 particles with diameter of ca.30 nm. using LB technique. A new method for preparation and purification of submicron SiO_2 hydrophobic particles has also been developed. Enzymatic ability measurement of immobilized glucose oxidase(GOD) have been conducted by measuring the fading of indigo camine dye oxidized by H_2O_2 released from the enzymatic reaction. Activity of GOD membrane measurement showed that the ultrafine hydrophobic SiO_2 particles immobilized in LB films could help GOD to be incorporated into films. After incorporated into the SiO_2-LB film GOD retained its enzymatic activity. On top of that, because of its firm adsorption on the SiO_2 particle surface,GOD activity per area of membrane increased. The life time of GOD in the lipid-SiO_2 LB film was much longer than in that without SiO_2 particles. (Table I,II)

REFERENCES
1.J.R.Li,M.Cai,T.F.Chen and L.Jiang, Thin Solid Films,180(1989)205.
2.F.Q.Tang,J.R.Li and L.Jiang, Chemical Sensors,Vol.10,No.1(1990)26(in Chinese).
3.H.Shinohara, M.Aizawa and H.Shirakawa, Chem.Soc.Jan.,3(1986)465.
4.T.Morizumi, Thin Solid Film,160 (1988)413.

IP23

PHOTORESPONSE OF LB FILM CONTAINING BACTERIORHODOPSIN

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Bacteriorhodopsin(BR) molecules in the purple membrane(PM) are organized into a two-dimentional hexagonal lattice of trimers which are surrounded by about 30 lipid molecules. In this work, purple membrane of Halobacterium holobium has been introduced into LB film of soybean phospholipid and the orientation of bacteriorhodopsin in multilayer LB films has been measured by linear dichroism. Experimental results showed that bacteriorhodopsin molecules had a preferential orientation, the angle(Θ) between the film plane and the transition dipole moment of retinal chromophore was 68.4° which is close to the value in native purple membrane, the shape and peaks position of PM LB film in visible absorption spectra and FTIR were the same as those in native PM suspension.

The relative amount of the photocycle intermediate M412 of PM in multilayer LB film was determined by measuring the amplitude of flash-induced absorbance changes at 412 nm with a single-kinetic spectrophotometer. Light-induced absorbance changes were initiated by a camera photoflash lamp (0.2 ms half-bandwidth) with appropriate filter. It has been found that the M412 decay rate of the PM fragment in LB film is slower than that in the suspension of PM fragment.

The photoresponse of PM fragment multilayer LB film has also been investigated with flash photolysis method. The study showed that not only at low temperature, but also at room temperature could be formed and detected the photocycle intermediate. Fig.1 shows the changes of photocycle intermediate in a multilayer PM LB film at a relatively longer time, providing a model for investigation of the primary process in visual exitation.

IP24

FUSION OF PHOSPHOLIPID VESICLES ON SUPPORTED MONOLAYERS: A NEW TECHNIQUE TO PREPARE SUPPORTED PLANAR BILAYERS.

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In recent years, single supported planar bilayers (SPBs) have become increasingly popular as model systems for biological membranes. These model membranes are especially useful for studying the binding of macromolecules by total internal reflection fluorescence microscopy (TIRFM) and the lateral diffusion of membrane constituents by fluorescence recovery after photobleaching (FRAP). Further, these membranes are ideal for structural studies, for device fabrication (biosensors), and for studies of cell-cell and cell-membrane interactions.

A major difficulty of the previous techniques to prepare SPBs was the functional reconstitution of integral membrane proteins into the planar membranes, since proteins which in a biological membrane are laterally mobile became immobilized in SPBs. Therefore, we investigated the fusion of unilamellar phospholipid vesicles on quartz slides which had been coated with a monolayer of 1-palmitoyl-2-oleoyl-phosphatidylcholine (POPC). The formation of the second phospholipid monolayer was followed by TIRFM and a complete bilayer was formed after incubation with POPC vesicles (containing 0.2 mol% NBD-eggPE) at concentrations as low as 25μM. However, rates and amounts of fusion are highly dependent on ionic strenghts and divalent cation concentrations in the fusion buffer. Adsorbed vesicles could be removed by washing with buffer. Lateral diffusion experiments confirmed that extended continuous bilayers had been formed. SPBs prepared by the new monolayer-fusion technique were compared to SPBs of which both layers were transfered by Langmuir-Blodgett techniques. Fluorescence intesities were usually about 10-15% lower in the fused SPBs. The lateral diffusion coefficients of NBD-eggPE were identical in both membranes [$(3.5+0.5)*10^{-8}$ cm^2/s]. Preliminary results indicate that about 50% of the reconstituted integral membrane protein cytochrome b_5 is mobile with a lateral diffusion coefficent of about $2*10^{-8}$ cm^2/s.

IP25

DEPOSITION AND X-RAY SCATTERING OF DNA CONTAINING LB FILMS

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Thin oriented films of DNA could be useful for biosensors based on the complanar binding of specific pieces.

In this work LB films of hexadecylamin - DNA were deposited to solid substrates and investigated by small-angle X-ray scattering.

Hexadecylamin monolayer was compressed to the surface pressure π=25 mN/m. DNA solution was injected under the monolayer. The resulting consentration was $c=10^{-2}$ mg/ml. The interaction was done during 1 hour. The film was deposited to a substrate by horizontal lift technique.

X-ray measurements have indicated a lamelar structure with a spacing D=60.5 A. The spacing corresponds to the amin bilayer thickness (40 A) plus DNA diametre (20 A).

IP26

STRUCTURE AND PHOTOELECTRIC PROPERTIES OF LB–FILMS BASED ON BACTERIORHODOPSIN

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Ordered mono– and multilayer films consist of 1–75 or approximately 1000 layers were fabricated from purple membranes (PM) of Halobacteriun halobium by Langmuir and electrosedimentation techniques, respectively. PM monolayers formed from hexan suspension on the air/water interface were deposited onto different solid supports. Circular dichroism and kinetic absorption spectroskopy were used to investigate the effect of organic solvents on chromophore structure and functional properties of bacteriorhodopsin (BR).

PM monolayers oriented with it's cytoplasmic side to the support were prepared by making use of LB–technique and PM monolayers with opposite orientation to the support – by Langmuir–Shefer method. The lattice spacing and long–range ordering correlation were measured using a small angle X–ray analysis. Specific structure features of PM monolayers fabricated by Langmuir–Blodgett and Langmuir–Shefer techniques were investigated by scanning tunneling microscopy (STM). STM was used to characterise the PM surface structure in LB monolayers as well as local conductivity properties and types of the structure defects. The resalts of STM study of PM surface structure are compared to the resalts of similar study obtained by atomic force microscopy.

The specific photoelectrical activities as estimated per one BR monolayer for LB (˜ 0.4 mV/monolayer) and electrodeposited (5 mV/monolayer) preparations are compared. The possible applications of oriented BR structures in information processing systems as well as technological aspects of their fabrication are discussed.

IP27

CONDUCTIVITY IN SPREAD LIPID MONOLAYERS

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The literature provides conflicting data concerning the effects of spread monolayers on measurement of electrical conductivity in the air-water interfacial region. The dependence of such conductivity on several monolayer parameters--lipid type, surface pressure, subphase composition-- has been investigated here to elucidate the mechanisms by which spread monolayers may affect ion mobility near the water surface. Utilizing an AC bridge at 1600 Hz and rigorous control of water levels throughout the period of measurement, conductivity changes have been determined for a series of lipids which differ from one another principally by the characteristics of their headgroups. Lipids used have been predominantly those which do not undergo phase transitions short of their collapse point. These compounds include: Dioleoylphosphatidylglycerol, (DPG), which bears a negative charge; Dioleoyl 1-[N-(trimethylammonium propyl)]carbamoylglycerol, (DOCA), a positively charged lipid; Dioleoylphosphatidylcholine, (DOL), which is switterionic. For reference, conductivity has been measured with dioleoylglycerol, a compound bearing no charge. In addition to lipids, several metal bearing surface active phthalocyanines have also been investigated.

In order to describe conductivity changes in these systems, the following relationship has been utilized:

$$\rho_P = \frac{G_p - G_{35}}{G_{35}} \qquad (1)$$

where G_P is the conductivity taken at surface pressure P and G_{35} is the conductivity measured at the reference point of 35 dyne/cm.

It has been shown that in all cases the measured conductivity *decreases* with increasing lipid surface pressure, indicating an inhibiting effect on ion mobilities. However, this behavior is markedly dependent upon the type of lipid employed, with the positively charged species exhibiting the smallest change and the phthalocyanines the largest. For DOL and DOG alterations of about 2.5% are observed over the range of compression while 1.5% was obtained with DOG and 0.8% with DOCA. Very much higher numbers (6-10%) were found for Zn and Al phthalocyanines. Consistent with previous photophysical measurements, irreproducible values were observed in the pressure region below 10 dyne/cm for most systems, while above this point values of ρ_P were well behaved.

These results are interpreted in terms of layer organization, the mobility of ions, principally H_3O^+ or OH^-, and characteristics of the electrode-water interface.

Session JP

Molecular recognition, self-assembling systems

JP1

Surface Modification and Functionalization of Gold by Sulfur-Containing Polymerizable and Polymeric Monolayers

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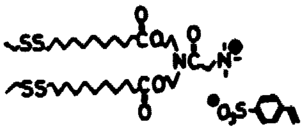
The recent interest in self-assembled monolayer systems stems from a recognition of the potential for their use in detailed studies of surface-function relationships at the solid-liquid interface. The monolayers prepared from the sulfur-containing species, such as thiols and disulfides, at gold surface have been especially well studied because of their tendency toward forming monolayers with well-defined structures. In this paper, preparations of a variety of *polymerizable* and *polymeric* monolayers on gold electrode and their electrochemical properties are described.

Photopolymerization of monolayers[1] The photopolymerization at a spontaneously-assembled polymerizable monolayer (1) on gold could be traced electrochemically by using $Fe(CN)_6^{4-}$ as an electroactive species and was successfully carried out in the presence of a photoinitiator (2) fixed near polymerizable groups, but not in the absence of 2.

Polymeric monolayers Two types of the polymeric monolayer were prepared on gold surface. One of them is a poly(methacrylic acid)(3) or poly(*L*-glutamic acid)(4) carrying a thiol group at one terminus of the polymer chain. The pH-induced conformational transitions were observed for both adsorbed monolayers as an electrochemical information. The another polymeric monolayer is a polyion complex (5) bearing pendent thiol groups. A mechanism and influences of the chemical structures of these complexes for electrical responses are discussed.

Polymerizable System



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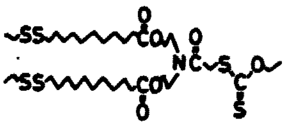

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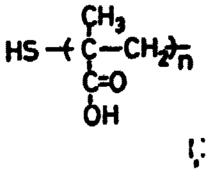
Polymeric System



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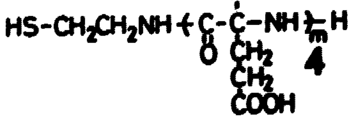

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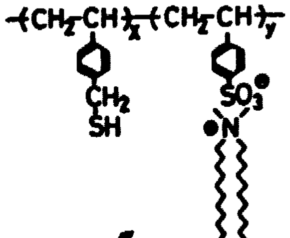

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[1] N. Higashi, T .Mori, M. Niwa, *J.Chem.Soc., Chem.Commun.*, 1990, 225

Control of Reactivity of Adsorbed Monomolecular Films from Polydiacetylene Derivatives to Energy Beams

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Reactivity depending on molecular arrangement or density to energy beams such as ultra-violet (UV) light or electron beam (EB) has been investigated on chemically adsorbed (CA) films having diacetylenic (DA) bonds.

Materials used for the CA films were 18,20-Heneicosadiynoxytrichlorosilane (18-DATS), 7,9-Tetradecadiynyloxypropyltrichlorosilane (7-DATS), and Propyltrichlorosilane (PTS).

The CA films were deposited on silicondioxide/aluminum/silicon substrates by using the CA technique already recommended by Netzer[1)] at different composition ratios of the mixture of the surfactants (18-DATS and PTS or 7-DATS and PTS) in a nonaquaous CA solution. The photo-reactivity of the CA films from the DA derivatives to the UV light (50 uW/cm^2 at 365 nm) was measured by a multichannel UV-visible spectrophotometer.

On the polymerized CA films from the mixture of 18-DATS and PTS (4:1) by the UV irradiation, two absorption peaks appeared at about 560 nm (red) and 675 nm (blue). On the polymerized CA films from the other different mixtures (6:1 and 8:1), one absorption peak appeared at about 560 nm. The CA film from 18-DATS did not react by the UV light irradiation at all. The CA films from pure 18-DATS or the mixture of 18-DATS and PTS (2:1 and 1:1) did not react by the UV light irradiation.

On the other hand, on the polymerized CA film from the mixture of 7-DATS and PTS (2:1), two absorption peaks appeared at about 550 and 675 nm. The CA films from pure 7-DATS or the mixture of 7-DATS and PTS (1:1) did not react by the UV light irradiation. Both the CA films from the mixture of 7-DATS and PTS (3:1 and 4:1) had one absorption peak at about 550 nm.

The reason for the preparation of the blue and red films may be explained as follows. On the blue film from 18-DATS and PTS (4:1), as the length of PTS molecule is very short relative to that of the 18-DATS molecules, one vacancy is formed to the four 18-DATS molecules near the DA group. Thus, the occupied area of DA group increased and became 29 A^2. On the other hand, on the red films (6:1 and 8:1), the density of a DA group in the 18-DATS was estimated to be ca. 27 and 26 A^2, respectively. We had reported the photopolymerization mechanism of Langmuir films having DA bonds[2)], in which a blue film was produced at molecular area of about 29 A^2 and a red film was produced at molecular area of about 27 A^2. These results were similar to those obtained in the previous report. On the CA films from the mixture of 7-DATS and PTS, the preparation of the blue and red film may be explained by the same reasons mentioned above.

In conclusions, we have prepared some CA films from DA derivatives. By changing the molecular area of the DA molecules, photoreactivity of the films was controlled, and the blue and/or red films were obtained.

On the blue and/or red films made from the different mixtures the molecular area of the DA molecules in the CA films obtained are similar to those calculated on L films. The other results obtained by EB irradiation will be presented at the conference.

(1) L.Netzer, and J.Sagiv, J.Am.Chem.Soc.,105,674(1983).
(2) H.Tamura, N.Mino, and K.Ogawa, Thin Solid Films,179,33(1989).

JP3

STERIC AND ELECTROSTATIC ASPECTS OF ANTIBODY BINDING TO HAPTEN FUNCTIONALIZED LIPID MONOLAYERS

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The binding of an antibody to membrane-bound haptens depends critically on the relative geometric arrangement of the hapten and the membrane, and on electrostatic interactions. In order to characterize the requirements for specific binding, the membrane surface and the position of a hapten with respect to the interface was systematically varied. For this study a number of DNP-haptens were synthesized with spacer groups of different lengths (0 to 10 Å) between the epitope and a membrane-anchoring fatty acid. The binding of labeled anti-DNP-antibodies to hapten doped (2 mol%) lipid monolayers was studied by means of fluorescence microscopy at the air/water interface.

With monolayers of DMPC, unspecific antibody adsorption is shown to predominate over specific binding due to electrostatic interactions. The adsorption is reversibly reduced by compressing the monolayer to lateral pressures above π = 10 mN/m. On account of the bulky choline head group, the minimum spacer length which is required for specific antibody binding to occur is, d = 10 Å. Still, at high surface pressures ($\pi > 20$ mN/m), the bound antibody is detached because of steric interference with the lipid head groups.

No unspecific binding is observed to hapten doped monolayers of cholesterol, which carries a small dipole moment and presents a small hydrophilic part to the aqueous phase. As the spacer length on the hapten is increased the epitope protrudes more deeply into the water subphase and binds progressively better to the antibody. Two-dimensional phase separation is observed in the system of protein-bound hapten and cholesterol.

At low π, mixed hapten doped monolayers of cholesterol and DMPC separate into two fluid phases with preferential antibody binding to the cholesterol-enriched phase. For $\pi > 7.5$ mN/m the constituents of the monolayer mix homogeneously and neither specific nor unspecific binding is observed. This is, again, attributed to steric hindrance by the large choline head groups and to the reduced electrostatic interaction of the protein with the interface.

JP4

LANGMUIR-BLODGETT FILMS OF PHOTODYNAMIC STREPTAVIDIN CONJUGATED PHYCOERYTHRIN BOUND TO BIOTINYLATED LIPID MONOLAYERS

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The Langmuir-Blodgett technique has been used to simultaneously orient and couple the photodynamic "antennae" protein, phycoerythrin, to a biotin derivatized phospholipid monolayer film. Phycoerythrin is a highly pigmented, intensely fluorescent but water soluble protein and thus required modification of the traditional Langmuir-Blodgett technique for monolayer preparation. Our approach has involved utilization of the well known, highly specific, and nearly irreversible, streptavidin-biotin complexation. Biotinylated phospholipid monolayers were prepared at the air-water interface and streptavidin conjugated phycoerythrin was then injected into the subphase.

The streptavidin conjugated phycoerythrin was found to preferentially adsorb to the biotinylated monolayers while at the air-water interface. Pressure-area isotherms indicated that oriented monolayer films are formed with the hydrophilic biotin containing head groups exposed to the four biotin binding sites on the streptavidin conjugated proteins. An increase in surface pressure at expanded areas indicated protein adsorption to the monolayer. The binding of protein was confirmed by transferring the monolayers to solid supports and probing the characteristic phycoerythrin fluorescence at 576 nm. The samples were excited with 496 nm light and then scanned from 515 to 670 nm for the emission signal. It was determined that the streptavidin conjugated phycoerythrin binds by what appears to be only a specific (biotin-streptavidin) mechanism.

An extension of this work has included mixture of these biotinylated monolayers with conducting polymerized surfactant systems in an attempt to enhance the mechanical integrity of the films and elicit novel electronic and optical properties. These results suggest a perfectly general technology for the two-dimensional ordering of water soluble protein monolayers with potential bioelectronic, optical and protein structure research applications.

JP5

Molecular Arrangements of Liquid Crystal on Langmuir–Blodgett Monolayers and in Langmuir–Blodgett Multilayers

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Liquid crystal compounds have been attracting attention in display devices, optoelectronic devices and physical investigations, However, one of the most improtant problems with these materials is controlling molecular arrangements. For this purpose, various techniques have been devised(1–2). Recently. There has been much interest in the control of molecular arrangement and packing of liquid crystal by LB technique(3–5). In this work, we investigated the alignment of liquid crystal molecules(8CB) on DPPC LB monolayers with varions packing densities and the aggregation states of liquid crystal molecules (8CB) in multilayers by mixing with strearic acid as the supporting matrix.

Alignment properties of liquid crystal on DPPC monolayers strongly depend on the surface pressure of DPPC monolayers. At the surface pressure of $5 \mathrm{mNm}^{-1}$, $10 \mathrm{mNm}^{-1}$ and $15 \mathrm{mNm}^{-1}$. The molecules of liquid crystal align pendicular to the surface of monolayer. when the surface pressure is over $20 \mathrm{mNm}^{-1}$, the homeotropic alignment of liquid crystal lose. A possibe mechanism has been proposed to account for the alignment properties.

In mixed multilayers, many crystalline domains are observed. These domains are aggregates of liquid crystal molecules in the multilayers. The size and the density of the domains increase with the numble of deposition. Uv–visible absorption spectra shows that the absorption band of the multilayers shifts about 60mm from the monomer band of liquid crystal in chloroform solution. This implies formation of aggregates in the multilayers.

Reference

1. D.Armitage, Appl. phys. Lett, 56 (1990) 1723.
2. K.Ogawa, N.Mino and K.Nakajima, Jpn.J.Appl. phys.29 (1990) L1689.
3. T.Sakuhara, H.Nakahara and K.Fukuda, Thin Solid Films 159 (1988) 345.
4. S.Baker, A.Seki and J.Seto, Thin Solid Films, 180 (1989) 263.
5. J.Y.Fang, Y.Wei, Z.Sun, P.Stroeve, to be published in Phys. Lett, A.

JP6

ULTRATHIN ORGANIC FILMS ON GOLD

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Abstract

Spontaneous formation of ordered organic films can be achieved by the self-assembly technique. In contrast to conventional Langmuir-Blodgett technique self-assembly methods allow rapid film formation. Therefore, this technique is of interest for potential industrial applications. For many practical applications of ultrathin organic films mechanical and thermal stability is mandatory. To stabilize the films on the substrate chemical bonding is required. To this end we synthesized numerous disulfides 1 and thiols 2 with functional terminal groups and investigated their chemisorption on polycrystalline gold surfaces.

1 : $R-(CH_2)_n-S-S-(CH_2)_n-R$ $n = 10,11$

$R = NH_2$, OH, Br, COOH, COONa, $COO-(CH_2)_3-COOH$, COOEt, N-Phthalimidyl, CH_3

2 : $HS-(CH_2)_n-R$ $n = 10,11$ $R = OH$, COOH, $CH=CH_2$, CH_3

Spontaneous formation of a monolayer occurs by dipping the gold substrate in a solution of the thiol or disulfide. Film formation makes use of the strong preference of the sulfur containing group to bind to the gold surface as compared to the other functional groups. The properties of surfaces modified in this way such as chemical reactivity, hydrophilicity and wettability are mainly determined by the terminal groups. Self-assembled monolayers of thiols and disulfides on gold are stable up to 150° and can not be washed off by rinsing with excess solvent. On silver surfaces similar results are obtained.

The terminal functional groups (i.e. OH, NH_2, COOH) of the first monolayer allow the build-up of a second monolayer. We applied esterification and amide formation to self-assembled monolayers in order to build up multilayer structures. Hydroxyl groups could be reacted with cyclic anhydrides forming an ester bond and a new terminal acid group simultaneously.
Transformation of the acid groups to acid chlorides and reaction with stearylamine led to the third monolayer. The long alkyl chain of stearylamine creates a new hydrophobic surface. Simple immersion of the acid terminated surface in a solution of stearylamine results only in partial salt formation as indicated by lower contact angle as compared with the amide modified surface described above.

We have investigated the self-assembled mono- and multilayers by averaging methods suchs as contact angle measurements and reflection infrared spectroscopy, as well as local methods such as scanning tunneling and scanning force microscopy.

JP7

MOLECULAR RECOGNITION BY AMPHIPHILIC CYCLODEXTRIN IN THE LB FILMS

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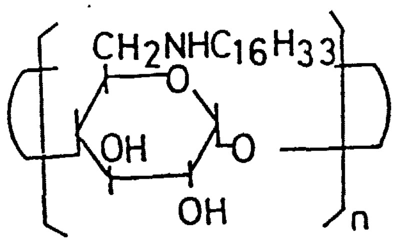
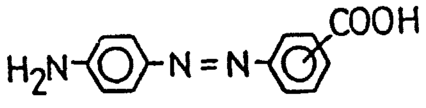
We have examined the structures of LB films of amphiphilic cyclodextrins (CDs), and found that various azobenzene molecules are incorporated in the films.1-3) Among others, azobenzene molecules in the films show a reversible cis-trans photoisomerization, indicating the feasibility of the LB films of this type as optical memory devices.4-6) These LB films are prepared by spreading chloroform solutions of equimolar mixtures of alkylamino derivatives of CDs and azobenzene derivatives on a water surface. In this system, however, the amount of azobenzene molecules incorporated in the film depends on the structures of both CD and azobenzene derevatives. In other words, the quantity of azobenzene molecules incorporated in the films can measure the interaction between the two. This provides us with a means of molecular recognition.

In this study, the possihilities are examined to use amphiphilic cyclodextrins (Fig. 1) for molecular recognition of o-, m-, and p-isomers of azobenzene derivatives without alkyl chains (Fig. 2). The amount of azobenzene derivative incorporated in the resultant LB film was determined spectroscopically by dissolving the LB films into methanol. The amount incorporated depends both on the size of the cavity of CD and on the molecular structure of the azobenzene derivative.



n=6: α-CD
n=7: β-CD
n=8: γ-CD

Fig. 1. Molecular structures of CDs.



ortho isomer: o-MR
meta isomer: m-MR
para isomer: p-MR

Fig. 2. Molecular structures of azobenzene derivatives.

1) Y.Kawabata et al., Chem. Lett., 1933 (1986).
2) M.Tanaka et al., ibid., 1307 (1987).
3) Y.Kawabata et al., Thin Solid Films, 159, 353 (1988).
4) A.Yabe et al., Chem. Lett., 1 (1988).
5) H.Niino et al., ibid., 1227 (1988).
6) A.Yabe et al., Thin Solid Films, 160, 33 (1988).

JP8

Self-Assembled Monolayers on Gold: Sulfone Group Enhancing Two-Dimensional Organization

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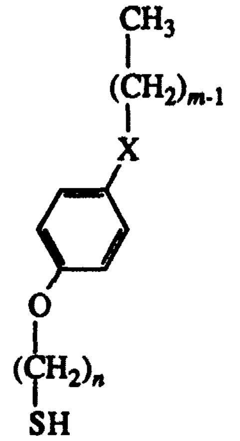
ABSTRACT

Monolayers were formed from molecules having large in-plane dipole moments [CH_3–$(CH_2)_n$–SO_2–$(CH_2)_m$–SH]. It was found that the incorporation of the sulfone group strongly affected the molecular conformation within the monolayer. The effect of varying the position of the sulfone group in these molecules, while maintaining constant molecular length, was studied and the results compared to those found for a octadecylethaniol (CH_3–$(CH_2)_{17}$–SH, ODT).

The effect of incorporating polar aromatic groups into self-assembled alkanethiol monolayers was studied using the series:



molecule	X	*m*	*n*
I	SO_2	4	12
II	SO_2	8	8
III	SO_2	12	4
IV	S	4	12
V	S	8	8
VI	S	12	4

A variety of techniques including ellipsometry, wetting, reflection-absorption FTIR, surface (contact) potential, surface enhanced Raman spectroscopy (SERS), and XPS were used to characterize these monolayers. In both series, the quality of the monolayers was found to be dependent on the length of the aliphatic chain above the polar group.

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JP9

Wettability of Heterogeneous Surfaces: Experimental and Theoretical Results for Mixed Alkanethiol Monolayers on Gold

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ABSTRACT

Wettability studies of mixed monolayers containing hydrophobic (OH) and hydrophilic (CH_3) terminal groups are discussed. We are reporting the first observation of an apparent concentration-driven transition in the contact angles of liquids on mixed monolayers. It is suggested that this phenomenon is due to a possible (true or rounded) surface phase transition, resulting in the formation of a prewetting water layer. This formation is triggered by variations in the quenched distribution of random surface fields.

The current treatment of wettability of heterogeneous surfaces is discussed. It is suggested that this treatment represents concentration-weighted interpolation between two extremes. Thus, once those two extremes are fixed, environmental parameters, such as temperature and relative humidity, play no role in the interpolation. A new way of calculating the wettability of heterogeneous surfaces is presented, based on a proper statistical mechanics methods. These involve the thermal average of the related partition functions at *each* fixed configuration of surface functionalities and not only at the two extreme cases corresponding to the homogeneous surfaces. Subsequently, a quenched average of the resulting interfacial free energies, relative to a frozen probability distribution of those surface functionalities, is performed.

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JP10

SURFACE–PLASMON STUDIES OF SPECIFIC RECOGNITION REACTIONS AT SELF–ASSEMBLED MONOLAYERS ON GOLD

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Surface–Plasmon spectroscopy and microscopy provides a powerful method for studies of interfacial phenomena. With a high sensitivity for subtle thickness changes of the surface geometry and without the need for labeling (e.g. fluorescence) the target molecules, this novel technique offers certain advantages for investigations of molecular recognition reactions at interfaces.

As a modell system for biological receptor–ligand pairs we used the well known Biotin–Streptavidin system. These molecules show a specific and strong (_K_m_$\sim 10^{-15}$ m) binding and can be chemically modified in various ways, e.g. Biotin bond to alkanethiols. Alkanethiols (besides disulfides and thioethers) were shown recently to form very stable monolayers at gold surfaces, (because of the strong Au–S_bond.

Due to the defined molecular geometry of such an ultrathin organic film, further adsorption processes can be performed. Especially in the case of specific attached Streptavidin, free binding sites are still exposed to the surrounding medium (_because of the four–fold symmetry of the molecule). This offers the very interesting perspective of attaching further layers of (various) biotinylated molecules and by this a specific functionalizing of an interface.

JP11

ORIENTED CRYSTALLIZATION AND NONLINEAR OPTICS : TOOLS FOR STUDYING STRUCTURAL CHANGES OF AMPHIPHILIC MOLECULES AT INTERFACES.

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Two independent techniques, oriented crystallization and second harmonic generation techniques were used to probe the existence of ordered aggregates of amphiphilic molecules at air-solution interfaces from which the crystal nucleation of suitable solutes can start. The strong interactions between the solute molecules in the solution and the surface aggregates lead to changes in the latter as compared to their presumed structure at the air-pure water interface.

In this study we report the results of the oriented crystallization of the 4-hydroxybenzoic acid monohydrate (HBA) at the solution-air interface as induced by insoluble 4-alkoxy-, 4-acyloxy-, and 4-alkylaminobenzoic acid molecules used in the form of Langmuir films. Spreading such molecules on a HBA supersaturated solution induces fast nucleation of HBA crystals attached at the interface with their newly developed (401) face. Based on the analysis of the molecular arrangement at this crystalline face, one may assume that the amphiphilic molecules when spread over the solution adopt a tilted orientation so that to form hydrogen bonded dimers lying almost parallel to the surface. This arrangement may serve as a matrix for the (401) oriented crystal nucleation and is very different from the orientation of the same molecules when spread over pure water.

Surface pressure - area isotherm measurements show a larger limiting area per amphiphilic molecule as increasing the solute concentration of the subphase, being consistent with a change in the molecular tilt.

Further corroboration for this model has been obtained using optical second harmonic generation (SHG), a surface sensitive technique which can detect the presence and orientation of an amphiphilic monolayer at the air-solution interface. Our SHG experiments have shown a drastic difference between the orientation of 4-(hexadecyl)-oxybenzoic acid and 4-(hexadecyl)aminobenzoic acids when spread on water and spread over the HBA solutions, in complete agreement with the crystallization experiments.

These results demonstrate the potential use of crystallization processes combined with SHG as surface sensitive techniques.

JP12

MONOLAYERS AND BILAYERS CONTAINING THIOLIPIDS

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For studying the basic mechanisms of many cellular signal transduction processes and as well as for adapting the biological principles of signal transduction to bioelectronic devices, it is of great importance to realize stable supported lipid membranes. For this purpose we have synthesized lipids carrying hydrophilic spacers of different length with a disulfide bridge at their ω-position allowing the molecules to anchor on a gold substrate. The goal of this mode of attachment is to preserve a water layer between the support and the membrane in order to incorporate proteins with large extra membraneous domains into the bilayer.

The deposition of the film was carried out by self assembly techniques. Simultaneous monitoring of the formation of the layer by capacitance measurements and by plasmon surface polariton (PSP) fields indicates a binding kinetic with a fast component (minutes) and a slow component (hours to days). The latter may be due to steric problems. The steady state values of both techniques are in accordance with a complete bilayer, probably in the fluid state. After washing with an aqueous n-octyl glycoside solution the outer monolayer of this system can be substituted by a conventional lipid layer.

Characterisation of dry films on gold by gracing incidence reflection IR-spectroscopy showed a high degree of order within the film.

Mixed monolayers of thiolipids and various lipids were investigated by fluorescence microscopy on the water surface.

Furthermore we present first results on the incorporation of membrane proteins into these films.

JP13

ELECTROCHEMICAL AND RAMAN STUDIES OF AMPHIPHILIC VIOLOGENS: EFFECTS OF COUNTERIONS

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Viologens are redox-active compounds recognized as efficient promoters of electron transfer at interfaces, e.g. electrode surfaces. When derivatized to produce surface-active species, monolayer techniques can be used to demonstrate various electrochemical effects during modulation of secondary factors such as counterions.

Monolayers of N-methyl-N'-hexadecylviologen were prepared on silver electrode surfaces, using both the self-assembly technique and Langmuir-Blodgett transfer. Cyclic voltammograms were determined as a function of the associated counteranion, and spectroelectrochemistry used to obtain Raman spectra of the various species generated during redox events.

From the results based on spectroelectrochemistry, it was determined that the counterion associated with the viologen had a pronounced effect on the operative mechanism of enhancement. When strongly adsorbed counterions (e.g. bromide) are present, the viologen appears to be oriented nearly perpendicular to the surface. This indicates that only the electrochemical mechanism of enhancement is operating. Monolayer and solution spectra were similar, differing only in intensity. In contrast, with only weakly adsorbing counterions present, the viologen appears to form a strong complex with the Ag surface. The solution and surface spectra differ radically and large (40 cm^{-1}) band shifts are seen. Analysis of these spectra suggest that the aromatic ring system is parallel to the surface.

Electrochemical studies support the conclusions based on the Raman results. In addition, a splitting of peaks in cyclic voltammograms was seen in those systems having e.g. bromide or iodide counterions. This phenomenon is attributed to reduced solubility of the viologen in these systems, but also may be rationalized in terms of a theoretical model describing the nature of one-electron transfer peak splitting. It has been predicted that no splitting should take place with random orientations of adsorbed species, but should be observed in regular, close-packed arrays such as are present in Langmuir-Blodgett transferred monolayers or self-assembled systems.

Results for systems prepared by adsorption (self-assembly) were similar to those obtained from LB transfer.

JP14

GOLD SERS OF AMPHIPHILIC SULFUR VIOLOGENS DURING ELECTRON TRANSFER

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Surface-enhanced Raman scattering (SERS) from appropriate metal surfaces results in an increase of orders of magnitude for observed scattering intensities, and in favorable cases submonolayer amounts of materials may be detectable. Although silver surfaces have been the traditional choice for invoking the SERS effect, gold can also produce SERS using appropriate red wavelengths. To date, monolayers detected through gold enhancement have been little studied. This report provides SERS spectra of substituted viologens which are self-assembled on roughened Au electrodes, and compares their spectra with those of a previous study of the same compounds on Ag surfaces. This is evidently the first such comparative study for self-assembled monolayers on Au and Ag.

The compounds used were sulfides with the general structure: [octadecyl]-S-[CH_2]n-[viologen]-R. The values of n were 5, 7 and 10, and R was varied to make a constant chain length for the branch containing the electroactive viologen group. Thus, the viologen could assume various known distances from the metal because of the variable number of intervening methylene groups, provided that the chain is not parallel to the interface. Electron transfer thus must take place through nonconjugated carbon bonds if the viologens are extended away from the surface. Monolayers were formed on Au by spontaneous self-assembly; it has been previously shown that thiols with long alkyl groups form dense monolayers with the sulfur interacting strongly with the Au surface.

Using Au electrodes, cyclic voltammetry of monolayers of these compounds indicated highly efficient electron transfer, the kinetics for which was a function of the length of the spacer methylene groups. Spectroelectrochemistry was also carried out, to detect SERS spectra, on both smooth (original) and roughened Au surfaces. Roughening was effected by varying the potential of the Au electrode from +1.3 v. to -0.6 v. for 25 cycles, after which the original surface color was changed from gold to coppery hues. Self-assembled monolayers were then prepared by adsorption from solution. Well-defined spectra were observed from roughened Au surfaces, using the 647.1 nm line of a krypton-ion laser. Spectra were observed for the neutral, cationic and anionic species. In contrast to the previous study on Ag, it was found that the nature of the counteranion had little effect on the character of the spectra. Analysis of the data shows agreement with previous studies using Ag, which indicated that the saturated hydrocarbon chain containing the viologen is nearly perpendicular to the metal surface.

JP15

SPONTAINEOUS FORMATION OF MULTI-LAYERED CAST FILMS FROM ORGANIC SOLVENTS USING NOVEL FLUOROCARBON AMPHIPHILES

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Novel double-chain ammonium amphiphiles, whose alkyl tails are composed of fluorocarbon and hydrocabon segments are synthesized. They are used to make multi-bilayer cast films from water as well as from organic solvents.

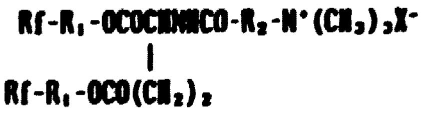
Newly synthesized amphiphiles are summarized in the Table. X-ray diffraction comfirmed that most of them can form multi-bilayer structures by casting from water or appropriate organic solvents. Especially, amphiphiles that have olefin unit in the tail exhibit higher solubility (dispersibility) in many organic solvents than the others. They produce well-ordered cast films rather readily. By measuring π-A isotherms, it is found that these amphiphiles produce expansion-type monolayers on water. These characteristics would be related to their casting behavior.

Among the amphiphiles newly synthesized, compound 10 exhibits the best results. It can form a transparent, self-supporting film even from perfluorohexane solvent. The thickness of the individual layer is seen to be 500Å or less, as observed by scanning electron microscopy.

The present study broadens the scope of the cast films, for example as molecular templates.

Table Newly synthesized fluorocarbon amphiphiles.

Compound No.	Rf	R_1	R_2	X
1	C_8F_{17}-	$-(CH_2)_{11}-$	$-CH_2-$	Cl
2	C_8F_{17}-	$-(CH_2)_{11}-$	$-(CH_2)_{10}-$	Br
3	C_8F_{17}-	$-(CH_2)_3O(CH_2)_2-$	$-(CH_2)_{10}-$	Br
4	$C_{10}F_{21}$-	$-(CH_2)_6-$	$-CH_2-$	Cl
5	$C_{10}F_{21}$-	$-(CH_2)_6-$	$-(CH_2)_{10}-$	Br
6	$C_{10}F_{21}$-	$-(CH_2)_6-$	-⬡-$(CH_2)_{10}-$	Br
7	$C_{10}F_{21}$-	$-(CH_2)_{11}-$	$-CH_2-$	Cl
8	$C_{10}F_{21}$-	$-(CH_2)_{11}-$	$-(CH_2)_{10}-$	Br
9	$C_{10}F_{21}$-	$-CH=CH(CH_2)_9-$	$-CH_2-$	Cl
10	$C_{10}F_{21}$-	$-CH=CH(CH_2)_9-$	$-(CH_2)_4-$	Br
11	$C_{10}F_{21}$-	$-CH=CH(CH_2)_9-$	$-(CH_2)_{10}-$	Br
12	$C_{14}F_{21}$-	$-CH=CH(CH_2)_9-$	$-CH_2-$	Cl
13	$C_{14}F_{21}$-	$-(CH_2)_{11}-$	$-(CH_2)_{10}-$	Br



$$\begin{array}{l} Rf\text{-}R_1\text{-}OCOCHNHCO\text{-}R_2\text{-}N^+(CH_3)_3X^- \\ \qquad\qquad | \\ Rf\text{-}R_1\text{-}OCO(CH_2)_2 \end{array}$$

JP16

BUILDUP OF ULTRATHIN MULTILAYER FILMS BY A SELF-ASSEMBLY PROCESS: II. REPEATED ALTERNATING ADSORPTION OF ANIONIC AND CATIONIC POLYELECTROLYTES

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INTRODUCTION

The state of the art technologies for the preparation of well defined ultrathin films in the submicron range are the Langmuir-Blodgett (LB) technique and self-assembly (SA) methods based on chemisorption [1]. Whereas the LB-technique requires sophisticated apparatus and is generally limited to small film areas [2], the SA-methods are rather straightforward [3,4], but have not been employed for the preparation of films thicker than 8 layers (≈ 20 nm) [4], probably due to the loss of chemical functionality. Similar limits are encountered in the Merrifield peptide synthesis. Our approach, which was recently introduced employing a low molecular weight system [5], avoids these limits and extends the SA-concept by using salt formation as the driving force for the construction of multilayered supramolecular assemblies.

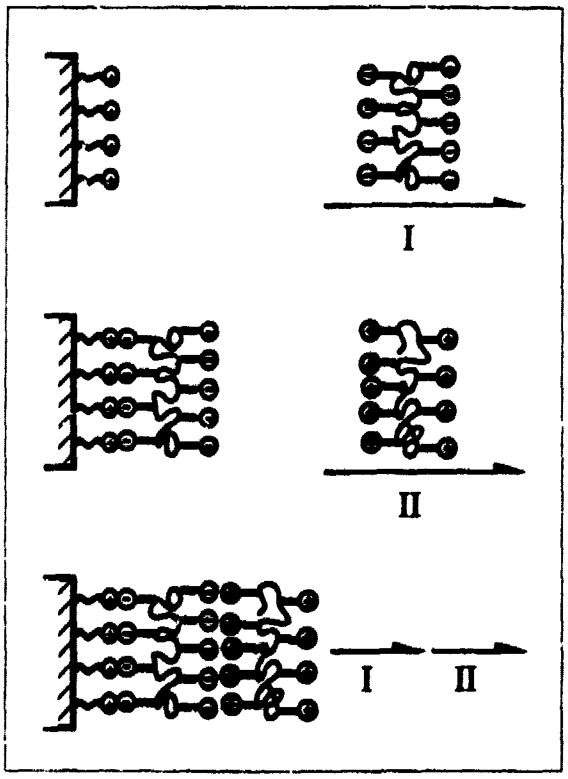

Figure 1. *Illustration of the adsorption process. Both the solution structure of the polyelectrolytes and their structure after adsorption are highly idealized. Step I symbolizes the physisorption of an anionic polyelectrolyte on a positively charged surface, thus reversing the surface charge. Step II depicts the adsorption of a cationic polyelectrolyte, whereby the original surface charge is restored. By repeating steps I and II in a cyclic fashion, any type of superlattice, containig at least two polyelectrolytes, can be prepared.*

RESULTS AND DISCUSSION

In addition to the stepwise buildup of films using charged bipolar amphiphiles with a rigid core [5], the process can also be carrierd out utilizing polyelectrolytes (Fig. 1). Multilayered structures are prepared by simply dipping a substrate with a positively charged surface into an aqueous solution containing the anionic polyelectrolyte, then rinsing it with clean water. This way the substrate is covered with one layer and its surface charge is reversed. The substrate is then immersed in a solution of the cationic polyelectrolyte, thus adding a second layer and restoring the original surface charge. Thicker films are easily obtained by repeating steps I and II in a cyclic fashion.

As previously observed in the case of the adsorption of single polymeric layers [6], the adsorption of the polyelectrolytes depends on time, concentration and concentration of added salt. By UV/Vis-spectroscopy we have demonstrated that at least 80 polymeric layers can be deposited consecutively. The constant film thickness is further evidenced by the observation of homogeneous interference colors when aminopropylated silicon wafers are used as substrates.

REFERENCES

[1] J. D. Swalen et al.
Langmuir 3 (1987), 932-950

[2] G. L. Gaines, Jr.
"Insoluble Monolayers at Liquid-Gas Interfaces"
Interscience Publishers, New York 1966

[3] R. Maoz, L. Netzer, J. Gun and J. Sagiv
J. de Chim. Phys. 85 (1988), 1059-1065

[4] H. Lee et al.
J. Phys. Chem. 92 (1988), 2597-2601

[5] G. Decher and J. D. Hong
Proceedings of the ECOF '90 Conference
Makromolare Chemie, in press

[6] J. Blaakmeer et al.
Macromolecules 23 (1990), 2301-2309

JP17

Modulated Photoregulation of Liquid Crystal Alignment by Azobenzene Langmuir-Blodgett Layers

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In recent years we have been investigating reversible homeotropic $\rightleftarrows$ parallel (planar) photochemical alignment controls of nematic liquid crystals (LC) induced by highly photoreactive Langmuir-Blodgett layers comprised of side-chain type azobenzene (Az) amphiphilic polymers.[1-3]

This paper presents how the preparation process of LB films and the way of the light irradiation influence the LC alignment controls. In the parallel mode under non-polarized UV irradiation, the LC molecules are homogeneously oriented parallel along the dipping direction. Under certain conditions, polarized UV irradiation induces subsequent rotation of the in-plane direction of the homogeneous LC alignment. These alignment modulations strongly depend on the molecular structure of Az polymers and the number of deposition. Details on these results are reported.

References
1) K. Ichimura et al., Langmuir (1988), 4, 1214.
2) T. Seki and K. Ichimura, Thin Solid Films (1989), 179, 77.
3) T. Seki et al., Macromolecules (1989), 22, 3505.

JP18

LB FILM FORMATION OF A NOVEL AMPHIPHILIC POLYMER PAMC$_{18}$S

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The application of amphiphilic polymers in LB film formation has attracted great attention in recent years. Poly(2-acrylamido-hexadecyl-sulfonic acid) (PAMC$_{18}$S) is a novel comb-type amphiphilic polymer, each repeat unit of which contains a hydrophilic sulfonic acid group, an amido group and a hydrophobic long aliphatic hydrocarbon chain. This paper involves the formation of LB films of PAMC$_{18}$S by Langmuir-Blodgett (LB) and self-assembly (SA) techniques.

The spreading behaviours of PAMC$_{18}$S on the water-air interface have been investigated. It is found that PAMC$_{18}$S forms rather stable condensed solid films, and that the limiting area of PAMC$_{18}$S is strongly dependent on the subphase: pure water results in a larger area/monomer, whereas the area/monomer decreases markedly when the subphase contains $CaCl_2$ or $CdCl_2$.

Ordered thin films of PAMC$_{18}$S have been obtained on gold surfaces (clean gold and anodized gold), glass, and quartz by SA technique. Water does not wet the monolayer-covered gold surfaces, indicating that the films are hydrophobic with the hydrophilic sulfonic acid groups ajacent to the metal surfaces and with the hydrocarbon chains extended from the surfaces. On the other hand, films on glass and quartz are hydrophilic, according to the contact angle results.

XPS and electrochemical analysis have further been used to characterize the self-assembled monolayers on gold surfaces.

The results of XPS measurements show that the gold oxide layer of the anodized gold surface has not been completely stripped during the adsorption process, and has partly reacted with the sulfonic acid groups of the monolayer to form gold sulfonate.

Electrochemical analysis is a sensetive probe for the monolayer coated on an electrode. For the polymer-coated gold electrodes, peak current attenuation and peak potential shift have been found, especially for the first scan. The variation of peak currents and peak potentials with scan number reveals that the self-assembled monolayers of PAMC$_{18}$S exhibit great adsorption stability during the faradaic reactions, illustrating the advantage of polymer LB films in potential applications. The stability of PAMC$_{18}$S monolayers during the redox reactions makes possible the further sweep-rate studies. The data of sweep-rate studies show that polymer monolayer has not changed the pattern of the redox reaction, except for the reduced peak currents and shifted peak potentials. The resulting monolayer-covered gold surfaces behave as relatively stable blocked electrodes containing pinhole defects.

References

1. A. Laschewsky, H. Ringsdorf, and G. Schmidt, Thin Solid Films, 134, 153(1985).
2. Y. Tsukahara, A. Hayakawa, Y. Tachibana, Y. Yamashita, and R. Tatematsu, Polym. J. , 17, 959(1989).
3. M. Niwa, T. Hayashi, and N. Higashi, Langmuir, 6, 263(1990).

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