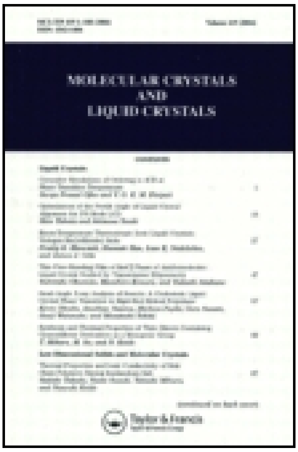

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Solid State Architecture in LB Films: Towards a Magnetic Molecular Memory

P. Coronel [a] & A. Ruaudel-teixier [a]
[a] CEA-IRDI-DESICP-DLPC-SCM CEN-SACLAY, 91191, GIF SUR YVETTE CEDEX, France

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SOLID STATE ARCHITECTURE IN LB FILMS : TOWARDS A MAGNETIC MOLECULAR MEMORY.

P. CORONEL, A. RUAUDEL-TEIXIER
CEA-IRDI-DESICP-DLPC-SCM
CEN-SACLAY
91191 GIF SUR YVETTE CEDEX
France

Supramolecular engineering in solution has already led to exciting results. The same challenge can be tried in the solid state. The Langmuir-Blodgett technique allows the positioning of organizates at the molecular level. The structural order obtained by sequential depositions of mixed or alternate monolayers can be increased by introducing possible reactivity between sets of molecules or sets of assemblies. This coupling of struture and reactivity has already given examples of solid state architectures and active machineries. Ordering molecules in the monomolecular plane is still a challenge. We describe here an example of 2D cooperativity in a molecular assembly which is the first approach towards a molecular magnetic memory.

Introduction

Supermolecular architecture has been a great challenge for the past decade and led to exciting results as exemplified by D. CRAM, PEDERSEN, J.M. LEHN[1] and others[2]. In solution these supermolecules are relevant in specificity and efficiency to biological models.
The solid state is highly preferred for development purposes and organizing molecular assemblies is made possible by using the Langmuir-Blodgett technique[3]. It often requires less synthetic work, since sets of molecules, when properly designed, can interlock easily under the geometrical strains involved in this technique. The art of solid state architecture is to interlock sets of molecular assemblies by in-plane and interplane connections. These organizates can be able to

propagate and modulate signals or information from moving particles, such as electrons, protons or ions, as in biological systems. In this paper we shall review the state of the art in the LB technique. The first example of molecular bistability involving cooperative phenomena in a 2D architecture will be described shortly.

Supermolecular engineering in LB films.

The sequential deposition of monolayers formed at the air water interface and transferred onto solid substrates allows us to govern both structure and reactivity. The technique is associated with specifically designed molecules often called "Langmuir-Blodgettable" molecules. The main requirement is the amphiphilic character. Hydrophobic aliphatic chains of at least 18 carbons provide, by a close packed arrangement, a crystalline structure through lateral Van der Waals forces. The polar heads insure the affinity for water when the monolayer is formed at the air-water interface. It is possible to choose these polar moieties so as to introduce reactivity and even to modify the overall structure . If the possibility of lateral bonds has been previously introduced in the design of the molecule, interlocking will appear between the set of molecules in the same plane. Complexation (in the broader sense) will increase the 2D organization. In some cases, this lateral order produced by reactivity is stronger than the lateral order of the chain lattice and imposes its own structure.

This concept is highly fitted to the LB technique where mixed layers and/or alternate layers can be fabricated. (Fig. 1).

a) mixed layers.

In pure monolayers (only amphiphilic molecules A) the packing is usually that of the chain lattice When two amphiphilic molecules, A and B, are mixed in the spreading solution, two situations appear :

i) no interaction exists between the polar heads of A and B. The structure is only governed by the chain lattice which can be different for A and B. Hence the monolayer is heterogeneous or biphasic : domains of A and domains of B are obtained.

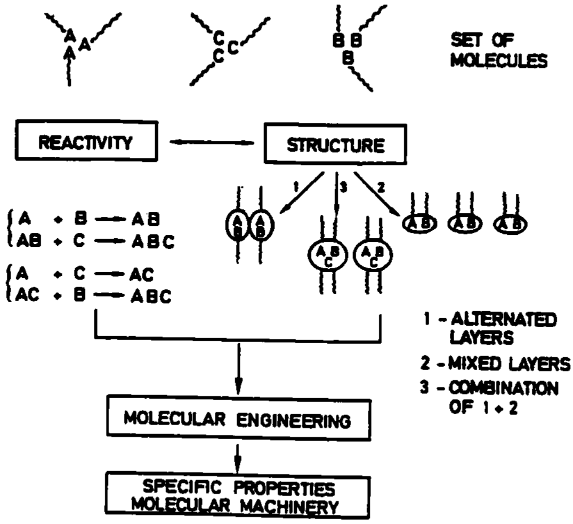

Fig. 1 : General concept for molecular engineering in L.B. films.

ii) the polar heads A and B can interlock each other due to an attractive interaction or,better,a specific complexation. Then a homogeneous monophasic system is obtained.

This is exemplified by the studies of PALACIN et al.[4] where a carotenoïd mixed with behenic acid forms a biphasic system : domains of aggregated carotenoïds, λ_{max} = 350 nm (no interaction between the fatty acid and the polyene). A monophasic system forms when a host-guest complex is built by mixing the same carotenoïd with amphiphilic cyclodextrine (1-1).

2) Alternate layers.

In a modified Langmuir trough the substrate can alternatively cross through a monolayer of molecule A and a monolayer of molecule B. In the polar plane, A can face B and chemical reactivity occurs if the set A and B has been properly chosen. Then the film exhibits new properties due to the in situ synthesized compound.

3) Mixed + alternate layers.

By mixing the above possibilities given by the LB technique, it is possible to interlock sets of molecules in the same plane giving a 2D assembly and interlocking set of assemblies of successives layers giving rise to a supermolecular network. This molecular architecture is conceptually obtainable by pairing the effects of structure and reactivity. Therefore, in this concept, the monolayer building molecules require a highly sophisticated design (Fig. 2). The polar head is the "heart" of the machinery. It holds the chemical functionalities :

A) the in-plane connecting sites
B) the interplane connecting sites
C) the reactive center.
E) *Structural site (aliphatic chains)*

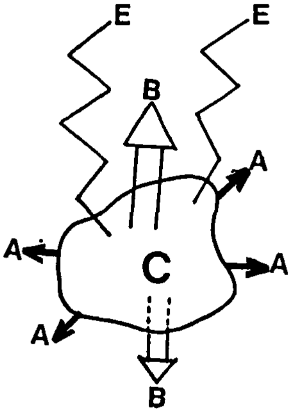

Fig. 2 : General concept for molecular engineering in L.B. films.

The propagation of a signal is then allowed in the same plane and from plane to plane. Such a solid state architecture has never been fully achieved until now. But some steps have been already reached : the dioxygen trap which mimics hemoglobin[5], the molecular wire[6], the in-plane electron transfer in conductive LB films[7] and more recently, in the field of molecular bistability, the spin transition complex in LB films can be cited[8]. Hereafter, an abstract of this study is given so as to illustrate the solid state architecture in LB films by at least one example[9].

Spin transition complex in LB films.

Some organometallic complexes exhibit a spin multiplicity : two stable configurations of spin (high spin and low spin) exist depending on an external strain (temperature, pressure etc...). The transition from the low spin state to the high spin state can be very abrupt (a few degrees when temperature variation is involved), and it exhibits an hysteresis connected with the cooperativity of the assembly. Examples of such complexes have been studied in monocrystals or powders i.e. in a 3D

structure[10]. We decided to explore these phenomena in the 2D structure of the LB films since it could bring a new stone to the building of the solid state engineering in LB films and open the door to passive information storage devices.
The archetypal compound $[Fe^{II}$ phen$_2$ NCS$_2]$,thoroughly studied in the literature[10,11],was rendered amphiphilic by grafting three aliphatic chains on each phenanthroline ligand (Fig. 3).

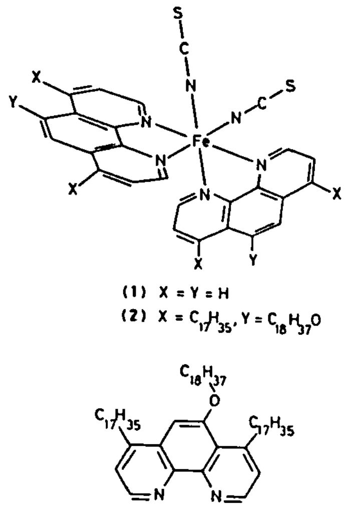

Fig. 3 : Spin transition complex.
1 - archetypal compound.
2 - Amphiphilic complex. (OP$_3$)

Two strategies were worked up to obtain the molecular assembly :

1. Pure LB films : method 1.

The designed and synthetized complex$[Fe_{II}$ (OP$_3$)$_2$ NCS$_2]$was dissolved in cyclohexane (as spreading solvent) and transfered onto CaF$_2$ substrates. Characterization by IR spectroscopy shows the presence of the desired complex for the major part, and beside, other species derived from an hydrolysis in the solvent and at the water surface.

2. Solid state synthesis : method 2.

LB films of the amphiphilic ligand were treated by aqueous solutions of $FeCl_2$, 7 H_2O then NH_4 SCN. The only compound obtained was $[Fe(OP_3)_x (NCS)_y H_2O]$ where x = 3, y = 2, which exhibits no spin transition. This preparation was ruled out and the studies performed on the samples of method 1 in spite of the presence of chemical impurities.

3. Physical studies.

The magnetic behaviour was deduced from the infrared absorption bands of ν NCS[10] at various temperatures from 77 K to 300 K . The high spin state exhibits a doublet at 2075-2065 cm^{-1} and the low spin state at 2116-2108cm^{-1}. During the transition, both absorptions are seen and the relative intensities of the bands are proportional to the molar fraction of each species. The curve x = f(T) , x being the molar fraction of the high spin species, is plotted in Fig. 4 for cooling and warming modes.

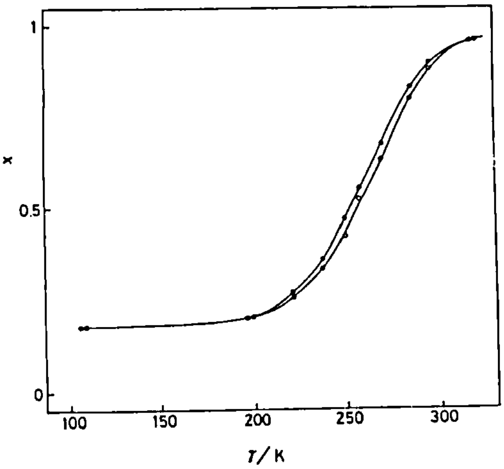

Fig. 4 : Temperature dependence of the molar fraction, x, of the high spin species in both the cooling mode (●) and the warning mode (o).

The transition is far from being abrupt but the presence of either chemical or structural defects always smooths the slope as described in ref. 12,13. However it is different from a Boltzman distribution law and hysteresis (4 K) is clearly seen. This hysteresis,representing a metastable equilibrium in a local minimum of free energy[14],is related to cooperative phenomena during the spin transition[13,15]. This cooperativity, already observed in 3D crystals, seems to be retained in our 2D architecture. Hence the LB method provides an in plane coupling of the spread molecules as shown by observing a given physical property (spin transition) However for a first stage, we can conclude that domains of pure complex exist beside domains of impurities (a biphasic system) and that the observed spin transition phenomena are due to the first domains alone. Attemps to get LB films of the pure complex $[Fe(OP_3)_2 NCS_2]$(monophasic system) are now in progress, since these first results are highly promising to move forward molecular magnetic memories.

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