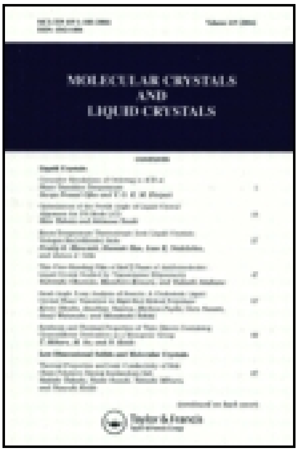

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Annie Ruaudel-teixier [a]
[a] CEA, Service de Chimie Moléculaire, Centre d'Etudes de Saclay, 91191, Gif sur Yvette Cedex, France

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SUPRAMOLECULAR ASSEMBLIES FOR MOLECULAR ELECTRONICS

Annie RUAUDEL-TEIXIER
CEA, Service de Chimie Moléculaire, Centre d'Etudes de Saclay,
91191 Gif sur Yvette Cedex, France

Abstract The Langmuir-Blodgett technique and its modern variants are collective organisation methods of molecules. This allows to fabricate artificial assemblies, programmed for specific properties which are the "modules" of advanced materials for the future molecular electronics.

INTRODUCTION

For the past decade, the concept of molecular electronics prompted Physico-Chemists to create molecular assemblies monitoring simple functions. This molecular micromachinaries are yet very coarse compared to their complex and refine biological models but can already exhibit physico chemical properties such as molecular recognition and intermolecular cooperativity.

This new track, named molecular architecture explores two fields : the building of supramolecules, where the various functionnal groups are interlocked by strong covalent bondings and the fabrication of supramolecular assemblies made of various functional molecules, interlocked by weak physical forces[1]. These two strategies are very different : the first involves chemical synthesis and leads to stable macromolecules, but the second involves the manipulation of organized media, less stable, often in dynamic equilibria such as micelles, emulsions, vesicules, liquid crystals but the method of choice to organize molecules in a real solid state, is the Langmuir-Blodgett technique which allows the fabrication of monolayers sequentially deposited onto a substrate[2].

CHEMICAL MANIPULATION OF LB FILM

Chemical reactions can be performed "in situ" by diffusing external species either from their dissolution in the water of the trough so the reaction proceeds at the air-water interface, before the transfer or after the transfer onto substrate, by aqueous solutions or by vapours so that the reactions proceed in the solid state, and are diffusion and matrix controlled[3].

By these means 2D polymerisations or copolymerisations can take place, as well as other syntheses giving rise to covalent bonds superimposed to the weak physical forces which have been responsible for the former organized assembly. This illustrates both the strategies described above. The stoichiometry and the structure is insured if preprogrammed molecules have been designed prior to built the assembly. Then by monitoring "structure and reactivity" that is to say the LB technique joined to chemistry in this solid state, advanced materials of specific properties can be obtained[4].

ARTIFICIAL SUPRAMOLECULAR EDIFICES

In LB films all the reactivity is displayed in the polar planes where hydrophilic groups are gathered. These groups can be chosen among the various reactive chemical functions to program the reactivity in the solid state.

Control of the structure for specific properties

The variants of the LB techniques are mixed monolayers and adjacent monolayers made of several different molecules which can react and interlock each other, leading to the building of "modules". But the in-plane organization of these modules must be controlled by choosing the set of molecules in such a way that they could react and give rise to a controlled interlocking. This can be monitored by the means of molecular interactions. Such as, host-guest chemistry and more widely molecular recognition. In the solid state these interactions are governed by adequation of the geometries. A simple example is given by LB films of amphiphilic cyclodextrins : the Van der Waals interactions between the aliphatic chains allows the fabrication of stable monolayers and the geometry of the cavity (α β γ cyclodextrins) can select the guests as monomers[5]. In the field of photoreactive dies, in the solid state, aggregation occurs and quentches the fluorescence but in LB films designed in that way, monomers can be obtained and the fluorescence properties are kept.

The structure is also very important in the field of Non Linear Optics where non centrosymetric assemblies are needed : the fabrication of adjacent monolayers of different molecules offers the possibility to align highly polarised molecules in one direction and this illustrates the cooperativity of the whole assembly leading to NLO properties[6].

1-D organization of polymers or stacks

In the field of conducting materials, monomers such as thiophene[7], pyrrole[8], aniline[9], TCNQ complexes, TTF can be polymerized or stacked in the polar planes where these polar heads are settled. A partial oxydation reaction is performed either by diffusing $FeCl_3$,H_2SO_4 solutions solutions or by iodine vapours ; the mixed valent compounds obtained exhibit electrical conductive properties.

Amino-Acids can be polymerized under a matrix-control of the aliphatic chains and either coil or helix polypeptides are obtained at will[10].

But in these cases the overall in-plane order of these macromolecules is disrupted by the formation of domains of low size, (few microns) which can be each regarded as 2-D monocrystals. The whole monolayer behaves like a powder which is a mixture of tiny monocrystals and this discreases the physical properties. For example in the field of conducting materials, the highest conductibility is obtained with monocrystals and a compressed powder of the same compound exhibits a lower conductivity of two orders of magnitude. For this reason an in-plane organisation of a long range order is needed.

2D polymers

Mixed monolayers of cationic and anionic modules (amphiphilic phtalocyanines and porphyrines) have led to the fabrication of an ionic bidimensional polymer[11], the stability of which is poor because hydrolysis taking place with time. But the strategy of polycondensation of the above modules leads to a highly stable 2D polymer where covalent bonds replace the ionic ones[12] (Fig. 1). This polycondensation can be

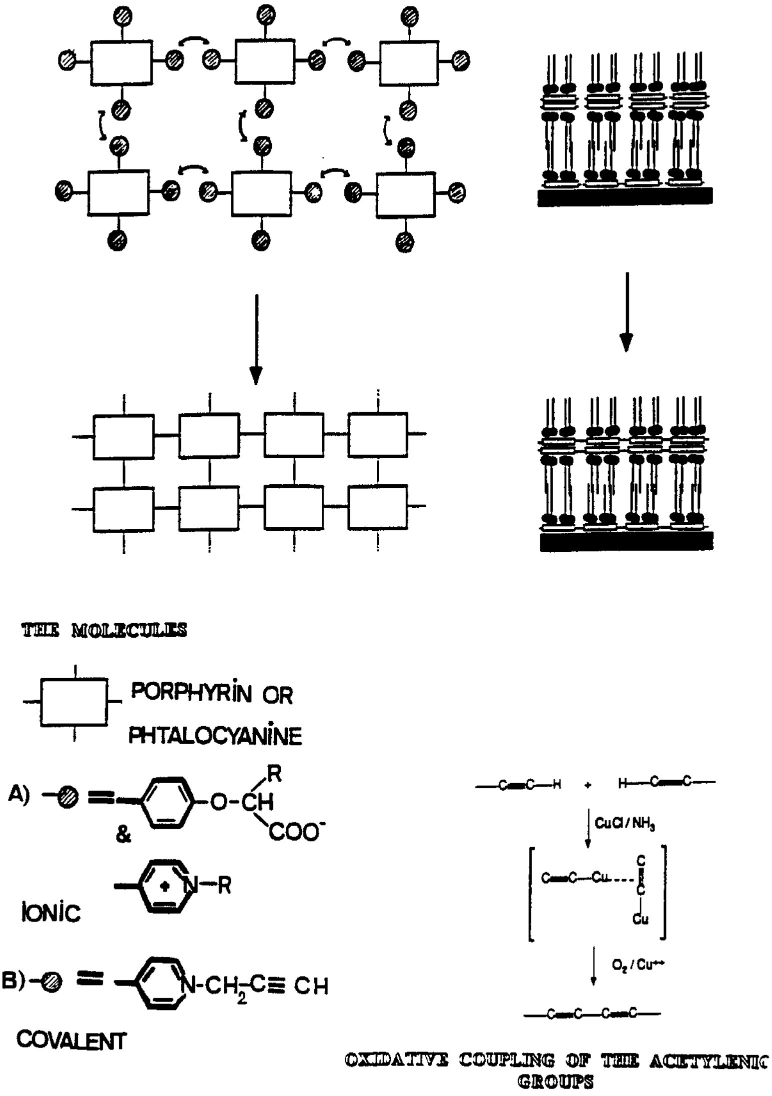

FIGURE 1 Strategy for the 2D polymer

performed at the air-water interface where the reaction takes place between the floating monolayer of monomers and the reactive species dissolved in the water of the trough, as well as in the solid state on the transfered monomers onto substrate and the reactive species diffused from their aqueous solution. The resulting polymer is insoluble and strong enough as one monolayer thick to cover without tearing holes of 0.01 mm^2. XRays measurements exhibit a square 2D network of 27 Å with 1 module by unit cell[13].

In this case by a simple ionic exchange reaction, the aliphatic chains can be discarded by solvent ; the monomolecular-thick sheets superimpose upon each other on the substrate. This manipulation opens the way to future alternate active polar planes.

Another 2D organization is examplified by molecular recognition strategy with biological molecules such as the couple biotin/streptavidine. An amphiphilic biotin designed an synthesized for that purpose is built as a floating monolayer, and the streptavidine is dissolved in the water of the trough ; after a time necessary for the recognition of the holes and keys a 2D crystal of streptavidine is formed at the air water interface and transferred onto substrates for further characterizations[14]. Other examples have been described[15].

Towards the 3D systems

If molecular electronics is to rise as a reality, it must offer an attractive alternative to present inorganic semi-conductors and devices. In the field of integration and parallel treatment of information, progresses are to be performed and 3D molecular structures are necessary.

With LB films epitaxy of successive mono or bilayers is seldom controlled by a simple self-assembling. Here again chemistry is the by-pass to 3D dimensions, to link successives planes so that information or signal carreers could circulate not only in the same plane but also be driven to upper planes in controlled ways. Various already published experiments are pionners for that purpose :

i) The rigid rod-like polymers described by Wegner's team is the first example of composite alternate structures, but with few activity at the moment[16].

ii) The 2D polymers of the team of Saclay where aliphatic chains can be removed (as well as in the case of inorganic insertion compounds of the same team) is also a possibility to superimpose different actives monolayers from alternate layers built from the Langmuir-Blodgett technique.

iii) Sagiv's technique has been presented for more than a decade now and allows also the 3D supra molecular structures : epitaxy is there controlled by sequential chemical reactivity as in the Merrifield syntheses[17].

PROSPECTS FOR MOLECULAR ELECTRONICS

Supramolecular architectures in the solid state, as organized assemblies, have bloomed during the past decades. Anyway the above cited experiments are not exhaustive of the tremendous breack through in this field. Molecular engineering is the basic effort to design active molecules preprogrammed for long range interaction sequences. Every technique of organizing molecules has its own drawbacks and qualities : the future will see the handling of hybridations of these various technologies,sequentially fabricated towards 3D molecular assemblies, superimposing their own capability in ordering, for a specific activity, like a molecular machinary. Pr. Hans KUHN has often spoken for this goal for he was familiar with biological supermolecules. This is a challenge for imaginative chemistry and physics which may lead to molecular electronic devices for the future

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