REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE
7/31/01

3. REPORT TYPE AND DATES COVERED
final 6/1/98 - ~~6/1/01~~ 31 May 01

4. TITLE AND SUBTITLE
Pyridinium-Coupled Porphyrin-Based Molecular Grid Membrane

5. FUNDING NUMBERS
DAAG-55-98-10310

6. AUTHOR(S)
Michl, J.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Colorado, Department of Chemistry
Campus Box 215, Boulder, CO 80309-0215

8. PERFORMING ORGANIZATION REPORT NUMBER
153-4017

RECEIVED
AUG 06 2001
By

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
37675.14-CH

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

ABSTRACT

Several types of molecular connectors have been synthesized and used for the preparation of two kinds of regular two-dimensional molecular grids on liquid surfaces. The connectors are connected into square or hexagonal networks by hydrogen-bonding couplers such as hydroquinones or by mercury cations. The electrochemistry, spectroscopy, and scanning tunneling imaging of the structures have been investigated, and in some cases extensive long-range order was observed. In addition, the relation between the conformation of saturated linear silicon chains and their electronic states have been investigated by methods based on photophysics, spectroscopy, and quantum theory.

14. SUBJECT TERMS

20010831 032

15. NUMBER OF PAGES
7

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Page)

1. List of Manuscripts Submitted or Published

Magnera, T. F.; Michl, J. “Towards a More Regular Square Grid Polymer”, *Atualidades de Físico-Química Orgânica,* **1998**, 50.

Brotin, T.; Pospíšil, L.; Fiedler, J.; King, B. T.; Michl, J. “Towards a Square Grid Polymer: Electrochemistry of Tentacled Tetragonal Star Connectors, C_4R_4-Co-$C_5(HgY)_5$, on Mercury”, *J. Phys. Chem. B*, **1998**, *102*, 10062.

Albinsson, B.; Antic, D.; Neumann, F.; Michl, J. “The Conformers of *n*-Si_5Me_{12}: A Comparison of Ab Initio and Molecular Mechanics Methods”, *J. Phys. Chem. A* **1999**, *103*, 2184.

Raymond, M. K.; Michl, J. "Quantum Confinement Induced Collapse of a Large to a Small Radius Self-Trapped Exciton in a Permethylated Polysilane Chain", *Int. J. Quant. Chem.*, **1999**, *72*, 361.

Crespo, R.; Teramae, H.; Antic, D.; Michl, J. "Calculation of the Conformational Dependence of Valence and Rydberg States in *n*-Tetrasilane," *Chem. Phys.*, **1999**, *244*, 203.

Fogarty, H. A.; Ottosson, C. H.; Michl, J. “Conformations of Oligosilanes with Ethyl and Methyl Substituents”, *J. Mol. Struct.*, **2000**, *556*, 105.

Zink, R.; Magnera, T. F.; Michl, J. “The Transoid, Ortho and Gauche Conformers of *n*-Si_4Cl_{10}: Mid-IR and Raman Matrix-Isolation Spectra”, *J. Phys. Chem. A*, **2000**, *104*, 3829.

Fogarty, H. A.; Ottosson, C. H.; Michl, J. “The Five Favored Backbone Conformations of *n*-Si_4Et_{10}: Cisoid, Gauche, Ortho, Deviant, and Transoid”, *J. Mol. Struct.* (*Theochem*) **2000**, *506*, 243.

Ottosson, C. H.; Michl, J. “Conformers of *n*-Si_6Me_{14}: Ab Initio, Molecular Mechanics, and Additive Increment Methods”, *J. Phys. Chem. A*, **2000,** *15*, 3367.

Michl, J.; West, R. “Electronic Structure and Spectroscopy of Polysilanes”, in *Silicon-Containing Polymers: The Science and Technology of their Synthesis and Applications*, Jones, R. G.; Ando, W.; Chojnowski, J., Eds., Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000, p 499.

Crespo, R.; Merchán, M.; Michl, J. “Electronic Excitation in a Saturated Chain: An MS-CASPT2 Treatment of the Anti Conformer of *n*-Tetrasilane”, *J. Phys. Chem.* **2000**, *104*, 8593.

Michl, J.; West, R. “Conformations of Linear Chains. Systematics and Suggestions for Nomenclature”, *Acc. Chem. Res.* **2000**, *33*, 821.

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Page)

Peter Schwab, "Toward a Hexagonal Grid Polymer," Ph. D. dissertation, University of Colorado, Boulder, 2000.

Tsuji, H.; Toshimitsu, A.; Tamao, K.; Michl, J. "UV, MCD, and LD Spectra of a Conformationally Constrained *ortho*-Tetrasilane: Support for the Avoided Crossing Model of Conformational Effects on Excited States", *J. Phys. Chem.*, in press.

Schwab, P. F. H.; Fleischer, F.; Michl, J. "Preparation of 5- and 5,5'-Brominated 2,2'-Bipyridines and 2,2'-Bipyrimidines", submitted for publication.

Piqueras, M.; Crespo, R.; Michl, J., "Multiconfigurational Second-order Perturbation Calculation of the Electronic Absorption Spectrum of Trisilane, Si_3H_8", submitted for publication.

2. Scientific Personnel Supported by This Project, Awards, Honors, and Degrees

A. John Downing (senior research associate)
B. Raul Crespo (visitor)
C. Natalia Varaksa (post-doctoral)
D. Gregg Kottas (graduate student)
E. Heather Fogarty (graduate student); was awarded a Marion L. Sharrah Grad. Fellowship for the academic year 1999, presented a poster at the 32nd Organosilicon Symposium, March, 1999 in Milwaukee, WI; and attended the Fifth Annual Rocky Mt. Symposium on Photons and Chemistry, November, 1999. She presented posters at 220th American Chemical Society National Meeting, Washington DC, August 2000 and at the 33rd Organosilicon Symposium, Saginaw MI, April 2000. In May 2001, she placed second in the Graduate Student Research and Creative Work Award and won the Chemistry Department's Ekeley Award at the University of Colorado. She presented her work at the Inter-American Photochemistry Society meeting in Ascochinga, Cordoba, Argentina in May, 2001.
F. Peter Schwab, as a graduate student was awarded Quadrille Ball Scholarship from the Institute of International Education in 1998 and an Enrollment Enhancement Fellowship in 1999. He presented a paper at the European Research conference at San Feliu de Guixols, Spain, on September 23, 1999. He earned a Ph. D. in 2000, and won the Marie Curie Fellowship awarded by the European Commission in 2001.
G. Thorsten Schepers (graduate student)
H. David Lee (undergraduate)
I. Erin McElory (undergraduate)
J. Joanna Brown (undergraduate)

3. Inventions

None

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Page)

4. Scientific Progress and Accomplishments

The project involved two unrelated parts; the synthesis of two-dimensional grids and the investigation of the elementary units of polysilanes.

1. Grids. The work on molecular grids was performed by graduate students, Mr. (now Dr.) P. Schwab and Mr. G. Kottas, assisted by undergraduate research assistants, Ms. E. McElroy, Mr. D. Lee, and Ms. J. Brown, and a postdoctoral fellow, Ms. N. Varaksa, with part-time guidance from a senior research associate, Dr. T. Magnera. We were fortunate to secure the collaboration of an experienced electrochemist from Prague, Czech Republic, Dr. L. Pospíšil. The work fell into two categories. The first involved organic chemistry, namely the synthesis of rods and connectors, and was done by the two graduate students. The second involved physical chemistry, namely the electrochemical characterization of the elementary modules and their assembly in two dimensions, and was done by the Czech collaborator and the postdoctoral fellow, respectively. The results of the organic work have been published in a dissertation and a paper, with two more papers under preparation. The results of the more physical work have been published in two papers, with two more nearly ready for submittal and several more under preparation.

The synthetic work concentrated on the preparation of constituents of two types of grid, square (G. Kottas) and hexagonal (P. Schwab). The former type of module is based on cross-shaped tetraaryl derivatives of a cyclobutadienecobaltcyclopentadienyl complex, with the para positions of the four aryls available for coupling (e.g., pyridyls), and the five positions on the cyclopentadienyl ring available for attachment of "tentacles" carrying groups that adhere well to a surface. We have chosen mercury as the surface of choice and used thioether or pyridine groups for adhesion. Currently the best procedure for introducing substituents into the five-membered ring is mercuration. Several suitable square connectors of this type were synthesized for use in the physicochemical part of the project.

The modules for the hexagonal grid are trigonal in shape and several of these were also synthesized, based on 1,3,5-trisubstituted benzenes. Two of these had 10-vertex or 12-vertex *p*-carboranes as the three substituents, and coupling is to take place at the acidic CH groups in the *p* positions. Several others had longer rods as the three substituents, with nitrogen heterocycles at the end. For instance, a pyridine termination offers the possibility of either metal ion coupling or coupling through quaternization. In the process, new synthetic routes were developed to several basic building blocks of molecular rods (5- and 5,5'- brominated bipyridines and bipyrimidines), and these will be of general utility. An attempt to synthesize a macrocycle containing a single element of a hexagonal grid, as a model of the final grid structure, is very close to completion.

Attempts to attach metal atoms to the face of the central benzene rings of either type of these trigonal connectors, with formation of sandwich complexes, whose second deck could then carry thioether-containing tentacles as described above for the square modules, have however not been successful so far. An alternative utilization for use in the construction of molecular grids was sought in that flexible thioether-containing tentacles were attached directly to the carborane CH carbon atoms, and physical measurements performed with these gave very instructive results.

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Page)

The physico-chemical studies required considerable instrumental development; they rely heavily on the use of the STM/AFM and polarization modulation FTIR units purchased from a DURIP grant, and on a home-built electrochemical Langmuir-Blodgett trough working with mercury, which we believe to be unique in the world. These studies were of two main kinds. In one research direction, we examined the self-assembly of grids composed of two types of molecules, a connector and a linker, on a liquid surface under reversible conditions, and looked for conditions that would produce highly regular large domains with a minimum of defects. Reversibility of the assembly was assured by the use of weak interactions (hydrogen bonds) between the connectors and the linkers ("phantom couplers"). Here, the long-term plan is to convert the self-assembled weakly knit networks into sturdy covalent grids suitable for practical use by gradual exchange of covalently bound real couplers for the phantom ones. In a second research direction, we examined the electrochemistry of tentacled modules on mercury and the formation of surface networks that result from their interaction with mercury ions. Little is known about such grids and quite a few fundamental scientific issues remain to be investigated. In this case, the long-term plan again is to use these regular metal-bound networks as templates for the covalent coupling of modules into sturdy grids.

The assembly of a grid with phantom couplers used tetrapyridylporphyrin as the connector and hydroquinone as the coupler. This works very well both on water and on mercury surfaces, and STM images show large defect-free domains of highly regular grids. Trimethylhydroquinone works equally well, and LB isotherms agree nicely with the expected area changes upon grid formation. A continuation of this direction, with exchange of covalently attached *p*-xylylene units for the hydrogen-bonded hydroquinone, is planned.

The assembly of metal-ion-bound networks on mercury was initially discovered accidentally. These potentially very useful networks have now been investigated by a combination of electrochemical measurements and measurements on an LB trough. We have reached the conclusion that physisorption of the thioether tentacled modules on mercury surface is insufficient for our two-dimensional grid-building purposes, in that reduction of the mercury surface area by compression causes them to desorb into the supernatant solvent. Under these conditions, an attempt at coupling by addition of a linker to the solvent would lead to at least some coupling in solution and therefore in three dimensions, causing problems with the formation of a purely two-dimensional grid. Only in the range of mercury surface (electrode) potentials in which a compact chemisorbed film forms is the adsorption of our modules complete. This is not a problem in itself since we can choose such potentials when attempting to form the grids.

However, we now came to realize that if each tentacle carries only one functionality, these compact films form only when thioether or pyridine functionalities in neighboring modules bind to each other through mercury ions, and the range of compact film stability is restricted by the reduction of these mercury ions at potentials that are too negative. The resulting network seems to be highly regular and the distances between neighbors are dictated by the length and conformation of the tentacles. This means that in effect the mercury ions are acting as phantom couplers, and that we may not need to artificially add the latter, e.g., hydroquinone, before adding the real coupler, in order to achieve our goal of a simultaneously regular and sturdy two-dimensional grid. It now appears that it will be possible to effect an annealing of the structure of the network by cycling between the reduced and oxidized form of the mercury ions. The use of mercury cations thus promises to be a great advantage in all respects, and we are pursuing this possibility vigorously. Of course, it will impose a constraint on the length and nature of the tentacles that we can use, as they must be compatible with the length and nature of the arms of the modules that we are trying to couple. This is not a serious constraint, because of the ease with which the synthesis of various types of tentacles can be achieved.

We have also examined cases in which each tentacle carries two thioether functionalities. These modules adhere to mercury at all potentials, also when any initially present mercury ions have been reduced, but in that case exhibit a much smaller surface area per molecule. This observation raises interesting possibilities for practical utilization of the associated very large conformational changes as a function of electrode potential and we plan to examine the situation further.

2. Silicon Polymers. This part of the project benefitted from the efforts of a postdoc who came from Sweden with his own funding, Dr. Carl-Henrik Ottosson, and another who came from Austria with his own funding, Dr. R. Zink, of a Japanese graduate student, Mr. (now Dr.) Hayato Tsuji, who was half-supported from Japan in a collaborative effort with Prof. K. Tamao of the University of Kyoto, a German student, T. Schepers, who was partially supported from Germany, and from collaboration with a group of Spanish theoretical chemists at Valencia, Spain, led by Prof. Raul Crespo. Their activities complemented nicely the work of my graduate student, Ms. Heather Fogarty, who was engaged primarily in experiments and expects to submit her Ph.D. dissertation in about half a year, and a senior research associate, Dr. John Downing, who spent a fraction of his time working on computer code and program development for this project.

The results have been mostly published (12 full papers) and summarized (a book chapter and a brief review article, both written jointly with Prof. R. West of the University of Wisconsin, Madison), but about half a dozen articles remain unpublished, in various stages of preparation.

The primary objective of this work was the development of an understanding of the conformational behavior and electronic structure of peralkylated saturated silicon chains, and most of all, of the relation between the two. We believe that an understanding of short model chains, with anywhere from two up to sixteen concatenated silicon atoms, is essential for the ultimate understanding of high molecular weight polymers.

The unusually rich conformational behavior of the silicon chains carrying methyl or longer alkyl substituents, responsible for their striking thermochromism, solvatochromism, and ionochromism, is now understood in terms of elementary van der Waals repulsive interactions among the substituents. In particular, the existence of the uncommon "ortho" and the even more exotic "deviant" (corresponding to the 7/3 helix observed in certain polysilanes) and "cisoid" (so far, only an unverified prediction) conformations follows logically from first principles. Matrix isolation Raman spectroscopy combined with annealing procedures was used to detect the existence of all three conformers predicted for a tetrasilane, including the novel "ortho" structure. We have calculated the structures of all the several dozen conformers of permethylated chains containing up

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Page)

to six silicon atoms and worked out an increment system that permits the prediction of relative energies of various conformers of longer chains by extremely simple means. Although solvent effects still remain to be incorporated, these result have already proven to be very valuable for the interpretation of spectral data obtained on conformer mixtures, particularly electronic absorption and emission spectra.

Electronic structure of the all-transoid chains, whose absorption and emission spectra are available, is the easiest to understand. Here, we have addressed the issue of separation of valence and Rydberg states, and after considerable effort settled an existing controversy and established beyond doubt that the first several singlet excitations are of valence nature even in chains as short as trisilane. We have detected both the σ to π^* and the previously unobserved σ to σ^* singlet excitation in the basic disilane unit.

We have further shown how the length of the chain dictates the size of the vibrationally relaxed singlet excimer through quantum confinement effects: the excited state is fully delocalized only in medium-length chains. It was not surprising to find that the excitation is localized in a fraction of a chain of excessive length, but the high degree of excitation localization observed in chains that are not long enough initially came as a surprise ("small-radius self-trapped exciton") until we realized that it is in perfect agreement with expectations based on classical exciton theory of solid state physics. In permethylated oligosilanes, the six-silicon chain is the longest that always supports a localized excitation. The seven-silicon chain is on the borderline in that some conformers support a localized and some a delocalized excitation. This localization of excitation on a single SiSi bond leads to bond-stretch isomerism in the excited states of the shorter oligosilanes, manifested by multiple fluorescence. In an attempt to characterize the exact location of excitation in the various species, a deuterium labeled sample was synthesized and photolyzed at temperatures characterized by emission from one or another of the excited bond-stretch isomers, while trapping the dimethylsilylene extruded from the oligosilane chain photochemically in the hope that its label will pinpoint the chain segment that carried the excitation. However, it was discovered that the photochemical process was ultrafast and always gave the same isotopic result; clearly, it did not compete with fluorescence. Although the original goal therefore could not be attained, this observation is of considerable interest for photochemistry in its own right.

Another important issue in electronic structure was the detection of additional singlet excited states using less usual forms of spectroscopy, magnetic circular dichroism, linear dichroism, and two-photon excitation spectroscopy, and their theoretical interpretation.

However, most effort concentrated on the development of an understanding of the effect of conformational change on ionized and electronically excited states. We have chosen tetrasilanes as the simplest chromophores in which a backbone SiSiSiSi dihedral angle can be defined and synthesized a whole series of conformationally constrained peralkylated molecules in which this dihedral angle varied from 0 to 180 °. This effort has paid off handsomely, and more recently we also synthesized longer conformationally constrained oligosilane chains, up to octasilane.

The effects of dihedral angle changes on ionization potentials of tetrasilanes are clearly noticeable and follow expectations based on simple MO theory and Koopmans' theorem; indeed, we found a Hückel-type scheme that permits an easy prediction of ionization potentials for any conformation and any chain length. This is a parameterization of the "ladder C" model that

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Page)

recognizes explicitly not only the presence of primary bonding interactions and geminal interactions between sp^3 hybrid orbitals on silicon atoms, but also the presence of dihedral angle dependent vicinal interactions.

The effects of dihedral angle changes on electronic spectra of tetrasilanes were even more dramatic. They did not show the expected decrease in excitation energies as the dihedral angle grew from 0 to 180 ° and the excitation energies of the various transitions remained roughly constant. However, the band intensities changed entirely, such that the spectra of species differing strongly in the dihedral angle looked completely different. The behavior suggested the presence of an avoided crossing between two low-lying B symmetry states, one strongly allowed (σ to σ^*) and one nearly forbidden (σ to π^*). This interpretation is supported by analysis of correlation diagrams and by calculations at all levels of ab initio theory that we were able to employ, except that the best calculations also suggest the presence of yet another valence state of B symmetry, so far undetected. These measurements however permitted us to detect one new transition, assigned to an excited state of A symmetry. The best calculations suggest the presence of two additional A states, so far unobserved.

In spite of these remaining issues to be addressed in the case of the tetrasilane chromophore, we believe that the stage is now set for an examination of conformational dependence in longer silicon chains, with the understanding of the spectra of the high polymers themselves as the ultimate objective.