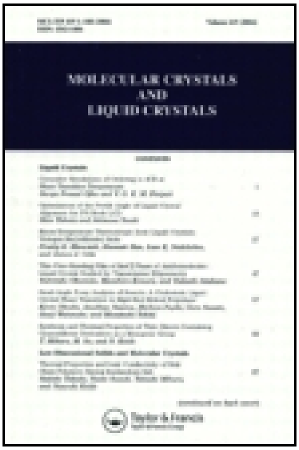

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Control of Supramolecular Architecture in LB Films: Tiling the Plane With Macrorings and Interlocking the Modules

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CONTROL OF SUPRAMOLECULAR ARCHITECTURE IN LB FILMS : TILING THE PLANE WITH MACRORINGS AND INTERLOCKING THE MODULES

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Abstract A strategy to control a solid state supramolecular architecture is reported and illustrated by the elaboration of a two dimensional polymer of molecular thickness.

INTRODUCTION

In the field of organic conductors (mixed valence complexes or polymers) the defects at the molecular organisation level have shown to be of tremendous importance. Improving the quality of these new materials comes up against the fragile 1-D conductivity. As Heeger[1] mentioned, infinite aligned 1-D conductors represent the theoretical approach. From a practical point of view, this sensitivity to defects can be of great use for gas sensing devices : physisorbed or chemisorbed molecules create perturbations in the supramolecular conducting assembly related to the variations of the electronic conductivity [2] . This mechanism involves both the sensing and transducing functions. But increasing the performance in strength and conductivity for new materials is a challenge which has been already reached for $(CH)_x$ by Shirakawa[3,4] , the Durham team[5,6] and Heeger's group [7,8] . For polythiophene, highly purified oligomers proved to have better performance than the long disordered chains . Organizing the polymer chains at the molecular level so as to obtain supramolecular ordered materials is now extensively developed by many groups : epitaxy on surfaces, template synthesis on ordered liquid crystals, insertion in rigid frameworks such as zeolite channels or layered inorganic matrices.

Another strategy is to get rid of the 1-D conductivity by synthesizing a 2-D conducting polymer. The mechanical strength and the electronic conductivity are connected because one origin of their fragility is the same : deviations from the theoretical infinite aligned chain ; fracture on elongation occurs mainly at chain ends, as well as electron delocalization stops. In a rigid orthogonal network, a defect represented as a chain end can be by-passed in another direction during the charge transport.

For the time being, the Langmuir Blodgett technique conjugated with solid-state chemistry is the only tool which provides a control on solid state supramolecular architecture. Here we describe an attempt to elaborate a rigid planar network controlled at the molecular level.

DESCRIPTION OF THE STRATEGY

According to the symbols of Figure 1, the paving stones" and the "joints" have to be translated into chemical language. The module units must possess a fourfold symmetry, a planar configuration and be ordered flat on a substrate. The joints, as well as the chemical be ordered flat on a substrate. The joins, as well as the chemical reactions, have to be tailored to undergo the interlocking of the modules. To control the overall architecture a precise molecular engineering is needed. The following requirements are to be

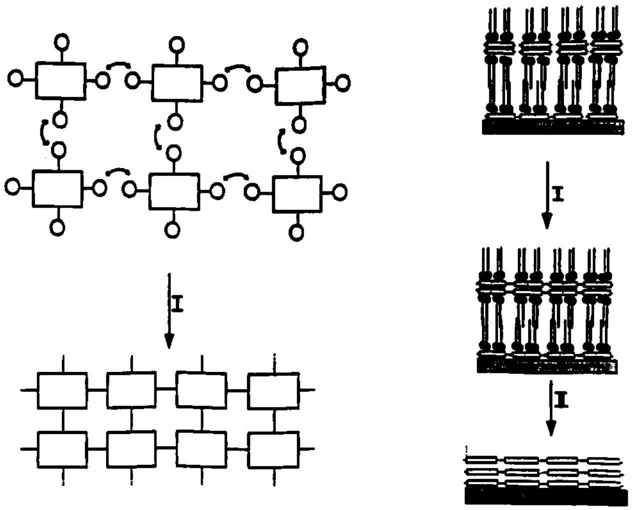

FIGURE 1 Control for planar molecular network

fulfilled for the modules and for the interlocking :

for the modules

1. to be amphiphilic or semi-amphiphilic to allow the Langmuir Blodgett technique
2. to be planar i.e. highly conjugated to fit with electron delocalization
3. to lie flat at the air-water interface taken as the 2-D template
4. to possess a symmetry so that four orthogonally oriented chemical groups can be grafted ; these groups must be conjugated to the module unit.

for the interlocking

5. the coupling reaction must occur under mild conditions: at room temperature and in aqueous media, to preserve the pristine ordering of the modules;
6. the orbital overlaps between the modules and the interlocking joints must be preserved after the coupling to ensure the overall localization of electrons;
7. the final polymer must undergo redox reactions able to confer the mixed valence state;
8. the aliphatic chain matrix, necessary for building the film at the first stage must be released, also under mild conditions.

Assuming these requirements are fulfilled, one might expect a fully conjugated planar molecular network.

MOLECULAR ENGINEERING

Module units

Many "modules or paving stones" can be imagined. We decided to choose macrorings of the family of porphyrins and phthalocyanines for their square symmetry, highly conjugated fused ring structure and their potential chemical (redox) reactivity. This is in accordance with requirements 2 and 4 and maybe 8. To render these macrorings amphiphilic and to force them to lie flat at the air-water interface, we replaced the phenyl rings by pyridines. Hence the peripheral nitrogen atoms can be quaternized.

This easy reaction allows to simultaneously achieve requirements 1 and 3 : to add a hydrophobic moiety as a long aliphatic chain (1) and to provide four polar groups (pyridinium cations) on the four edges of the planar macroring, which anchor it parallel to the surface of water or substrates (3).

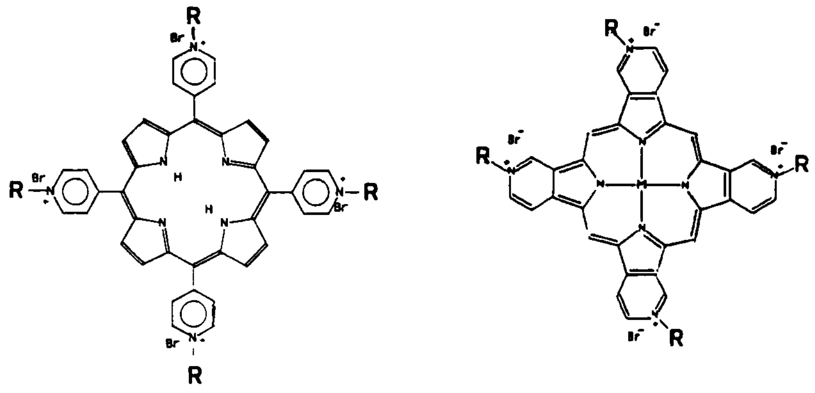

FIGURE 2 Molecular engineering for modules

A more refined engineering consists in quaternizing by short conjugated chains tailored for the future coupling : the macroring is then soluble in the water subphase and is adsorbed and oriented as well by an anionic Langmuir film acting as the 2-D template. In both cases amphiphilic or semi-amphiphilic, very stable films are built and transferred onto substrates. It has been checked by ESR experiments that, indeed, the macrocycles lie flat ($\theta \sim 20°$) and by spectroscopic measurements that the covering also is the same in both experiments[12,13] .

The first part of the project "tiling the plane" is achieved.

Interlocking

The paving stones need joints to be interlocked with each other in two orthogonal directions of the plane. For our specific purpose, covalent bonds are the ones of choice. We selected the Glaser reaction, i.e. an acetylenic coupling as shown in Figure 3.

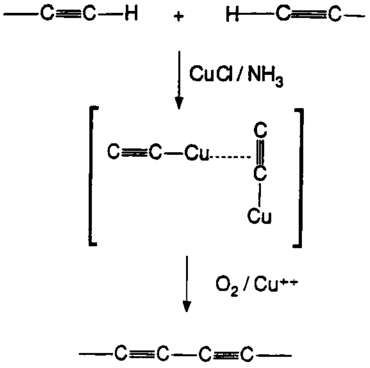

FIGURE 3 The Glaser coupling

This route can fulfil requirements 6 and 7, because a fully conjugated diacetylenic group is synthesized (6) and the reaction is completed at room temperature in cuprous ammoniacal solution (7). This coupling has been previously explored as a means of solid state reactions in LB films[10].

For this purpose, the semi-amphiphilic way has been selected: tetrapyridinoporphyrin quaternized by four acetylenic bonds, tailored for the Glaser coupling, is water soluble and adsorbed beneath an anionic Langmuir film of dihexadecyl phosphate. The covering and the planarity were checked and fully described else where[11-12] .

The first drawback registered along these studies is the impossibility to graft directly the mono acetylenic group on the four nitrogens of the periphery and a methylene group has to be inserted to achieve the quaternization (Figure 4).

This precludes requirement 5 which is prerequisite to the engineering of a fully conjugated polymer : indeed the σ bond, disrupts the conjugation.

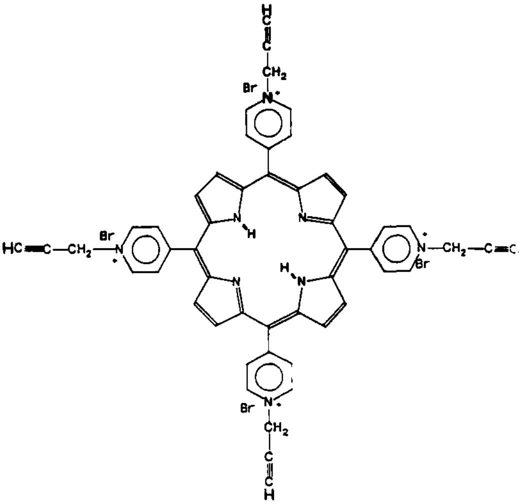

FIGURE 4 The module unit

However to test the method of interlocking, we went on with this joint. The Glaser coupling was checked, as solid state cross-linking as well in the monolayer at the air water interface (the reactants being in the subphase) as in LB films on substrates. Infrared and Raman spectroscopies were used to follow the reaction: the increase of the band intensity of the diacetylenic bond vibration at the expense of the mono-acetylenic one. For the experimental part, this study has been throrougly handled and reported by F. Porteu[11,12] and the detailed physical properties of the polymer are to be published elsewhere by S. Palacin et al[13].

At this stage of the project, a 2-D planar, molecular thick but insulating polymer is obtained and this strategy proved to be efficient.

Removal of the aliphatic matrix

To fulfil the listed requirements, 9 has also to be achieved. The ionic bonds between the cationic polymer and the anionic matrix (dihexadecylphosphate) can be broken by an ion exchange with HCL gas: the regenerated dihexadecyphosphoric acid is easily dissolved and removed, leaving the insoluble molecularly defined polymer sheets or domains, layered on the substrate[13]. The pristine controlled order imposed to the monomeric modules by the LB technique is preserved in the supramolecular structure obtained through this strategy.

DISCUSSION

Other syntheses are in progress to graft fully conjugated chemical links onto the macrorings, to fulfil all the listed conditions, namely 5, to study the doping process, if any.

But whatever the future will be concerning the 2-D conducting polymer, it was intended here to demonstrate that precise molecular engineering conjugated to appropriate solid state structure and reactivity can offer tremendous possibilities to find new materials for nanotechnologies. Although not yet conducting, the present 2-D polymer exhibits already some of the required high performances : the high strength has been checked by deposition of one bilayer on calibrated microscope grids until the membrane bridging the holes breaks. The largest area found is about 10^2 microns in diameter for a membrane thickness of 5.10^{-2} micron. From these data it can be calculated that at least 5.10^9 molecules are cross-linked. This accounts for a high molecular weight connected with the mechanical properties. If the electron delocalization can be related to the same geometrical coherence of the network, high conductivities can be expected, with such 2-D architectures[14].

CONCLUSION

This strategy intends not only to give an example of solid state molecular materials, but to inspire other models, tailored to the goal to be reached[15]. Another outstanding feature, the last but not the least, is that the aliphatic matrix can be released and the thermic stability highly increased. We handle now, various molecular paving stones and only one (a porphyrin) has been discussed here. But other architectures are also in progress by mixing all of the macrorings; phthalocyanines and porphyrins connected with more sophisticated 2-D structures such as alternate layers.

The chemical properties of the polymers preprogrammed by the chemical properties of the individual unit are also to be investigated.

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