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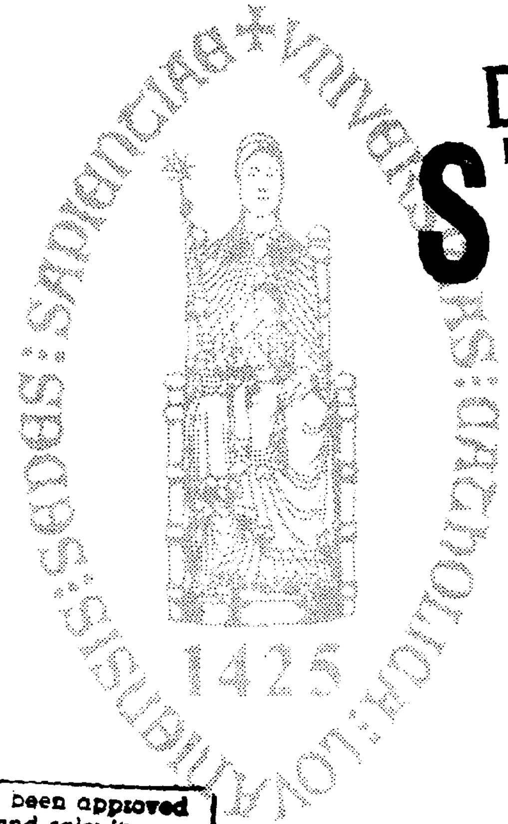
6th Symposium on Unconventional Photoactive Solids

Leuven August 15-19, 1993



ABSTRACTS

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Dear Participant,

In name of the organizing committee and of the executive committee I have the pleasure to welcome you at the occasion of the 6th Symposium on Unconventional Photoactive Solids. Over the last two years the organizers have tried to arrange optimal conditions for scientific exchange. I would like to take the opportunity to thank all those who through advise, sponsoring, fund raising or organizational skills have contributed to provide for these initial conditions . Each of you through your personal contribution and scientific activity can and will now make this Symposium one in an outstanding series of meetings.

This volume contains the abstracts, reproduced as submitted by the authors, of the scientific contributions that will be presented at the Symposium as plenary lecture, short invited lecture, oral presentations or as poster presentations. In an effort to force each of you to read or discuss as many posters of different subfields as possible, the abstracts were arranged in a non topical order but placed in alphabetical order based on the name of the participant presenting the poster.

I sincerely hope that this meeting will contribute to further enhance the scientific and personal contacts between the participants and advance and strengthen the field.

Leuven, August 1993

F.C. De Schryver

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PLENARY LECTURES

RECENT DEVELOPMENTS IN PHOTOREFRACTIVE POLYMERS

D.M. Burland, G.C. Bjorklund, M.C.J.M. Donckers , W.E. Moerner,
S.M. Silence, R.J. Twieg and C.A. Walsh

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Photorefractive materials have a variety of potential applications including holographic optical storage, real-time optical processing and beam switching, interconnections in neural networks, restoration of phase distorted images and coherent light amplification. Until quite recently all of the photorefractive materials investigated have been inorganic: examples include $LiNbO_3$, $BaTiO_3$, GaAs and InP:Fe. Organic systems, polymeric or crystalline, might be expected to have advantages over inorganic ones. A critical advantage arises from the lower DC dielectric constant of organic materials. This directly affects the figures of merit for holographic efficiency and high speed electrooptic modulation in photorefractive systems. Further, the organic systems may be processed at lower temperatures. If the materials are polymeric they can be spin-coated and cured using well established photoresist technology. Because physical properties of organic molecules may be extensively modified by chemical substitution, the potential for optimization and engineering of organic systems is greater than for inorganics.

Figure 1 illustrates the origins of the photorefractive effect. In a typical photorefractive experiment the sample is illuminated by two interfering mutually coherent light beams producing an interference pattern. Charge carriers are generated by the absorption of light producing, in the particular case shown in the Figure, mobile electrons and ionized donors. The electrons diffuse or drift in a large external electric field into the unilluminated regions resulting in a space charge as shown. This space charge produces an electric field that is 90° out of phase with the exciting light. This results in an index of refraction variation across the sample that is itself 90° out of phase via the linear electrooptic effect

$$\Delta n = \frac{1}{2} n^3 r E \tag{1}$$

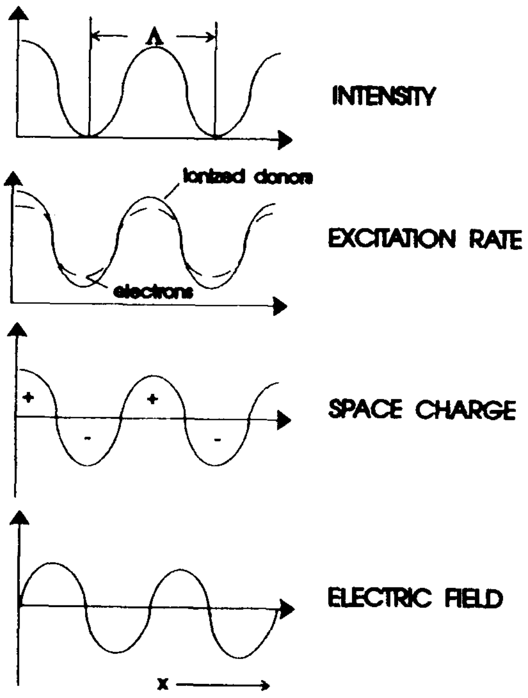

Figure 1. Elements of the photorefractive effect

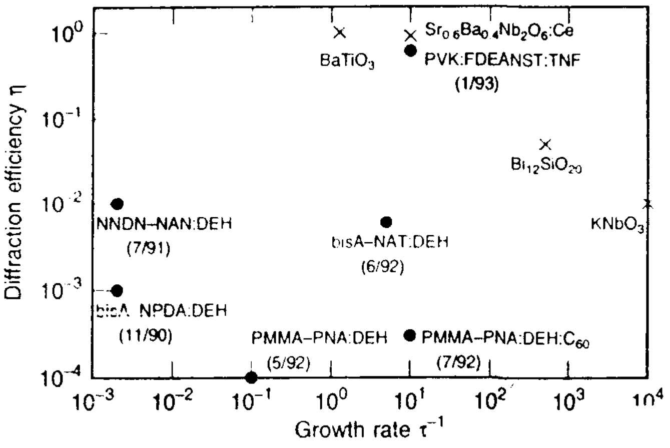

Figure 2. Comparison of organic and inorganic photorefractive materials

where r is the linear electrooptic coefficient. To exhibit a photorefractive effect the following necessary conditions must be present:

- Noncentrosymmetric structure → nonzero r
- Photo-charge generation mechanism (intrinsic or extrinsic)
- Charge mobility
- Charge trapping (internal space charge formation)

However the presence of these properties is not sufficient to guarantee that the photorefractive mechanism of grating formation is dominant over other mechanisms such as heating or photochemistry. These alternative mechanisms must be ruled out before a material can be considered photorefractive.

The first organic photorefractive system to be identified was a crystalline system consisting of an electro-optic single crystal doped with a charge generating molecule[1]. This discovery was followed shortly by the identification of a photorefractive polymer[2].

This system consisted of an electrooptic polymer made photoconductive by doping with a hole-transport agent. These early materials had low diffraction efficiencies and slow growth rates. This is indicated in Figure 2 where a variety of organic polymers (indicated by •) and inorganic crystals (indicated by X) are compared. A considerable enhancement in speed was obtained by using C_{60} as a sensitizer[3].

Recently a new class of photorefractive polymers has been identified exhibiting speeds and efficiencies equivalent to some of the best inorganic crystals (see PVK:FDEANST:TNF in Figure 2)[4]. These systems utilize a photoconducting polymer, instead of an electrooptic polymer as in previously studied systems. The system is made electrooptic by doping the polymer with an optically nonlinear chromophore. A sensitizer molecule is also added to enhance charge generation at the laser wavelength. These systems have efficiencies several orders of magnitude larger than previous polymeric systems due to a new orientational enhancement mechanism. The photorefractive effect is enhanced by the *orientation of the nonlinear chromophore in* the modulated internal space charge field[5].

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Non-Dispersive and Dispersive Transport in Random Organic Photoconductors

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There is a recurrent pattern of features associated with charge transport in disordered organic photoconductors such as molecularly doped polymers and pendent groups as well as π- and σ-conjugated main chain polymers. The charge carrier mobility is both activated and field dependent in a way that is reminiscent of, albeit not identical with Poole-Frenkel behavior. The slope in a $\ln\mu \propto SE^{1/2}$ relation decreases with increasing temperature and may even change sign above a certain temperature. At lower temperatures time of flight (TOF) signals become dispersive but even non-dispersive TOF signals feature anomalously broad tails often bearing out universality. Presence of dipoles reduces the carrier mobility and raises the temperature at which TOF signals become dispersive.

It has been shown before [1] that a model based upon charge carrier hopping in a system of energetically and positionally random sites is able to recover the basic observations. The emphasis of this lecture will be on the effect static dipoles have on transport as well as on the phenomena of universality and dispersion associated with TOF signals.

1. The effect of dipoles

It has been shown before that presence of dipoles associated with either the transport molecules themselves or the matrix lowers μ [2,3] and simultaneously increases its temperature sensitivity [4] and renders TOF signals more dispersive. One way to account for the increases of the activation energy - yet not the increasing tendency towards dispersion - is to invoke polaron formation [6] via dipole reorientation in the vicinity of a charge carrier. The rigidity of the structure at temperatures near or below the glass transition temperature, evidenced by the absence of dipolar relaxation on a time scale comparable with that of charge carrier hopping, argues against this notion, though. On the other hand, summation of the contribution of randomly positioned dipoles to the electrostatic potential of a charge carrier shows that random dipolar fields do, in fact, generate a Gaussian distribution of the energies of localized hopping states of the magnitude determined from the temperature dependence of μ. Its variance σ increases with the dipole concentration in a $\sigma \sim c^{1/2}$ fashion as borne out by the recent experimental work of Borsenberger et al.[7] for 1,1-bis(di-4-tolylaminophenyl)cyclohexane (TAPC) doped into polycarbonate or polystyrene at variable concentration.

2. Transition from non-dispersive to dispersive transport

Relaxation towards dynamic equilibrium is an inherent feature of an ensemble of charge carriers initially started at random within a Gaussian distribution of localized states (DOS). Since the equilibration time increases faster with decreasing temperature than does the time needed by a sheet of charge carriers to traverse a sample under the action of a bias field, TOF signals must become dispersive upon lowering the temperature, the transition temperature being related to the energetic disorder parameter $\hat{\sigma}=\sigma/kT$, σ being the variance of the DOS. The phenomenology of this transition has been delineated in the course of Monte Carlo simulations [8]. Although qualitatively similar to the predictions of Scher and Montroll's continuous time random walk treatment [9] the quantitative results are different. Pre- and post-transitional slopes of lnj vs lnt plots do not add up to two, no strict power laws are observed and universality is not fulfilled. Experimental results on vapor deposited amorphous films of DEH and DEASP are in quantitative agreement with model predictions. The transition temperature and the evolution of TOF shapes can be quantitatively recovered in terms of the disorder parameter derived from non-dispersive TOF signals.

3. Universality

The dispersion of what are usually referred to as non-dispersive TOF signals (documented by well-developed plateaus) can be quantified by

$$w = \frac{t_{1/2} - t_0}{t_{1/2}}$$

where $t_{1/2}$ is the time after which the current has decayed to one half of its plateau value and t_0 marks the intersection of the tangents. Since

$$w = (\pi D/\mu E L)^{1/2}$$

L being the sample thickness, universality is observed when the ratio of the apparent diffusivity, determined from the spatial evolution of a carrier packet under the action of an applied electric field E, to mobility increases linearly with both E and L. This is the case for $\hat{\sigma}=4$. At lower degree of energetic disorder, $w \propto L^{-1/2}$. Recent experimental data on both the temperature and field dependence of w will be discussed. The results indicate that the observed temporal pattern of TOF signals is in full accord with the predictions of the disorder formalism and no polaronic effects have to be invoked.

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PRESSURE PHENOMENA IN SPECTRAL HOLE BURNING

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Pressure seems to be an important parameter in elucidating the interaction of a probe molecule with its host lattice. There is a large variety of host-guest forces with a rich variation in their interaction range. The various interactions may affect the properties of a probe in a specific way. In optical spectroscopy, these properties are the width, the center frequency of the transition and the line shape. Pressure studies in optical spectroscopy are well established. Yet there is a big problem: In disordered systems, the inhomogeneous width is very large so that large pressure changes are needed to induce measurable line shifts. An evaluation of band broadening under pressure is, for glass-like systems, impossible.

Persistent spectral hole burning brings in novel features: First of all, since a hole may be several orders of magnitude narrower than the inhomogeneous width, extremely small pressure changes are sufficient to induce significant changes.

The most important feature of the technique is, however, its frequency selectivity /1/. By burning holes at various positions in the inhomogeneous band, probe ensembles with specific solvent shifts can be selected. They respond in a specific way to pressure. Hence, through the frequency selectivity, the solvent shift can be varied and, therefore, is a parameter of the experiment.

This has important implications: It seems that for many dye probes, the pressure induced line shift is proportional to the solvent shift /2/. In this case, the frequency dependence of the pressure shift is solely governed through the compressibility of the system which can be measured this way.

Clearly, if the pressure shift is proportional to the solvent shift, there must be a sharply defined frequency where the pressure shift vanishes. This frequency is the vacuum absorption frequency. For polar probes in polar solvents this frequency can fall into the inhomogeneous band and can be measured directly. The pressure shift changes sign as the burning laser is tuned across the vacuum frequency.

We applied the technique to glasses, Shpol'skii matrices, crystals, aggregates and proteins. All of these materials show surprising features. However, the most attractive field is the spectroscopy of proteins /3/.

If one succeeds in measuring the compressibility of a protein molecule, one knows the relative volume fluctuations which seem to be an important quantity for a proper functioning.

Surprisingly, we found that the compressibility of protein molecules is not a well defined quantity but is, instead, subject to dramatic variations. This can be understood within the frame of a model which we call the 'correlated phase space model'. It is assumed that certain structures of the chromophore support specific structures of the apoprotein. This means that the structural phase space of the chromophore and that of the apoprotein are correlated. Hence, if one selects specific structures of the chromophore (e.g. tautomers) by tuning the laser properly, one simultaneously selects different areas in the structural phase space of the apoprotein. It turned out that the properties, e.g. the compressibility, in these different structural substates can be very different. The question is whether structural differences like these can also be seen in the X-ray diffraction patterns. A simple calculation shows that this is not the case. Despite the drastic changes in their compressibility, the associated overall structural changes seem to be small and below are or just at the edge of the X-ray resolution.

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TIME-DOMAIN OPTICAL PROCESSING AND MEMORY IN HOLE-BURNING MATERIALS

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Coherent time-domain optical memory (CTOM), also known as stimulated echo memory, offers the potential of ultrahigh density data storage, temporal and spatial signal processing, at high data rate. Like the frequency-domain optical memory (FOM), such as persistent hole-burning memory, CTOM stores information in the spectral domain of an inhomogenously broadened material in addition to the spatial dimension in conventional two-dimensional optical memories.

Unlike FOM, where the information is stored bit by bit directly in the frequency dimension, the information stored in CTOM is the Fourier transform of a structured data pulse, which is nominally an amplitude-modulated binary stream. The high speed inherent to the echo process enables CTOM to store and retrieve data at much higher rates than FOM. The storage density in a spatial address is a time-bandwidth (TB) product where T is the length of the data stream and B is the data rate. The theoretical limits on T and B are usually considered to be the homogeneous dephasing time (T_2) and the inhomogeneous bandwidth (Δv) of the storage material, respectively. In rare-earth doped crystals, T_2 is typically ~10^{-5}-10^{-4} s and Δv ~10^{9}-10^{10} Hz, yielding maximal TB products of ~10^{4}-10^{6}. Theoretically estimated maximal TB products up to 10^7 have been reported for some Eu^{3+} doped oxides. When dealing with a lower data rate, one can divide the inhomogeneous profile into frequency subchannels and hence obtain a similar storage density. The potential to store large data packets (~100 μs long) at a data rate of tens of megabits per second up to 10 gigabits per second makes the CTOM very attractive for many applications.

We have experimentally demonstrated that performance of the CTOM close to the theoretical estimates can indeed be obtained. In our experiment, a 1.6 kbit data packet 40 μs long was stored at a data rate of 40 Mbit/s in a single frequency channel at one spatial location. Multiplying the total frequency channels available ($\gtrsim$ 32), we obtained an inferred storage capacity of $\gtrsim 5 \times 10^4$ bits per spatial spot.

A key factor for achieving such performance was the application of a novel spread-spectrum technique. This is because it was found that the length of a purely amplitude-modulated data stream was not simply determined by the dephasing time. Significant distortion of the retrieved data was observed long before it reached a fraction of the dephasing time, causing coherent saturation.

NEAR-FIELD PHOTOFABRICATION AND OPTICAL NANOPROBES

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We have nanofabricated subwavelength light sources as small as 40 nm in diameter and exciton sources that are probably smaller. These include micropipette tips with nanocrystals such as perylene as well as polymeric matrices. They also include fiber-optic tips with polymeric or crystalline tips. Further miniaturization is achieved by the addition of crystalline or polymeric supertips [1].

The first step in the nanofabrication process is the pulling of micropipette and fiberoptic tips of appropriate size and shape. The second step is the metal-coating of such tips (side but not front). This is followed by crystal (or polymer) growing. A variety of growing techniques have been employed, for both organic and inorganic crystals. Polymers are also grown by polymerization at the tip.

Optically controlled nanofabrication has been mainly utilized for the second stage of optical nanoprobe preparation. After silanization of the metal coated fiberoptic tip, the photopolymerization is controlled by the light emanating from this near-field light source. The size of the light source, and the near-field evanescent photon profile, control the size and shape of the immobilized photoactive polymer [1,2].

The above technology has been used to prepare both light sources [1] and submicrometer intracellular chemical optical fiber sensors [1,2]. Such 100 nm optical sensors have been used to monitor pH inside blood cells, early rat conceptuses, etc. They have extremely high absolute detection limits (zeptomoles) and fast response times (ms or less) combined with excellent sensitivity and reliability. Some of them contain as little as 400 photoactive molecules (*e.g.*, fluoresceinamine) and still are mechanically, optically and chemically stable over a series of measurements.

The near-field photo-polymerization has also been used for stepwise nanofabrication of optical probes, growing supertips onto tips [1]. This is an ongoing effort to produce the ultimate photon or exciton nano-tip, consisting of a single active molecule or chromophore. Various designs exist for maximizing the output while minimizing photobleaching.

A special point of both theoretical and practical interest is the increased photoexcitation cross-section of optically active molecules in the near-field range. This factor is important for both the photofabrication process and the utilization of such probes. The promise of near-field photon sources for the nanofabrication and monitoring of electronic devices and optical memories is obviously of much current interest [3,4]. So is the use of optical nanoprobes for microscopy, spectroscopy and biochemical sensing [1-4].

We acknowledge support from NSF grant DMR-911622.

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PHOTOACTIVE MOLECULAR SYSTEMS TOWARDS ADVANCED MATERIAL

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Molecular engineering of photoactive molecular systems with their tailor-made properties is one of the most essential way to construct advanced material which involves a molecular device. In this paper, several conceptional aspects are presented with examples such as multi-functionalization of functional molecule, intramolecular systematization of donor sensitizer acceptor moieties, intermolecular systematization of photoactive molecule, materialization of functional molecule and construction of structure-depending quantum functional material.

1. Multi-mode signal transducer molecules [1]: A new class of chemical signal transducer molecules which have plural transformation modes switchable by independent stimulations are shown. The molecules have plural functional groups responsive independently to stimulations and appropriate interactions of these groups through a conjugated system makes the response controllable.

2. Wheel and axle donor-acceptor polymer [2]: One-dimensional phosphorus(V)porphyrin molecule linked with the various length of oligothienyl molecular wire toward the axial direction of the porphyrin ring is demonstrated. The phosphorus(V)porphyrin unit tending to be an electron acceptor acted as a photoinduced hole generator, and the oligothienyl moiety tending to be an electron donor are able to transfer the positive hole just as molecular electric wire. The conductivity of these donor acceptor polymer is strongly enhanced by the photoirradiation, indicating that the

photoinduced carrier formation and transfer occur efficiently along the polymeric chain. A molecular photo- switching system is suggested.

3. Accordion-type photoactive molecular clusters[3]: A series of self-assembled metal porphyrin clusters are investigated. Some have capabilities to store electrons for a considerable time as a charge separated state.

4. Functional molecule materials [4]. A series of negatively charged functional molecule are efficiently incorporated in conducting polymers by electropolymerization, as a dopant. The resulting functional molecule incorporating conducting polymers show specific functions attributed to the incorporated molecule.

5. Ultrathin conjugating polymer multilayers [5]: To realize the organic superlattice, a novel potential programmed electropolymerization method which enables us to fabricate any microscopic depth structures in conjugating polymer ultrathin films, such as a multi-heterolayers and a sloped layers, is introduced. The depth profiles of the heterolayers, thickness and polymer composition are controlled by applied electrode potential. By this method, organic conjugating polymer superlattice, type I and type II heterostructures, are fabricated and structure-specific properties such as a quantum size effect are demonstrated.

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CHARGE CARRIER PHOTOGENERATION AND TRANSPORT IN ORGANIC CRYSTALS AND MOLECULAR ASSEMBLIES

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INTRODUCTION

In organic molecular crystals (OMC) the domination of molecular properties over the crystalline ones, caused by the weakness of Van-der Waals interaction, leads to pronounced tendency of localization of charge carriers (and excitons) on individual molecules of the crystal [1-3]. As a result, a typical localization (residence) time of an excess charge carrier τ_h on a lattice site is larger by about two orders than the characteristic relaxation time of electronic polarization of *surrounding molecules* τ_e, ($\tau_h >> \tau_e$), and usually lies in the same time domain as nuclear intramolecular relaxation time τ_v. Due to prevailing many-electron interaction phenomena charge carriers in OMC do not apear as free (bare) electrons or holes, but emerge as polaron-type quasi-particles, viz. as electronic, molecular, and, more rarely, as lattice polarons [3].

Consequently, for the description of charge carrier photogeneration and transport processes in OMC one should apply the approaches of contemporary polaron theories.

PHOTOGENERATION IN ORGANIC CRYSTALS

The charge carrier photogeneration and separation phenomena in OMC proceed via multistep processes. They include autoionization of excited neutral Frenkel exciton state, thermalization of the hot ejected electron, and, finally, thermally activated escape of the thermalized electron from the Coulombic well of the parent ion, stimulated by external electric field [3,5].

At the near thereshold spectral region of intrinsic photogeneration there emerge two competitive photogeneration mechanisms, viz. autoionization of excited molecular states and direct optical charge transfer to nearest neighbour molecules. At higher excitation energies the autoionization mechanism becomes dominant and appears in two possible modes, viz. as direct ionization of photoexcited neutral molecular states, and autoionization from fixed electronic levels after intramolecular relaxation [5].

Experimental and computer-simulated studies confirm the viability of the modified ballistic Sano-Mozumder model and an extended Onsager's approach for the description of photogenerated charge carrier thermalization and separation processes [3,4]. They also confirm the plausibility of the molecular polaron model for interpretation of these phenomena. It has been shown that the adiabatic nearly small molecular polaron may be formed as a result of selective interaction of a charge carrier with intramolecular vibrational modes of the molecule on which it is localized during the residence time, and also with polar, IR-active vibrational modes of nearest-neighbour molecules [3,4]. The formation energy of a molecular polaron has been evaluated from reported data on optical E_G^{opt} and adiabatic E_G^{ad} energy gap values [6] and substantiated by quantum chemical calculations.

TRANSPORT PHENOMENA IN ORGANIC CRYSTALS

The transport processes of charge carriers in OMC are also predetermined by the interaction and localization phenomena. The dynamics of the charge carrier motion in a crystal depends on two opposing and competing trends, viz. on delocalization of the carrier in the form of a Bloch wave, and on localization of the wave packet as a result of interaction with the surrounding electronic and nuclear subsystems of the lattice.

The contemporary transport theories, based on generalized stochastic Liouville equation and generalized master equations (GME), allow to describe both the coherent (wave like) and diffusive (hopping type) motion of charge carriers in a framework of a single model, as well as time and temperature *dependent loss of the carriers coherence* [3].

It has been demonstrated that a modified Sano-Mozumder approach, based on the Fokker-Planck equations, allows, in the framework of a model description, to simulate reported [7-9] experimental carrier transport characteristics in polyacene and α-perylene crystals, including hot carrier generation at high electric field values [3,10]. These studies confirm the plausibility of molecular polaron (MP) approach for phenomenological description of charge carrier separation and transport phenomena in polyacene and α-perylene crystals over a wide temperature (4.2-300 K) and electric field ($\mathcal{E}$ - 10^3 - 10^6 V/cm) range both in hot and thermalized carrier regimes. In this approach the charge carrier appears as a polaron-type heavy quasi particle with effective mass dependent on temperature, carrier sign *and direction of motion in the crystal* [3,10]. The molecular polaron presumably moves by hopping via tunnelling. In addition to phenomenological approaches [10], the MP model has also been analyzed in terms of Hamiltonian description [3].

PROCESSES IN MOLECULAR ASSEMBLIES

Langmuir-Blodgett (LB) multilayers may serve as excellent model systems of highly organized molecular assemblies. If an LB film consists of a conjugated amphiphilic compound like phthalocyanine (Phc) with aliphatic "tails" it may be envisaged as a multilayer of two-dimentional sheets of semiconducting molecules separated by insulating aliphatic spacers. *Energetically such a superlattice forms a* sequence of quantum wells.

Experimental studies of vanadyl Phc LB films show that at lower electric fields ($\mathcal{E} < 10^6$ V/cm) the charge carrier transport is trap controlled. At higher electric fields ($\mathcal{E} > 10^6$ V/cm) "quasi trapfree" carrier transport can be reached with zero activation energy ($E_a \rightarrow 0$) (11). This temperature-dependent effect may be regarded as indirect evidence of electric field-induced hot carrier generation. This assumption has been confirmed by computer simulation of carrier transport processes in LB films. In hot carrier transport regime ultrashort carrier transit times of picosecond and subpicosecond range can be reached in thin LB films. The transport of injected or photogenerated charge carriers in LB multilayers presumably proceeds by tunnelling through the quantum wells of oriented layers of polar ampiphilic molecules. This assumption has been substantiated by inelastic electron tunnelling spectroscopy studies of vanadyl Phc LB monolayers. These findings may be relevant for future applications of LB films in molecular electronics and optronics.

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Single Molecule Spectroscopy

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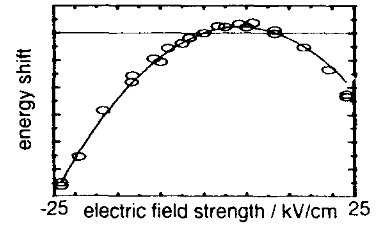
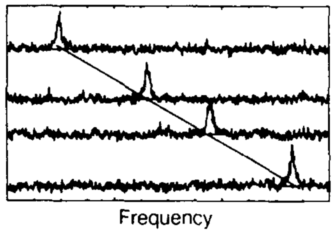
Fluorescence excitation spectra of single guest molecules of pentacene in a p-terphenyl crystal can be observed with high spectral resolution at low temperatures. These molecules are excellent probes for studying the effects of external fields such as an electric field or hydrostatic pressure. Fluorescence lifetime and polarization measurements have been performed on single molecules.


Stark Effect [1]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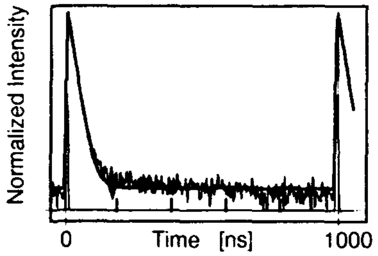
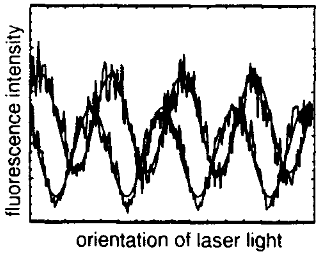

Fluorescence Lifetimes [3]


Polarization Spectra [4]

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INVITED LECTURES

LIGHT-EMITTING DIODES BASED ON CONJUGATED POLYMERS

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Since our first report that conjugated polymers could be used as the emissive layer in thin-film light-emitting diodes [1], there have been important advances in the understanding of the semiconductor processes that determine device performance, and major improvements in device performance have beeen achieved through selection of the polymers and optimisation of device architecture. We will report on several aspects of device operation, including the detection of both charged and neutral excited states by means of induced optical absorption. We will also report new results on heterostructure devices fabricated with two or more semiconductor layers which are arranged to ensure the balancing of electron and hole currents from the two injection electrodes.

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SCANNING FORCE MICROSCOPY OF ORGANIC SURFACES

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The scanning tunneling (STM) and atomic force microscopes (AFM) have established a strong presence in studies of surfaces and interfaces, principally with work on semiconductors and metallic surfaces. In order to study organic materials with the STM, the organic materials are configured as adsorbates on conducting surfaces [1]. With the AFM, the requirement of conductivity is lifted and the studied organic materials are found in a variety of environments, e.g., atop their three-dimensional crystals, layered with other materials, or as a component of mixtures.

The ability of the AFM to document surface features of organic thin films has, by now, been fairly well-demonstrated [1]. A challenge lies in differentiating subtle features, such as compositional changes *within* a film. An ideal system to extend the capabilities of the force microscopes for sensitivity to differences between materials is a film composed of two chemical species. Films composed of multiple chemical species are being studied [2], addressing the issues molecular miscibility and domain formation. In mixed films, molecular heterogeneity *within* a film plane yields local variations in response, such as friction or elasticity, providing a contrast mechanism *in-situ* for comparing material behavior on a very local scale. Also associated with domain size is the question of the origin of bulk properties, e.g., how properties measured on the nm-scale scale up to the macroscopic whole.

Comparative imaging studies are performed on series of films as well as on single films composed of multiple components. In films prepared from different classes of molecules, e.g., fatty acids, fluorocarbons, and liquid crystals, it is seen that the relative strengths of the intermolecular and interfacial interactions can be probed with these instruments. Film composition affects the ease with which intentional modifications in the film are made with the AFM stylus [3,4].

An alternate imaging mode in AFM is lateral force microscopy (also known as friction force microscopy). Additional information about the sample is provided by measuring the lateral force between probing tip and sample. For example, it has been preliminarily observed by AFM that the lateral response of an organic thin film can be associated with its elastic response. In another example, reduced friction is found on organic film-covered areas compared to the inorganic substrate, demonstrating lubrication on a microscopic scale [5]. On multicomponent films, friction measurements are found to be material-specific, distinguishing between domains of different molecular species or different molecular orientation [2].

Non-contact modes are now available as an alternative to repulsive contact measurements, particularly for imaging soft organic materials. Surprisingly, on the nanometer scale it appears that resolution is not sacrificed when scanning with the probe physically backed off the sample [6].

Finally, the phase-separated films of mixed chemical species are employed as substrates for adsorbates. Selective adsorption on particular film domains is observed [7].

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PHOTOCHEMICAL PRODUCTION OF HIGHLY ORDERED SPINS IN ORGANIC SOLIDS

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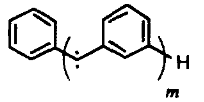
Poly(*m*-phenylenemethylene)s, poly(*m*-phenyleneethynylene)s and other conjugated polymers to which photolabile diazo or azido groups are attached in every repeating unit have been obtained by stepwise syntheses. When photolyzed and studied *in situ* at cryogenic temperatures by means of EPR spectroscopy and magnetometry/magnetic susceptometry, the corresponding high-spin polycarbenes and polynitrenes (e.g., **1** and **2**) were obtained. In particular, hexa- and nonacarbenes with pseudo-two-dimensional structural arrangement (**3**(m = 6 and 9)) were found to be with S = 6 and 9 ground states, respectively, highest magnetic moments ever reported. Attempts to synthesize real polymer samples capable of showing $S = 10^{2\sim3}$ were made. These included polymers due to *p*-(α-diazobenyl)phenylacetylenes and diacetylenes. The magnetic properties so far obtained are only partly satisfactory. These materials would serve as prototypes for organic optomagnetic recording devices.



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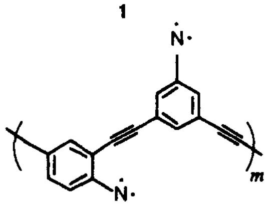

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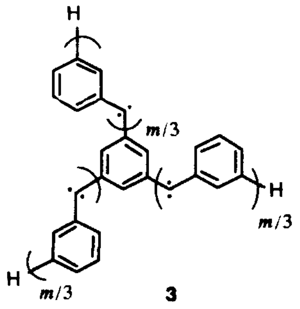

3

PHOTOELECTROCHEMISTRY ON SEMICONDUCTOR-BASED MICROELECTRODE ARRAYS

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Interdigited electrode arrays (IDA) have been so far studied in reference to development of chemical microtransistors and sensors as well as to high performance measurements of redox intermediates based on platinum, silver, or gold microelectrode arrays [1]. Recent advances in microfabrication techniques engage preparation of IDA with various chemical functions in addition to the role as an electrode array itself. Semiconductor-based IDAs have a high potential for photochemical and electrochemical control of reactions along the array. In this talk, we show characteristic features of a TiO_2/Pt microelectrode array and demonstrate effects of spatial arrangement of the electrodes on photoelectrochemistry of TiO_2 [2].

A photograph of a TiO_2 (**#1**)/Pt (**#2~8**) microelectrode (100 μm long x 10 μm wide x 0.3 μm thick, 10 μm spacing) array is shown in Figure 1. A photocurrent (I_p) on the TiO_2 electrode (**#1**) accompanied by photoelectrolysis of water is strongly dependent on a bias voltage (V_{Pt}; -0.7 ~ -1.1 V) applied to the Pt electrode as well as on the distance between the TiO_2 and Pt electrodes (d ; 20 ~ 140 μm). The present results are explained on the basis of electrolysis of water on TiO_2 and Pt;

on TiO_2 : $TiO_2 + h\nu \rightarrow e^- + p^+ + TiO_2$ (1)

$p^+ + 1/2H_2O \rightarrow 1/2O_2 + H^+$ (2)

on Pt : $H_2O + e^- \rightarrow 1/2H_2 + OH^-$ (3)

I_p on TiO_2 depends on pH of a solution, so that OH^- generated on the Pt electrode (eq.3) influences I_p. Since OH^- reaches to the TiO_2 electrode through diffusion along the electrode array, Ip decreases with increasing the distance between the TiO_2 and Pt electrodes. However, the decrease in I_p with increasing d is much smaller than that expected from a collection efficiency of OH^- by the TiO_2 electrode. OH^- generation on a Pt electrode leads to an increase in the local pH around **#1**, so that I_p is determined primarily by band bending of the depletion layer in TiO_2 through the change in local pH near the electrode, but not directly by the collection efficiency.

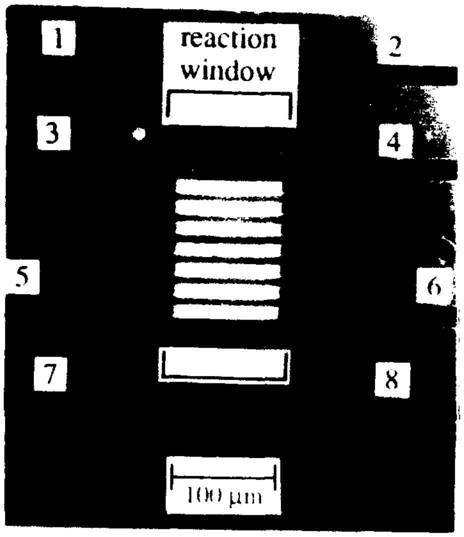

Figure 1. A photograph of the TiO_2/Pt microelectrode array. The array was protected by a Si_3N_4 film except for a reaction window.

The present results clearly indicate that chemical reactions along an array can be controlled electrochemically and photochemically. As one of the important advantages of IDA, furthermore, a reaction site in an array can be arbitrarily addressed through an outer circuit or selective photoirradiation under a microscope. A combination of IDA with semiconductor electrodes and photochemical techniques is thus highly promising to conduct and/or control various redox reactions in minute dimensions.

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Forbidden Delights: Emission Spectroscopy of AgBr Nanocrystals

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Abstract

Since AgBr is an indirect gap material, excitonic emission is formally (momentum) forbidden and thus extremely weak ($\phi < 10^{-5}$). However, AgBr can be grown as extremely small crystals using modified "reverse micelle" approaches. For crystals with R < 100 Å, excitonic emission becomes quite strong ($\phi \sim 0.1$)! This increase reflects not only "defect exclusion" in nanocrystals but also a change in selection roles associated with quantum restrictions. Radiative lifetime measurements provide a direct measure of how the selection roles change with size: down to 30 Å radius, the change in radiative lifetime remains modest ($\tau \approx 400$ µs, for 30 Å AgBr, vs. $\tau \approx$ 1 ms for "bulk" AgBr). Implications of these results for other indirect gap materials, e.g., "porous Si" are briefly discussed.

SOME RECENT RESULTS IN SINGLE MOLECULE SPECTROSCOPY

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The inhomogeneously broadened spectrum of a sufficiently small and diluted sample of a solid solution displays the homogeneous lines of single molecules. The experimental method giving the best results so far is fluorescence excitation with a high collection efficiency of the emitted light [1]. For well-chosen host-guest systems, the single molecule's signal is high above the background of Raman scattering from host molecules and of residual fluorescence. Single molecule lines are intense enough for a wide series of experiments, ranging from dependence on temperature or on exciting power [2] to external field effects [3,4] and to correlation studies of the time-distribution of emitted photons [5].

The correlation method allows us to investigate the dynamics of the local disordered environment of the molecule at liquid helium temperature. The experiments were performed on single terrylene molecules in a polyethylene matrix [6]. The histogram of measured linewidths shows a cutoff at the natural linewidth of the terrylene molecule, showing that some molecules have negligible dephasing and spectral diffusion, even in an amorphous matrix. The linewidths of different molecules show different temperature dependences. We applied the correlation method to study the intensity fluctuations of single molecule fluorescence. The relaxation times obtained span many decades. Sometimes, two excitations peaks appear on the spectrum (Fig1). The identity of their correlation times show that they stem from the same molecule, coupled to a nearby two-level system. The variation with temperature of the jumping rate between the peaks shows that the responsible mechanism, most often, is tunneling assisted by one or two acoustic phonons.

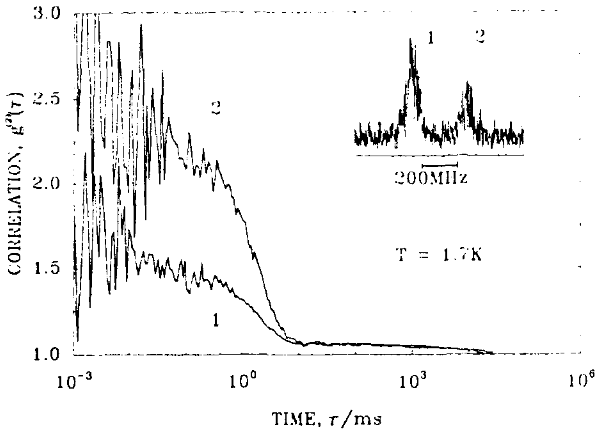

Fig1: Correlation functions of two peaks stemming from the same single terrylene molecule in polyethylene. The frequency of the molecule jumps from one peak to the other as a nearby two-level system flips. The jumping time is about 3 ms.

The study of fluorescence correlation for single pentacene molecules in para-terphenyl crystal directly shows saturation of the signal due to intersystem crossing transitions to and from the triplet subspace [5]. When a microwave field is applied, transitions between triplet sublevels affect the average fluorescence intensity and the correlation function. Two of the three possible zero-field transitions are observed. Their transition frequencies are not fixed on the timescale of the experiment. It is thus possible to study magnetic resonance on a single molecule [7], so enhancing by several decades the sensitivity of conventional techniques.

The variety of experiments performed to date on single molecules show the potential of single molecule spectroscopy (SMS) for the study of the structure and dynamics of molecular solids at nanometer level. In order to become a full-fledged spectroscopic method, SMS needs now to be generalized to other guest-host couples.

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DESIGN OF ORGANIC ELECTROLUMINESCENT MATERIALS AND DEVICES

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Using three 9,10-bis-styrylanthracene derivatives (BSA's) with different substituents for emission layer materials, various types of electroluminescent (EL) devices were fabricated. Combining with triphenylamine derivatives as a hole transport layer material and an oxadiazole derivative as an electron transport material, two-layer type and three layer type devices were fabricated. We found that the performances of two- and three-layer type devices were largely dependent on the electronic nature of emission layer materials. We found that the BSA's attached with electron-donating groups have the specific electronic nature which allowed the transport of both electrons and holes. A single layer devices with about 100 nm-thick BSA layer showed high luminance comparable with convenient two-layer type devices. Two-layer type devices which consisted of two different BSA layers were prepared in order to confirm that BSA layer surely behave as both electron and hole transporting materials. BSA with an electron-accepting substituent surely behave as an electron transport material. In contrast, BSA's with electron-donating groups showed the bipolar charge transporting characteristics, which means the capability of transport of both electrons and holes.

Size effects in organic EL devices were studied. Requirements for accomplishing the confinement of the singlet excitons generated by the recombinations of injected electrons and holes were discussed by using three-layer type devices with extremely thin emission layer. We found that the confinements of injected charges and generated excitons were achieved even within bimolecular emission layer.

Then the emphasis was laid on the control of spontaneous emission from the emission layer by using three-layer type EL devices. We found an interference effect of the emitted light and an optical micro-cavity effect on the spontaneous emission; variation of the intensity and pattern of outer emission through semitransparent ITO glass substrate with spacing between the emission layer and the metallic electrode were discussed theoretically and experimentally. And variation of the fluorescent lifetime or the radiative decay rate with the spacing was also discussed theoretically and experimentally.

TRANSPORT IN MOLECULARLY DOPED POLYMERS: DISPERSIVE OR NON-DISPERSIVE?

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Charge transport in molecularly doped polymers occurs by hopping among random sites. Anomalous diffusion is revealed in the ratio of diffusion constant to mobility which greatly exceeds the Einstein relation. We describe a method which allows the analysis of experimental current transients to determine the distribution of arrival times at the collecting electrode and find that the distribution of *inverse* arrival times closely approximates a Gaussian, with a relative width approaching unity. Theoretically we show that such behaviour can arise when either or both distributions of waiting times and hopping distances are wide relative to their means. It is not necessary that the transport be dispersive in the sense that the mean waiting time be infinite, as it is, for example, with a power law distribution of waiting times. These ideas are used to describe experimental data on a variety of materials.

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Charge & Energy Transport in Phthalocyanine Based Columnar Mesophases

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Columnar liquid crystals offer the possibility of studying charge and energy transport in quasi ^{1}D-systems. The use of liquid crystalline phases has important consequences on the transport properties in these media. In particular, the characteristic times associated must be compared with the residence time of the charge or energy at every site. Moreover, detailed informations on the structures within the columns must be known to avoid misleading interpretations of experimental results.`

These phenomena will be reviewed in the case of phthalocyanine based liquid crystals.

SCANNING PROBE MICROSCOPIES FOR THE CHARACTERIZATION OF STRUCTURE, DYNAMICS AND ELECTRONIC PROPERTIES OF MOLECULAR MATERIALS

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Scanning probe microscopies, in particular scanning tunneling microscopy (STM) and scanning force microscopy (SFM), can be used for both characterization and manipulation of molecular materials at interfaces. For STM, two classes of materials are accessible, namely molecular conductors and ultrathin molecular layers on conducting substrates (for a review see [1]). We will focus here on monomolecular layers, obtained by self-assembly from their melts or organic solutions at interfaces with atomically flat surfaces of graphite, MoS_2 and $MoSe_2$ [2-5]. We will show that molecular structure, dynamics and electronic properties can be determined down to the scales of 10 pm and 10 μs.

The structure analysis is based on the fact that the image contrast depends critically on substrate, adsorbate, as well as on the tunneling bias. Using the substrate lattice as an internal reference the analysis of moiré patterns due to adsorbate and substrate lattices allows to determine molecular packings, orientations, conformations, as well as epitaxy between adsorbate and substrate. Dynamic processes, which have been followed by STM, include the motion of domain boundaries as well as cooperative molecular reorientations. Molecular motions which are too fast to be observed directly, result in smearing of the images with respect to the respective coordinates. In these cases molecular dynamics computer simulations yield valuable complementary information. We report in particular on temperature and composition induced order-disorder transitions, including roughening of alkane lamellae with increasing temperature, as well as the transition from two-dimensional crystallites to smectic or columnar phases.

At molecular defects and domain boundaries it can be demonstrated that the current is determined by individual molecular segments, which means that current-voltage characteristics through them can be measured. For instance, at a bias between about 0.5 and 1 V the current through aromatic segments (e.g., benzene, naphthalene, triphenylene, azobenzene) or sulphur is in general considerably larger than through alkyl chains, while the difference between oxygen containing functions and alkyls is relatively small.

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PHOTOCHEMICAL AND PHOTOTHERMAL DYNAMICS IN SUBMICROMETER ORGANIC FILMS BY TRANSIENT GRATING SPECTROSCOPY

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Recently, submicrometer organic films of macrocycles and conjugated polymers have attracted much interest due to their potential applications in nonlinear optics. For the fundamental understanding of nonlinear optical processes, the analyses of photophysical, photochemical, and photothermal properties in thin films are indispensable. Transient absorption spectroscopy, being very powerful for nonfluorescent samples, cannot be applied to submicrometer films for the analyses these properties, because it requires high densities of transient species in thin layers. We have recently proposed transient grating spectroscopy using a femtosecond white light continuum as a probe pulse [1]. Using this spectroscopy, the diffraction spectrum corresponding to the transient absorption spectrum can be obtained with high sensitivity, and transient species in thin films can be identified. Here, we report the photophysical and photochemical dynamics of phthalocyanine and poly(2,5-thienylene vinylene) (PTV) thin films, and photothermal properties of cyanobiphenyl liquid crystal near the sapphire interface by transient grating spectroscopy combined with total internal reflection.

Thin films of phthalocyanines were obtained by a vacuum evaporation method. PTV film was prepared by the thermal conversion of a PTV precursor polymer at 200 - 250 °C [2]. Samples were excited by crossed two laser beams (~ 360 nm, 150 fs fwhm) with an appropriate angle to make a sinusoidal distribution of the change in complex refractive index $\Delta\tilde{n}$. Submicrometer liquid crystal/sapphire interface layers were excited by an interfering, evanescent wave under total internal reflection conditions. Relaxation of $\Delta\tilde{n}$ was probed by a femtosecond white light continuum. The diffraction efficiency was measured as functions of probe wavelength and delay time, which corresponds to a diffraction spectrum. Fig. 1 illustrates diffraction spectra of copper phthalocyanine thin film (~50 nm thickness) observed at various delay times. It was found that the peak position of the diffraction spectrum is independent of the delay time and excitation power. Diffraction decays, however, strongly depend on the excitation photon density, and the second-order diffraction with rise components was easily observed. On the other hand, diffraction decays of PTV film are approximately independent of the excitation power. A typical decay curve observed at $\chi^{(3)}$ peak of ~ 650 nm is illustrated in Fig. 2, which consists of a fast decay component of ~ 0.85 ps. From these results, temporal and spatial profiles of the grating in organic thin films are interpreted in terms of exciton diffusion and relaxation of self-trapped exciton. In μs time scales, the thermal diffusion of a sample is given by transient grating spectroscopy. The thermal diffusion of a liquid crystal/sapphire interface layers was found to be different from those in the bulk. The phase transition behavior in thin layers is also discussed in relation to the thermal diffusion.

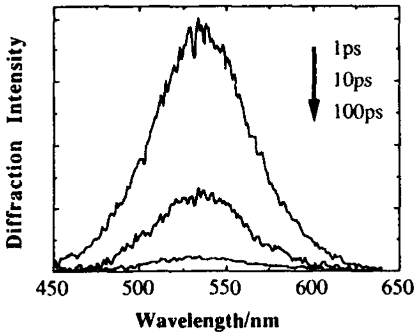

Fig. 1 Diffraction spectra of copper phthalocyanine thin film.

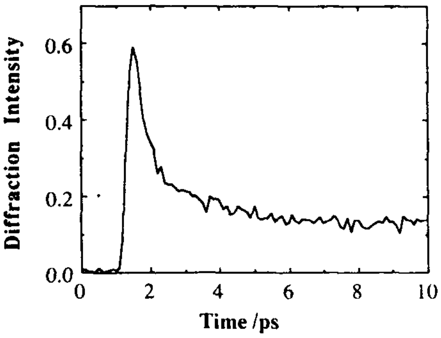

Fig. 2 A decay curve of diffraction intensity of PTV thin film observed at 650 nm.

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TIME RESOLVED LUMINESCENCE, PHOTOCURRENT, AND REACTION SCHEME FOR THE FOLDED DYE-SENSITIZED TiO_2 ELECTRODE

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This paper addresses the behavior of a dye-sensitized solar cell with a high surface area that was described recently by Grätzel's group in Lausanne. It is an improved version of a cell suggested earlier by Tsubomura et al. Photocurrent excitation spectra and picosecond time-resolved luminescence difference spectra reveal that the adsorbed Ru-dye-molecules are indeed the electron injecting species on the folded surface of the polycrystalline TiO_2 electrode. Stationary luminescence spectra are dominated by color-centers that are not active in the electron injection process. Absorption and luminescence spectra and luminescence decay curves show aggregation and intersystem-crossing of the adsorbed dye molecules and shed light on the stability of different ruthenium dyes. The reaction scheme of the cell involves at least four different stages and reveals cases where there is no trivial direct relationship between the photocurrent and the dye-luminescence in this cell, the latter would be expected to hold true for an essentially 2-level scheme. Injection of majority carriers from the excited dye molecules into an extremely thin TiO_2 layer allows for employment of TiO_2 material with extremely high trap density without involving at the same time serious losses in the cell. We will discuss possible mechanisms resulting in the observed fairly small recombination losses between oxidized dye molecules adsorbed on the folded TiO_2 surface and electrons injected from this surface into the TiO_2 material. Strategies will be considered for achieving long-time stabilization of this type of majority-carrier injection solar cell.

Ultrafast Dynamics of Excited States of J-Aggregates

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The excited state dynamics of J-aggregates formed from carbocyanine dye BIC have been studied with picosecond transient absorption and fluorescence spectroscopy. With the former method, we created many excitons per aggregate. The observed dynamics are intensity dependent and reflect exciton-exciton annihilation processes. In addition, the zero time spectrum is also intensity dependent, probably due to a reduction of k-space at high exciton concentrations. J-aggregates in glass are studied at liquid helium temperature and broadening and red-shift of time-resolved fluorescence spectra on the picosecond timescale are observed. The fluorescence lifetimes decreased with increasing temperature in the range of 20 - 60 K. The possible mechanisms of these phenomena are discussed.

ORAL PRESENTATIONS

ORGANIC/INORGANIC MOLECULAR BEAM EPITAXY (O/I-MBE): FORMATION AND CHARACTERIZATION OF ORDERED ORGANIC/SEMICONDUCTOR, ORGANIC/METAL, AND ORGANIC/ORGANIC' HETEROJUNCTIONS AND SUPERLATTICES

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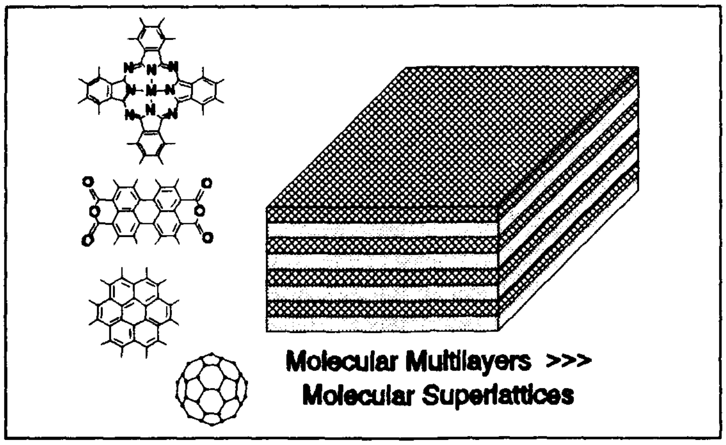
A combination of molecular beam epitaxies has been developed to create highly ordered thin films of trivalent and tetravalent metal phthalocyanine dyes on metal dichalcogenide semiconductors such as SnS_2 and MoS_2 [1]. MBE deposition of the semiconductor thin film produces a semitransparent substrate for the dye layers which then supports characterization by both photoelectrochemical and optical means, including linear absorbance and reflectance/absorbance spectroscopies and femtosecond transient hole-burning spectroscopies [2,3].

The development of the O/I-MBE process has been driven by the interest in studying dye sensitization, exciton coupling, electroluminescence, fast optical switching and other optical nonlinearities in organic materials with long range order as thin films, and the capability to form molecularly sharp interfaces with both inorganic and organic dye substrates. The O/I-MBE process should be viewed as complimentary to other casting or LB deposition strategies, and provides for the deposition of dyes not amenable to these solution deposition procedures, with no need for hydrocarbon spacer layers between the dyes.

Surface electron diffraction techniques are applied during the MBE deposition process to verify long range order of the dyes and to determine the architecture of the monolayer→multilayer dye assemblies [1,2]. On the six-fold symmetric basal planes of SnS_2 and MoS_2 the four-fold symmetric phthalocyanines form 3-6 equivalent domains, rotated to optimize the van der Waals interactions between the first dye monolayer and the substrate chalcogenide atoms (sulfur-sulfur spacing distances apparently control orientation of these domains). Perylene dyes form pseudo-hexagonal arrays, also rotated to optimize interaction with the substrate, while high symmetry molecules such as C_{60} form perfectly coincident six-fold symmetric surface layers [4].



Photoelectrochemical studies of Pc/SnS_2 interfaces show that dye sensitization by the ordered Pc monolayer is quite efficient, with quantum yields per absorbed photon in the first monolayer of up to 50% and photocurrent spectral lineshapes nearly as narrow as those for the monomer in solution [3]. Provided that long range order is sustained in the deposition of the second and subsequent layers, the spectral shapes remain narrow and the QYAP values decrease to 1-5%. Systematic shifts in the Q-band maximum are seen as the epitaxial layer growth is continued, up to ca. 10 ordered monolayers. The exciton coupling model (point dipole approximation) has been extrapolated to these systems to model the interaction between adjacent epitaxial dye layers [3b], confirming that this type of exciton coupling should saturate at epitaxial dye layer thicknesses of 6-10 monolayers.

Femtosecond differential hole burning spectroscopies (DTS) of both disordered and ordered phthalocyanine layers have been carried out [2]. For the disordered films, pumping anywhere in the Q-band region produces a spectral hole, temporally coincident with the pump, at the bottom of the excited singlet manifold. For epitaxial Pc thin films (e.g. InPc-Cl/SnS_2) the spectral hole is at the Q-band maximum, consistent with the more homogeneous enviroment for the chromophore in these MBE-grown materials. In both types of materials there is a significant induced absorption (IA) event on the high energy side of the Q-band, better resolved in the epitaxial thin films, which suggests a "biexcitonic-like" process following the initial excitation. Relaxation rates for both the DTS and IA events are strongly temperature and polarization dependent and occur on time scales that are encouraging for the envisioned fast optical switching applications for this type of organic thin film.

Success in creating highly ordered phthalocyanine, perylene and C_{60} thin films has now led to attempts to grow true organic/organic' superlattices based on these materials [4]. Starting with ordered Pc layers on substrates such as MBE-grown-SnS_2, it is possible to form ordered $[(InPc\text{-}Cl)_{1\text{-}4ML}/(C_{60})_{1\text{-}4ML}]_{20}$ or $[(InPc\text{-}Cl)_{1\text{-}4ML}/(PTCDA)_{1\text{-}4ML}]_{20}$ multilayers [4a]. Provided that the Pc coverage per layer is 1-2ML, narrow Q-band lineshapes can be sustained, and the excitonic interaction between adjacent Pc layers can be carefully regulated by controlling either the C_{60} or the PTCDA film thickness. Photoelectrochemical and DTS/IA studies in progress suggest that formation of such multilayers will be an attractive way to study excitonic interactions which have been largely confined to two-dimensional ordered layers.

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PHOTOINDUCED PROCESSES IN RIGID SUPRAMOLECULAR SYSTEMS

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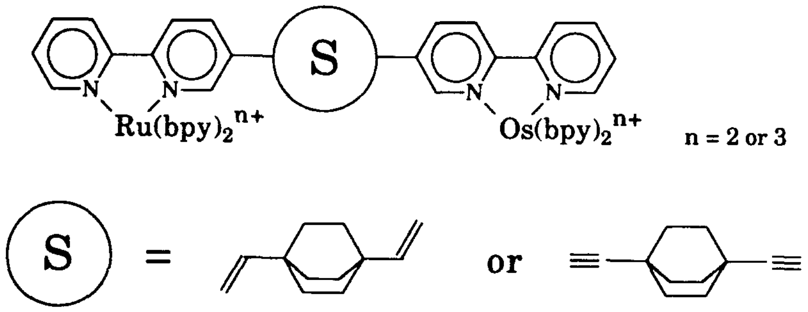
There has been considerable interest in photochemical and photophysical processes of molecular assemblies consisting of polypyridine complexes. Recently our main effort concerned with covalently linked polynuclear complexes of Ru(II) and Os(II) in which optical excitation is followed by spatially directed energy and/or electron transfer. The mono- and dinuclear complexes containing rigid bridging ligands and $Ru(bpy)_2^{2+}$ and $Os(bpy)_2^{2+}$ units have been synthesized and their electrochemical and photophysical properties investigated. Such rod-like, nanoscale supramolecular species exhibit intense absorption spectra, strong and long-lived luminescence, and reversible redox properties. In the mixed metal $[(bpy)_2Ru(bpy\text{-}S\text{-}bpy)Os(bpy)_2]^{m+}$ complexes (see figure) long-range energy and electron transfer take place. Their rate constants and mechanisms are discussed.



PHOTOCONDUCTIVITY IN DISCOTIC LIQUID CRYSTALS: A NEW CLASS OF HIGH MOBILITY MATERIALS

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Organic photoconductors have penetrated many areas of technical applications such as laser-printing, offset-printing etc. Their major disadvantage has, so far, been their low charge carrier mobilities, which are mainly due to disorder phenomena. The latter lead to a hopping conduction of rather localized charge carriers.

In organic crystals one can see the onset of band-like carrier propagation due to the good overlap of the molecular wave functions and due to the long range order of crystalline materials.

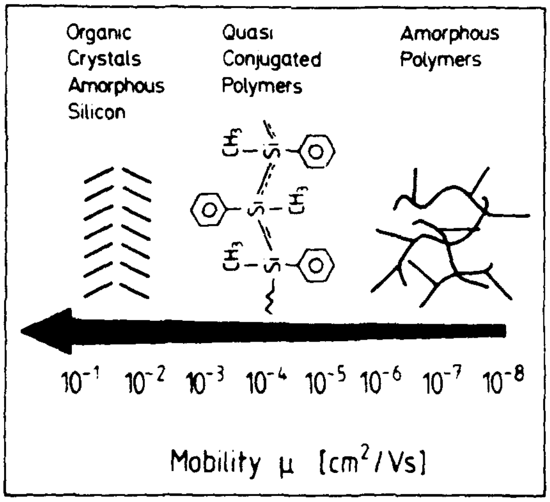

Fig. 1: Mobilities of typical organic solids (see text).

We have, for the first time, been able to perform dynamical photoconduction experiments in a discotic liquid crystal [1]. Whereas the crystalline (multicrystalline) phase shows heavy trapping, the meso-phase shows rather high hole mobilities (10^{-3} $cm^2/Vsec$) and moderately high electron mobilities (10^{-5} $cm^2/Vsec$).

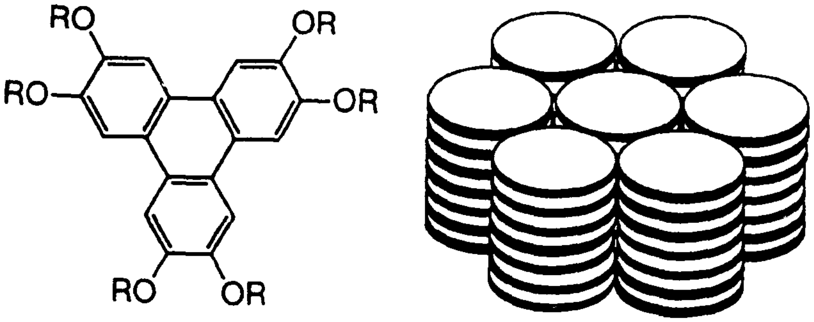

Fig. 2: Structure and packing of hexapentyloxytriphenylene. The R-group corresponds to R = C_5H_{11}.

The temperature- and field-dependence of charge carrier mobilities will be discussed in some more detail.

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MECHANISM OF LASER-INDUCED HOLE FILLING IN PHOTOCHEMICAL HOLE BURNING AT 4-20 K

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Laser-induced hole filling (LIHF) in persistent spectral hole burning is a phenomenon in which the decrease in hole depth occurs without changing its width for a previously burnt hole during laser irradiation at a different wavelength. There are several papers concerned with the LIHF [1-3]. Among them, our previous paper [3] showed that LIHF due to structural relaxation of matrix polymers is an important factor controlling the hole formation of porphyrin derivatives at 80K depending on the nature matrix polymers, since the temperature dependence of quantum efficiency for hole formation, Φ, markedly deviates at 50- 80 K from that of Debye-Waller factor while the former coincides well with the latter at 4- 30 K. The mechanism of LIHF due to the structural relaxation was also suggested by the fact that polymers with hydrogen bonding (polyvinyl alcohol and epoxy resin) and capable of hole formation at 80 K showed excellent resistance against LIHF at 50 and 80 K during temperature cycle experiments.

The LIHF at lower temperatures, e.g. 4-20 K, is also important topic since it is related to non-site-selective phonon-assisted excitation process of the host-guest systems and it would be the principal factor for limiting the achievable recording density of photochemical hole burning (PHB) memory. A convincing mechanism of LIHF at 4-20 K [4] is proposed in the present contribution.

The extents of LIHF at 4-20 K were precisely measured as a function of energy difference from the newly burnt wavelength, of burning power, and of an originally burnt hole depth for sulfonated tetraphenylporphin (TPPS) in poly(vinyl alcohol)

(PVA) film. The hole profiles during hole filling experiments (Fig.1) and the wavelength dependence of hole filling extent γ at 20 K (Fig. 2) are shown below. Dyes doped in amorphous hosts can be excited non-site-selectively through three types of transitions in addition to the site-selective purely electronic zero-phonon transition. These three types are : excitations from thermally excited S_0 states, excitations to lattice vibronic states in S_1, and to vibronically excited states of dye molecules in S_1 with lattice vibrations. The main mechanism of LIHF at 4-20 K is supposed to be these non-site-selective excitations and reactions, which lead to smaller decrease in absorbance in the previously burnt wavelength region compared to the region that was not previously burnt.

$$\gamma(\lambda) = \lim_{E_B \to 0} [1-\Delta A_{E_B}(\lambda) / \Delta A_0(\lambda)] / E_B$$

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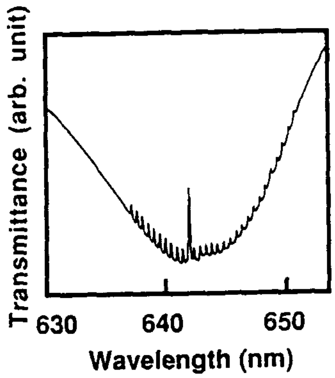

Fig. 1. Example of quantitative experiment for laser induced hole filling at 20 K. The hole at 642.0 nm is formed with burning energy E_B. Depth changes of other holes are measured as a function of E_B. Note that the holes in the lower wavelength region are more filled compared to the holes in the shorter wavelength region.

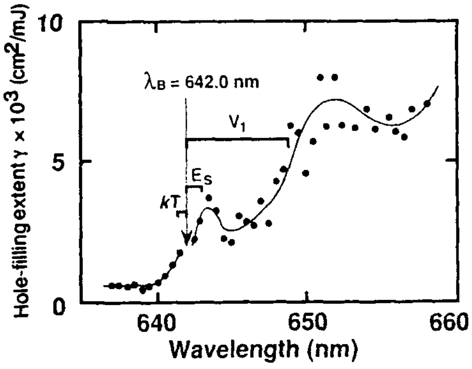

Fig. 2. Wavelength dependence of hole -filling extent γ of TPPS/PVA at 20 K. Burning wavelength λ_B is 642.0 nm. This figure also shows the phonon energy E_s (23.5 cm^{-1} or 0.96 nm), energy difference between the first main satellite hole and the resonant hole V_1 (169 cm^{-1} or 6.94 nm), and kT at 20K (13.9 cm^{-1} or 0.57 nm).

ATOMIC FORCE MICROSCOPY ON PHOTOREACTIVE ORGANIC SOLIDS

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INTRODUCTION

Stereoselective photolyses of crystals include absolute asymmetric syntheses [1]. The stereoselectivities have been rationalized in terms of the well known topochemistry principle. However there are numerous severe drawbacks with hardly understood positive and negative exceptions [2]. With the advent of atomic force microscopy (AFM) it has become apparent, that phase transformations, which largely had not been acknowledged previously, are vital for photoreactivity and that those involve far reaching spatially directed transport phenomena [3]. At present, eight different mechanisms are known and these will be interpreted on a molecular basis.

RESULTS AND DISCUSSION

Numerous **enantioselective syntheses** by solid-state photochemistry are known. However, in most cases ee-values are poor [1]. Thus, most of the chirality advantage of the crystal may be wasted upon photolysis via conformational racemization during the phase transformation.

The photodimerizations of **α- and β-cinnamic acid** yield α-truxillic and β-truxinic acid predominantly. However, in contradiction to previous belief, there are spatially directed formations of flat covers with trenches (followed by floes) or craters (β-, (100)) and volcanoes (β-, (010)) followed by flattening. Crystal structure will be discussed.

In the photodimerization of the **chalcone** 2,5-dibenzylidene *cyclopentanone* three products are formed. From those, the h/h-anti-cyclodimer puts an incredible world record in terms of topochemistry principle with a skew angle of 135°. However, AFM on (001) clearly indicates materials' transport over more than 10 nm even in the initial phases of the reaction.

Anthracene forms topochemically forbidden its [4+4]photodimer. The reaction starts along one-, two-, three- and four-molecular steps, which behave as independent crystal face already. Those are easily depicted within a simple AFM run on (001) and provide a new approach to nanotechnology. 9-Cyanoanthracene yields the head to tail photodimer in opposition to crystal structure. The product formation occurs on multimolecular steps upon (010) which again behave as distinct submicro crystal faces.

Crystalline **diphenyltetrazole photoeliminates** nitrogen. Escape of nitrogen occurs through newly formed submicroscopic holes. This points to applications in submicrofabrication techniques.

CONCLUSION

AFM is a versatile new experimental technique for elucidation and interpretation of solid-state photolyses. The results are directly seen in 3D-pictures. Furthermore there are new approaches to nanotechnology.

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Energetic topography of organized molecular systems*

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A model for the description of electronic excitations in organized molecular systems of finite size in which intermolecular distances are comparable to molecular dimensions is presented**. A methodology based on the excitonic theory coupled to quantum chemistry is developed and applied to columnar aggregates of triarylpyrylium tetrafluoroborates and triphenylenes. Excitation energy and interactions among transition moments (diagonal and off-diagonal terms of the matrix Hamiltonian) are calculated taking into account the precise geometry of the aggregate. The energetic topography of triariaryl pyrylium aggregates shows that diagonal energy is sensitive to edge and orientational effects. Conversely, the relative orientation triphenylene cores has not a big influence to the excitation energy. Diagonalization of the electronic Hamiltonian in the strong exciton interaction limit, provides the eigenstates from which localization indexes, radiative lifetimes, absorption and fluorescence spectra are calculated. Previously published experimental data are discussed in the light of the theoretical calculations.

* the present work has been performed within the frame of a COST D4 project entitled "Columnar liquid crystals as energy guides for molecular electronics".

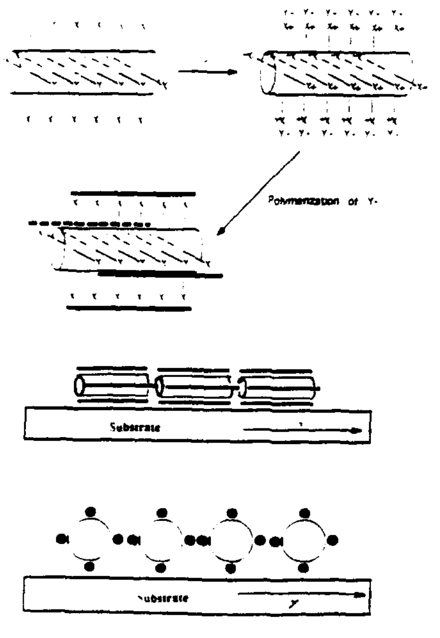
** Chem. Physics, *in press*

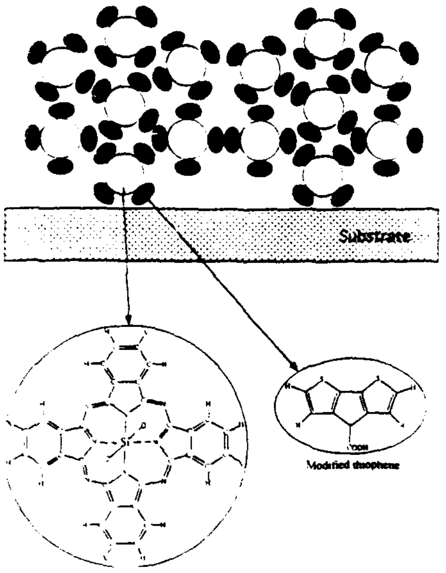
. CEA CE SACLAY (France) - Dr. A. RUAUDEL-TEIXIER
. Universidad Antonoma de Madrid (Spain) - Pr. TORRES
. Universita degli studi de Milano (Italy) - Pr. SANNICOLO

Title : Oriented conducting polymers in a Langmuir-Blodgett supramolecular architecture

The electrical conductivities of organic polymers are known to be severely affected by structural defects such as dispersed length (chain ends), misorientation and tilting of the chains (polymers are seldom grown as monocrystals).

The goal of this proposal is to control the primitive organization of monomers and to polymerize them topochemically in the solid state, so as to obtain long monodispersed aligned polymer chains. From this ordering in a supramolecular architecture, the conductivity, when monomers are from the thiophene, pyrrole or aniline family is expected to increase by several orders of magnitude. To reach this goal the proposed strategy consists in the design and the synthesis of a matrix, made of rigid polymeric rods, preprogrammed to interlock with designed monomers, along the long axis of each rods, at well defined intervals (allowing C-C bonds when the polymerization will be performed in the solid state). The alignment of the matrix will be given by the Langmuir-Blodgett technique and so the conducting polymer chains will grow along, at the periphery of the template rod like polymer. The chemistry and synthesis of the rod like template (siloxo phthalocyanines) will be realized by the team of Pr. TORRES (SPAIN). The monomers will be synthetized by Dr. SANNICOLO (ITALY) and the work-up by the L.B. technique, as well as solid state reactions (interlocking and polymerization by the SACLAY team (M. VANDEVYVER, S. PALACIN, A. RUAUDEL-TEIXIER).





PHOTOPHYSICAL PROCESSES INVOLVED IN CREATION OF DARK SPATIAL SOLITONS IN COMPOSITE PHOTONIC MEDIA

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A dark spatial soliton is a self-guided dip in the intensity profile of an optical beam propagating in a nonlinear medium. It is a stable spatial structure with a constant shape and size where diffraction of the beam is exactly cancelled by the action of the nonlinearity of the medium [1]. A dark soliton requires the medium to have a negative nonlinearity, i.e., the nonlinear refractive index n_2 or third order susceptibility $\chi^{(3)} <0$ (self-defocussing behaviour) as opposed to the condition for a bright soliton which can be formed in nonlinear media with $n_2>0$ [2].

An exciting feature of spatial solitons is their ability to create waveguide structures including Y and X-junctions [3,4]. In the simplest case, a π phase jump introduced across the centre of a Gaussian beam leads to the formation of a (1+1)D black soliton which writes a refractive index profile in which the bright regions have a lowered refractive index due to the negative n_2 ($n=n_0+n_2I$), while in the centre of the dark soliton the index is unperturbed. The waveguide formed in this way can be used to guide a separate probe beam coaxially along the soliton. Dark spatial solitons can thus be used for guiding light beams by other light beams and this is of great interest to all-optical processing of information.

We have started a project to develop materials suitable for a technology which uses dark spatial solitons for creation of permanent and transient waveguiding structures. Such materials involve polymers as well as organic/inorganic composites fabricated using the sol-gel process. Our interest is in materials which show self defocussing behaviour, i.e. in which the action of light is to reduce the magnitude of the refractive index. Three classes of photophysical processes which are of interest here are:

- photochemical transformations of the dye molecules. These can lead to transient or permanent bleaching of absorption, which, through the Kramers-Kroning transformation causes a decrease of the refractive index,

- thermally induced changes in absorbing media. The major component of these changes is due to thermal expansion leading to a defocussing behaviour, however, other processes may also contribute to the total refractive index change,
- electronic third-order optical nonlinearity of molecules. As a rule, negative (defocussing) $\chi^{(3)}$ occurs for wavelength between the single-photon and two-photon absorption edges of the material.

We have investigated a large number of dyes of various chemical structures in various media (solution, molecularly doped polymer, sol-gel silica glass) and found that the refractive index changes necessary to create a dark soliton which, in turn creates a waveguide can be obtained through bleaching of several dyes. In particular, many fluorescein derivatives have been found to be suitable for writing permanent waveguide structures by bleaching. Thermally induced refractive index changes can also be of practical interest for relatively slow photonic switching using dark solitons. In both cases, however, the situation is complicated by the fact that the effective nonlinearity is a nonlocal function of both time and the spatial variables which is equivalent to saying that the nonlinear refractive index n_2 is a function of both the frequency (which determines the time response of the soliton switch) and the spatial frequency (which influences the ability to form highly spatially resolved structures such as soliton induced waveguides).

The formation of solitons and soliton induced waveguides in polymeric materials and viscous solutions has been found to be greatly influenced by the Soret-like thermodiffusion process. This nonlocal contribution to the effective thermal nonlinearity of a multicomponent medium is a slow process which, depending on the details of the composition of the medium, can either destroy the soliton or enhance its formation. This is of special importance for such media as dye-doped polymer-solvent systems.

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ELECTRON AND ENERGY TRANSFER IN LANGMUIR BLODGETT FILMS

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Langmuir Blodgett layers, allowing a control of molecular orientations and the formation of designed structure in one dimension are, the systems of choice to investigate electron and energy transfer in organized molecular assemblies. Due to the large local sensitizer concentration in Langmuir Blodgett films the photophysical behaviour of the sensitizer will be influenced by the formation of and (inter or intralayer) [1] energy transfer to aggregates [2]. Information on or suppression of those processes is therefore necessary for a quantitative study of excited state electron transfer processes in those films. Preliminary experiments suggested that this dimer formation can de reduced significantly [3] using a matrix of unsaturated phospholipids. This has been confirmed more recently using octadecyl substituted rhodamine B and octadecyl substituted crystal violet. When Cd-arachidate is used as matrix energy transfer to dimers or aggregates becomes for both molecules already an major decay processes when 0.3 % or less of the area of each layer is occupied buy dye molecules. On the other hand using the a matrix of dipalmitoyl phosphatidic acid or dioleoyl phosphatidic acid those processes become only relevant at a coverage of more than 3 %. In the latter system the non exponential decay observed at low concentrations of dioctadecyl crystal violet is not related to energy transfer to dimers but to the presence of two nearly degenerate transitions in the chromophore.

Global analysis [4] of simulated fluorescence decays suggested the possibility to discriminate between a homogeneous distribution of acceptors, a system with two phases and a distribution of acceptors characterized by a fractal dimension [1]. In this way it is possible to cover a range of dimensions that is accessible neither with X-ray or electron diffraction nor with optical spectroscopy. While at low acceptor concentrations energy transfer can be described using stretched exponential expressions more complicated expressions are necessary at higher acceptor concentrations [5]. Recently it has become possible to fit fluorescence decays simulated for a large range of acceptor concentrations to an approximate multi-exponential expression. The validity of this expression will be investigated for experimentally obtained fluorescence decays obtained for a large range of acceptor concentration. In a next step the expression will be adapted for the occurrence of donor-donor energy migration and be used for fluorescence decays obtained of a large range of donor concentrations.

As the investigation of sensitized photocurrents [6] and luminescence quenching [7] in multilayer structures suggested important contributions of the through bond interactions to the electron transfer a polychromophoric molecule, N,N'-di-(1-pyrenyl)-butyloxacarbocyanine (OXAPY) that could be incorporated in oriented way into a Langmuir Blodgett layer was synthesized [8]. Photoinduced electron transfer between covalently bound chromophores as OXAPY incorporated in a monolayer will be compared to electron transfer between similar chromophores situated at opposite sides of a monolayer. To the extent that the electron transfer is reversible, as was observed for OXAPY in solution, those experiments yield also information on the further decay processes involving the charge separated state. The latter processes will also be investigated using nanosecond flash photolysis. If important lateral movements of the hole occur they should also be detected by stationary ad time-resolved photocurrents in the plane of the monolayer.

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TOWARDS ORGANOMETALLIC CONDUCTING POLYMERS CONTAINING BIS-CYCLOMETALLATING BRIDGING LIGANDS

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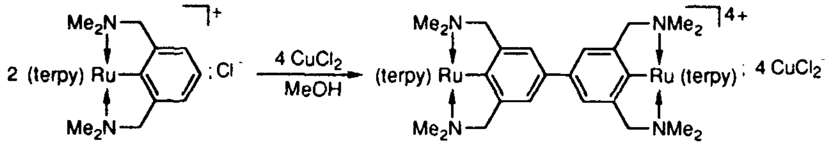
The search for bridging ligands allowing electronic communication between metal centres is an important target related to long-range electron transfer and photoinduced charge separation. Recently, Sauvage et al.[1] found a new type of biscyclometallated 3,3',5,5'-tetrapyridylbiphenyl ligand, tpbp, bridging two ruthenium centers in the complex $[(\text{tterpy})\text{Ru}]_2(\text{tpbp})^{2+}$, tterpy = 4'-p-tolyl-2,2':6',2"-terpyridine, as shown in Figure 1. Besides the way this compound was formed, this complex showed interesting photophysical and electrochemical properties. These properties originating from the fact that it can exist not only in Ru^{II}_2 and Ru^{III}_2 oxidation states but also in the mixed valence state $\text{Ru}_2^{\text{II,III}}$ (comproportionation constant K_c is ≈600). The most striking aspect of the $\text{Ru}_2^{\text{II,III}}$ state is related to its intervalence transfer (huge IT band at $\lambda_{max} \approx 1820$ nm, $\varepsilon \approx 27000\ \text{M}^{-1}\text{cm}^{-1}$) that indicates significant delocalization.

In a collaborative project the Utrecht group is exploring the use of the bis-*ortho*-chelating ligand 2,6-bis[(dimethylamino)methyl]phenyl, *trans*-pincer, in ruthenium chemistry. In the course of these studies the reaction shown in eqn 1 was realized and the resulting dinuclear ruthenium complex with a bridging bis-*trans*-pincer was isolated and characterized by X-ray diffraction. The planar biphenyl part of this ligand is a striking structural feature of this complex (see Figure 2) that was not present in $[(\text{tterpy})\text{Ru}]_2(\text{tpbp})^{2+}$.

Eqn. 1



terpy = 2,2':6',2" terpyridine

The easy oxidative coupling of $(\textit{trans}\text{-pincer})\text{Ru}(\text{terpy})^+$, which has a highly reversible Ru(II)/Ru(III) couple (i.e. the *trans*-pincer is a strong electron donor), opens the way to a new family of complexes combining two different C-bonded aromatic nuclei disposed in a *para*-fashion with respect to the metal-carbon bonds. Such back-to-back bis-chelated metal centres could form the basis for interesting switchable devices with controllable conformational changes (e.g. rotation around the central C-C bond). The current status of the project will be discussed.

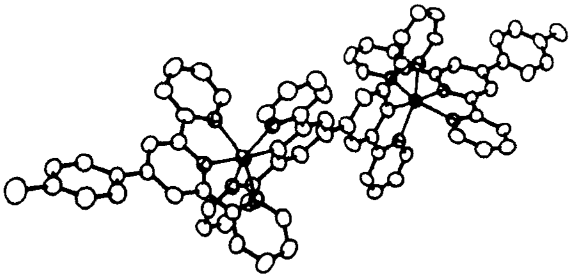


Figure 1. Molecular structure of $[(\text{tterpy})\text{Ru}^{II}]_2(\text{tpbp})^{2+}$: Ru•••Ru distance, 11.009(2) Å, torsion angle around the central C-C bond of the tpbp ligand, 22.2(7)°.

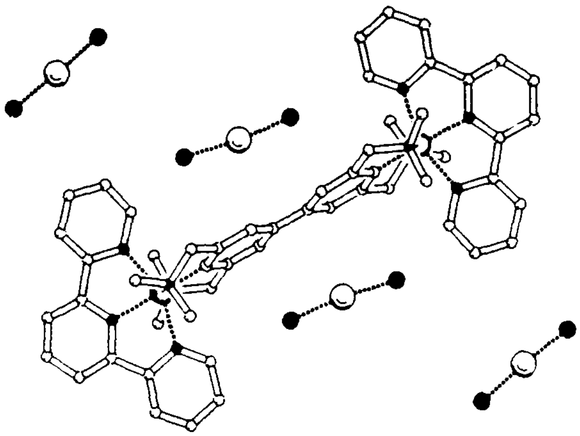


Figure 2. Molecular structure of $[(\text{terpy})\text{Ru}^{III}]_2\{\text{bis-}trans\text{-pincer}\}^{4+}$; 4 $(\text{CuCl}_2)^-$: Ru•••Ru distance, 10.829(2) Å, torsion angle around the central C-C bond, 0°; length of that bond, 1.436(12) Å.

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OPTICALLY INDUCED TRANSIENT CONDUCTIVITY IN QUASI-METALLIC DCNQI RADICAL ION SALTS

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ABSTRACT

Multi-component conductivity changes in metallic radical ion salts are induced by optical excitation. The measurements stimulate the search for new models describing the charge carrier generation and transport in these salts. First experiments on polycrystalline films of the quasi-three-dimensional 2,5-dimethyl-dicyanoquinonediimine copper salt, $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$ and the corresponding low-dimensional chlor-methyl and brom-methyl salts, $(\mathrm{ClMe\text{-}DCNQI})_2\mathrm{Cu}$ and $(\mathrm{BrMe\text{-}DCNQI})_2\mathrm{Cu}$, respectively, are presented. The experiments raise the question whether there is a considerable contribution of higher conduction bands which might explain the fast signals ($\tau < 5$ ns).

INTRODUCTION

Conventional photoconductivity in highly conducting materials, e.g. DCNQI salts [1], is unlikely to be observed because of considerable charge carrier concentrations in the conduction bands. We are interested in switching the conductivity mechanism in materials which show extremely high dark conductivities. In systems of limited dimensionality, a possible mechanism is the reversible optical modification of the Peierls distorted state [2]. Apart from optically induced phase transitions one might speculate about the existence of higher conduction bands in molecular solids which could contribute to very fast charge transport via delocalized electronic states.

EXPERIMENTAL

Substrates of quartz were contacted with 50 Ohm stripline technique. Covering these substrates partly with evaporated Cu, films of DCNQI salts have been grown by submerging the substrates into a solution of the corresponding DCNQI molecules in $\mathrm{CH_3CN}$. This technique yields films which are less ordered than those obtained by a solid state diffusion reaction applied to alkaline salts [3]. Figure 1 gives a top view onto the network like film structure. The films were irradiated by light of a $\mathrm{N_2}$-laser (337 nm, 5ns, max. 1mJ) and the changes of the electrical conductivity were detected by a fast digital storage oscilloscope (1 Gigasample/sec). In order to scope with the low signal levels at broad band detection, a differential averaging technique was applied.

Figure 1
Top view on a $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$ film processed by the solution technique. Thickness 10 μm. Dimensions of area 50 μm × 70 μm.

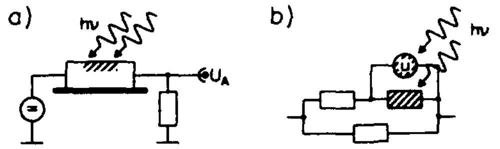

Figure 2
Experimental set-up a), and equivalent circuit b) of the film. In the irradiated area (shaded) a voltage is produced. The parallel resistance is only heated by light. The two remainig resistances account for not illuminated material and the contacts.

RESULTS AND DISCUSSION

The electric signals are discussed according to the equivalent circuit of fig. 2. In the (DMe-DCNQI)$_2$Cu films, we find a superposition of three contributions. The fast signal is not yet resolved ($\tau < 5$ ns). Figure 3 gives an example of the signal at 135 K and 300 K. Within the field strength of 2 V/m to 100 V/m it seems to be independent of the field. While its origin is uncertain, the fast pulse is best described as being created by a photovoltaic source. The fast response and the non-Ohmic behaviour raises the question for a possible contribution of higher conduction bands or a large delocalisation of the excited electronic states. This signal is also detected in monocrystals of (DMe-DCNQI)$_2$Cu. The second contribution consists of a tail following the fast signal at elevated temperatures (see fig. 3, T=300K). This hints at the depletion of shallow traps which might be localized at the grain boundaries in the films. The third contribution is slow (fig. 3, inset). It is ascribed to the thermal heating of the thin film sample because the signal shows a linear increase with the electrical field and its amplitude is proportional to the derivative $\partial\sigma/\partial T$ at the corresponding temperature.

The three contributions were found in the ClMe and BrMe derivatives of the salt films, as well.

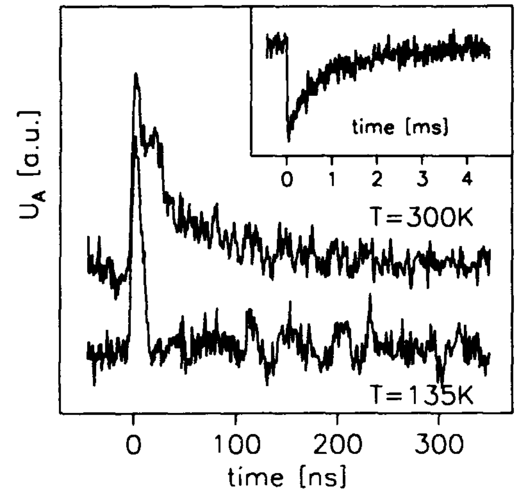

Figure 3
Electrical response of (DMe-DCNQI)$_2$Cu films to laser irradiation at $\lambda = 337$ nm, pulsewidth 5 ns, 1 mJ. Electric field E=1.5 V/m. At low temperature the fast signal cannot be resolved i.e. the laser pulse is reproduced. At 300 K a tail follows the fast pulse. This is tentatively assigned to the detrapping of charge carriers. The inset gives the thermal effect as detected at E=100 V/m at T=300 K (range of metallic conductivity).

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POSTER PRESENTATIONS

Photo-induced Tunneling Spectroscopy on ReS_2: Dramatic increase of the quantum efficiency by chemical treatment

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In this work we present a systematic study of the local photovoltaic properties of ReS_2, using a scanning tunneling microscope (STM). The tunneling junction of the STM was optically illuminated during the tunneling process. The phase sensitive detected photo-induced tunneling current (PITC) was studied as a function of wavelength and surface topography. In order to improve the performance of ReS_2-solar cells, the samples were treated with NaI/I_2- and EDTA-solutions. Relative to the untreated sample, the EDTA-treated samples show an increase in the photo-induced tunneling current by a factor of 8-10 in the whole spectral range, the NaI/I-treated samples by 2-3. Two dimensional mapping of the PITC was performed on an atomic scale and compared to the surface topography.

FLUORESCENCE OF CATIONIC DYES IN PHOSPHOLIPID LANGMUIR BLODGETT FILMS.

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With the intention of studying the excitation energy transfer process in organised Langmuir Blodgett films, a study of fluorescence of cationic dyes in several matrices was initiated to use them in a later stage as donor- and acceptor-probes .

In literature [1.,2.] difficulties in making Langmuir Blodgett films from phospholipids were mentioned. Phosphatidic acids appear to have good properties to build up multilayers, although poor deposition of phosphatidyl-cholines and -ethanolamines, who were first suggested as a dilution matrix for cationic dyes, was achieved. In practice, monolayers of dipalmitoyl phosphatidic acid spread on a $CaCl_2$ water subfase could be transferred consecutively onto a quartz-substrate. In the case of unsaturated hydrocarbon chain phosphatidic acids, double alternated films (AABBAABB...), composed of dioleoyl phosphatidic acid and arachidic acid were used as a dilution matrix for cationic dyes.

Multilayers of 0.5 - 5 mol% of N,N'-dioctadecyl crystal violet [3.,4.,5.,6.], diluted with dipalmitoyl phosphatidic acid were prepared using the Langmuir Blodgett technique. Absorbance and fluorescence excitation spectra show an absorption band at 585 nm together with a shoulder at a shorter wavelenght (540 nm). These splitting of the absorption peak can be caused by dye aggregation or ground state absorption into two neighboring excited electronic states. In the concentration range studied, the relative intensity of the band at 585 nm, compared to the band at 540 nm, remains constant. In comparison with arachidic acid as a dilution matrix, the intensity of the 555 nm band increases at the expense of the intensity of the 590 nm absorption, as the concentration of N,N'-dioctadecyl crystal violet increases. Time resolved fluorescence measurements of mixed multilayer films of N,N'-dioctadecyl crystal violet and dipalmitoyl phosphatidic acid can be analysed as a two exponential decay with a fast component lifetime of 400 ps and a longer living component of 1.4 ns, indicating that two species are present in the film. These experiments indicate that N,N'-dioctadecyl crystal violet can be used as a suitable acceptor for energy transfer in Langmuir Blodgett films.

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LOW–TEMPERATURE PHOTOCONDUCTIVITY OF DOPED AMORPHOUS SEMICONDUCTORS

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Recently, experiments were carried out [1] in order to reveal the sign of dominant photocarriers in a–Si:H at very low temperatures which show that electrons are the dominant photocarriers in the n–type and holes in the p–type samples. The result seems to be surprising because all carriers from the dopants are frozen in and do not contribute to the photocurrent.

Here we suggest a theory of low–temperature hopping photoconductivity in doped amorphous semiconductors and show that the observed behaviour can be interpreted in the framework of the energy–loss hopping model [2]. In this theory, the contribution of carriers to the photocurrent is determined by the dipole moment, produced by the carriers prior to their nongeminate recombination. In a p–type sample an electron recombines with the nearest hole and at high enough doping levels it does not contribute much to the photocurrent. A hole hops along the tail states until a new electron is generated so that the considered hole is its nearest neighbour in space. Hence holes hop usually to much higher distances than electrons in p–type samples, which explains the observed asymmetry in the contributions of holes and electrons to the photocurrent in doped amorphous semiconductors.

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SECOND ORDER OPTICAL NONLINEARITY OF "IN-PLANE" POLED POLYMER FILMS INDUCED BY CHARGE INJECTION

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Second order nonlinear optical properties such as second harmonic generation (SHG) can be induced in polymers containing hyperpolarizable dyes when the isotropic symmetry is broken, such as by the application of electrostatic fields (poling). This is usually explained in terms of dipolar alignment of the dye molecules along the field direction.

We have previously reported [1] the creation of asymmetry and second order nonlinearity by a different mechanism when an electric field is applied in the "in-plane" geometry using thin electrodes (see Figure 1). The strongest nonlinearity is induced *perpendicular* to the applied field, and has been attributed to surface charge injection during poling, followed by diffusion into the bulk and trapping on dye molecules, particularly aggregates.

Our model system in the earlier study [1] was polymethyl methacrylate (PMMA) doped with dimethyl amino nitrostilbene (DANS). When an electrostatic field of 10^4 V/cm is applied in the "in-plane" geometry, we obtain $\chi^{(2)}$ in excess of 10^{-8} esu perpendicular to the poling field. This is more than an order of magnitude stronger than the nonlinearity *parallel* to the field. We now report that in-plane poling of DANS in other commercially available polymeric matrices (polycarbonates, polysulfones, poly vinyl chloride) yields similar nonlinearities perpendicular to the poling direction. These polymer hosts exhibit greatly enhanced temporal stability of the nonlinearity i.e. the decay of the nonlinearity after poling is much slower than in PMMA.

We have also varied the amount of charge injection into DANS/PMMA by varying the metal electrode material, and the conductivity of the substrate. Results will be presented showing how the perpendicular nonlinearity can be enhanced or diminished by these means, and its correlation with the charging current during poling.

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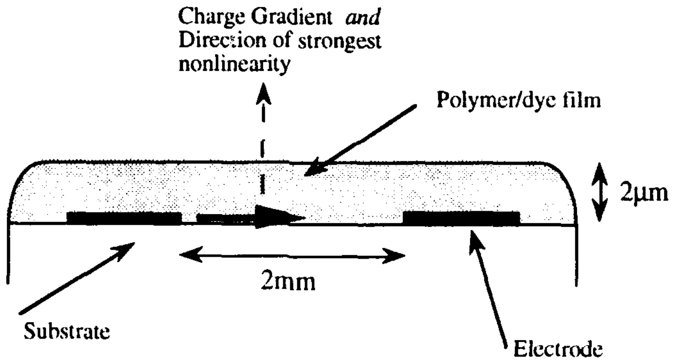

Figure 1. Side view of geometry for in-plane poling. Charge injection along the substrate surface is indicated by the thick arrow.

A NEW FLUORESCENCE PROBE FOR NETWORK FORMATION WITH INTERESTING NONLINEAR OPTICAL PROPERTIES.[1]

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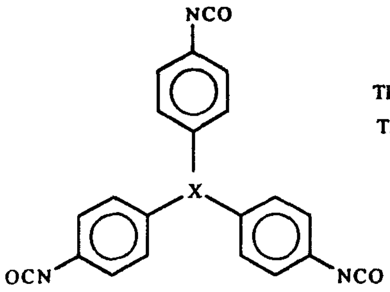
The polymerisation of linear polyimides , polyurethanes and polyamides and the formation of epoxy networks have been analysed by means of labelling the polymer chain with a molecular sensor and studying changes in the photochemical and/or photophysical behaviour of this reactive label. This technique offers the possibility to distinguish several intermediate species where other spectroscopic techniques such as IR cannot. We synthesised two trifunctional, highly symmetric probes, namely tris(p-isocyanatophenyl)amine (TIPA) and tris(p-isocynanatophenyl)benzeen (TITPB) and their 1-butanol adduct, TUPA and TUTPB.



TIPA : X=N

TITPB : X=1,3,5-phenyl

These probes can be used to study the kinetics and mechanisms of network formation of polyurethane modelnetworks and the mobility of the crosslink and segments where TIPA and TITPB both act as crosslinking site and as chemical sensor. The fluorescence intensity changes drasticly upon urethane formation. TIPA and TITPB do not show fluorescence neither in apolar nor in polar solvents but upon transformation to their urethane derivative a drastic change in the fluorescence is observed. In addition, tris(p-isocyanatophenyl)amine, TUPA tris(p-isocyanatophenyl)benzeen and TUTPB show remarkable high third order susceptibilities $\chi^{(3)}$. Incorporation of TIPA or TITPB in a modelnetwork of polyurethanes will allow the synthesis of nonlinear optical thermoharders.

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ORGANIC MIXED VALENCE SYSTEMS : INTERVALENCE TRANSITION IN PARTLY OXIDISED AROMATIC POLYAMINES.

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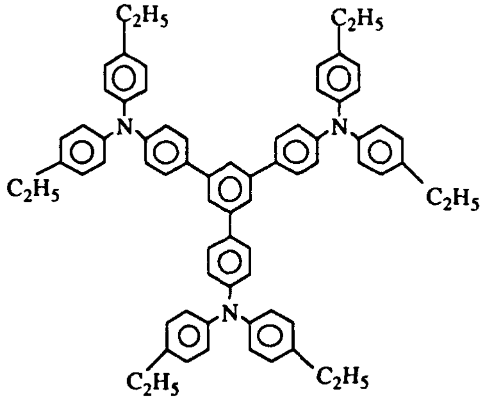
Electron transfer is a subject of great fundamental importance, particularly in the field of Molecular Electronics. It is indeed crucial to devise molecules allowing an intramolecular electron transfer between at least two redox sites linked by a bridge and to establish rules allowing the prediction and mastery of the electron propagation through this bridge. This paper is expected to be a contribution in this field.



The above molecule, noted p-EFTP has been studied by electrochemistry, UV-visible-near-IR and EPR spectroscopy. It is known for its photoconductive (1) and luminescence (2) properties.

The cyclic voltammetry shows a unique and reversible oxidation wave. The coulometry unambiguously shows a three electron process. This is explained by the fact that the oxidizable sites are far away and interact weakly with each other.

Simultaneously, the oxidation reaction is followed by UV-visible-near-IR spectroscopy which shows an increase and a decrease of a weak and wide band in the near-IR area. This is characteristic of intervalence transitions.

From the variation of the intervalence absorption bands versus the average oxidation state, we developed an original analysis from which we determined the two comproportionation constants in order to get the corrected spectra of the mixed valence mono- and di-radicals species. This method is derived from the one applied in mixed valence dinuclear ruthenium compounds (3,4). We have thus extracted the shape of the intervalence bands through deconvolution for both mixed valence radicals, which permits an evaluation of the effective intramolecular couplings between the nitrogen sites.

EPR can also be recorded during the oxidation reaction. This technique should provide crucial informations on the electron transfer rate and this study is presently in progress.

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SYNTHESIS AND ELECTRICAL PROPERTIES OF A NEW MOLECULAR SEMICONDUCTOR: THE UNSYMMETRICAL LUTETIUM PHTHALONAPHTHALOCYANINE

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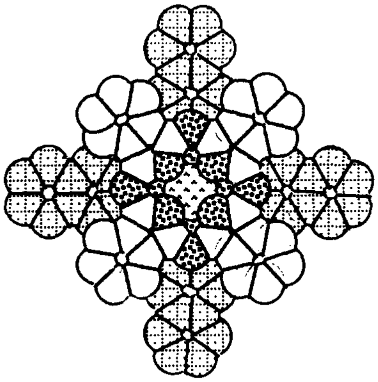
The first two intrinsic molecular semiconductors are the lutetium bisphthalocyanine, $LuPc_2$, and the lithium monophthalocyanine, LiPc. We prepared and characterized a new molecular semiconductor, the unsymmetrical lutetium phthalonaphthalocyanine PcLuNPc.



PcLuNPc is synthesized from 2,3-dicyanonaphthalene and lutetium monophthalocyanine LuPcOAc. This latter is obtained from orthodicyanobenzene and lutetium acetate $Lu(OAc)_3$. PcLuNPc is characterized by mass spectrometry, optical spectroscopy and elemental analysis. Single crystals obtained by very slow evaporation of chloroform solutions have been characterized.

We determined the redox potentials of PcLuNPc in solution (DMF/THF 50/50):
$E_0^{ox1} = +0.08V$, $E_0^{red1} = -0.39V$ vs ferrocene/ferricinium. Due to its radical nature, this compound is easily oxidized and reduced. We prepared thin films by sublimation under vacuum ($P = 10^{-6}$ torr). A conductivity of $5.10^{-5}\ \Omega^{-1}cm^{-1}$ has been measured for 500 Å thick

films deposited on gold electrodes. The corresponding thermal activation energy is equal to 0.48eV.

Using the redox potentials of the different molecular units A, A^+ et A^-, in solution, and in the solid phase, we demonstrated that the difference between the first oxidation and reduction potentials are in all cases equal to the thermal activation energy of conduction. Experimental and theoretical results are in good agreement for PcLuNPc (0.47 versus 0.48) and for the other compounds: LiPc, $LuPc_2$. These values are equal to the energies of the intermolecular charge transfer transitions E_{TC} observed in the near infra-red (1440 nm for PcLuNPc).

A NEW LB-FILM FORMING MOLECULE CONTAINING BOTH AN ELECTRO- AND PHOTOACTIVE PART

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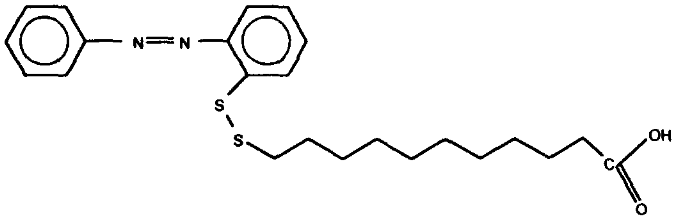
The new LB-film forming molecule (see structure below) has been synthesised and its monolayer behaviour at the air/water-interface studied. We succeeded in transferring the monolayer as a Y-type LB film onto a variety of substrates. Noteworthy, is that the molecule contains a relatively short alkyl chain and two (weakly) hydrophilic groups in the "hydrophobic" part of the molecule.

The LB films have been characterised by UV/Vis- and Fourier transform infrared spectroscopy in transmission and grazing incidence geometry. Layer thickness was determined by surface plasmon resonance experiments.

The molecule contains a photo reactive azo-group, which is capable of cis/trans-isomerization, and an electroactive disulphide bridge, which can be cleaved by electron transfer from an underlying electrode in an LB-film monolayer. Consequently, we performed cyclic voltammetry-measurements on LB monolayers before and after photoisomerization of the azo-group.



EXCITED STATE PHENOMENA IN SOLID STATE FULLERENE

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ABSTRACT

Time resolved photoluminescence is employed as a probe of the highly excited state of fullerene powders and crystals. Above a threshold input intensity, a dramatic increase in the lifetime as well as a redshift and broadening of the spectrum is observed. The luminescence intensity is seen to increase with the cube of the input intensity. The phenomenon is interpreted as an abrupt onset of emission from the highly populated triplet state resulting from a banding of the intramolecular triplet states, a process which is dependent on a critical excited state density. Furthermore, the phenomenon may be photoexcited at photon energies which lie below the HOMO-LUMO transition energy, under which conditions an intensity dependence of the output luminescence on input to the sixth power is observable. Under "off-resonant" conditions the process is interpreted as a two photon assisted nonlinear emission. This transition from a molecular to solid state behaviour is similarily manifest in the transport properties, the photocurrent increasing with the cube of the input intensity above the nonlinear luminescence threshold. Whereas at low intensities the temperature dependence of the photoconductive response indicates that the transport processes are activated, characteristic of a molecular insulator or semiconductor, the photocurrent is almost temperature independent at high intensities, indicative of a metallic behaviour.

ELECTRON TRANSFER REACTIONS IN FERROELECTRIC POLYMERS

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A model for an electron transfer system in a ferroelectric is developed. The electron transfer system is assumed to consist of two coupled electronic states interacting with a ferroelectric background described by a continous order parameter. Time dependent equations describing the system are derived and it is shown that for sufficiently large dielectric susceptibility the rate of transfer is controlled by the nature of the dielectric fluctuations of the dielectric. Application of the theory to molecular switches are discussed.

Conductivity and Photoconductivity in Nanosize Conductors

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Spreading of a solution of monomers and polymers of hexa-alkoxytriphenylenes, which form bulk discotic mesophases[1], on a Langmuir trough allows to obtain stable monolayers. By successive deposition of monolayers it is possible to obtain multilayers, with a thickness between 2 and 200 nm which are characterized by a columnar packing of the aromatic moieties.

When the Langmuir-Blodgett films are deposited on interdigiting electrodes with a spacing of 100 μ, it is possible to obtain a dark current[3-4] which is one order of magnitude larger for the polymer compared to the monomer. Using this experimental configuration the controversy[5-7] arising for the conductivity normal to Langmuir-Blodgett films can be avoided. The dark currents are proportional[4] to the number of layers and depend in a superlinear way on the applied electric field. While doping with iodine[8] leads to an enhancement of the dark current addition of trinitrofluorenone[9-10] does not increase the dark current.

Upon illumination with ultraviolet light a photocurrent proportional to the applied field and the incident light intensity can be observed. The action spectrum of the photocurrent corresponds to the absorption spectrum of the Langmuir Blodgett films. The photocurrent is enhanced in the presence of oxygen. Doping the Langmuir Blodgett films by both iodine and trinitrofluorenone quenches the photocurrent. As observed for the dark current the photocurrent is an order of magnitude larger for the polymer compared to the monomer.

A similar behaviour is observed for the emission spectra of the Langmuir Blodgett films which consist for the monomer of a structured band and resemble those of a dilute solution. For the polymer they consist mainly of a bathochromic structureless band suggesting efficient excimer or dimer formation.

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HOLEBURNING IN THE RESTRICTED GEOMETRY OF MOLECULAR SIEVES

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Persistent spectral hole-burning has been established as an extremely sensitive tool for the investigation of chromophore-host interactions and as a probe of dynamical processes in the surrounding environments like glasses, crystals and surfaces [1]. We will present data from a variety of chromophores encapsulated in molecular sieves, inorganic crystalline structures like e.g. aluminosilicates (also known as zeolites) or aluminophosphates whose main characteristics is a well-defined porous structure (cages, channels etc.) on an Å-lengthscale. Fig. 1a shows as an example the so-called $AlPO_4$-5 structure which has channels with an inner diameter of 7.8 Å. Molecular sieves constitute an ideal system for the study of molecular dynamics in a confined geometrical environment [2], and they allow the isolation and stabilization of encapsulated chromophores and the synthesis of supramolecular structures.

Early investigations have shown that geometric factors, i.e. molecular size and form with respect to the confining void play a decisive role in the mobility and dynamics of the encapsulated chromophore [3]. However, for the molecules investigated so far (phenoxazines, thiazines, Zn-phthalocyanines and porphyrins) persistent spectral hole-burning is only possible if additional guest molecules like ethanol, water or chloroform are incorporated into the porous structure. These guest molecules form an amorphous environment within the pores with glassy two-level systems (TLSs) which are the base of a photophysical burning mechanism. Whereas characteristics of the spectral holes like the temperature dependence of the homogenous linewidth or the refilling of the hole with time are similar for the molecular sieve/solvent and the bulk solvent environment, spectral diffusion, i.e. broadening of the hole with time is very different. As shown for oxazine 1 in Fig. 1b the broadening in bulk ethanol is comparable to other glasses investigated

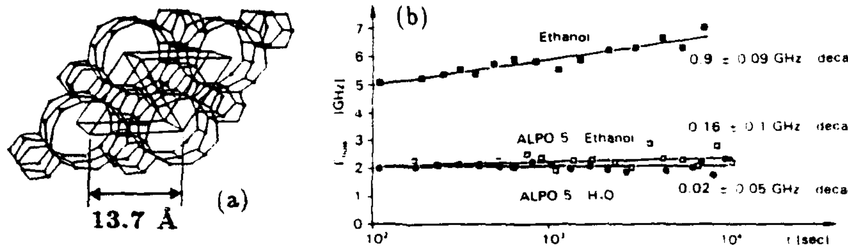

Figure 1: (a)Schematic structure of the aluminophosphate $AlPO_4$-5; (b) Temporal evolution of the width of the spectral hole for oxazine 1 at T = 2 K in (i) bulk ethanol, (ii) $AlPO_4$-5 with ethanol-filled porous channels, (iii) $AlPO_4$-5 with water-filled porous channels.

[4]. However, spectral diffusion is negligible for the solvents in the molecular sieve. This indicates that the long-range interaction with the TLSs is modified. The same system in the faujasite type molecular sieve SiAl100 which has pores of cage geometry has exhibited spectral diffusion. This demonstrates that not only the reduction of the number of TLSs but the *dimensionality of the* glassy environment plays a dominant role.

The encapsulated metal-doped phthalocyanins and porphyrins exhibit hole-burning with high quantum yield and up to a temperature of 80 K. However, no photon gating of the burning process is possible. One photon is enough to generate the spectral hole which obviously is purely photophysical and not due to the elctron transfer reaction found in polymer matrices.

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CONDITIONS REQUIRED TO OBTAIN HIGHLY PHOTOACTIVE PHTHALOCYANINES

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The most photoactive phthalocyanines (Pcs) are characterized by an extension ,in the solid state, of their Q band absorption toward the near infra red (NIR). It is the case, for instance, of the X polymeric form of PcH_2, whose structure is composed of dimers. It is also the case of a trivalent metallic phthalocyanine like ClGaPc (characterized by a slipped stacked aggregation of the molecules), or ClAlPc. For the latter material, a NIR absorption can be generated by its immersion in acidic solutions containing salts like KCl,KBr or KI. Anions are able to penetrate in the solid structure if it is mostly amorphous.

Another Pc able to display NIR absorption is oxotitanyl phthalocyanine (OTiPc). The most photoactive films of this material are obtained by sublimation on SnO_2 substrates maintained at temperatures around 130°C. SEM shows that they are made of tightly packed platelets. Diffraction rings obtained by TEM indicate that these films are crystalline (with amorphous regions). Their structure is triclinic.

A NIR absorption is however not the only condition required to obtain highly photoactive films. Indeed, when OTiPc films displaying the same absorption spectrum are evaluated under polychromatic illumination (35 mW/cm^2) , in photoelectrochemical cells with I_3^- /I^- , short circuit photocurrents J_{sc}, ranging from 0.3 to 1.5 mA/cm^2 are obtained. For comparison purposes, The best J_{sc} values measured in the same conditions for NIR absorbing ClAlPc are 1.0 mA/cm^2.

The large range of J_{sc} obtained for OTiPc can be related to the sublimation pressure used when the crude material was purified by repeated sublimation before being used for films preparation. The highest photocurrents are obtained for the lowest pressure (0.1-0.01 Torr). Besides the presence of a NIR absorption, an appropriate interaction of OTiPc with oxygen is, therefore, also essential for high photoactivities. Such an effect of the sublimation conditions is not found with ClAlPc. The oxygen content of the latter material has been estimated on the basis of the incorporation of anions in the material. It can be as high as 1 oxygen molecule per 2 phthalocyanines.

Influence of the molecular organisation on the photophysical properties: experimental and theoretical study of triarylpyrylium salts

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The photophysical properties of organized molecular systems (OMS) are very often very different of the corresponding "isolated" molecules. In the case of J or H aggregates it is well established that coherent excitation takes place leading to the formation of delocalized states. The same description is also valid for molecular crystals at low temperature. However, most of the OMS examined at room temperature (Langmuir-Blodgett films, liquid crystals, aggregates in solution..) exhibit only partial order. Moreover, at this temperature, the thermal fluctuations are larger than the intermolecuar interactions leading to energy localisation.

We have developped a methodology concerning the study of such systems using as an example a homologous series of triarylpyrylium salts. These compounds are particularly suitable for experimental work since they can form various types of molecular arrangements: aggregates of different sizes in solution[1], columnar liquid crystals[2], Langmuir-Blodgett films with a nematic discotic order[3]. The steady state and time-resolved spectra reccorded for all these systems, show a strong spectral diffusion of the fluorescence, proving the existence of emissive sites with different energy[1,4].

In order to elucidate the origin of the spectral diffusion we have undertaken a theoretical study. First, we have determined the electronic structure of the "isolated" chromophore. Then, taking into account the charge distribution within each chromophore, we have studied the excited states of the organized assemblies. We have determined the influence of the structure (relative position of the chromophores, position of the counter-ions...) on the excitation energy (diagonal and off-diagonal in an excitonic model) and its consequences on the transition moments and the localisation behaviour of the excitation.

Such an approach brings a better insight in the understanding of the energy migration processes in columnar phases and provides selection rules for the elaboration of efficient energy guides for molecular electronics.[5].

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STM-INVESTIGATION ON HETEROEPITAXIALLY GROWN OVERLAYERS OF CU-PHTHALOCYANINE ON AU(111)-SURFACES

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A detailed investigation of the initial growth structure of ultrathin films is essential to the understanding of the growth mechanism and heterogeneous interface formation between layers of different materials. Molecular beam epitaxy (MBE) has long been successful in exploring such problems, especially in the field of inorganic semiconductors. Since the first organic molecular beam epitaxy (OMBE) was performed with *in situ* reflection high energy diffraction (RHEED) during the film growth of copper phthalocyanine (CuPc) monolayers on MoS [1], considerably interest has been centred on developing OMBE techniques for the controlled growth of organic assemblies at molecular length scales [e.g.: 2,3]. More recently, scanning tunnelling microscopy (STM) has opened up an entirely new approach to the study of organic molecular systems. Actually, there has been strong interest of the combination of diffraction methods with real space imaging of STM.

In our experiments we introduced *in situ*-prepared Au(111)-surfaces as a substrate for OMBE studies and here we report the first real images of a heteroepitaxially grown organic thin film on gold. The artificial lattice structure of the organic film, being different from those in bulk, is commensurable with the Au(111)-surface as revealed by both STM and *in situ* RHEED investigations.

The heteroepitaxial growth of copper-phthalocyanine (CuPc) monolayers was carried out in an UHV-OMBE system with a base pressure better than $3x10^{-}$[illegible] torr ($2x10^{-}$[illegible] torr during deposition, resp.). Prior to the deposition of the CuPc, epitaxially grown Au layers were prepared on freshly cleaved mica, showing a flat and almost perfect surface with the typical triangular facets of growing [110]-lines in a larger scale or hexagonal alignment of the Au atoms at atomic resolution.

The STM system used in this study was a commercially available NanoScope II (Digital Instruments Inc., Santa Barbara, USA). A sharp platinum/iridium tip was scanned over the sample in air. All images were obtained in the constant current mode. The CuPc monolayer (fig. 1, 2) exhibits a nearly square lattice with a lattice angle of 9±5 degrees and a lattice constant of about 14.9±0.5 Å. Furthermore, directions of all the four-leaf-like parts are ordered in a parallel fashion to each other and inclined at an angle of approx. 30 degrees. It should be noted that fig. 2 shows unusual contrast, i.e., the molecules appear dark on a bright Au layer.

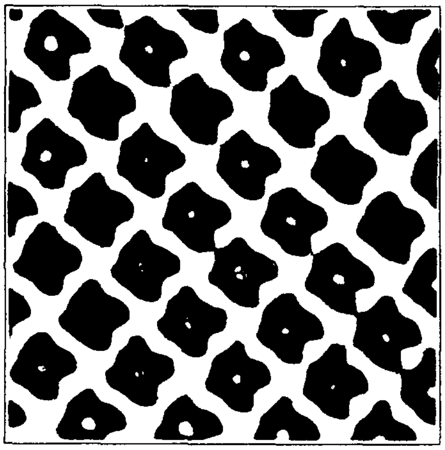

fig. 1: CuPc-monolayer on Au
- area 9x9 nm^2
- bias 50 mV
- current 7.7 nA

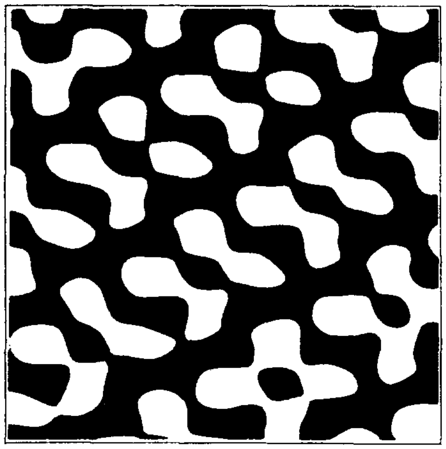

fig. 2: CuPc-monolayer on Au
- area 4.5x4.5 nm^2
- bias 50 mV
- current 20.7 nA

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THE STUDY OF PROPERTIES OF ORGANIC BULK MATERIALS BASED ON THE NEW KNOWLEDGE OF THEIR RADIOLUMINESCENCE MECHANISM

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The radioluminescence phenomenon usually was studied only as an aim of scientific or technical (certification of scintillation detector, for example) investigation. The material discussed allows not only to enunciate the radioluminescence theory of organic molecular solids, but to consider the radioluminescence study as the new method for investigation of structure features of organic bulk materials and the process of the charge transport in them as well [1,2].

The analysis of the experimental data on radioluminescence spectra, light yield and fast component pulse shape for organic molecular crystals, plastic and liquid scintillators shows that for organic solids the localization of charge carriers on shallow traps ($<$ 0.2 eV) of polarization origin results in the additional delay of their recombination, hence of molecular excitation, and consequently results in additional delay of a photon emission. This delay is described by the Gaussian function owing to the statistical nature of the processes discussed. The duration of these processes is by more than an order of magnitude greater than the duration of the electron excitation energy transfer. Thus the investigation of the scintillation pulse fast component rise gives the information about the system of charge carrier shallow traps. The existing radioluminescence theory based on the principles which ignore such effects. The description of the radioluminescence excitation mechanism for organic condensed matter is presented.

The origin of the charge carriers or exciton trap is caused by structural features of organic molecular solid. The results of the investigation discussed allow to judge such features.

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THE RADIOLUMINESCENCE EXCITATION MECHANISM FOR AN ORGANIC BULK MATERIALS.

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The new estimates for a cross-section radius of regions of the high density of activation in organic scintillators been made using the experimental data. It allows to revise the present-day knowledge of a charge density distribution in such regions. In contrast with existing theory it is in a good agreement with the present-day results for organic tracking detectors.

The investigation of organic single crystals and cross - linking copolymers shows that the intensity and shape of their radioluminescence pulse slow component correlate with structure perfection of the crystal studied or dimension of a mean cross-linking area of the polymer. The radioluminescence technique allows to estimate dimensions of the mean cross-linking area (≥ 50 nm) by the choice of radiation source, as well as to detect the presence of deep traps of charge carriers (≥ 1.0 eV) formed at aggregations and ensembles of dislocations. The measurements of the shape of the radioluminescence pulse slow component allow to investigate the features of charge transfer process in the high activation density regions of a bulk material studied.

X - RAY - EXCITED PHOTOCURRENT OF ANTHRACENE CRYSTAL

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1. INTRODUCTION

Mechanism of charge carriers generation by x-rays in anthracene crystal has been studied by several authors [eg.1,2,3]. In paper [1] it has been shown that the amount of generated charge carriers is independent of temperature, what is in discrepancy with Onsager model [5]. However, Hughes showed that mechanism of charge carrier separation follows the Onsager model [4]. The purpose of this communication is farther analysis of mechanisms of charge carriers production in bulk and on electrodes of anthracene crystals.

2. EXPERIMENTAL DATA

Experimental data were obtained on thin anthracene crystals with evaporated metallic electrodes with a steady-state x-ray source. Our experimental data include: (i) an efficiency of charge carrier generation, (ii) current-electric field characteristics and (iii) photoinjection of charge carriers from metallic electrode to anthracene crystal. Efficiency of charge carriers generation is practically independent of energy within 7 keV to 12 keV range. Current-electric field characteristics (Fig.1) seem to follow the Onsager model [4.5] but with a slope dependent of x-ray flux.

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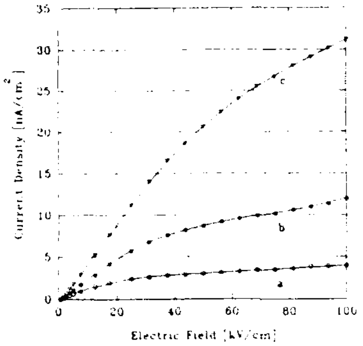

Fig. 1.

Current-electric field characteristics for x-ray generated charge carriers in anthracene crystal. Total spectrum of lamp for different currents (a-10ma, b-33mA, c-100mA) was used. Lamp voltage U=15kV. Crystal thickness d=40μm. Gold electrodes in sandwich system.

The spectral dependence of quantum efficiency of photogeneration (Fig. 2) near the strong change of electrode absorption (K_α line for copper) shows the step increase caused by photoinjection from electrode.

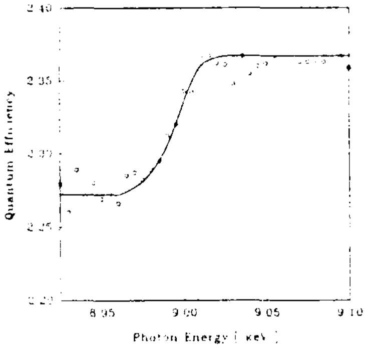

Fig. 2.

Spectral dependence of quantum efficiency of photogeneration. Crystal thickness d=120μm and voltage 50V.

3. CONCLUSIONS

Our data and their analysis show that Onsager model is not applicable to describe the separation of charge carriers by x-rays. The data indicate also that some part of photocurrent is a result of photoinjection from electrode.

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A STUDY OF THE CHARGED EXCITATIONS IN THIN FILMS OF THIOPHENE OLIGOMERS BY VOLTAGE-MODULATION SPECTROSCOPY AND PHOTOIMPEDANCE MEASUREMENTS

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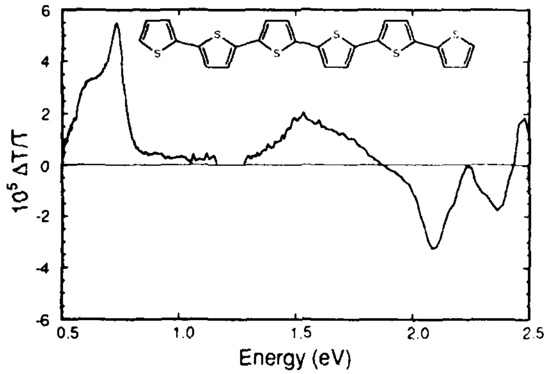
We have fabricated metal-insulator-semiconductor (MIS) structures, in which a thin evaporated film of the thiophene hexamer, α-sexithienylene (α-6T) acts as the semiconductor layer. The charged states of the oligomer are studied by voltage-modulation spectroscopy, as described previously [1, 2]. The voltage-modulation spectrum clearly shows features at 0.6-0.8eV and 1.5-1.7eV, in agreement with the spectra of dilute solutions of chemically-doped oligomers of sexithiophene, [3, 4, 5, 6, 7] where they have been assigned to transitions of the radical cation. We also observe electro-absorption close to the HOMO-LUMO transition. For the charged excitations, there is good correlation between the voltage-modulation spectrum and that obtained by the novel technique of photo-impedance spectroscopy.



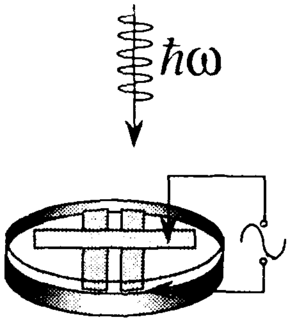


Fig. 1 Voltage-modulated transmission spectrum of an α-sexithiophene MIS device

Fig. 2 Voltage-modulation experiment - schematic

VOLTAGE MODULATION SPECTROSCOPY

By applying a sinusoidal AC electric field to the gate contact of the MIS structure, the concentration of field-induced charge within the device may be modulated and the corresponding change in absorption detected using a lock-in amplifier referenced to the modulation frequency of the applied electric field.

PHOTOIMPEDANCE SPECTROSCOPY

The charged states can also be detected by the novel technique of photo-impedance spectroscopy, whereby a change in the electrical properties of the device (capacitance and conductance) is detected in response to optical population and depopulation of charged states as the wavelength of the light incident on the sample is varied throughout the spectral range (IR-visible-UV). To the best of our knowledge, this technique has not previously been applied to the study of intra-gap charged states of conjugated polymers and oligomers, although photoimpedance measurements on GaAs and CdSe [8, 9] have yielded further insight into the nature of states which lie deep within the band-gap of inorganic semiconductors.

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Photoconductive Liquid Crystals: Calamitic and Discotic Systems

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Liquid Crystals as the "fourth state of matter", combine within themselves the order of a crystal and the mobility of a disordered liquid. Since their discovery more than hundred years ago[1], they have developed from a lab curiosity to a well known and studied system, yet today they are most famous for their use in display technology. From a scientific viewpoint however, liquid crystals *offer far more opportunities* in many different fields, e.g. high performance polymers, materials for optical information storage and processing, etc.[2]. In energy transfer studies however, until now, there are very little studies employing liquid crystals as a matrix or as anisotropic media[3].

Combining the self organizing properties of electron rich, disc- or rod- like molecules with their photophysical behaviour in thermotropic liquid crystals either in bulk or at the air water interface it was shown[3,4], that these arrangements yield rather high charge carrier mobilities (1×10^{-3} cm^2/Vs) in the organized mesophase, whereas the photoconducitivity drops to low values in the crystalline phase as well as in the isotropic melt.

This behaviour was observed and studied systematically for both types of liquid crystal systems, rigid rod (calamitic) and flat disc- like (discotic) molecules, as shown below.

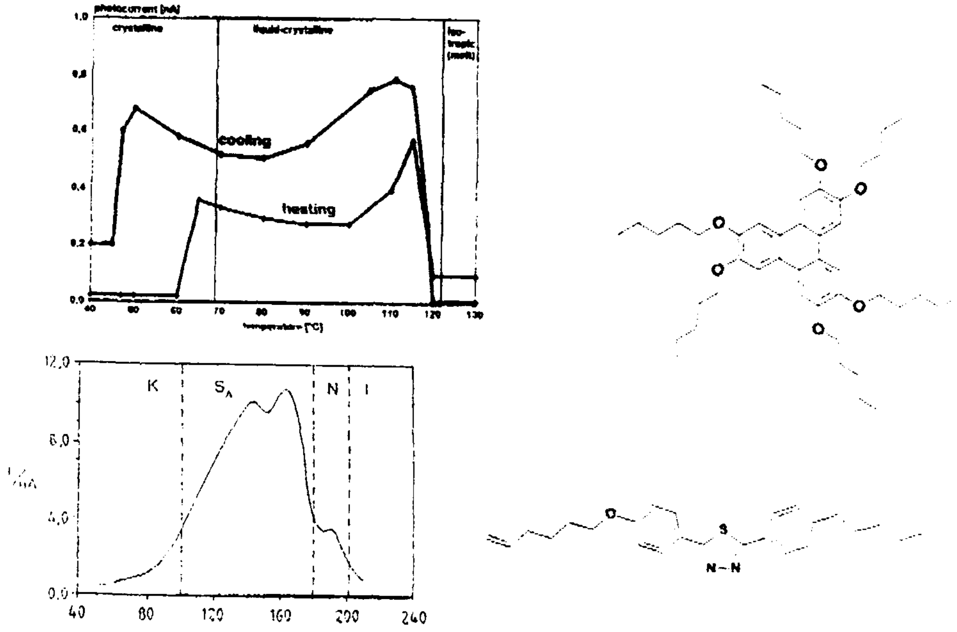

Fig.1: Photocurrent vs Temperature for lc hexapentyloxy-triphenylene and 4-alkylphenyl-4'alkoxy-phenylthiadiazol

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DISPERSION OF THE POLARIZABILITY TENSOR IN DNP

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The crystal structure of 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne (DNP) is centrosymmetric (monoclinic, space group $P2_1/n$, $Z = 2$). The electric dipole moments of the dinitrophenoxy substituent groups R in the disubstituted molecule $R\text{-}C\equiv C\text{-}C\equiv C\text{-}R$ are compensated antiferroelectrically due to the molecule center of symmetry [1].

In single crystals of DNP the indicatrix orientation, the optic axes angle, the birefringence, and the absorption tensor were measured in the VIS and NIR spectral range. The optic normal Y (intermediate polarizability) is found parallel to the b crystallographic axis, i.e. the optic axial plane coincides with the symmetry plane (010). The optic direction Z (maximum polarizability) is acute bisectrix. The angle between a axis and Z is about 110° (into obtuse ß). The bisectrix dispersion is small ($\approx 10^\circ$). But a strong dispersion of the optic axes angle $2V_Z$ was measured: in violet light the angle $2V_Z$ is about 100° (optical sign negative). Going to larger wavelengths the angle decreases (optical sign positive) and becomes zero in red light, i.e. the crystal changes from biaxial to uniaxial.

Examination of the crystal structure shows that the indicatrix orientation is governed by the orientation of the R groups. Furthermore the polarizability of hydrogen bridged intermolecular C-O contacts must be involved. The optic direction Z is found approximately parallel to the directions of these contacts. Calculations of the polarizabilities confirm this behaviour.

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CONDENSED STATES AND OPTICAL PROPERTIES OF THE DENSELY DISSOLVED ORGANIC COMPOUNDS IN POLYMER MATRICES BY COPRECIPITATION

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In recent years, optical properties of associated molecules, such as J- and H-aggregates, have been widely investigated because the localized electronic states in aggregates, typically known as molecular exciton, exhibit interesting phenomena.[1] Such investigation has also been stimulated by a measurement that analyzes the ultrafast response to incident light.[2] The condensed states of these molecular systems may be estimated by analyzing spectroscopic data.[3] For elucidating the relation between condensed states and optical properties of molecular aggregates, fabrication and characterization of 3,3'-Diethyloxadicarbocyanine Iodide (DODCI) dissolved polymer film are carried out.

DODCI dissolved polymer (e.g. poly(methyl methacrylate)(PMMA)) powder is formed by coprecipitation method, in which acetone solution of DODCI and the polymer is quickly injected into a poor solvent (e.g. n-hexane). The obtained polymer powder is dried under vacuum ($5x10^{-5}$ Pa) for more than 2 days at just bellow a glass transition temperature of the polymer. Thin film is formed from the powder by hot-press method.[4,5] Condensed states of the film are analyzed by ^{1}H- and ^{13}C-NMR spectroscopy and small angle X-ray scattering. Optical properties (absorption, emission and emission lifetime) of the film are measured by using a spectrophotometer and a time-correlated single photon counting method with a synchronously pumped picosecond dye laser / mode-locked Nd:YAG laser system. The emission lifetime of DODCI dissolved PMMA film showed double exponential decay with increased DODCI contents, which indicates the existence of condensation of DODCI molecules.

Another method for making a DODCI contained thin film is performed under high vacuum. An organic solvent (e.g. acetone) dissolving both DODCI and polymer is sprayed directly from liquid phase into the vacuum chamber through a modified needle valve. The solution produces mists through the valve, and the carrier solvent in mists evaporated very quickly on adhering to a temperature-controlled substrate. Thin film formation is done by the same method mentioned above.

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TEMPERATURE AND FIELD DEPENDENCE OF HOLE TRANSPORT IN CHLORO-ALUMINUM PHTHALOCYANINE DETERMINED BY TIME OF FLIGHT MEASUREMENTS

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Using the time of flight technique described previously [1], drift mobility measurements were performed on the p-type semiconductor chloro-aluminum phthalocyanine (ClAlPc). The field dependence of hole mobilities was examined at different temperatures, and the results were found to be interpretable within the context of the disorder formalism developed by Bassler and Coworkers [2-5]. In the region of low applied fields the mobilities are seen to first decrease with increasing field, for all temperatures in the range studied. The mobility then reaches a distinct minimum at intermediate fields which is followed by an increase at higher fields. The high field behavior for all temperatures studied shows a linear dependence of ln μ vs $E^{1/2}$, the slope of which decreases with increasing temperature with values ranging from 8×10^{-3} (cm/V)$^{1/2}$ at 275 K to 5×10^{-3} (cm/V)$^{1/2}$ at 330 K. Mobilities at all applied fields were found to increase with rising temperatures showing a linear dependence of ln μ vs T^{-2}. At each temperature, measurements were taken for applied fields ranging from 2.5×10^{4} V cm^{-1} to 1.6×10^{5} V cm^{-1}. The mobilities at the highest applied field ranged from 4.4×10^{-5} cm^2 V^{-1} s^{-1} at 275 K to 1.1×10^{-4} cm^2 V^{-1} s^{-1} at 330 K.

In view of the apparent consistency of this systems behavior with that predicted by the disorder formalism, the relevant constants were calculated and their relationships examined to better determine the existing correlation with the proposed model. From $\mu\ (E=0) = \mu_0\ exp\ -(T_0/T)^2$ and the appropriate plot, the values for μ_0 and T_0 are 2.5×10^{-3} cm^2 V^{-1} s^{-1} and 777 K, respectively. This yields a distribution width σ of 0.1 eV and corresponding $\hat{\sigma}$ values varying from 3.5 to 4.25 within the temperature range studied. Finally the parameter related to off-diagonal disorder, Σ, was determined to be 1.73. All of these results are self-consistent within the disorder formalism and tend to support its application to describe charge transport in ClAlPc films.

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ANALYTICAL DESCRIPTION OF EXTERNAL-FIELD EFFECTS ON PERSISTENT-HOLE SPECTRA IN DISORDERED MATERIALS

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The technique of persistent spectral hole burning is very well suited for studying the effects of small external perturbations such as pressure or electric fields on amorphous dye–matrix systems under near-equilibrium conditions. A few years ago, a stochastic theory of dye–matrix interaction, which had originally been used for modelling inhomogeneous absorption bands [1], was extended to describe the effects of hydrostatic pressure on persistent-hole spectra [2]. Within the so-called Gaussian approximation, which is valid if the density of the matrix molecules is sufficiently high, the theory yields analytical results and predicts the pressure shift parameter of a hole to vary linearly with optical frequency within the inhomogeneous absorption band. The pressure broadening, on the other hand, is calculated to have the same value for all frequencies, in contrast to experimental findings [3].

In the present paper, the theory is extended further to describe also the wavelength dependence of the broadening parameter. In this way, a general analytical framework is obtained which can be applied to external perturbations of any kind. Moreover, the results are generalized to take correlation effects [4] between the matrix units into account which are always present, even in totally amorphous systems, and consist at least in the fact that two molecules cannot be located at the same position. The calculation predicts a Gaussian shape of the kernel describing the effects of the perturbation and yields detailed results for the dependences of both its maximum position and width on the interaction potentials between dye and matrix molecules, the density of the matrix units and the optical frequency within the absorption band (see Figure 1).

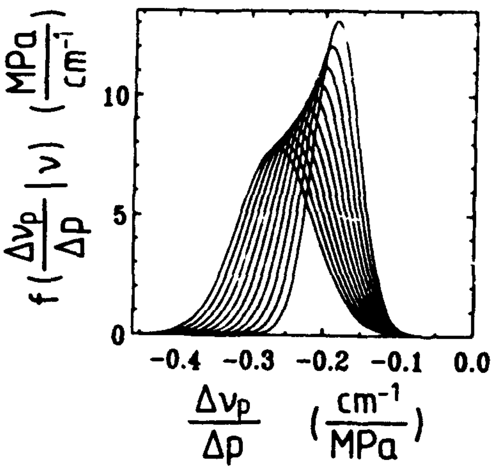

Figure 1: Distribution of the pressure shift $\Delta\nu_p/\Delta_p$ of molecular absorption lines for the amorphous system free-base phthalocyanine in poly(styrene). Each profile corresponds to a certain frequency position ν within the inhomogeneous band.

The analytical results are compared to numerical calculations [5] for the special case of hydrostatic pressure.

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PHOTOCONDUCTIVE PROPERTIES OF PHTHALOCYANINATO-POLY(SILOXANE) LANGMUIR-BLODGETT FILMS

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The photoconductive properties of organic materials have been investigated with respect to many applications including solar cells and photo detectors. Phthalocyanine compounds have been widely studied in this regard and high photogeneration quantum yields have been observed. However the molecular stacking arrangement of these molecules in the solid state is found to have a profound influence on their photoconducting properties. Recently rigid-rod phthalocyaninato-poly(siloxane) polymers (PcPS) have been synthesized that can be processed by the Langmuir-Blodgett (LB) technique. These LB films show extremly well-defined structures and molecular composites can be assembled by including different types of molecules into the films. Furthermore the linear absorption spectrum of PcPS shows a broad absorption across the visible region.

Prototype devices consisting of a gold or platinum bottom electrode, a defined number of PcPS layers and top electrodes of various metals, were investigated with respect to photogeneration properties. Figure 1 shows the action spectrum of a sandwich device consisting of a platinum bottom electrode, twenty layers of PcPS and an aluminium top electrode. Even though the spectrum reveals the general shape of the linear absorption, the photogeneration efficiency (η) is notable greater at shorter wavelength. From the current-voltage characteristics under illumination in the near UV, a fill factor of 0.43 was calculated. Strong kinematic effects have been observed that suggest internal changes of the space charge region under illumination.

Similar results were obtained by using gold bottom electrodes. However both the open-circuit voltage (U_{OC}) and the short-circuit current (I_{SC}) as function of the incident light intensity P showed unusual power laws of $P^{1.0}$ and $P^{0.3}$ respectively. Surprisingly, devices with bismuth top electrodes did not show any relevant photogeneration. In this context the influence of intermediate insulation layers will be discussed.

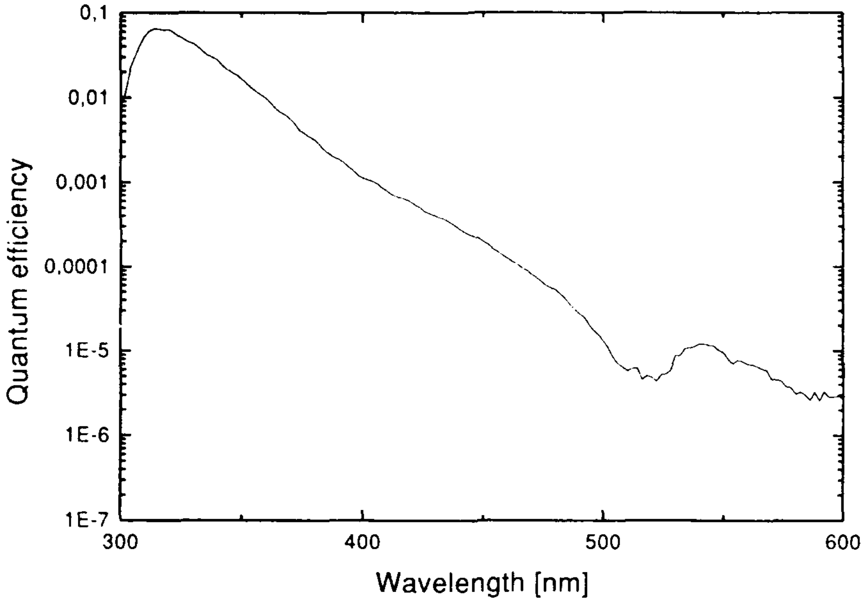

Fig. 1 Typical photoaction spectrum of an Al/PcPS/Pt sandwich device

MICROPARTICLE LASER: TEMPORAL CHARACTERISTICS AND INTRACAVITY ABSORPTION EFFECTS

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Dye-doped spherical microparticles act as laser cavities if the refractive index of the particles is higher than that of the surroundings [1]. Since the laser cavities are formed along the particle-surroundings interface the lasing phenomenon is sensitively affected by optical perturbations such as absorption near the interface. Thus, by analyzing lasing spectra and its dynamics, photophysical / photochemical properties at the interface of particles can be elucidated. We report here lasing of a single laser-trapped polymer microparticle in water and discuss its lasing dynamics and applications to unconventional time-resolved intracavity spectroscopy.

Laser trapping technique, which enables us to perform non-contact and three-dimensional position control of a microparticle, was applied to place it under the ideal optical condition [2]. A dye-(Rhodamine B; RhB)-doped PMMA microparticle was trapped in water by a focused cw beam (1064 nm) of a YAG laser under a microscope. Besides the trapping beam, a frequency-doubled pulse (532 nm, 40 ps fwhm) of a Q-switched YAG laser was irradiated to pump the dye molecules. Figure 1 shows an emission spectrum of a 26-μm-sized lasing particle. Intense emission peaks are ascribed to the spherical resonant modes according to the Mie scattering theory [1]. Nonlinear increase of the peaks with the pumping intensity indicates that the laser oscillation occurs in the trapped particle.

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Figure 2 gives temporal profiles of the laser emission. The decay of the laser emission is much faster than that of RhB fluorescence in PMMA (~3.3 ns), which indicates that the stimulated emission was induced. The dye concentration and wavelength dependences of the lasing dynamics can be explained in terms of reabsorption of the dye in the cavity.

Transient absorption of guest molecules at the interface also affects the lasing dynamics. It was demonstrated that Sn-S1 absorption of 9,10-diphenylanthracene (DPA), doped into a PMMA particle, perturbs the lasing of RhB. The lasing was strongly quenched immediately after the excitation of DPA, while lasing emission recovered again as the delay time is later. The results indicate a transient absorption measurement based on intracavity absorption effects is possible. The enhancement factor for the sensitivity was theoretically deduced to be about one hundred, and the time resolution was obtained to be ~50 ps. We believe that the intracavity spectroscopy of microparticle laser is useful to study the photophysical / photochemical processes at the interface.

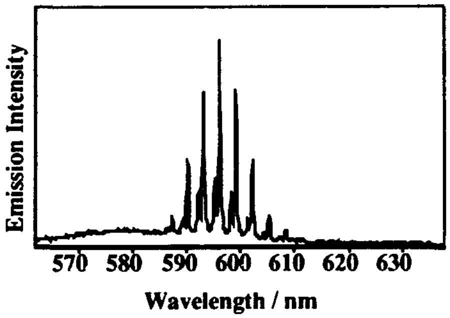

Fig. 1 A Lasing Spectrum of a microparticle.

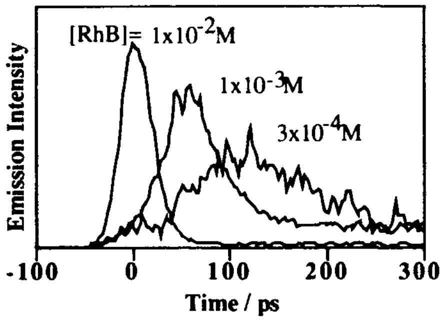

Fig. 2 Temporal profiles of laser emission from microparticles in various RhB-concentrations.

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Efficient Organic Photovoltaic Cells: The Role of Excitonic Light Collection, Exciton Diffusion to Interfaces, Internal Fields for Charge Separation and High Charge Carrier Mobilities

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Organic photovoltaic thin film structures made by vacuum vapor deposition, including molecular beam epitaxy, have been studied. From the spectral response as a function of the absorption coefficient of different organic materials we conclude that electron-hole separation takes place at the interface between the organic thin film and one or both of the semitransparent cover electrodes, (depending on the relative energy level positions of the materials employed and the internal fields thereby generated). The observed short circuit currents, however, are too large to be explained on the basis of a *direct* light-induced charge transfer at the layer/electrode interface. Rather, a contribution of the bulk-absorbed photons is necessary to account for the observed quantum yield. Transfer of the energy to the interface sites, where electron-hole generation and separation takes place, can be explained by diffusional migration of excitons; (bulk charge carrier generation can be ruled out). The bulk molecules of the organic layer thus play a similar role as the chlorophyll antennae molecules in photosynthesis. This is a very promising aspect for tayloring efficient photoelectric energy conversion. The efficiency of charge separation can be improved by combining donor and acceptor type partners in organic double and triple layers. The efficiency of power conversion, however, not only depends on a suitable choice of the absorption spectra and of the ionic energy levels of the materials employed, but also on the internal cell resistance, a fact that calls for high charge carrier mobilities, and hence for using strongly interacting molecules, and achieving high chemical purity and structural perfection in the organic layers.

THE INVESTIGATION OF NON RADIATIVE DEACTIVATION OF EXCITED STATES IN THIN FILMS BY LASER INDUCED OPTO-ACOUSTIC CALORIMETRY

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Laser induced photo-acoustic calorimetry (LIOAC) is at present recognised as an important technique for the measurement of quantum yields of radiationless photophysical processes in solutions. The energy released by those processes is converted into an ultrasonic wave that can be detected by a transducer.

Two major types of the cell configurations are used for such investigations: a front face configuration and a side face configuration. In the side face configuration the laser beam that excites the sample is parallel to the plane of the transducer, while in the front face configuration it is perpendicular to it.

The majority of set-ups used for the photo-acoustic study of liquid samples have the side face configuration while the front face type is used mostly for studying solid samples. The main disadvantage of front face set-ups is their high background signal due to the light absorption on the face of transducer, especially at frequencies larger than 1 MHz[2].

This contribution describes a new side face cell design that allows one to switch between the reference and the investigated sample, being in identical conditions, without detaching the film from the transducer. It can be used both for investigation of optically thick and thin samples.

The mentioned cell design for photo-acoustic studies of thin solid films can be successfully used for quantum yield measurements of photochemical processes. This set-up requires from the film forming substance a good mechanical contact with the sound conducting medium (glass or quartz) and optical transparency. For this purpose such polymers as polymethylmetacrilate or cellulose triacetate can be successfully used. The set-up shows a linear performance in the range of excitation energy up to 0.1 mJ/pulse and a large dynamic range.

Iron (III)-tris(2,4-pentadionate), 2-aminobenzophenone and 2,2'-dihydroxybenzophenone can be used as reference compounds for the LIOAC experiments in PMMA and Cellulose Triacetate films.

PHOTOCARRIER GENERATION VIA SINGLET EXCITON IN AROMTIC HYDROCARBON CRYSTALS

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We propose that charge carrier generation through photoionization of singlet exciton in anthracene, p-terphenyl and trans-stilbene crystals can be understood in the following way.

Charge carries are generated through either of two processes. Below a threshold energy for external photoemission carriers are generated by electron transfer from a higher excited state of a molecule to a neighboring molecule after a fast vibrational relaxation. Above that energy an electron is emitted from an excited molecule into the crystal bulk with finite kinetic energy. This may ne termed as direct ionization.

The picture is based on the following experimental findings. Ionization efficiency Φ can be defined as $\Phi = \sigma_{PI}/\sigma_A$, where σ_{PI} is the cross section of photoionization of singlet exciton and σ_A is that of absorption. This quantity Φ has been deduced as a function of excitation energy for anthracene (ANTH) [1], p-terphenyl (PTP) [2] and trans-stilbene (TST) [3] crystals (Fig. 1). A common feature is: Φ is insensitive to the excitation energy for relatively low energies and it increases steeply above a critical energy. The critical energy coincides with the threshold energy for external photoelectron emission [4]. Efficiency for generating a geminate electron-hole pair, which is estimated by photoconductivity measiuements at high fields, increases drastically above the threshold energy for external photoemission [5].

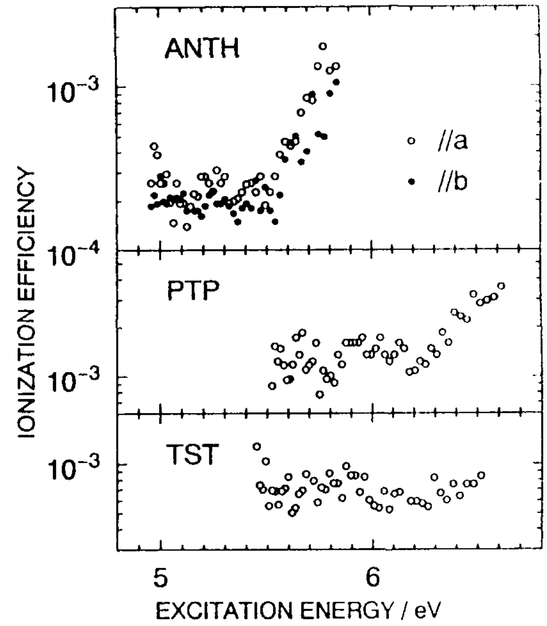

Fig. 1 Dependence of Φ on excitation energy.

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GENERATION OF OPTICAL EVANESCENT WAVES IN VACUUM-DEPOSITED THIN FILMS OF α-OLIGOTHIOPHENES.

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Vacuum-deposition of linear α-coupled oligothiophenes α-nT (with n=4-8 thiophene rings) yields highly homogeneous thin solid films with specific electrical and optical properties [1]. We recently demonstrated that these organic films have potential applications in various high technology fields such as integrated microelectronics [2] and all-optical information devices [3]. But up to now, few informations were available on the structure and morphology of these organic films. Evanescent optical waves, particularly plasmons surface polaritons (PSP) hereafter called "surface plasmons", and waveguide (WG) modes, have recently proved to be very useful to characterize organic ultrathin films and afford valuable structure-properties relationships [4,5]. We report here on the generation of evanescent optical waves in thin films of three model α-oligothiophenes, namely the tetramer α-4T, the hexamer α-6T and the extended octamer α-8T.

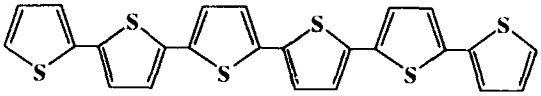

Figure 1- Molecular structure of α-6T, the linear hexamer of thiophene.

α-nT thin films (thickness=20 nm to 1.1 mm) are deposited onto silver films by evaporation of the powdered oligomers under reduced pressure (10^{-4} Pa). It affords polycrystalline films, as checked by X-ray diffraction and scanning electron microscopy. SEM reveals the high uniformity and homogeneity of the film surfaces, whatever the oligomer length, and evidences the extremely fine granular texture and high density packing of the evaporated films. The film morphology consists in a crystalline network made of inter-connected linear segments whose average diameter and length are respectively 30 nm and 100 nm. The crystallite size is far smaller than the wavelength of visible light and thus explains the perfect transparency of our α-6T and α-8T samples in the visible region.

The optical setup for PSP and WG modes generation has been described elsewhere [4]. The intensity of the reflected light R of an He-Ne laser is recorded as a function of the incident angle θ while rotating the whole setup. At a given angle θ_i, the reflectivity R of the α-nT film decreases sharply, thus creating a narrow dip in the R-q curve. This indicates the resonant excitation of an evanescent wave travelling at the α-nT film/air interface. As an example, Figure 2 shows the R-θ curve of an α-6T film (thickness=1.128 μm) under TM-polarized incident light. In such a thick film, two WG modes are generated at θ_i=40.0° and θ_i=66.6°. Surface plasmons and WG modes are also observed with α-4T and α-8T films of various thicknesses. The experimental curves (square points) are fitted with calculated ones (full lines) by applying Fresnel formalism which allows an accurate determination of the refractive index at a given wavelength.

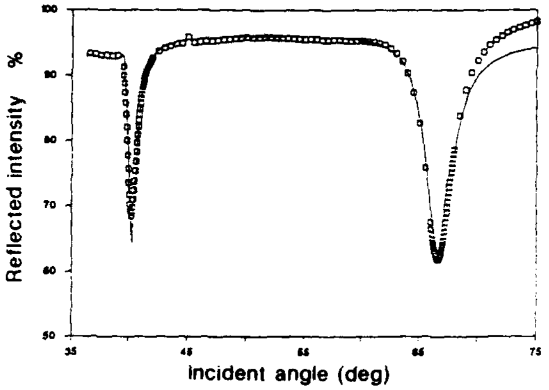

Figure 2- R-θ curve of a α-6T film under TM-polarized light showing two waveguide modes.

Importantly, the refractive index of the films rapidly and linearly increases with the oligomer length from α-4T to α-8T. No leveling off of n seems to appear for long chains, resulting in values as high as n=1.965 for α-6T and n=2.076 for the extended octamer α-8T. Such high n values are quite unusual for organics in their transparency region. They can be ascribed to the combined effects of a long π-conjugated system (electronic factors) and a high film crystallinity and density (morphology factors). The details of the present study will be published soon [6].

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STUDY OF SINGLE CRYSTAL SURFACE WITH SECOND-HARMONIC GENERATION: p-NITROANILINE

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It has been recognized that generation of optical second-harmonic (SHG) can be a powerful tool for studying surfaces [1]. SHG is forbidden in a medium which has an inversion symmetry. Since surface lacks inherently a center of inversion, any second-harmonic signal originated from a centrosymmetric medium should come from the surface and should bear information of the surface. This is an optical method and can be applied to many surfaces and interfaces, including those of insulating media.

Molecular solids are unique in that orientation of molecules which constitute the solids is an important parameter. Second-harmonic generation is especially suited for studying orientation of molecules. Here we report a SHG study of crystal surface of a highly nonlinear compound, p-nitroaniline (p-NA).

p-NA crystallizes in a centrosymmetric structure and the crystal is inactive in SHG. However, second-harmonic (SH) at 532 nm is observed in the specularly reflected light when cleaved surface of a single crystal of p-NA is irradiated with a pulse from a Q-switched Nd:YAG laser (1064 nm, 10 ns). The intensity of SH is the largest when the fundamental is incident normal to the surface. This, together with the polarization characteristics, indicates that molecules are lying flat in the surface and are aligned in a direction, making the surface polar. All the measurements give results which are in harmony with the symmetry of the crystal, as if the signal comes from a single layer of perfecltly aligned molecules which covers the surface.

When the surface is scanned with a tightly focused beam of light from the YAG laser, while SHG is monitored, it becomes evident that the surface is not uniform: There are spots at which SHG is very efficient. Most of the intensity detected with an unfocused beam comes from such spots. The area of the spots is comparable to, or smaller than, the area of the focused beam spots. We assign these "hot" spots to regions in which molecules are aligned unidirectionally.

Additional support for this assignment comes from measurements of the phase of SHG. The phase of the SH generated at the surface of a p-NA crystal can be measured by observing interference with SH from a thin quartz plate inserted in the incident beam. No interference can be detected at regions of the surface where SHG is weak, whereas some "hot" spots exhibit clear interference, indicating that strong SHG originates from regions where molecules are well oriented.

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DYNAMICS OF THE PHOTO-INDUCED PHASE-TRANSITION IN LOW-DIMENSIONAL ORGANIC CRYSTALS AND A ROLE OF PHOTOCARRIERS

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Various organic crystals with quasi-one-dimensional structures show the phase transition due to the strong electron-lattice and/or electron-electron interactions. For example, some charge-transfer (CT) complex crystals with half spins on each constituent molecules show the spin-Peierls like transition. The other example is the chromic transition in π-electron conjugated polymer crystals as observed in polydiacetylenes (PDAs) [1]. In previous reports, we have shown that local and small number of photo-excited species can trigger those spin-Peierls like and chromic phase-transitions over a macroscopic region [2,3]. In this study, we report the dynamics of such unconventional phenomena, i.e. photo-induced phase-transition (PIPT), with changing the excitation photon-energy, excitation intensity and sample temperatures.

A nano-second pump-and-probe technique has been applied to the dynamical study on phase-transitions in a few kind of CT and PDA single crystals [2,3]. It was confirmed that an initial process of the PIPT occurs much faster than 50 ns, if the sample is kept at nearby the phase transition temperature. In addition, a time-resolved photo-conductivity *measurement* has *made* clear that the photo-generated bipolaron-like carriers play an important role in driving PIPT.

Pico-second pump-probe experiments on CT compound (TTF-Chloranil(CA)) [2] and PDA crystals are also executed to reveal the early dynamics of the PIPT, i.e. the evolution from the photo-injected local excited species to the macroscopically converted phase. From preliminary results on TTF-CA single crystals, we found that it takes about 1 ns for the growth of the photo-injected domain.

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PHOTOCONDUCTIVITY OF POLY(ARYLENEVINYLENE)S AND POLY(HETARYLENEVINYLENE)S

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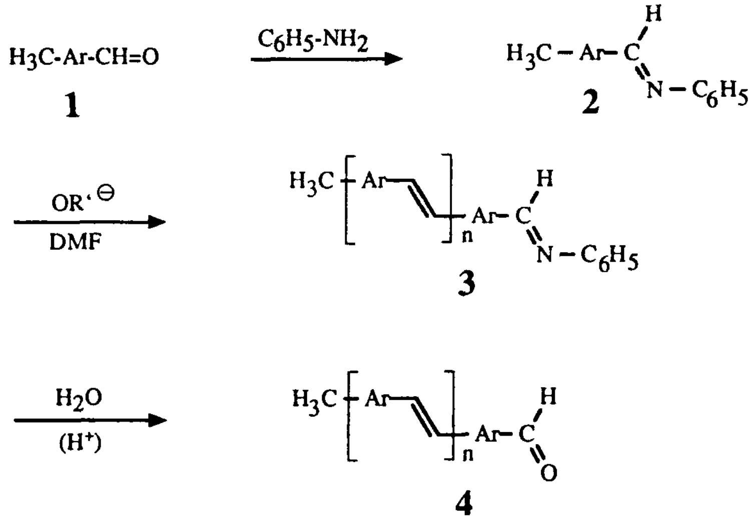
INTRODUCTION

Poly(arylenevinylene)s and Poly(hetarylenevinylene)s are highly interesting systems in materials science. Due to their physical properties they can be used as organic semiconductors, photoconductors, NLO-materials, laserdyes, scintillators or electroluminescence displays. The electronic structure of the conjugated polymers is essential for all these applications[1].

SYNTHESIS

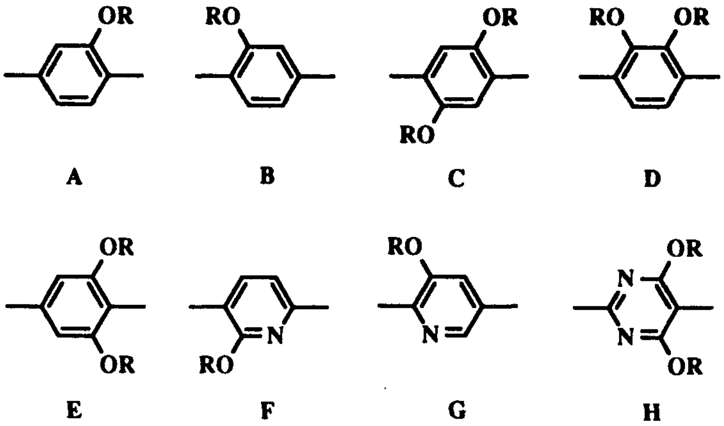
Applying the stepwise selfcondensation of the Schiff bases **2** in a strongly alkaline medium, we isolated the orange to deep red oligomers and polymers **3**, which can be hydrolyzed to the compounds **4**.



The main advantage of this new method of preparation consists in the extremely high structure reliability. The olefinic double bonds for example are formed with an (E/Z)-selectivity greater than 1000:1.

The 1,4-arylene or hetarylene units bear alkoxy side chains in order to enhance the solubility and to decrease the band gap. Altogether the eight building blocks **A** - **H** were investigated.

-Ar-:



R = CH_3, C_2H_5, ..., $C_{16}H_{33}$; $C_2H_4OC_2H_5$, $(C_2H_4O)_3H$ a.o.

PHYSICAL AND PHOTOCHEMICAL PROPERTIES

The arene systems **3/4 A-E** show a high photoconductivity on direct irradiation in dispersion layers. Increasing length of the side chains OR enhances the average length of the main chain in the process of preparation and decreases the band gap till the limit of convergence ($n \approx 8$) is reached. The optimum results were obtained for the 2,5-dipropyloxy system **3/4 C**. Longer side chains render the charge transfer from chain to chain more difficult. (Delocalisation of the charge carriers in the main chain seems to be almost activationless). Nevertheless, longer side chains ameliorize the generation of thin transparent photoconducting films. The highest sensitivity for the generation of photoconductivity is observed for wavelengths λ lying close to the absorption maxima λ_{max}. The hetarylene compounds **3/4 F-H** exhibit a much lower photoconductivity; however, they deserve interest because of the multiple quaternization at the nitrogen atoms. All oligomers and polymers **3/4** are completely photostable in the visible region. UV light (254 nm) leads finally to non-conjugated crosslinked polymers which neither fluoresce nor show a photocurrent.

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PHOTOELECTRO-POLING OF AZOBENZENE CHROMOPHORES IN MOLECULAR FILMS

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Azobenzene chromophores have been intensively investigated as prospective candidates to perform as functional entities in advanced molecular materials for integrated optics, non-linear optics and molecular electronics applications [1]. Photoreorientation of azobenzenes embedded in polymer or liquid crystal matrices has been observed by several groups [2–5]. For polymers it is assumed that trans-cis-trans isomerizations of the chromophores induce a rotation of the excited molecules' transition dipole moments out of the polarization direction of the illumination [4]. Recently, a similar behavior has been reported for molecular films of some 4,4'-substituted azobenzene dyes [6]: Chromophores were observed to reorient collectively on photoselective electronic excitation, which lead to a depletion of transition moments parallel to the light polarization, and thus to the formation of anisotropic samples. These were, however, still centrosymmetric.

We report on the first photoelectro-poling experiments with azobenzenes in LB films, where this symmetry is broken by the application of an external electric d.c. field during illumination [7]. This leads to macroscopically polar, stable solid state structures. Samples have been characterized macroscopically by Stark spectroscopy and microscopically by AFM and electron diffraction. Interaction energies of ~ 1 meV between the field and the ground state dipole moments are sufficient to control the reorientation. The manipulated structures are stable at room temperature under ambient light.

We suggest for the photo-reorientation mechanism a rotational diffusion process, governed by the interaction of light with the chromophores, which are aggregated in anisotropic domains and experience therefore an anisotropic mean molecular field. On excitation of a chromophore, the molecule may reorient within this mean field, according to Boltzmann statistics, and this reorientation affects in turn the orientation of the domain's director. After relaxation to thermal equilibrium, a slight change in the macroscopic orientation of the system has occurred. One possibility for the increase of the rotational diffusivity of *excited* chromophores may be local dissipation of the excitation energy, possibly into thermal channels. This is suggested by experimental observations and by the fact that azobenzenes in general show low fluorescence quantum yields.

We have simulated the photo-reorientation process of the molecules within a domain under the influence of an external electric field. The molecules are placed within the mean field of a nematic Maier-Saupe potential. Such simulations reproduce the experimentally observed behavior without any 'fitted' parameters. The collective behavior of the molecules is well accounted for; a decay of the molecular order was observed if the magnitude of an interaction potential, that stabilizes the polar orientation of the molecules across the interface, was reduced to below 0.3 eV.

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RELAXATION PROCESSES IN ORGANIC MOLECULAR CRYSTALS UNDER VUV EXCITATION

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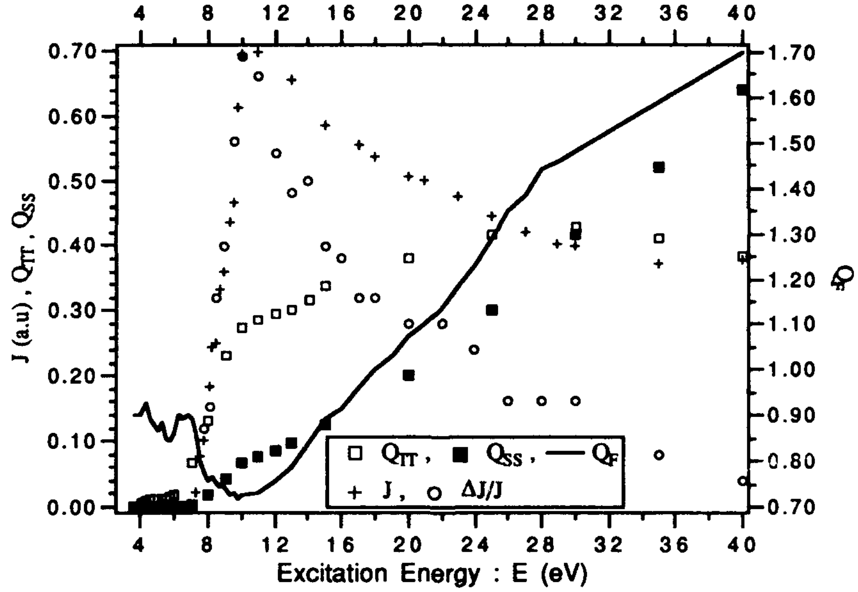
91405 ORSAY, FRANCE

In this contribution we propose a discussion of some recent results about charge carriers delayed recombination and dominant fast electronic relaxation processes in organic molecular single crystals (anthracene and p-terphenyl), under VUV exitation up to 40 eV.

We have studied the production of geminate electron-hole pairs induced by the initial photoionization. We detect the fraction of the pairs which have a delayed recombination (in the ns range). This approch is based on the analysis of the time dependent observation of the modulation by a *low magnetic field*, B, of the recombination fluorescence emission. The direct evidence of the formation of such separated charge states is the existence of a magnetic modulation with an hyperfine structure (HFS) type [1] in a time scale fixed by the spins precession periods in the hyperfine interaction field (some ns).

In these crystals, a delayed geminate recombination fluorescence is detected above a threshold energy caracteristic of a new particular mecanism. The decay law of this component is found to be proportional to $t^{-3/2}$. The properties of the HFS modulation also give the initial spin state of the electron-hole pairs which is found exclusively triplet. The excitation spectra of the integrated (over a small interval of time) intensity, J, and the well known HFS modulation ratio, $\Delta J/J$ $(\Delta J/J=(J^{(B\neq 0)}-J^{(B=0)})/J^{(B=0)})$, of the delayed recombination fluorescence (see the figure) and its decay form are interpreted by a sequential intermolecular mecanism with the implication of a primary excited deep hole leading to the formation of a triplet exciton on a neighbouring site and a charge transfert state in a triplet spin multiplicity. This bi-excited system can be stabilized in a metastable complex with a long lifetime or rapidly destroyed by the recombination of the charges pair; in the last case, the result is similar to a fast fission of an excited singlet state into two triplet excitons. The delayed recombination rate is controlled by the anisotropic transport properties of the thermalised primary ionization electron in the coulomb field of the heavy and quasi-fixed complex.

By measuring the excitation spectrum of the total fluorescence quantum yield of the crystal, Q_F, we have renormalized the spectra of the global fast fission into triplet and singlet excitons given elsewhere [2]. We show that the behavior of the corresponding large quantum yields respectively, Q_{TT}, and, Q_{SS}, and of Q_F (see the figure) is determined by these intermolecular transitions from deep holes.



Anthracene crystal: excitation spectra

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Laser Ablation Dynamics of Polymer Films: A Time-Resolved Interferometric Study

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Irradiation by an intense laser pulse to a polymer surface produces etching of the surface instantaneously [1]. To reveal the dynamics of morphological changes of the surface just upon the laser irradiation, we have developed a nanosecond time-resolved interferometer with nanosecond time resolution [2]. The preliminary works have shown that expansion of polymer surfaces took place at laser intensities lower than the ablation threshold. The expansion continued in the ms region, but the surfaces returned to the initial flat surfaces after a few seconds. We consider that this transient expansion is a key to clarify the mechanism of the laser ablation.

Poly(methyl methacrylate) (PMMA) thin films (2μm thickness) doped with 2 wt% biphenyl (BP) were prepared on quartz or PMMA substrates by using a spin coater. A Nd:YAG laser (532nm, 9ns) and an excimer laser (248 nm, 30ns) were employed for the light source of a Michelson interferometer and the ablation irradiation source, respectively. In Figure 1, an optical set is shown, where a transient interferogram was recorded with a CCD camera system. Irrespective of the substrate material, polymer surfaces expanded to the same height within several tens of ns after the irradiation of an excimer laser pulse. The decay time of the expansion was, however, faster on quartz substrates than those on PMMA ones, as shown in Figure 2. The results suggest that transient heating by laser irradiation is responsible for the expansion. An accompanied change of refractive index of the film is also examined, and ablation mechanism will be considered.

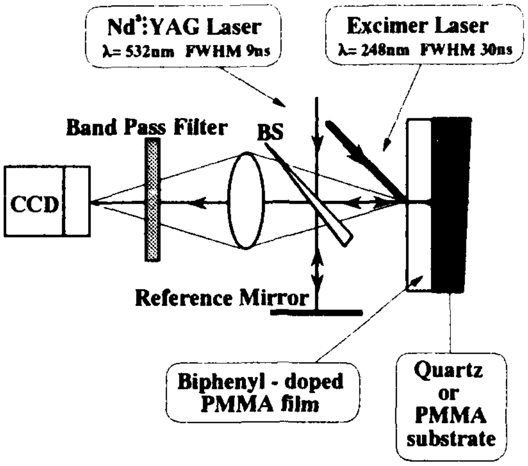

Fig. 1 Optical setup of Michelson interferometer and Sample substrate

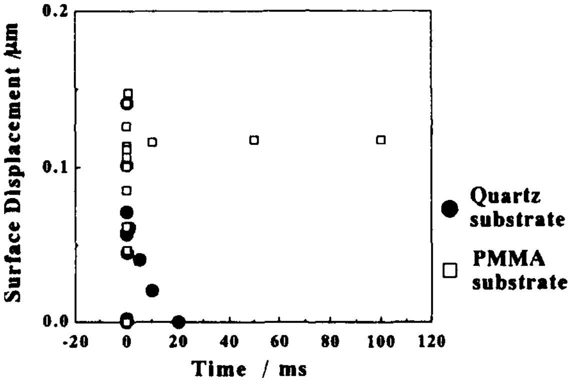

Fig. 2 Temporal Behavior of Surface Displacement of 2 wt% Biphenyl- doped PMMA films (fluence 80 mJ / cm²)

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SYNTHESIS OF A "STARBURST"-TYPE DODECADIAZO COMPOUND AND MAGNETIC PROPERTIES OF ITS PHOTOPRODUCT

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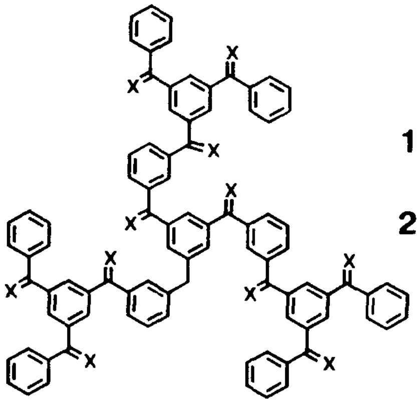
"Starburst"-type dodecacarbene **1** is considered to have a super-high spin ground state because of its topological symmetry of the π-orbitals. **1** was generated by photolysis of the corresponding diazo compound **2**. Trimerization of ethynyl ketones was performed twice in the key steps of the synthetic route to **2**. The photoproduct showed a single EPR line with the width of 10 mT. The magnetization curves as determined by a Faraday balance did not necessarily satisfy the Brillouin function with $S = 12$, suggesting the following two possibilities: a) antiferromagnetic interactions might operate within and/or between the high spin molecules, and b) species with lower-spin ground states might be generated in the reaction. Once these difficulties are solved, the chances are that strongly magnetic materials will be formed photochemically.



1: X=:

2: X=N_2

ON THE SPECTROSCOPIC AND NONLINEAR OPTICAL PROPERTIES OF 3-(1,1-DICYANOETHENYL)-1-PHENYL-4,5-DIHYDRO-1H-PYRAZOLE (DCNP)

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3-(1,1-dicyanoethenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (hereafter DCNP) has been reported as an excellent electrooptic organic crystal [1] with a reduced half-wave voltage of 370 V at 632,8 nm wavelength. Such a very high figure of merit of linear electrooptic effect (Pockels) is the result of favorable molecular packing in a unit cell and a large resonance enhancement of a molecular second order hyperpolarizability β. We undertook investigations of DCNP crystal in order to better characterize its spectroscopic, nonlinear optical and other properties such as photoconductivity and pyroelectricity which are essential to possible photorefractive applications of this interesting crystal.

In this paper we present spectra of DCNP in various organic solvents with different polarity. Assuming a two level quantum-mechanical model being operative for the molecule on the basis of the observed solvatochromic shifts of the dominant lowest lying electronic transition we calculated three molecular parameters: ground state dipole moment μ_g = 3.283 D, first excited state dipole moment μ_e= 11.77 D and a diluted vapour transition frequency ν = 23154 cm^{-1}. We also calculated the transition dipole moment μ_{eg} = 5.79 D from the absorption spectrum in hexane. Such a set of parameters allowed us to calculate the dispersion of the vectorial part of molecular second order hyperpolarizability $\beta_{CT}(-2\omega;\omega,\omega)$. The $\beta_{CT}(-2\omega;\omega,\omega)$ dependence calculated from purely spectroscopic data can be improved when one employs a separately measured ground state dipole moment of DCNP (in benzene $\mu_g = 4.5 \pm 0.5$ D). The experimental results are compared with quantum-mechanical calculations of electronic spectrum, ground and excited state dipole moments of DCNP by GRINDOL method [2]. The obtained results are discussed in detail in order to evaluate their respective relevance.

Some preliminary studies show that the excitation of the DCNP crystal within the interstack CT transition (e.g. by means of HeNe laser irradiation $\lambda = 632.8$ nm) produces a size able bulk photoconductivity. The photoconductivity is strongly dependent on light wave polarization within the (010) plane due to polarization dependent absorption coefficient in that spectral region. Occurrence of photoconductivity combined with large electrooptic coefficient should allow one to observe photorefractive properties in this material, this, however, is beyond the scope of the present paper. We also show that the crystal is pyroelectric then it should also be useful in formation of pyroelectric transient gratings [3].

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A SPECTROSCOPIC STUDY ON A PYRENE LABELED POLYMER MICROPARTICLE PREPARED BY PHOTO-THERMAL PHASE TRANSITION

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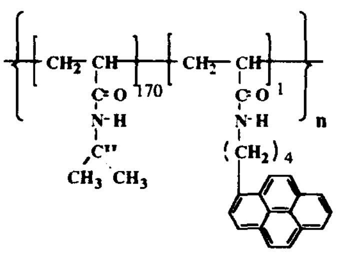
An aqueous poly (N-isopropylacrylamide) (PNIPAM) solution exhibits a thermal phase transition at 31°C (a lower critical solution temperature : LCST), giving water-insoluble subμm-sized polymeric particles [1]. Recently, we reported that thermal phase transition of PNIPAM in water could be induced by irradiation of an infrared 1064 nm laser beam and a produced single μm-sized polymer particle could be laser manipulated simultaneously [2]. It was also suggested that radiation pressure has a key role in a microparticle formation. To elucidate the mechanism of molecular aggregation during the microparticle formation, we performed fluorescence studies on photo-thermal phase transition of pyrene-labeled PNIPAM (Py-PNIPAM, scheme 1) in water.

An aqueous Py-PNIPAM solution (Mw ~10^6, 0.75 wt%) placed between two glass plates was set on a temperature-controlled stage of an optical microscope and was irradiated by a focused 1064 nm laser beam from a CW Nd^{3+} : YAG laser. Upon laser irradiation at 24 °C, a Py-PNIPAM microparticle was produced instantaneously and prolonged irradiation rendered growing-in of the particle. Fluorescence characteristics of pyrene during the microparticle formation was studied by a ns spectroscopy system (355 nm, Nd^{3+} : YAG laser, a polychromator, and a multichannel plate/photodiode array). A fluorescence spectrum from the Py-PNIPAM microparticle produced by photo-thermal phase transition is shown in Fig. 1a. A broad structureless fluorescence band overlapped with vibrational structures of the monomer extends to the long wavelength. The spectrum is quite different from that observed from the Py-PNIPAM microparticle prepared by thermal phase transition above LCST in the dark (Fig. 1b). The broad fluorescence band seen in Fig. 1a can be assigned to one-center-type excimer [3], while that in Fig. 1b is responsible for sandwitch excimer of pyrene. This indicates that molecular aggregation in the particle produced by 1064 nm laser irradiation is different from that prepared by thermal phase transition in the dark, demonstrating that radiation pressure of the laser beam influences aggregation of polymer chains.

The present results will be applicable to laser regulation of polymer conformations in soution as well as to controlled-preparation of polymer microparticles.

Scheme 1



Py - PNIPAM

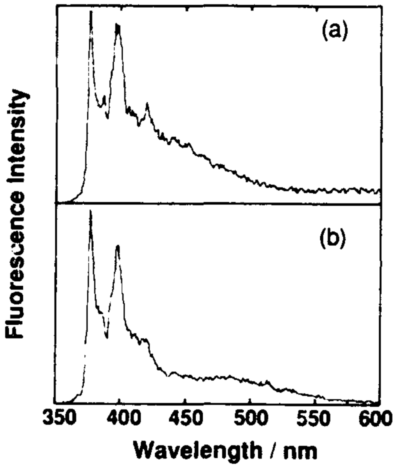


Fig. 1 Fluorescence spectra of Py-PNIPAM microparticle.

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MAGNETIC INTERACTION BETWEEN THE TRIPLET CENTERS THROUGH PPV SKELETON

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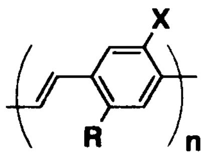
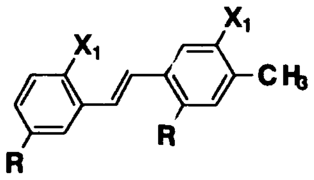
PPV polymer **1** is considered to be a high-spin organic molecule from its topological symmetry and expected to have interesting magnetic properties. The *E*/*Z* geometrical isomers of 1-(2-azidophenyl)-2-(3-azidophenyl)ethylene **2** and **3** were prepared and photolyzed in a 2-methyltetrahydrofuran matrix at 10 K to generate the corresponding dinitrenes **4** and **5**, respectively, prototypes of **1**. The ESR spectra of **4** and **5** showed intense quintet signals which obeyed Curie's law in the temperature range 13-85 K. The D value of **4** was smaller than that of **5**. It is concluded that two triplet phenylnitrene moieties in **4** and **5** interact sufficiently through the double bond to form quintet states, which are likely to be ground states of **4** and **5**, as predicted by theory. The difference in the D values between the isomers suggests that the *trans*-form of the PPV skeleton is preferable to the *cis*-form as a ferromagnetic coupling unit.

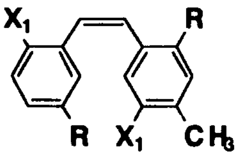


X : spin source

1



(trans)
2 X_1 : N_3
4 X_1 : N:



(cis)
3 X_1 : N_3
5 X_1 : N:

R : $OC_{18}H_{37}$

PHOTOCHEMICAL PROCESS OF p-PHENYLENEDIACRYLIC ACID MONOESTERS IN THE CRYSTAL AND MONOLAYER/MULTILAYER

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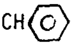
A series of long-alkyl chain monoesters of p-phenylenediacrylic acid (p-PDA, HOOCCH=CHCH=CHCOOR, R=n-C_nH_{2n+1}) is an interesting amphiphlic compounds. These compounds are liquid crystalline, some of them are photoreactive and have monolayer forming property. These properties are attractive from the view point of study on photochemical process in nano-dimensions and led us to investigate photoreaction of these compounds in the crystal and monolayer/multilayer. For this purpose decyl ester (p-PDAmC_{10}) and dodecyl ester (p-PDAmC_{12}) of p-PDA were prepared. In the crystal, two p-PDAmC_{10} molecules are paired with carboxylic acids by hydrogen bonding as a dimer. The pairing units are displaced to form parallel plane to plane stacks. The distance between double bonds is 4 433 A, which affords photoreaction to proceed by cycloaddition of double bonds resulting in formation of dimers. This causes disorder of crystal structure and some of double bonds became closer leading to the formation of amorphous mixture of dimers and trimers. p-PDAmC_{12} crystal is rather photo-stable, probably due to longer distance between double bonds.

Regarding to monolayer/multilayer, both p-PDAmC_{10} and p-PDAmC_{12} form stable monolayers and they could be transferred onto a substrate as multilayer by LB method. The surface area and spectroscopic data of monolayer/multilayer indicated that p-PDA monoesters in the layer are arranged side by side closing each other to form excimers. Photoreaction of the monolayer at an air/water interface is remarkable resulting in increase of surface pressure due to movement of p-PDA monoester by reaction. This suggests the formation of more ordered structure in the monolayer on irradiation. Proceedong of photoreaction in the multilayer was monitored by change of UV and fluoresence spectra. The result of measurement of contact angle of irradiated multilayer supports improvement of the ordered structure in the layer on irradiation. Based on spectroscopic data and molecular weight of products, it is concluded that cycloaddition of double bonds takes place giving oligomers/polymers on irradiation. In conclusion it is shown for photoreaction of p-PDA monoester that cycloaddition is common reaction in crystal and monolayer/multilayer,but each photochemical process is different depending on reaction system.

Organic Microcrystals for Photonics and Microelectronics

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Microcrystals, differing from both bulk crystals and isolated molecules, would have striking properties for photonics and microelectronics. Preparation of microcrystals of π-conjugated molecules, however, have been little investigated except for the evaporation method. Organics are, in general, not stable at elevated temperature. Thus, in the present study, preparation of organic microcrystals by reprecipitation methods has been examined.

Compounds used were chromophers with particular relevance to nonlinear optics, including solid-state polymerizable diacetylenes. Microcrystals of several tens nm to 1 μm in size were successfully prepared (1) by dispersing solutions of organics into vigorously stirred poor solvents at room temperature, or (2) by salting out from aqueous solutions.

Microcrystals of diacetylene monomers could be polymerized to give microcrystals of the conjugated polymers. Interestingly, the molecular weight of poly-4BCMU from microcrystals became greater than that from large bulk crystals, suggesting that single conjugated polymer chains are elongated from one end to the other end of the microcrystals.

Merocyanine microcrystals were obtained in the form of very stable water dispersion, which looked like a solution. By ammonia-treatment the dispersed microcrystals were converted into J aggregates with sharp absorption. In addition, J-aggregates of pseudo-isocyanine bromide, that has surprisingly sharp excitonic absorption, were obtained for the first time at room temperature by salting-out technique. The finding led to the formation of polymer thin films containg the J-aggregates.

In conclusion, it has been found that organic microcrystals can easily be obtained by simple reprecipitation methods.

CONDUCTIVITY IN LANGMUIR BLODGETT FILMS OF PHTHALOCYANINATO-POLY(SILOXANE) POLYMERS

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There has been strong interest in organic semiconductors for their application as basic materials in molecular electronic devices such as transistors or photocells. In particular, materials that can be processed by the Langmuir-Blodgett (LB) technique can be prepared into ultrathin films with well-defined structural order and thickness. Recently a novel class of hairy rod molecules has been designed for manipulation by the LB technique. These molecules are superior to traditional amphiphilic molecules in the realisation of LB films with high thermal stability and good mechanical properties. Among these, phthalocyaninato-poly(siloxane) (PcPS) is of particular interest for application in sensing and photonics devices.

We present detailed studies on the conduction properties of PcPS-LB films. Prototype sandwich structures have been prepared using a gold or platinum bottom electrode, a defined number of PcPS layers and top electrodes of various metals and the current-voltage characteristics was recorded under various conditions. Figure 1 shows the current-voltage characteristics of such a sandwich structure with aluminium as the top electrode and a platinum bottom electrode.

Rectifying, Schottky-type behaviour typical for a surface barrier between a metal and a p-type semiconductor is observed. However the semilogarithmic plot of the current density versus applied voltage shows the non-exponential nature of the current-voltage characteristics under forward bias. The relative low value for the conductivity (σ) of around 10^{-10} Scm^{-1} deduced from these measurements may be due in part to the formation of an aluminium-oxide layer. Larger values for σ up to 10^{-8} Scm^{-1} were observed if bismuth was used as the top electrode material. The influence of an insulating layer was further studied by inserting a few layers of a cellulose derivative into the multilayer assembly. Thermoelectrical measurements provided further information on the charge carrier transport mechanism in these structures. Data on oligomeric model compounds will also be presented and the effect of electrochemical doping will be discussed.

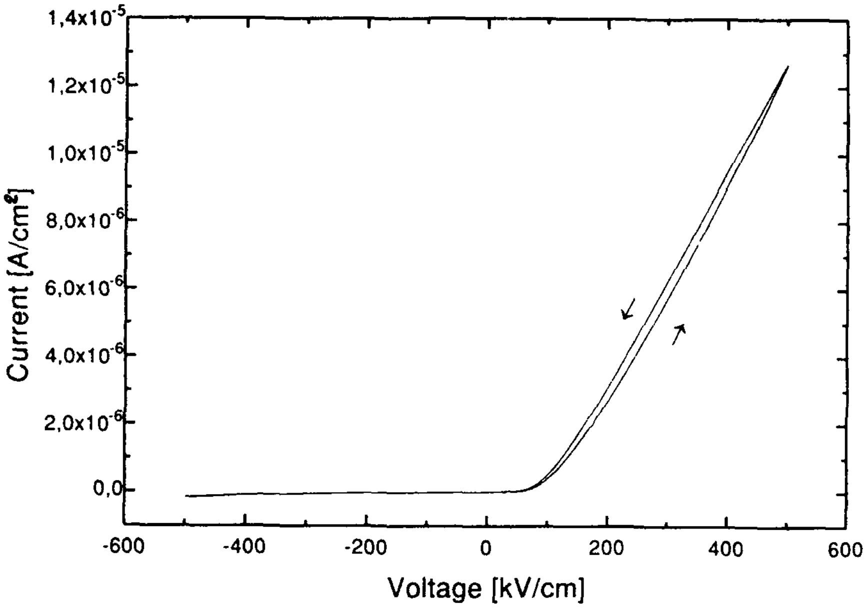

Fig. 1 Current-voltage characteristics of a Pt/PcPS/Al sandwich structure

PHOTOSENSITIZED ELECTRON INJECTION FROM ORGANIC DYES INCORPORATED IN LB FILMS INTO SnO_2

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Spectral sensitization of semi-conductors has been a wide and very active field of research the last three decades, driven mainly by its importance in photographic processes and solar energy conversion. In a early attempt [1] to elucidate the mechanism of sensitization of silver halides, the energy transfer mechanism was favoured, while for other semi-conductors [2] both energy and charge transfer were thought to be possible. The mechanism of spectral sensitization is still not completely understood, although nowadays charge transfer is believed to be the predominant process [3].

In our study, LB films of a cyanine dye, Bis-[1-octadecyl-benzothiazol-2-] monomethine perchlorate (MBT) and arachidic acid (ARA) in different mixing ratios, were transfered onto n-SnO_2 plates. By inserting various numbers of layers of ARA between the semi-conductor and the dye, their mutual distance could be controled. The voltage dependance of the sensitized photocurrent in presence of Hydroquinone was investigated using a three electrodes set-up. Interestingly, both anodic and cathodic photocurrents were observed, their magnitude and ratio being dependant upon the distance between the n-SnO_2 surface and the MBT.

The photocurrent studies together with the results obtained by fluorescence technics will be presented. They strongly suggest that in the present case, energy transfer is the mechanism responsible for the "long range" sensitization of anodic and cathodic photocurrents, while electron transfer accounts for the generation of anodic photocurrent when the dye is in contact with the semi-conductor. Details on these two mechanisms will also be discussed.

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RADIATION DEFECTS IN A NEUTRON-IRRADIATED DIAMOND, INVESTIGATED BY PERSISTENT SPECTRAL HOLE BURNING

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In this work we present the results of a study of photoactive processes in neutron-irradiated natural diamond crystals of type IaB. Originally this type of diamond contains nitrogen in the form of platelets in the <100> plane and in the form of considerable amount of N3 centers. One of the peculiarities of the diamond is its extremely high Debye temperature (1900 K). In particular the longitudinal optical modes have energies corresponding to this temperature. Very few of these high-energy modes are excited at room temperature and this is the reason ,why several zero-phonon lines can be detected even at RT.

In our study a piece of natural type IaB crystal was prepared by irradiating it with a fast neutron flux of 10^{19} neutrons/cm ^{2} and annealing it subsequently at 950 ^{o} C for 30 minutes. As a result of irradiation the sample changed completely dark and became partially transparent at wavelengths > 600 nm after annealing. It should be mentioned that interstitials and vacancies become mobile at T=300 K and T=800 K respectively. The migration of nitrogen atoms and the decomposition of a pair nitrogen may occur around 800 K also. The above described treatment yielded a rich optical spectrum in the region of 600 - 820 nm. Seven comparatively sharp lines were observed in absorption and twelve, in luminescence.

The spectra of polarized luminescence (Fig.1) were recorded for different orientations and polarizations of detection and excitation to determine the orientation of the dipole moments.We conclude that the electric dipoles corresponding to the 723.8 nm transition, are orientated along the <100> axis in the crystal lattice.

Persistent spectral hole burning is performable in the 723.8, 730.7 , and 734.1 nm spectral lines by using a cw dye laser. This gives evidence of inhomogeneous broadening of these lines. The exposures typically of 10 minutes at 100mW/mm^2 yielded spectral holes with the depth of 40% in case of 730.7 and 734.1 nm luminescence lines and 80% in case of 723.8 nm line. The widths of the holes varied from 0.02 nm to 0.2 nm. The temperature dependence of the spectra shows that the holes in the 730.7 nm line are detectable up to 70 K. The holes in the 723.8 line are restored after a thermal cycle to 50 K. In the latter case a strong cross-talk effect is observed: burning a hole in the 723.8 nm line fulfils the preceding hole in the same line. The enhancement of the 734.1 and 738.9 nm lines on irradiation at 723.8 nm line indicates the location of the photoproduct. Proportional decrease of the 723.8 and 731.8 nm absorption lines after burning the sample at 723.8 nm with a pulsed laser gives evidence of the common origin of these lines.

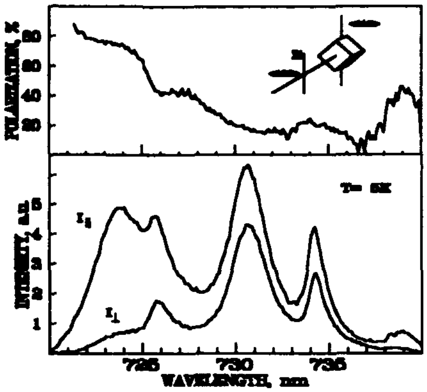

Figure 1.

OPTICAL AND RELATED PROPERTIES OF SOME NATURAL THREE- AND LOWER-DIMENSIONAL SEMICONDUCTOR SYSTEMS

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During the last few years, rapid advances in materials tehcnology have lead to the fabricatyion of novel electronic and optoelectronic devices based on low-dimensional (L-D) systems, i.e. quantum wells (2-D), quantum wives (1-D), and quantum dots (0-D). Artificial systems are fabricated by using several techniques, such as molecular beam epitaxy. However, in addition to manmade structures, natural L-D systems have long been known.

In this paper the optical and related properties (i.e. luminescence, photoluminescence excitation, resonance Raman excitation profiles etc) of some natural three- and lower- dimensional semiconductor systems are briefly reviewed and some new results are reported. The following kinds of systems are investigated. 1) 3-D systems: Compounds of the formula $(CH_3NH_3)MX_3$ (where M=Pb, Sn, Ge; X=Cl, Br, I). These have a cubic perovskite structure and some of them are 3-D semiconductors. 2) 2-D systems: Compounds of the formula $(C_nH_{2n+1}NH_3)_2MX_4$ and compounds of the formula (CH_3NH_3) $(C_nH_{2n+1}NH_3)M_2X_7$ have a perovskite structure and are 2-D semiconductors. 3)1-D systems: Compounds of the formula $M(L\text{-}L)_2M(L\text{-}L)_2X_2(ClO_4)_4$ (where M=Pt, Pd, Ni; L-L= diamine; X=Cl, Br, I) show 1-D semiconductor ' ehaviour. 0-D systems: Small particles of CdS and similar compounds as well as compounds of the formula $(NMe_4)_8M_{20}X_{13}$ $(SPh)_{22}$ (M= Cd, Zn; X=S and/or Se) show 0-D semiconductor behaviour (quantum dots). In all cases, the excitonic or charge transfer (absorption and luminescence) bands in the visible-near infrared is the common feature of these systems. In some cases, a blue shift of the bands has been observed by decreasing the dimensionality.

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STABILITY OF ORGANIC ELECTROLUMINESCENT DIODE

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Organic electroluminescent (EL) diode which cosists of a hole trasport layer and an emitter layer has been reported to give a high brightness and good efficiency [1]. However, lifetime of the EL cell is the most important problem to be overcomed for its application to flat panel diplay [2].

We conducted an investigation of the stability of organic EL diode during operation and storage using analytical methods such as SEM, XPS, cyclic voltammetry, etc. We found that one must pay attention to the following points; 1) morphological stability of organic thin films, 2) electrochemical stability of organic materials themselves, 3) oxidation and/or peeling-off of the cathode, 4) environment of a fabrication process.

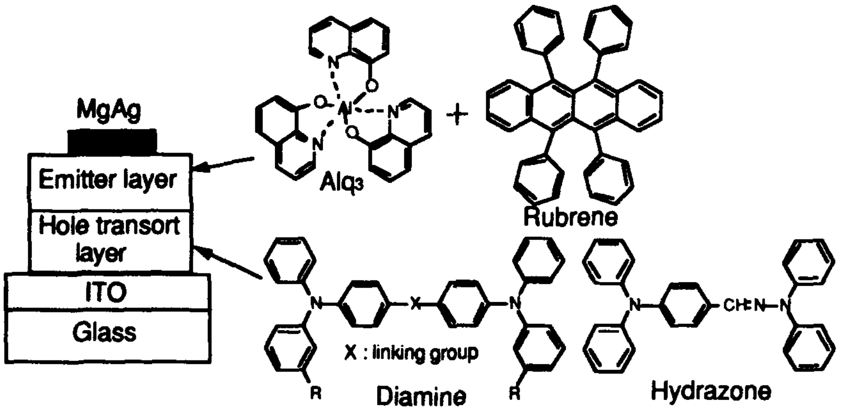

Fig.1 Configuration of EL cell and molecular structures of materials.

The first point, morphological stability of organic thin films, plays an important role in long-term stability of the EL cell. When more than one hole trasport materials were mixed together by means of co-evaporation method, uniform thin films were often obatined. This was quite effective for the suppression of dark spots (non-emissive area) formation, in the cell during its operation and storage.

The similar effect was also observed when the emitter layer was doped with an organic dye. An example is shown in Fig.1, where the Alq$_3$ layer was doped with 7.5 mol.% of rubrene.This doping significantly suppressed dark spots during a long-term storage, compared with the undoped cell (see Fig.2). The grain structure of the Alq$_3$ layer almost disappeared with the doping.

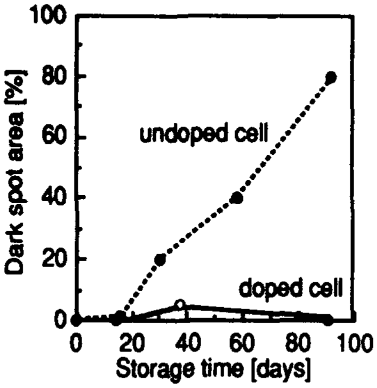

Fig.2 Rubrene doping effect on dark spots

A hydrazone compound shown in Fig.1 decomposed elecctrochemically in a repeated cyclic voltammetry measurement. The EL cell using this hydrazone compound as a hole transport layer degradated very quickly even at low temperature. Degradation due to the third and forth points already mentioned could be avoided when an appropriate encapsulation structure was introduced into the EL device and it was fabricated carefully under a dust-free and dry environment. These results will also be discussed in detail.

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"PHOTOCHEMICAL NON - RECIPROCITY BEHAVIOUR NEW 1,2-NAPHTHOQUINONE-DIAZIDE-(2)-4-SULFONIC ACID ESTERS"

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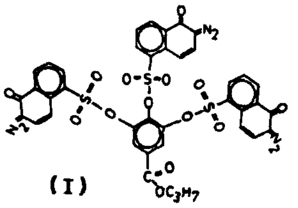
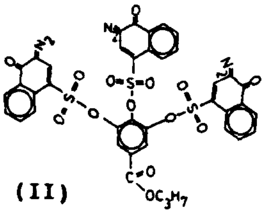
Positive photoresists contain trifunctionally 1,2-naphthochinondiazide-(2)-5- (I) or -4-sulfonic esters (II) as sensitizers. The structure of the NCD molecule play an important role in the performance of these resists. During photolysis the 4- and the 5-sulfonic acid esters show different reaction behaviour resulting in different final products.

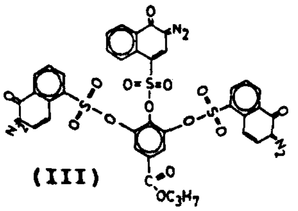


(I)



(II)

Intrinsic new lithographic properties might be generated using the hitherto actinic compound (III) based on the different photolytic properties of compound (III).



(III)

The preparation of the trifunctionaly sulfonic acid esters (III) and the spectroscopic behaviour and the photolytic reactions were described in detail.

FACTORS WHICH INFLUENCE THE "n-TYPE" OR "p-TYPE" PHOTOELECTRICAL BEHAVIOR OF MOLECULAR SEMICONDUCTOR THIN FILMS

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There is presently great interest in the rectification properties of heterojunctions based upon modified phthalocyanine and/or perylene dye thin films, and the origin of the "n-type" or "p-type" behavior of these materials [1-4]. The creation and transport of photogenerated charges in these thin films is known to be strongly dependent upon concentrations of impurities, defects and traps, and upon the positions of the HOMO and LUMO levels of these dyes in the condensed state. There have been however, relatively few attempts to systematically study the HOMO and LUMO energies of such systems, and to correlate these energies with the dark and photoelectrical behavior in ultraclean environments, and upon initial exposure to gases such as O_2, NH_3, etc.

Thin crystalline films (10 nm) of phthalocyaninatozinc(II) (PcZn), and its derivatives tetrapyridotetraazaporphyrinatozinc(II) (TPyTAPZn) and naphthalocyaninatozinc(II) (NcZn); as well as of perylenetetracarboxilic dianhydride (PTCDA) and its derivative N,N-dimethylperylenetetra-carboxilic diimide (MePTCDI), have been prepared by vapor deposition under UHV conditions. The electrical conductivity and photoconductivity of these films were measured on interdigitated microelectrode arrays of $PtSi_x$ on Si. The films were studied as prepared and during exposure to rising partial pressures of oxygen and ammonia. Changes of dark conductivity and photoconductivity wit O_2 or NH_3 exposure (Figure 1), as well as changes in their activation energies, showed striking differences among the studied compounds. These differences are explained by a changing tendency towards charge exchange with acceptor or donor molecules. These interactions were only partly reversible, as confirmed by XPS analysis. While derivatives of PTCDA generally show n-type conduction, the conduction type of phthalocyanines and their derivatives is strongly dependent on the type of ligand.

To rationalize these photoelectrical results a detailed analysis of positions of energy levels in the solid is crucial. The positions of the ground-state levels are derived from in-situ UPS experiments on an atomically clean gold surface during the deposition of the Pc and perylene dye thin films (Figure 2). The positions of the excited state levels are estimated from luminescence measurements of these films on transparent substrates. The results are discussed within existing models of molecular semiconductors, and their impact is emphasized on the use of these materials as photoelectrochemical and photovoltaic electrodes.

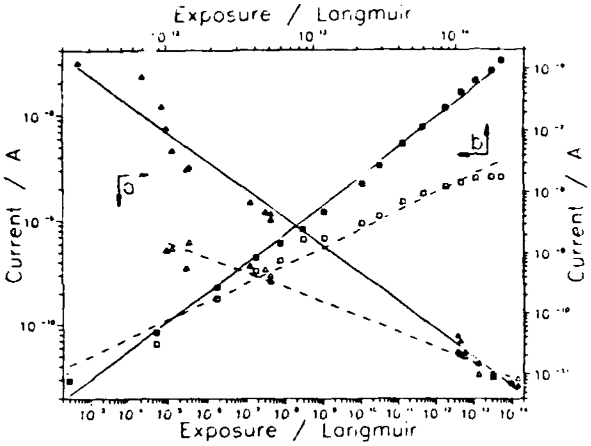


FIGURE 1:

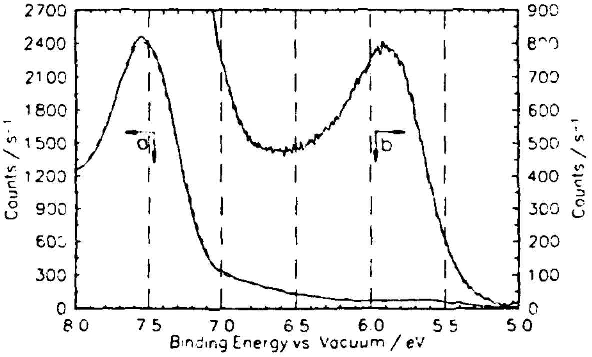
Changes of the current in the dark (solid symbols) and under illumination by a 5 mW He-Ne Laser (open symbols) obtained at films of

(a) MePTCDI and
(b) NcZn

FIGURE 2:

Photoelectron spectra arising from the highest occupied orbitals after excitation with ultraviolet light (HeI) obtained at films on Au of

a) MePTCDI and
(b) NcZn



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NEW LB HETEROSTRUCTURES CONTAINING ELECTRON DONATING AND ACCEPTING MOLECULES

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In the field of molecular electronics a variety of molecules and heterostructures prepared by the LB technique have already been investigated. In our work we want to combine the potential of the LB technique with the possibilities of thiophene chemistry to achieve precursor structures for one dimensional wires or devices which can store information on the molecular scale (e.g. by charge separation).

Newly synthesised derivatives of thiophene were investigated as pure films as well as in mixed monolayers with amphiphilic viologene derivatives. The pressure area isotherms were obtained on a commercial film balance (LAUDA FW1) and the occupied area per molecule indicates a tight packing of the hydrocarbon chains. We transferred the films on a variety of hydrophilic and hydrophobic substrates as a monolayer and as multilayers. The conditions of film preparation for the pure LB films have been presented elsewhere [1].

The work which we have done with the LB films of 3-thienylpentadecanoic acid (3TC15) comprises the following spectroscopic methods: Fourier transform infrared absorption experiments (commercial spectrometer, Brucker 113v) in transmission and grazing incidence geometry, surface plasmon resonance [2], and UV/VIS experiments. The results indicate that the saturated hydrocarbon chains are slightly tilted with respect to the substrate normal (10°) and that the thickness of the LB film is 23 Å per LB monolayer. This is the first example of an arrangement of monomeric thiophene derivatives in a two dimensional manner without supporting matrix molecules. The thiophene moieties, the plane of which is oriented perpendicular to the plane of the substrate, are separated by the isolating saturated hydrocarbon chains. We prepared isolating sandwich structures with thicknesses < 100 Å. Polymerisation of this structure should lead to highly anisotropic conductivities. In addition we prepared LB heterostructures which combine the electron donating character of the thiophene moiety of 3TC15 and the electron accepting character of a LB film forming viologene derivative (BPS) [3]. The mixture of 3TC15 and BPS (2:1) builds stable monolayers on the air-water interface on a subphase containing $NaClO_4$ (0.5 mM) and $CaCl_2$ (0.25 mM). In this heterostructure the thiophene can act as an electron donating moiety at the hydrophobic end of the LB film. The electron accepting viologene is located at the hydrophilic end of the layers and is separated via the saturated hydrocarbon chains. These structures were investigated with the above mentioned techniques and the results will be presented in this conference. In the heterostructures we expect a vectorial electron transfer from the excited thiophene to the viologene.

In conclusion we were able to prepare pure and mixed LB films of the new molecule 3TC15 and investigated the different systems which may act as precursor systems for future molecular device concepts with a variety of experiments.

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ELECTRICAL CONDUCTIVITY AND ELECTROLUMINESCENCE OF POLY-P-PHENYLENE-VINYLENE SCHOTTKY BARRIERS

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Due to its good processability and thermal stability poly-p-phenylene-vinylene (PPV) is well suited for large area electronic devices (colour plate) as well as for micro structures. Our PPV is prepared by the precursor route widely used for the synthesis of high polymer weight PPV [1]. We made only slight modifications, for example we used a methanol/water solution to improve the polymer yield [2]. Our devices have a typical Schottky diode configuration with an ohmic contact (ITO), the p-type semiconducting PPV layer (thickness 0.1 - 1 μm) and a vacuum evaporated rectifying electrode (Al, Ca) [3]. The fabrication of large light emitting diodes with active areas of more than 25 cm^2 is possible. The conversion of the PPV precursor polymer to PPV can also be done by UV radiation, giving the possibility of creating micro structures. The exposed places become insoluble while the dark remain soluble and can be removed with methanol [4].

In this paper we report on electrical properties of PPV-based light-emitting diodes and solar cells. At room temperature I-V-characteristics in the dark reveal a good diode behaviour (Fig. 1) with a maximum rectification ratio of 10^6. The threshold voltage for visible electroluminescence (EL) is as low as 2 V (Fig. 3). Due to the low drive voltage and the use of Al as top electrode, our devices have been run for more than one week under ambient conditions. In a glove box under argon atmosphere a continously driven device still emitted light after 4 weeks.

The EL spectrum together with optical absorption spectrum of an ITO/PPV/Al devices are shown in Fig. 2. In the EL spectrum a series of bands with an energy spacing of about 0.16 eV appears just below the band edge. According to Friend et al. [5] the sharp vibronic structure is due to coupling of vibrational excitations of the polymer chain to the electronic $\pi - \pi^*$ transition and the vibrational modes are ring stretching modes. Impedance measurements show that our diodes can be described within the Schottky barrier model, e.g. as a serial circuit of resistive and capacitive components, for both the bulk and the junction. Under illumination an open-circuit voltage of more than 1 V and a power conversion efficiency of about 0.1 % can be achieved, suggesting the possible application as solar cells (Fig. 4).

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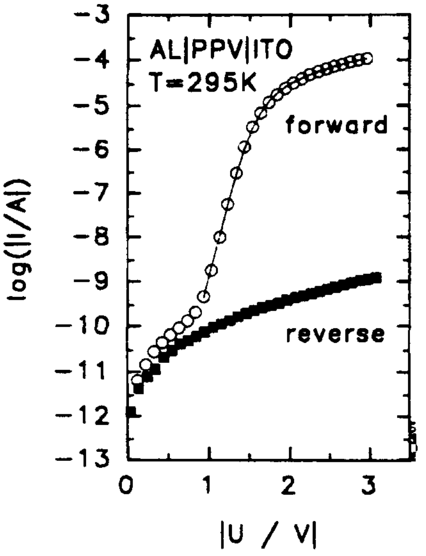

Fig. 1: I-V-characteristic

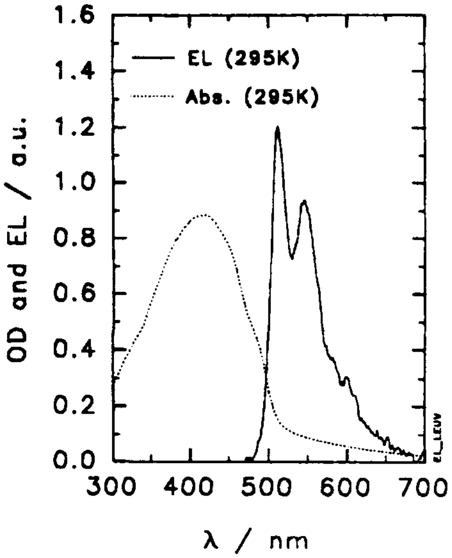

Fig. 2: EL and opt. Absorption

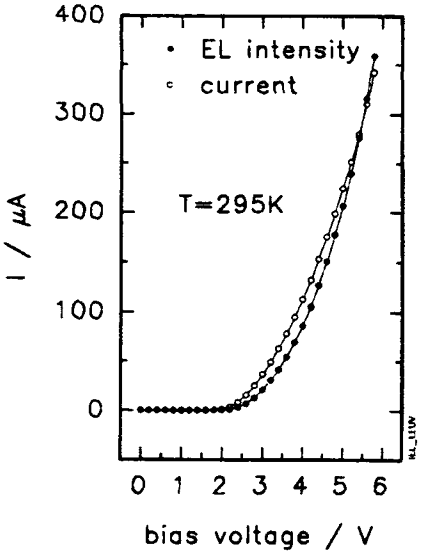

Fig. 3: EL signal and current versus bias

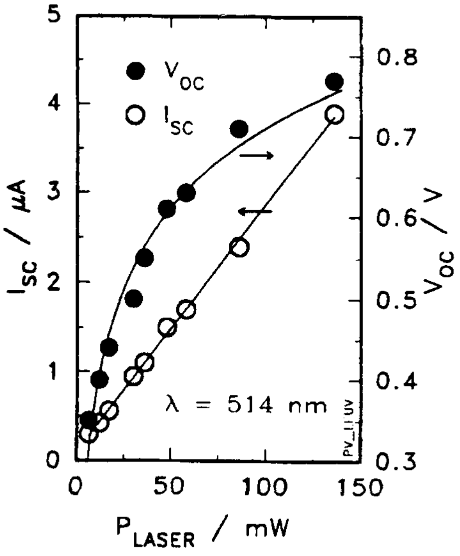

Fig. 4: Short circuit current I_{sc} and open circuit voltage V_{oc}

CHARGE TRANSPORT PROPERTIES OF ARYLALDEHYDE HYDRAZONES IN THEIR GLASSY STATES

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Charge transport in organic disordered systems, such as molecularly doped polymer systems where low-molecular-weight organic compounds are dispersed into polymer binders have been a subject of recent extensive studies. It has recently become recognized that the polymer binder, which was thought to be inert for charge transport, affects greatly charge transport.

In order to understand intrinsic properties of charge transport in disordered organic solids, we have been studying charge transport in the amorphous glassy state of low-molecular-weight organic compounds. We have found that a series of arylaldehyde hydrazones constitute a new family of amorphous molecular materials that form stable amorphous glasses.

We report here charge transport properties of a few arylaldehyde hydrazones, 4-diphenylaminobenzaldehyde diphenylhydrazones (DPH), 9-ethylcarbazole-3-carbaldehyde diphenylhydrazones (ECH), and 9-ethylcarbazole-3-carbaldehyde methylphenylhydrazone (MECH), and discuss the correlation between the molecular structure and hole drift mobilities. The effects of mixing two different hydrazones on charge transport properties are also discussed.

PHOTOACTIVE LANGMUIR BLODGETT FILMS OF INDANDIONE 1,3 PYRIDINIUM BETAINE.

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Novel amphiphilic derivatives of indandione 1,3 pyridinium betaine (IPB) with different length of the aliphatic tail, containing 11 (C11IPB) and 17 (C17IPB) carbon atoms, respectively, have been synthesized. Quantum chemical calculations of the electronic structure, absorption spectra and dipole moment measurements demonstrate pronounced dipolar nature of the first singlet transition ($S_0 \longrightarrow S_1$) of the IPB molecule resulting in change of the direction of the dipole moment of the molecule from d_g=4.5D in ground to d_e 5.1D in excited states.

The compression π-A isotherms of the C17IPB monolayers on water surface and computer simulation of molecular arrangement, performed in the framework of atom-atom potential and Coulombic interaction approaches, shows that there may exist two energetically most stable molecular configurations, i.e., two structural phases, of the C17IPB monolayer. The first stable configuration phase emerge at low pressure linear π(A) region (π = 10 to 32 mN/m) and limiting area per molecule A_0=37A². In this low pressure region simulation predicts a dimer type of configuration of the C17IPB "heads", with antiparallel orientation of the dipoles, the "dimers" lying sideways with respect to the water surface. After distinct phase transition at π - 33mN/m the IPB molecules rearrange in more dense packing and area per molecule equal to 33Å². In this high pressure region parallel configuration of both molecular "heads" and their dipole moments is predicted with tilting angle α relative to the substrate estimated to be about 50 degrees. The calculated areas A_0 per molecule were found to be in good agreement with experimentally determined A_0 values for both structural phases of the C17IPB.

The high pressure region yields a <u>linear</u> $\pi(A)$ dependence up to the collapse pressure at π = 50mN/m. The electronic absorption spectra of the C17IPB monolayer on the water surface and simulation data show that the phase transition caused by compression of the monolayer produce short-wave shift and decrease in intensity of the S_1 band as well as change of the tilting angle. These spectral changes reproducibly correlate with the compression π-A isotherms.

In case of C11IPB monolayers one can observe the presence of low pressure phase of molecular arrangement only, since the phase transition at π = 37mN/m coincides with the collapse pressure of the monolayer.

The multilayer LB assemblies of C17IPB on solid substrates have been obtained at high pressure linear $\pi(A)$ region at π = 40mN/m. Using deposition technique with different speed of up and downward motions of a hydrophilic substrate Z type of C17IPB multilayers can be obtained. This structure has been confirmed by ellipsometric measurements and simulation data. Applying intrinsic photoconductivity and photoemission data preliminary energy structure of the sequence of quantum wells of the C17IPB multilayer assemblies has been proposed.

The C17IPB multilayers possess pronounced non-linear optical properties, viz. effective second harmonic generation, excited at $h\nu$ = 1.17eV by Nd YAG laser pulses. These non-linear optical and photoelectric properties of 17IPB LB films, as well as predicted very fast optoelectrical response, caused by optical switch of molecular dipole moments, may be of considerable interest for applications in molecular optoelectronics.

PHOTOINDUCED CHARGE TRANSFER FROM CONJUGATED POLYMERS INTO MOLECULARLY DOPED POLYMER

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We describe here charge transfer from photoexcited π-conjugated polymers, linear poly(phenylenevinylene) (PPV) and a ladder type polymer, poly(benzimidazobenzophenanthroline) (BBL), into a molecularly doped polymer, [N,N-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine) (TPD) in polycarbonate] in the presence of an electric field. Both π-conjugated polymers are photoconductive in the region of wavelengths of absorbed light [1,2] but the drift of photogenerated carriers is severely range limited by trapping events. In a bilayer device schematically shown below the carriers which are photogenerated in a thin layer (0.1 μm or so) of PPV or BBL, are efficiently transferred into the adjacent TPD layer and transported without trapping to the counter electrode.

Time resolved photoinduced charge transfer from PPV and BBL into TPD in the presence of an electric field is analyzed. Transient photocurrent measurements were performed on these bilayer devices using the TOF technique. The study shows that the charge transfer from both BBL and PPV into the TPD/polycarbonate layer is complete and without delay. No interfacial trapping has been detected in either case. The shape of the TOF transients through the TPD layer at all measured electric fields is indicative of nondispersive charge transport. The transients are similar to those obtained by flash excitation of the bulk of TPD in the presence of an electric field or those obtained by flash photoemission from adjacent α-Se [3.4]. The photoemission from PPV or BBL thus occurs in times that are substantially shorter than the transit time through the TPD layer.

The TOF mobilities determined in the bilayer device using extrinsic photoexcitation in the conjugated polymers at peak absorption of 460 nm in the case of PPV and 560 nm in BBL are about the same as mobilities determined at reversed bias by photoexcitation directly in the TPD layer at 360 nm. The carrier collection efficiency η_c expressed as the product of η_g (the generation efficiency), η_t (trapping efficiency) and η_i (injection efficiency) in the PPV / TPD system at $E=4x10^5$ V/cm is near 25%. The collection efficiency in the BBL / TPD layered device is only 1%. In both cases, η_c is electric field dependent.

It is not clear whether the photogeneration is intrinsic (π-π^* transition followed by the carrier separation, migration in PPV or BBL, and injection), or extrinsic (TPD assisted dissociation of the π-π^* excitons at the polymer - polymer interface). If the photogeneration is intrinsic, the collection efficiencies η_c of 25% in the case of PPV and 1% in the case of BBL represent lower bound estimates of η_g if trapping in the generation layer is neglected and if the interfaces do not affect carrier injection. The actual generation efficiency could approach unity if a large fraction of photogenerated carriers is lost during the short transit through the π-conjugated polymers.

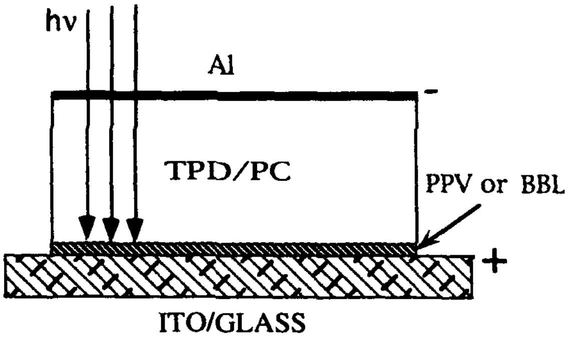

Figure 1. A scheme of the bilayer device

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PHOTOINDUCED OPTICAL ANISOTROPY IN FILMS OF PHOTOCHROMIC LIQUID CRYSTALLINE POLYMERS

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Photochromic liquid crystalline side-group polymers (LCP) have been recently attracting much attention as materials for optical data storage. A wide variety of optical phenomena may be induced in liquid crystalline materials, either through variation of order parameter or manipulation of director orientation.

Using linearly polarized light offers a fundamentally new approach to modify optical properties by angular-dependent photoselection.

We have studied laser induced modification of optical anisotropy of liquid crystalline polyacrylates and polymethacrylates containing different content of azo moieties below and above glass transition.

Our results show that the anisotropic properties of the LCP films such as dichroism and birefringence are changed on irradiation. The angle between the optical axis of the oriented LC film and the plane of polarization of light is continuously enlarged to as much as a maximum limit of perpendicular orientation. This effect is caused by a rotational diffusion in combination with angular-dependent photoselection process within the steady state of the E-Z photoisomerization.

Measurements of the induced birefringence, the IR dichroism of non-photochromic moities and microscopic studies suggest, that even in glassy state the optical axis of the whole system undergoes reorientation due to a cooperative effect of adjacent side groups. Thus, we characterize this type of variation of optical anisotropy in such polymers showing a long range order as a photochemically induced physical reorientation process.

The induced birefringence strongly depends on the operating temperature with respect to the glass transition as well as the chemical structure of the polymer. It can be frozen-in in the glassy state of the polymer, read out by a non-actinic laser beam, changed by further irradiation and erased thermically or photonically.

SCANNING TUNNELING MICROSCOPY/SPECTROSCOPY OF SURFACE OXIDE ON TITANIUM: PHOTOEXCITATION EFFECT AND NANOANODIZATION

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Among various semiconductors, titanium dioxide (TiO_2) is of special interest because of its unique properties of photoelectrochemical and photocatalytic abilities. For further applications of the material to microdevices, microfabrication of TiO_2 in arbitrary spatial patterns is worth to be explored on the basis of clear understandings of photoactivities of TiO_2 in minute dimensions. Along the strategy, we examined photoexcitation effects on scanning tunneling microscope (STM) images of a very thin TiO_2 layer on titanium (Ti) metal [1]. In this report, we show scanning tunneling spectroscopy (STS) of surface TiO_2 on Ti under optical illumination ; *optical tunneling spectroscopy*. Furthermore, nanolithography of Ti through STM tip-induced anodization [2] and its application to fabricate spatially-arranged photoactive surfaces are presented.

SCANNING TUNNLEING SPECTROSCOPY OF TiO_2/Ti

Ti surfaces exposed to air are covered with a very thin TiO_2 layer which is known to act as an n-type semiconductor. Therefore, conductivity of the surface layer is expected to be enhanced upon photoillumination. Current-bias (I-V) characteristics of STM-tip/TiO_2/Ti tunneling junction were measured under photollumination by a 100 W super-high-pressure mercury lamp at starting values of a sample bias (Vs) = -2.0 V and a reference current (i) = 0.5

nA. Fig. 1 shows typical I-V curves and the relevant differential conductivities of the junction under dark and photoillumination. Conductivity of the junction under photoillumination (Fig. 1B) is clearly higher than that in dark (Fig, 1A). Photoconductivity of the TiO_2 layer was confirmed by means of STS under optical illumination.

NANOANODIZATION

Nanoanodization of Ti was achieved by scanning an STM tip at Vs ≥ +3.0 V in the presence of adsorbed water [2]. An STM image in Fig. 2, acquired with Vs = -3.0 V and i = 0.1 nA, is a typical example of nanoanodized Ti where anodized TiO_2 lines of 30 ~ 40 nm in width are fabricated on Ti at Vs = +8.0 V, i = 0.2 nA, and a scan rate of 5 μm/s. An increase in the relative composition of oxygen to Ti in the fabricated area was confirmed by Auger electron spectroscopy. Chemical and photochemical properties of the fabricated patterns will be also presented.

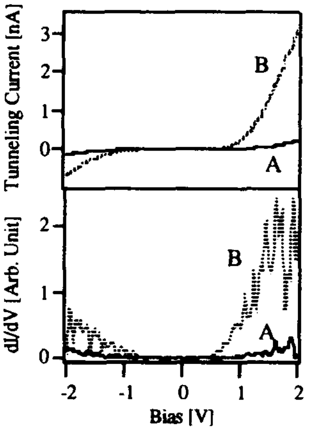

Fig. 1 STS of TiO_2/Ti
A: dark, B: photo

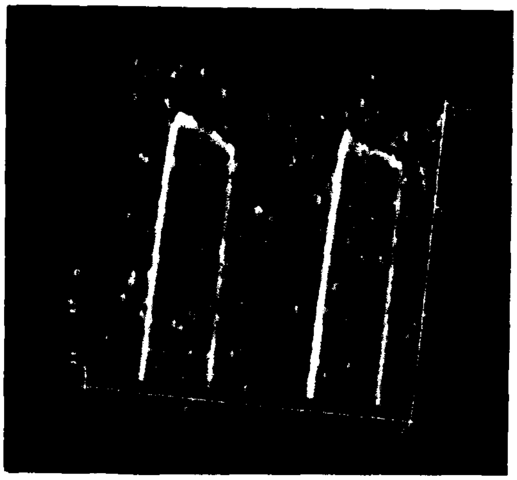

Fig.2 Line patterns fabricated by STM tip-induced anodization of Ti

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SPECTRAL HOLE BURNING IN DYE DOPED PLASTIC FIBER

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We report persistent spectral hole burning (PSHB) in metal-free tetraphenylporphyrin (TPP) doped polymethylmethacrylate (PMMA) fibers via the proton tautomerization of TPP. This combination was chosen because PMMA fibers exhibit their largest transmittance at around 658 nm, which is a convenient wavelength at which to use TPP as guest molecules.

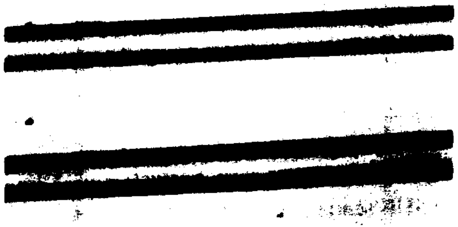

Fig. 1. Fiber PSHB sample (below) and SiO_2 multi-mode optical fiber with 125 μm diameter (above).

In PSHB storage scheme, materials development with sufficient guest molecules is vital to realize the burning of more than 10^3 spectral holes within a single focused laser spot. One approach is to prepare highly doped host-guest systems, in which, however, some drawbacks occur due to the competition between interguest energy migration and PSHB photochemistry. Another approach is to fabricate thick samples where the guest concentration should be low enough not to induce interguest energy migration and the focused laser light should remain localized in the samples. The fabrication of the fiber PSHB materials will meet these two requirements.

Table I Characteristics of fiber PSHB samples and spectral holes burnt in these samples

Sample[a)]	Diameter (μm)	Length (mm)	Hole Yield (10^5)	Holewidth (GHz)
1	600	55	2.4	4.66
2	400	52	43	4.42
3	125	10	0.021	8.04

a) [TPP] = 1.25×10^{-4} M

Table I lists the characteristics of fiber samples we fabricated in this study and spectral holes burnt in these samples (see also Figs. 1 and 2). Decrease of the hole formation yield (η) in comparison with the reported value (1.0×10^{-3}) in TPP/PMMA ($[TPP]=5\times10^{-4}$ M) is ascribed to an overestimation of the number of irradiated photons due to the propagation loss of the excitation laser light and the connection loss between samples and light guiding fibers. The marked decrease in the η value of sample 3 is due to the chemical change of TPP.

A simplified analysis for a bit by bit storage scheme revealed that the achievable areal storage density (S) increases in proportion to the increase in the sample length due to the accompanying increase in the number of guest molecules in the sample. Thus, the S value can be increased by one or two orders of magnitude in our fiber PSHB samples because most of PSHB samples studied so far have the thickness of 0.1-1 mm Further increase in the S value can be facilitated with the aid of recent breakthroughs in developments of high efficiency PSHB materials and high sensitivity detection schemes. However, it should be noted that the practical S value in fiber PSHB samples is determined by their core diameter. A more suitable application of fiber PSHB samples may be to use them in a holographic storage scheme when difficulties are taken into account to fabricate fiber PSHB samples with a core diameter of about 1 μm. In this storage scheme, advantages of fiber PSHB samples can be used more directly than in a bit by bit storage scheme. Additionally, the fiber structure of PSHB samples will facilitate their application to a variety of devices for optical data processing.

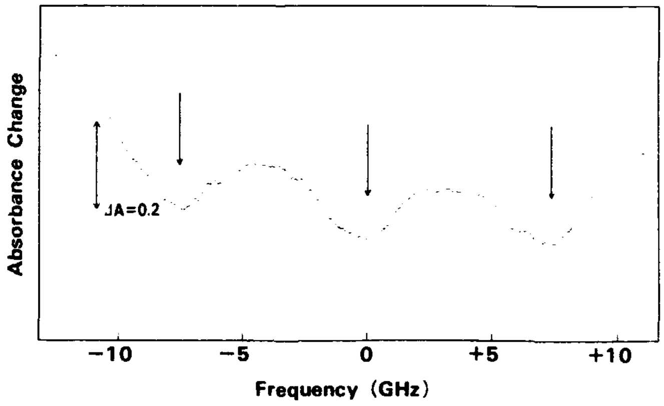

Fig. 2. Spectral holes burnt at every 7 GHz with an irradiation of 13.9 mW/cm^2 for 120 s in sample 2.

EFFECT OF DIPOLAR DEFECTS ON TRAPPING OF CHARGE CARRIERS IN STRONGLY ANISOTROPIC POLYDIACETYLENE CRYSTALS

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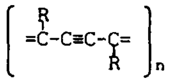
Single-crystalline polydiacetylenes



$$\left[=\overset{R}{C}-C\equiv C-\underset{R}{C}= \right]_n$$

are a unique class of solids consisting of extended conjugated π-electron chains, 10^2-10^4 monomer units long, well separated from and relatively weakly interacting with one another. Since the pioneering work of Wegner [1], structural, mechanical and electronic properties of this class of polymers have been extensively studied (see, e.g., [2-5] for reviews and collections of papers), and it has been commonly accepted that polydiacetylenes may be considered model quasi-one-dimensional solids.

One of the most striking features of polydiacetylenes is a pronounced anisotropy of their electronic properties. In particular, dark conductivities and photoconductivities in some polydiacetylenes capable of yielding single crystals of a reasonable quality (e.g., pTS, in which R = $-CH_2-OSO_2-\phi-CH_3$ or pFBS, where R = $-CH_2-OSO_2-\phi-F$) determined in the directions parallel to the polymer chains are 2 to 4 orders of magnitude higher than those measured in perpendicular directions [6,7]. These results, to a first approximation, seem to reflect the anisotropy of the mean free paths of the carriers. The latter parameter may be expected to amount to the length of the unperturbed chain in case of the carrier transport along the chain, and to the inter-chain distance in case of the lateral transport.

The length of unperturbed polymer chains is believed to critically depend on the concentration of defects, the most obvious of them being chain ends. These defects may influence the carrier transport not only on one polymer chain but also on neighbouring ones, nominally defect-free. It should be realized that in most cases the presence of defects in polydiacetylenes is likely to give rise to the appearance of uncompensated dipoles (*cf.* [8]). In this note, the effect of such dipolar defects on the transport of carriers in strongly anisotropic (quasi-1D) systems will be examined.

Simple calculations of electrostatic interactions yield the following results:

i) The presence of a dipolar defect gives rise to the appearance of local minima of potential energy of a carrier travelling on neighbouring polymer chains. Such minima may act as carrier traps.

ii) The depth and concentration of the traps depend primarily on the magnitude of the dipole moment; these parameters, however, can also be modified by biasing field and temperature. The latter effect may account for the field-dependent trap release recently described by Fisher and Willock [9].

iii) Since the thermally assisted release of a carrier from a trap is a ballistic process, one should expect the localization events to enhance the probability of inter-chain jumps, and consequently to reduce the anisotropy of parameters governing the carrier transport.

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RELAXATION DYNAMICS OF CHARGED SPECIES IN POLYSILANES FROM PICO-TO MILLI-SECOND TIME SCALE STUDIED BY PICOSECOND PULSE RADIOLYSIS COMBINED WITH PICOSECOND DIODE LASERS

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Recently considerable attention has been paid to polysilane derivatives containing polygermanes, so-called sigma-conjugated polymers, as a quite new category of newly developed polymer materials [1]. We have already reported on both the spectroscopic data of the transient charged species [2-5], electronic properties [6], and final products [6] in irradiated linear and network polysilanes[7] in solutions and solid films.

The present paper describes mainly the relaxation dynamics of charged species in polysilanes from picosecond to millisecond time scale studied by a new picosecond pulse radiolysis system.

The relaxation dynamics of charged species in polysilanes are very importamnt in not only their potential usefulness such as photoconductive materials and resists for microlithography but also their unusual photochemical and photophysical properties.

The new picosecond pulse radiolysis system, so-called LL-Twin pulse radiolysis system [8], uses mainly 10 ps electron pulses from a 28 MeV electron linac and picosecond diode lasers as irradiation source and analyzing light, respectively. The picosecond diode lasers are synchronized with 10 ps electron pulses.

Relaxation dynamics of charged species have been studied for previously reported transient absorption due to both radical anions and cations. Very intense transient absorption due to radical anions and cations of various kinds of polysilanes such as linear, network and branched polysilanes and polysilane copolymers from ultra violet to infrared wavelength regions have been observed by both pulse radiolysis and gamma-irradiated matrix isolation techniques [2-5,7,9,10]. Polygermane radical anions and cations have also been observed [5,11]. Polysilane radical anions and cations have also been observed in irradiated molten polysilanes and polysilane films in addition to polysilanes in solutions. Polysilane radical anions and cations have very similar UV absorption spectra [12]. It is a so-called pairing properties of radical ions of conjugated molecules. Red shifts of ultra violet absorption bands of radical ions of polysilanes from those of neutral polysilanes are observed systematically [13]. The formation processes of both radical anions and cations on picosecond and nanosecond time scale were observed very clearly in irradiated polysilanes in solutions such as tetrahydrofuran (THF) and methylene chloride (MeCl) solutions. The formation processes of radical anions and cations are mainly due to the reactions of solvated electrons in THF with polysilanes and the charge transfer from the radical cations of MeCl to polysilanes, respectively. The reactions of solvated electrons and the charge transfer processes were observed very clearly and rate constants of these reactions were determined, but the red shift of the absorption peaks couldn't be observed on picosecond and nanosecond time scale. It indicates the processes of red shift of UV absorption bands of both radical anions and cations are very fast.

The relaxation dynamics of very broad infrared absorption spectra of polysilane radical anions and cations on time scale from picosecond to millisecond have been observed by LL-twin picosecond pulse radiolysis system. The main relaxation processes of polysilane radical anions and cations in solutions occur on several microsecond time scale. The relaxation dynamics of polysilane radical cations and anions in solids are more complicated, because absorption spectra of radical anions and cations overlap and the time scale of the relaxation of radical ions overlaps the time scale of ion recombination. The time scale of the charge recombination in solids are several orders of length.

Relaxation dynamics of charged species in polysilanes play very important roles in potential usefulness, photochemical and photophysical properties, electronic properties, and radiation effects of various kinds of radiation, especially hole mobilities, resist sensitivities for microlithography and large LET effects in ion beam modification.

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HOLE BURNING OF PROTON(S) SUBTRACTED 1,4-DIHYDROXYANTHRAQUINONE: MECHANISM AND LOW-LYING ELECTRONIC STATE(S) IN INTRAMOLECULAR HYDROGEN-BOND(S) AND PROTON TRANSFER SYSTEM

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Among many photoreactive molecules in persistent spectral hole-burning (PSHB) we have been paying much attention to 1,4-dihydroxy-9,10-anthraquinone (1,4-DAQ) and its derivatives [1-3] as well as free-base porphyrins. This is because the comprehension of the structure of the excited electronic state(s) and the mechanism which drives the proton(s) transfer reaction from purely electronic excitation seem to be interesting [4,5]. Here we describe our recent results on the PSHB and absorption/emission properties of proton(s) subtracted 1,4-DAQ's in ethanol/methanol glasses mixed with Na-ethylate (EtONa) as titrant.

Mono- [AQ(OH)(ONa)] and di-substituted [$AQ(ONa)_2$] derivatives can be distinguished and separated by monitoring its spectral change with addition of EtONa. The solution of AQ(OH)(ONa) is so stable as to carry out various observations separately after degassed and sealed in the optical glass cell of 1.5-mm path length, while that of $AQ(ONa)_2$ precipitates so easily that the samples are quenched down to liquid He temperatures just after the preparation.

Absorption and emission spectra observed at 4.7K indicate that the Stokes shifts are sufficiently small for both derivatives and each of the lowest absorption band contains enough amount of 0-phonon transitions. Actually the formation of 0-phonon hole and pseudo-phonon sidehole is clearly observed in both derivatives [6]. Hole-burning was performed with pulsed dye laser (6ns, $\leq 0.06\ cm^{-1}$) pumped with 2nd harmonic from Q-switched Nd:YAG laser (10Hz).

PSHB properties are almost similar between the two but different from those of 1,4-DAQ. The widths are fairly large and the efficiencies are rather low; 1.4 cm^{-1} and 1.2×10^{-5} for AQ(OH)(ONa) and 1.5 cm^{-1} and 1.7×10^{-6} for $AD(ONa)_2$, respectively. Most significant difference between the two and non-substituted DAQ is the spectral profiles of anti-hole(s) or the product states. The observed absorption difference before and after large amount of burning for each derivative, as seen in the figure, shows that the spectra of the products seem almost similar to those of the educt states except that they are red-shifted by 20~30 nm. In case of 1,4-DAQ, the product appears just as a broad and featureless spectrum around 410 nm with reduced oscillator strength. We consider so far the mechanism of hole formation of AQ(OH)(ONa) and $AQ(ONa)_2$ is different from those in 1,4-DAQ [6,7,1] and seems photophysical in nature. The feature of the proton(s) transfer in 1,4-DAQ and related derivatives will be discussed. Further the possibility and role of non-bonding state(s) in O= groups will also be discussed based on these and our accumulated findings such as in heterogeneous 1,4-substitution by NH_2-group(s), QS/β-cyclodextrin/LB film, 1,4-DAQ/TMA/saponite [8] and 1,4-DAQ in two-component sol-gel glasses (5 mol% Al,B, Ti in Si) as well.

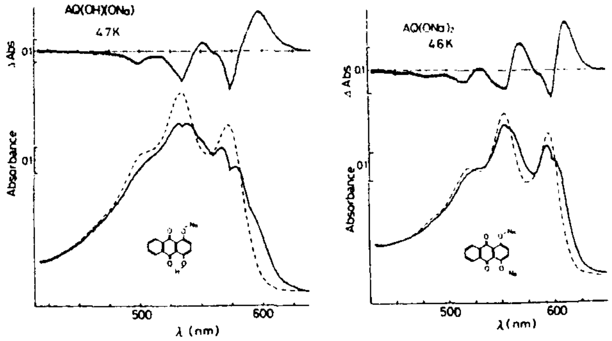

Fig.1 Absorption difference spectra after strong laser illumination; AQ(OH)(ONa): λ_I 573nm, 15J/cm^2, $AQ(ONa)_2$: λ_B= 595nm, 9J/cm^2.
——: after burning
·········: before burning

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LB-FILM EMBEDDED J-AGGREGATES:
ENERGY TRANSFER AND FAST DYNAMICS

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During last years some progress has been made in the understanding of the subtleties of the aggregate's optical dynamics in solution and in the condensed phase. The large concentration of dye molecules embedded in LB-films is attractive from fundamental point of view as geometrical restricted molecular systems with unusual energetic and electrical properties. The energy transfer between J-aggregates have been of interest in connection with photographic engineering as well as application to high-density optical memory.

New type J-aggregates are obtained by anion-cation dyes pairs in water solution under special conditions. The spectral and kinetical features of this compounds are investigated. Data are compared with the molecular dye aggregates features obtained separately and with well-known PIC J-aggregates.

The fluorescence lifetime measurements were performed by time - correlated single photon counting and by picosecond up - conversion (UpC) method (time resolution is about 1 ps). UpC-method is realised with cavity-dumped two-jet dye laser synchronsly pumped by mode-locked Nd-YAG laser and special detection systems: lock - in -amplifiers and photon counting. The dynamic range for kinetic measurements is more than three orders. The picosecond kinetics of fluorescence anisotropy is discussed as well.

The basic idea behind the energy transfer measurements is the construction of special geometrical positions for donors and acceptors by LB-technique. The particularity of fluorescence LB-film embedded J-aggregates are studied as new example of energy transfer in molecular systems with restricted geometries.

SUPRAMOLECULAR SYSTEMS FOR OPTICAL SWITCHING: CONTROLLING ULTRAFAST ELECTRON TRANSFER REACTIONS WITH FEMTOSECOND LASER PULSES

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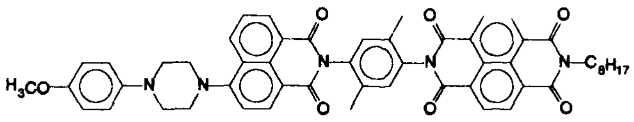
Rapid, reversible photoinduced electron transfer reactions are a class of photophysical phenomena that can be exploited to develop schemes for optical switching. Molecular electronic switches, wires, micro-sensors for chemical analysis, and opto-electronic components for use in optical computing are currently under active investigation. The principal advantages of using molecules in these applications are high component density, increased response speeds, and high energy efficiency. Since photoinduced electron transfer processes within molecules can take place on a picosecond time scale, it should be possible to produce efficient devices that respond very rapidly. Molecules that employ reversible electron transfer reactions for optical switching should possess both speed and photostability advantages over molecular switches based on photochemical changes in molecular structure.

We have designed a new series of electron donor-acceptor molecules, an example of which is **1**, consisting of a 4-aminonaphthalimide (ANI) chromophore attached to aniline (MeOPh) donors and a 1,4,5,8-naphthalenediimide (NPDI) electron acceptor. These molecules are designed to undergo ultrafast charge separation in non-polar media including glassy solids such as polymer films. They are also designed to be photochemically stable.



1: **MeOPHPIP-ANI-DMPH-NPDI-C8**

Excitation of the ANI chromophore with a 200 fs, 420 nm laser pulse from a frequency-doubled, amplified Ti-sapphire laser results in direct excitation of the ANI chromophore to a charge transfer state. This excited state is most likely a TICT state. The polar nature of this excited state polarizes the surrounding medium, which results in rapid (8 ps) electron transfer to yield the MeOPh cation and the ANI anion. The ANI anion then transfers an electron in a secondary, dark reaction (430 ps) to the NPDI acceptor, which yields the MeOPh cation - NPDI anion ion pair that lives for 300 ns before recombining.

After charge separation has occurred in **1**, the ANI chromophore is once again in its ground electronic state, and is flanked by both a good electron donor, $NPDI^{-}$, and by a good electron acceptor, MeOPh$^+$. When the ANI chromophore is re-excited with a second 200fs, 420 nm laser pulse 2 ns after the initial pulse, the charge recombination rate is perturbed by the excited ANI molecule. This perturbation results in collapse of the charge transfer state. These effects can be repeatedly cycled at high repetition rates. The nature of the interaction of excited ANI with the surrounding ions formed by the initial pulse is being probed by a variety of both linear and non-linear optical techniques.

This type of Bistable Electron Transfer Array or BETA switch has been proposed previously by Mehring[1], but has not been realized experimentally until now. Since the changes in electron transfer rates and corresponding optical properties of molecules such as **1** are produced solely by electron transfers, molecular switches based on these effects have no moving parts, and can be made to switch significantly faster than photochromic molecules that must undergo changes in molecular structure.

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VIBRATIONAL STRUCTURE OF THE $S_0 \rightarrow S_2$ ABSORPTION BAND OF CORONENE IN POLYMETHYLMETHACRYLATE, STUDIED BY TRANSIENT SPECTRAL HOLE-BURNING

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The $S_0 \rightarrow S_2$ absorption band of the aromatic hydrocarbon coronene in polymethylmethacrylate (PMMA) was investigated with the method of transient spectral hole-burning (TSHB), which uses the availability of a long-lived metastable triplet state [1]. The vibronic coupling of S_2 with S_1 in coronene belongs to the statistical limit [2]. This is a necessary condition for the determination of the homogeneous widths of $S_0 \rightarrow S_2$ vibronic transitions by spectral hole-burning. The $S_0 \rightarrow S_2$ transition is symmetry-forbidden, and the 0,0-transition is not observed. From the homogeneous widths of resonant holes lifetimes ≤ 2 ps are obtained for the S_2 vibronic states.

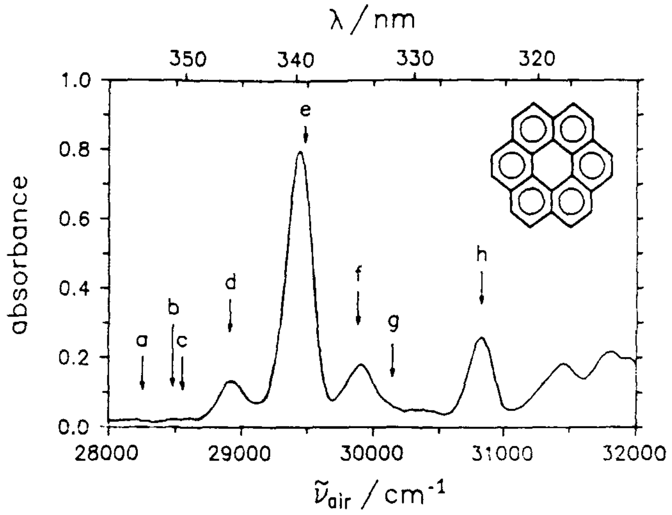

Abbildung 1: $S_0 \rightarrow S_2$ absorption spectrum of coronene in PMMA at 81 K. The arrows labeled by a, b, ..., h indicate the wavenumbers, at which resonant holes were burnt. Holes were burnt at 2K.

By the energy-selective TSHB the same vibronic transitions are observed as in the site-selective fluorescence excitation spectrum of coronene in a heptane Shpol'skii matrix [2]. The lowest e_{2g} mode gives rise to the lowest false origin and additionally forms progressions in combination with other false origins. The degree of polarization of transient zero-phonon holes is close to the theoretical value of 1/7 that is expected for in-plane polarized transitions of a molecule with the symmetry D_{6h}.

With optically thin samples, the lineshape of resonant zero-phonon holes remains Lorentzian in the steady state of TSHB despite nonnegligible ground-state depletion. The correlation of nonresonant holes is approximately Lorentzian.

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Second Harmonic Studies of Liquid Crystal-Langmuirfilms

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In recent years the investigation of the physical, especially optical properties of Langmuir- and Langmuir-Blodgett-Films has become increasingly important. In view of future applications it is of fundamental interest to understand the formation process of these molecular films.

Therefore, we have used the combination of surface balance and optical second harmonic generation (SHG) measurements to study the compression process of 4-n-octyl-4'-cyanobiphenyl films at the air-water interface. To get high quality films and reproducible results great attention was given to the purity of the samples and the environment.

A comparison of the polarization dependence of the generated SHG-light with the current theory shows a good agreement. From the obtained data, the molecular orientation of the chromophores as a function of the surface pressure was calculated.

The results for the two-component mixed films, measured with the same method, are compared with those of the pure films.

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