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TWO-DIMENSIONAL SYNTHESIS: ULTRATHIN POROUS MEMBRANES

FINAL REPORT

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Executive Summary. The proposed proof of concept has been accomplished. We have synthesized an ultrathin (7 Å) covalent molecular grid of the proposed type, composed of 2.5 nm × 2.5 nm squares with 1.5 nm × 1.5 nm square openings, we have demonstrated that it is sturdy (boiling with alcoholic HCl and surface-to-surface transfer), and we have obtained its spectral and STM characterization. The synthesis was based on the originally proposed two-dimensional linear cross-coupling of oriented molecular connectors mounted on pedestals that were constrained to a two-dimensional liquid mercury surface, but the molecules actually used in the successful experiment were different from those intended originally.

In this first attempt, only small sheets of the grid were made (up to 0.15 μ × 0.15 μ), and they did not have long-range order. Both of these problems were undoubtedly caused by the use of an irreversible coupling reaction in the polymerization process, and by the use of a coupler that was not strictly linear and thus permitted easy formation of defects (pentagons instead of squares, etc.). Neither of these limitations are inherent, and we have already submitted research proposals in which we outline how we propose to do the polymerization in a reversible way, yet produce a sturdy polymeric grid, and suggest chemical structures for linear couplers. Patent protection for these results has been applied for by the University of Colorado (following up on a previous conceptual patent already granted¹) and several publications have been written.^{2,3,4,5,6,7,8,9,10} Additional publications are in preparation.

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Detailed Results. About a third of our effort went into the development of infrastructure for the project, which represents an unusually interdisciplinary synthetic effort, which required much organic synthesis combined with the use of surface science techniques. The remainder went into the actual synthesis.

1. *Development of Infrastructure.* Although this is not especially glorious, it represented much effort and deserves to be mentioned in passing. We set up all the instrumentation needed for performing and monitoring surface-constrained synthesis (LB trough for mercury, grazing incidence IR and Raman, electrochemistry, LEED, UPS, and ellipsometry) in our laboratory, and learned how to use the departmental STM instrument. We have also written a molecular dynamics simulation program that permits the simultaneous tracking of the motion of up to 7 000 atoms of any elements in the periodic system in a time dependent electric field imposed from the outside, and have used it to model the passage of small gas atoms through a grid of the type that we have synthesized.

2. *Monomeric Module Synthesis.* We worked on the synthesis of three families of organometallic species of the metal sandwich complex type, to be used as monomeric modules, and prepared a large number of new compounds. The upper deck carries rigid radial arms suitable for linear coupling into a grid, while the bottom deck carries tentacles introduced to assure perfect adhesion to mercury surface, and thus serves as a pedestal that not only prevents escape of the monomeric module into the supernatant solution, but also holds it rigidly in an orientation appropriate for the surface coupling process, with the rigid arms parallel to the surface, and at a constant distance from it.

The structural type that led to success first was based on a *meso*-tetrapyridylporphyrin complex of lanthanum. Here, the four pyridines of the upper deck serve as rigid coupling arms and the four pyridines of the lower deck as sticky tentacles.

Work on the others was interrupted for the moment in order to concentrate on the successful breakthrough, but we believe that they would eventually lead to the goal, too. They were (i) a sandwich complex of cobalt with a cyclopentadienyl and a cyclobutadiene ring, with five sticky tentacles attached to the five-membered ring and four rigid arms on the cyclobutadiene ring, and (ii) a sandwich complex of 1,3,5-tris-*p*-carboranylbenzene, with the carboranes of the upper deck serving as rigid arms for the coupling reaction and those of the bottom deck carrying the sticky tentacles for adsorption to mercury. Sandwich complexes of type (i) have been actually successfully synthesized and close to being tested, whereas the synthesis of sandwich complexes of type (ii) ran into difficulties when the individually prepared decks, both with 12-vertex and with 10-vertex *p*-carboranes, would not combine with the requisite metal atom. Here, we now believe that it will be necessary to use extenders for the rigid arms (such as bicyclo[1.1.1]pentane) to make them less bulky and sterically demanding before the sandwich can be successfully formed.

3. *Grid Synthesis.* Before attempting the surface-confined synthesis, we examined the adhesion of the tentacled modules to metal surfaces. We started with gold since it is easier to work with, but rapidly realized that the properties of mercury are sufficiently different that gold cannot be used as a model surface. Using grazing incidence IR and Raman spectroscopy, we found that both the lanthanum and the cobalt complexes described above adsorb to a mercury surface from organic solutions extraordinarily strongly under open circuit conditions when 4-pyridyl or 4-carboxyphenyl substituents are used as tentacles. The triscarboranylbenzenes also adsorb very well when provided with thioether-containing tentacles, but only at positive electrode potentials.

We now believe that these adsorption phenomena are most likely mediated by the formation of a mercury-ion coupled net on the mercury surface and have reasonable electrochemical evidence for this belief in the one case that we examined in some detail. This is of fundamental interest and should be examined further.

Next, we worked on coupling reactions of the rigid arms. While pyridines are coupled easily via quaternization reactions, it is not simple to do this in a strictly linear fashion, and at first, we satisfied ourselves with an only approximately linear coupler, *p*-xylylene dibromide. This actually ultimately led to the desired goal. However, we have also worked out a strictly linear and surprisingly sturdy coupling procedure through a mercury

atom for the *p*-carboranyl arms, which uses reversible conditions and is likely to lead to superior results ultimately. We have also obtained good indications by Raman spectroscopy that the pyridine arms can be coupled in the desired fashion with transition metals.

The successful surface-confined polymerization of the lanthanum porphyrin sandwich compound was followed by IR spectroscopy. This, however, only proves local structure, and it was necessary to use an additional tool for determining the long-range structure of the product. We chose imaging by STM. Since it is not possible to obtain STM images on liquid mercury, we had to develop a technique for the transfer of the spectroscopically characterized product to a more suitable surface. We selected highly ordered pyrolytic graphite (HOPG), found a way to transfer the product largely intact, and imaging with STM indeed showed that it is the desired grid.

Specifics of the Successful Grid Synthesis. The first successful surface-constrained synthesis of a sheet of a strictly two dimensional polymer was done with a symmetrical module in which the upper and the lower decks were chemically identical (*meso*-tetrapyridylporphyrin), and they were joined by a lanthanum ion (the "pillar") into a sandwich complex, the lanthanum(III)bis[5,10,15,20-tetrakis(4-pyridyl)porphyrinate] anion (**1**). This particular porphyrin sandwich complex was not known before, but many similar complexes were. The synthesis of **1** was modeled on known chemistry: the porphyrin reacts rapidly with lanthanum acetylacetone to yield an open-face sandwich that still carries an acetylacetone group, and then more slowly with a further portion of lanthanum acetylacetone to give the desired symmetrical sandwich.

The four pyridine groups of the top deck of **1** served as the arms of a cross, while those of the bottom deck served the role of the tentacles that have high affinity for the surface of copper-containing mercury amalgam, and permit the lower deck to play the role of a pedestal. The tentacles cause strong adsorption and orient the pedestal-mounted connector with the pyridine arms up and parallel to the mercury surface (this was proven by consideration of polarization effects in grazing incidence IR). In separate experiments, the surface-confined sandwich **1** was treated with two different linking agents (*p*-xylylene dibromide and nickel(II) chloride), and in both cases the coupling reactions expected to lead to 2-D polymerization occurred, as judged by IR and Raman spectra.

The grid obtained with *p*-xylylene dibromide withstood 30 min boiling in 3% HCl in ethanol. Fig. 1 shows the grazing incidence FTIR spectra of **1** on a mercury surface before and after an irreversible coupling reaction with *p*-xylylene dibromide. It exhibits all the spectral changes expected from a previous study of the coupling of 5,10,15,20-tetra(4-pyridyl)porphyrin with *p*-xylylene linkers, performed by others in a different topology during their study of covalent multilayers of porphyrin stacked on a quartz surface.

The bis(*meso*-tetrapyridylporphyrinato)lanthanum sandwich ion **1** exhibits a strong tendency to self-assemble into a square planar array when given an opportunity. Fig. 2 shows an STM image of such an array crystallized on the surface of HOPG from an acidic solution. The size of the squares suggests that the pyridine arms of neighboring connectors are linked by hydrogen bonds. The high degree of order is undoubtedly due to the reversibility of the self-assembly process. Although this grid is too fragile to be of any immediate use to us, this tendency towards self-assembly is a good omen for future efforts to synthesize a sturdy and regular grid under reversible conditions.

The long-range structure of the sturdy but unannealed grid produced by the irreversible coupling of the lanthanum sandwich **1** with *p*-xylylene dibromide was examined by STM after removing HgO impurities by boiling with HCl in ethanol and transfer to HOPG. The transfer was effected by evaporating a thin layer of polystyrene from a THF solution onto the mercury surface, peeling the dried polymer layer off, placing it on the surface of HOPG, softening it with acetone, and carefully dissolving it in THF. Grazing incidence IR spectrum showed that none of the grid was left on the mercury surface, i.e., 100% was transferred, but only 5 - 50% was kept on the HOPG, the rest being apparently flushed with the solvent. The spectral features of the transferred grid were very weak, but they occurred reproducibly in the same places where they were located before transfer,

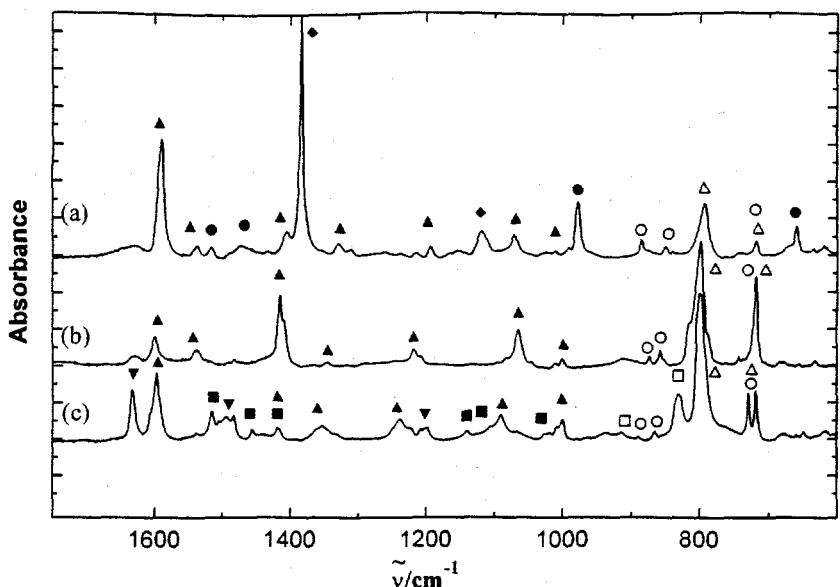


Figure 1 Reflectance FTIR monitoring of the coupling reaction of bis(*meso*-tetrapyridylporphyrinato)lanthanum with xylylene dibromide on Hg surface. Important in-plane (black) and out-of-plane (white) vibrations of porphyrin (●,○), pyridine (▲,△), pyridinium (■,□), and *p*-xylylene (▼,▽) rings are labeled

and we are confident that they were real. With polystyrene, the spectrum shows no polymer residue, but the weak IR intensity shows that only about 10% of the grid has been transferred successfully. With other polymers, we have observed transfers of up to 50%, but insoluble contaminants were present. Not surprisingly, uncoupled **1** was not transferred from mercury surface to the graphite surface by this procedure at all, even when the acid treatment step was omitted.

As shown by the STM image in Fig. 3, the irreversibly formed grid contains squares of exactly the expected size (~2.5 nm), but is much less regular than the reversibly assembled grid of Fig. 2. A diagonally disposed roughly square 50 × 50 nm domain in the center is fairly typical of numerous other regions of the sample. Considering the irreversible nature of the coupling reaction, and the rough transfer technique, the domain is surprisingly well ordered. It contains a few holes in which the partitions between two or even three adjacent squares are missing, and some quite long ordered rows of squares. As noted above, it is conceivable that the metal ions present (mercury or copper) have provided unanticipated help by preordering the monomer into a self-assembled grid on the mercury surface as discussed above, in effect acting as "phantom" couplers and aiding the regularity of the irreversible grid-forming process.

Even considerably larger partially ordered domains have been observed, up to 150 × 150 nm in size. A segment of a large domain is shown to the upper right of the diagonal in Fig. 4. Again, the presence of several holes is apparent. The left side of Fig. 4 appears to contain a portion of the grid that was presumably crumpled during the transfer. Overall, it is very reassuring that even a single-layer grid can apparently be transferred with only minor damage. We were concerned before that it might be impossible to handle a polymer grid this thin.

These results suggest very strongly that it will be possible to obtain large domains of regular two-dimensional grids by using a reversible yet sturdy mode of monomer coupling. It is possible that even the already available irreversibly formed irregular grid would have interesting separation properties when deposited on a perforated membrane.

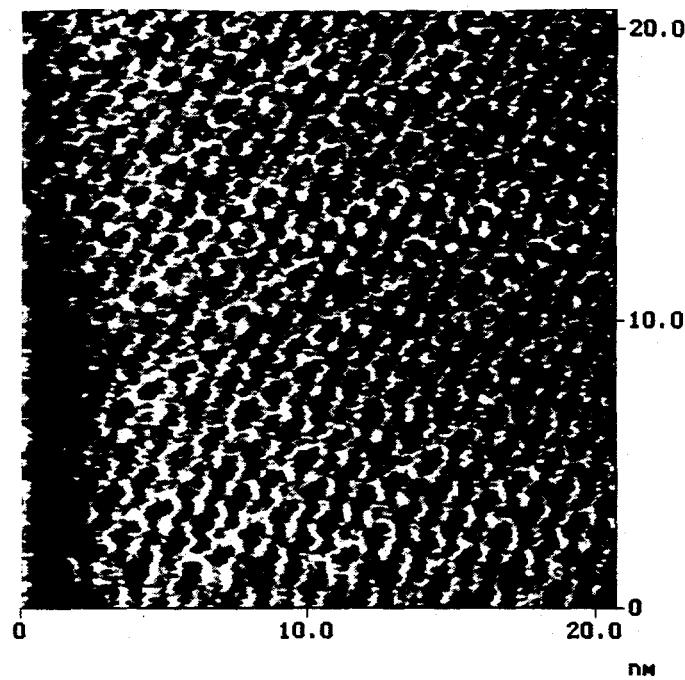


Figure 2 STM image of a square grid of **1** self-assembled on HOPG from an acidic solution, obtained with a Pt/Ir tip in the constant current mode (bias: 539 mV, current 317 pA)

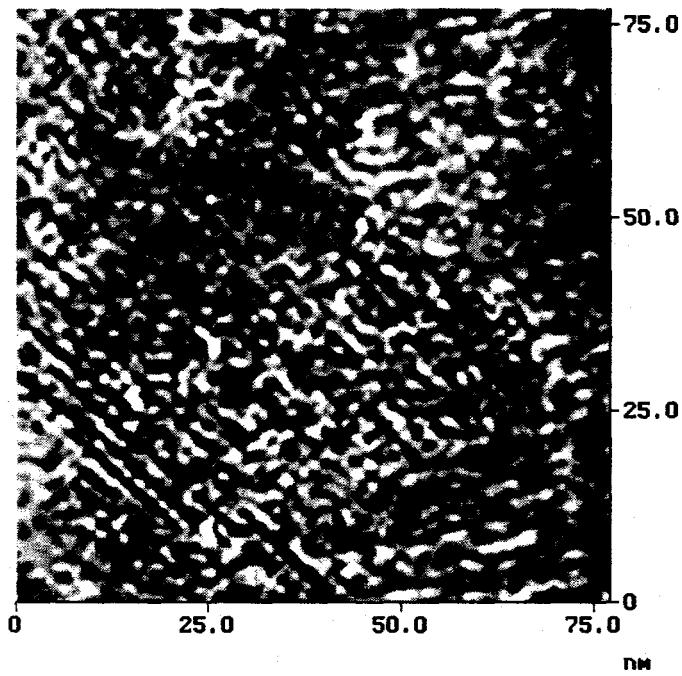


Figure 3 STM image of square grid formed from **1** and *p*-xylylene dibromide on mercury surface after transfer to HOPG. Pt/Ir tip, constant current mode (bias: -325 mV, current 131 pA).

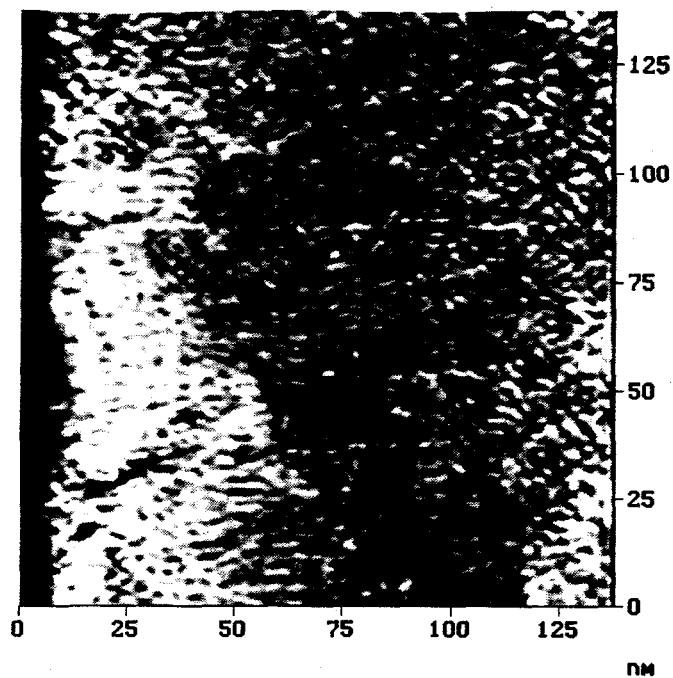


Figure 4 STM image of square grid from **1** and *p*-xylylene dibromide on mercury surface after transfer to HOPG. Pt/Ir tip, constant current mode (bias: -325 mV, current 131 pA).

C. List of all Publications and Technical Reports

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2. Magnera, T.F.; Pecka, J.; Vacek, J.; Michl, J., Accounts of Chemical Research, Moskovits, M. and Shalaev, V. Eds., American Chemical Society, in press.
3. Michl, J., "[n]Staffanes: Inert Rods for a Molecular Construction Set," *1995 McGraw Hill Yearbook of Science and Technology*, McGraw Hill, New York, p. 391.
4. Michl, J., in Applications of Organometallic Chemistry in the Preparation and Processing of Advanced Materials, Harrod, J.F. and Laine, R.M., eds., Kluwer, Dordrecht, The Netherlands, 1995, p. 243.
5. Harrison, R.M.; Magnera, T.F.; Vacek, J.; Michl, J., "Towards Designer Solids," in Modular Chemistry, Michl, J., ed., Kluwer, Dordrecht, The Netherlands, in press.
6. Schöberl, U.; Magnera, T.F.; Harrison, R.; Fleischer, F.; Pflug, J.L.; Schwab, P.F.H.; Meng, X.; Lipiak, D.; Noll, B.C.; Allured, V.S.; Rudalevige, T.; Lee, S.; Michl, J., "Towards a Hexagonal Grid Polymer: Synthesis, Coupling, and Chemically Reversible Surface-Pinning of the Star Connectors, $1,3,5-\text{C}_6\text{H}_3\text{CX}_3$," *J. Am Chem. Soc.*, 1997, 119, 3907.
7. Magnera, T.F.; Peslherbe, L.M.; Körblová, E.; Michl, J., "The Organometallic 'Molecular Tinkertoy' Approach to Planar Grid Polymers," *J. Organometallics*, in press.
8. Harrison, R.M.; Brotin, T.; Noll, B.C.; Michl, J., "Towards a Square Grid Polymer: Synthesis and Structure of Pedestal-Mounted Tetragonal Star Connectors, $\text{C}_4\text{R}_4\text{-Co-C}_5\text{Y}_5$," *Organometallics*, in press.
9. Vacek, J.; Michl, J., "A Molecular 'Tinkertoy' Construction Kit: Computer Simulation of Molecular Propellers," submitted for publication.
10. Pospisil, L.; Heyrovsky, M.; Pecka, J.; Michl, J., "Towards a Hexagonal Grid Polymer: Interaction of Tentacled 1,3,5-Tricarboranylbenzene Derivatives with Mercury Surface," submitted for publication.

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Sub: DOE Final Report, PI Josef Michl

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