Multifunctional organic-inorganic hybrid films deposited by the Langmuir-Blodgett technique

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Chapter 3

Introduction to Molecule-Based Conducting and Magnetic Langmuir-Blodgett Films

This chapter reviews the use of the Langmuir-Blodgett technique to produce molecule-based conductors and magnets. Some of the early and recent examples from the literature are highlighted with particular attention to the chemical systems that are studied. Hybrid Langmuir-Blodgett films, deposited with the purpose of mixing functionalities especially magnetism and conduction, are briefly discussed in the last section. This chapter provides a glimpse of the state of the art, mostly from the point of view of controlled deposition of heterostructures afforded by Langmuir-Blodgett films.
3.1. Introduction

In the last few decades, the Langmuir-Blodgett technique has been explored to design molecule-based materials not only for fundamental studies but also for possible applications in molecular electronics\textsuperscript{1-2}. The cooperative properties of molecule-based materials, such as conduction and magnetism, depend on the intermolecular distances and on the orientation of the molecules relative to each other\textsuperscript{3-4}. Hence, engineering of molecular assemblies with desired functionalities requires the ability to control the molecular organization. The Langmuir-Blodgett method has attracted much attention in the context of building supramolecular assemblies as it provides the opportunity to exercise molecular-level control over the mono- and multi-layer assemblies. Taking advantage of its ability to deposit thin films with a fine control of film thickness, several nanostructured functional materials have been organized on surfaces\textsuperscript{5-6}.

3.2. Molecule-based conducting Langmuir-Blodgett films

Organic conductors and semiconductors have attracted great attention, motivated by possible applications in molecular electronics\textsuperscript{7-8}. Since the discovery of the first metallic tetrathiafulvalene–tetracyanoquinodimethane (TTF-TCNQ) solid in 1973, much effort has been devoted to molecule-based (super)conductors\textsuperscript{9}. These materials show very interesting properties such as high anisotropy, low-dimensional electron transport and charge or spin ordering\textsuperscript{10}. These properties are mainly determined by the arrangement of molecules in condensed phases. Hence, control over the orientation and placement of molecules within the molecular assembly is required to achieve the desired material properties.

The Langmuir-Blodgett method requires amphiphilic molecules that are capable of forming the monolayer at the air/water interface. If molecular building blocks (figure 3.1: 1, 2, 3) with amphiphilic character are included in the synthesis of molecular solids, conducting films can be obtained using the Langmuir-Blodgett method. There are several approaches to self-assemble the molecules at the air/water interface, such as functionalizing the basic molecules with hydrophobic and hydrophilic groups\textsuperscript{11} or to associate the non-amphiphilic basic molecule with an amphiphilic counter anion\textsuperscript{12-13}. This section will review some of the molecular building blocks most commonly used to deposit conducting Langmuir-Blodgett films. A set of sophisticated analysis tools has been applied to generate a coherent picture of the physical and electronic structure of these Langmuir-Blodgett films.
These characterization results are not included here; this section emphasizes the molecular building blocks used to build conducting LB films and the corresponding conductivity results in the resulting films. The reader is referred to the original literature for details on the structural, spectroscopic and electrical transport measurements.

3.2.1. TCNQ-based conducting Langmuir-Blodgett films

One of the earliest examples of molecule-based conducting Langmuir-Blodgett films was prepared using N-docosylpyridinium TCNQ (figure 3.2; 4) by Raudel-Teixier et al. The deposited films were oxidized with iodine vapours to achieve mixed valency. X-ray diffraction along with other spectroscopic measurements was used to investigate the structure of the Langmuir-Blodgett films before and after iodine vapour treatment. It was found that (TCNQ)$_2$ dimers reorient upon oxidation with iodine vapours to align the long molecular axis perpendicular to the substrate surface. The intrinsic conductivity of LB film estimated from optical measurements was 200 S/cm after oxidation. However, the DC electrical conductivity was found to be 0.1 S/cm with an activation energy of 0.15 eV. It is understood that the macroscopic conductivity measured through DC electrical measurements is limited by grain boundary effects in a granular material. Since structural imperfections and a granular nature are common features in conducting LB films, the macroscopic DC electrical transport is significantly affected by inter-grain potential barriers.

Raudel-Teixier et al. also introduced another strategy for preparing conducting LB films, which did not require any post-oxidation treatment with iodine vapours. They used a mixture of neutral amphiphilic TCNQ (figure 3.2; 5) and fully reduced TCNQ to achieve stable monolayers. The transferred LB films were in a mixed valence state and exhibited a conductivity of 0.1 S/cm. The mixed valence nature of the LB films was confirmed by the presence of a charge transfer band in the IR spectrum. In another attempt hybrid LB films
were deposited using an amphiphilic pyridinium counterion with an azobenzene moiety (figure 3.2; 6)\textsuperscript{21} for the purpose of switchable conductivity. The resulting hybrid LB films showed changes in the in-plane conductivity upon irradiation at frequencies that induce trans-to-cis isomerization of the azobenzene.

![Chemical structures of molecular building blocks based on TCNQ derivatives](image)

**Figure 3.2. Chemical structures of molecular building blocks based on TCNQ derivatives**

### 3.2.2. Phthalocyanines-based conducting Langmuir-Blodgett films

Phthalocyanines have a strong tendency to self-organize from solution in common solvents into coherent columnar, rod-like assemblies; hence they hold great potential for solution-processed molecular electronic devices such as organic light-emitting diodes, organic field-effect transistors, photovoltaic cells and electrochromic displays. These materials exhibit long-range order and large electrical anisotropies which make them good candidates for any application that requires an anisotropic character in the molecular assemblies\textsuperscript{22-23}.

Considerable efforts have been spent to deposit phthalocyanine derivatives (figure 3.3; 7, 8, 9)\textsuperscript{22-29} using the Langmuir-Blodgett technique that provides the possibility to control the packing of these disk-like molecules. At low surface pressure (<10 mN/m\textsuperscript{2}), these molecules (7, 8, 9) form a monolayer with face-to-face stacking. However, further
compression leads to bilayer formation at the air/water interface. X-ray reflectivity studies together with atomic force (AFM) and optical microscopy on transferred LB films confirmed the picture of aligned columns of the phthalocyanines molecules. The structural properties of the resulting LB films were shown to be greatly influenced by several deposition parameters, especially by the surface pressures at which these were transferred. The conductivity in these LB films was found to be significantly larger along the column direction than perpendicular to it. The observed anisotropy$^{22-23}$ was as large as 1000:1.

![Chemical structure of phthalocyanine derivatives](image)

Figure 3.3. Chemical structure of phthalocyanine derivatives

### 3.2.3. TTF-based conducting Langmuir-Blodgett films

The amphiphilic TTF derivatives with hydrophobic alkyl chains (figure 4.4; 10)$^{30-32}$ have been studied in detail. The amphiphile EDT-TTF(SC$_{18}$)$_2$ (10) forms a stable monolayer only when mixed with long-chain carboxylic acids. The as-deposited LB films were subjected to post-oxidation treatment to achieve conduction. The oxidation process involved various steps and led to significant structural reorganization within the LB film. A DC electrical conductivity up to 1 S/cm was observed for multilayer LB films. Different studies gave a heterogeneous picture of these LB films in which conducting clusters of (EDT-TTF(SC$_{18}$)$_2$)$_2$I$_3$ were surrounded by insulating bilayers of carboxylic acid. The amphiphile derivative 11 has the ability to form films on its own and hence does not require any co-surfactant$^{11,33-34}$. The floating films were found to deposit forming a Y-type structure (see
figure 2.7 in Chapter 2) using normal dipping procedures. However, the resulting LB films are neutral and an iodine vapour treatment was required to obtain a charge-transfer salt. The two-point probe conductivity measurement gave 1 S/cm with an activation energy of 0.09 eV for oxidized LB films of amphiphile 11. To avoid the use of co-surfactants or long alkyl chains that hinder the optimal overlap between adjacent donors, several strategies have been used to prepare TTF derivatives that have improved film-forming properties. Some of them are illustrated very briefly in the following subsections.

Pyridine-containing TTF donors (figure 3.4; 12, 13):

Pyridine-containing TTF donors (12, 13) were reported to form Langmuir films without long alkyl chains35-36. The as-deposited LB films showed conductivity values up to $10^{-7}$ S/cm as measured by the two-point probe method; these values could even be increased to $\sim 10^{-3}$ S/cm with post-oxidation treatment35-36.

Azobenzene-containing TTF donors (figure 3.4; 14):

L. M. Goldenberg et al.37 coupled TTF derivatives to an azobenzene chromophore in order to deposit LB films with switchable conductivity. LB films with semiconducting properties were obtained from these molecules without adding any co-surfactant. However, the authors did not observe any change in conductivity upon irradiation.

Metal dithiolate complexes (figure 3.5; 15):

In the solid state, eleven superconductors with $T_c$’s of less than 8.4 K38, prepared from metal complexes of the dmit (1,3-dithiole-2-thione-4,5-dithiolate) ligand, have been reported. These complexes have also been studied in LB films as salts of alkylammonium or alkylpyridinium amphiphilic molecules39-40. LB films of monovalent or divalent salts acquire a mixed valence state upon post-oxidation. Room temperature conductivities up to 40 S/cm have been reported for a series of Au(dmit)$_2$ salts18. When electrochemically oxidized by a LiClO$_4$ electrolyte, LB films of ditetradecyldimethylammonium-Au(dmit)$_2$ (15) showed signatures of superconductivity in a series of AC susceptibility measurements.41-42
The majority of LB films based on molecular conductors require a post-oxidation treatment to achieve mixed valency, essential for conducting properties. The post-oxidation treatment most often consists in exposure iodine or bromine vapours which induce a significant structural reorganization. These structural changes are accompanied by inclusion of defects and insulating grain boundaries that limit the electrical conductivity. BEDO-TTF (16), when mixed with carboxylic acid, gives rise to conducting LB films without the need for further post-oxidation treatment. BEDO-TTF has a strong tendency to form a quasi-two-dimensional metal. When a mixture of amphiphilic carboxylic acid and BEDO-TTF is spread onto the water surface, the BEDO-TTF molecules self-assemble beneath the
amphiphile carboxylic acid molecular layer through hydrogen bonding. This Langmuir film is already in a mixed valence state characterized by an optical conductivity of $\sim 200$ S/cm. The deposited LB films display a Y-type multilayer structure and have been thoroughly studied for structural and electrical properties.

Figure 3.6. Chemical structure of BEDO-TTF

3.3. Magnetic Langmuir-Blodgett films

The earliest examples of low-dimensional magnetic Langmuir-Blodgett films were demonstrated in the late 1970s by M. Pomerantz et al. working at the IBM T.J. Watson Research Centre. These authors found evidence for an antiferromagnetic exchange within the monolayer of manganese stearate at low temperatures. Later on, Y. Ando et al. studied the stearate films of Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$ and Ni$^{2+}$. Their structural and EPR studies on manganese stearate LB films confirmed the findings of Pomerantz et al. The SQUID data on the stearate LB films of Fe$^{2+}$ and Co$^{2+}$ also showed antiferromagnetic exchange between transition metal ions; nickel stearate LB films showed ferromagnetic ordering at low temperatures. LB films of gadolinium stearate have also been studied in the same context of low-dimensional magnetism. EPR measurements indicated a magnetically ordered state with a transition temperature around 500 K. The same system was later investigated by Mukhopadhyay et al., but these authors did not observe any spontaneous magnetization down to 100 mK, although field-induced ferromagnetism was observed at low temperatures in the in-plane geometry.

Similar to fatty acids, alkyl phosphonic acids form LB films with a variety of divalent, trivalent or tetravalent metal ions. Among these, manganese phosphonate LB films have been extensively studied. The ordered state of manganese octadecylphosphonate LB films is reported as being a canted antiferromagnet and these films showed magnetic memory below the transition temperature. Magnetic LB films have also been deposited from different molecular complexes; some of the extensively studied examples are reviewed in the following subsections.
3.3.1. Metal cyanide networks – 2D analogues of Prussian Blue

Metal cyanide networks such as Prussian Blue analogues (PBAs) possess a rich palette of properties including high-spin clusters\(^6\), room temperature magnetic ordering\(^6\), metamagnetism\(^6\), photomagnetism\(^6\) and spin crossover. The very earliest examples of PBA-based LB films were prepared by Mingotaud et al.\(^6\) These authors used a very dilute colloidal dispersion of PBA as subphase and utilized positively charged dioctadecyldimethylammonium (DODA) ions to assemble PBA species at the air/water interface. The transferred films were of Y-type, with PBA species trapped within DODA bilayer as shown in figure 3.7 (a). These LB films exhibit a higher magnetic ordering temperature (\(T_c\)) than the corresponding PBA powder sample and a magnetic memory in the ordered state (figure 3.7 (b)).

![Figure 3.7. a) Schematic representation of the PBA-DODA LB film structure. b) Hysteresis loops of 300-layer-thick PBA-DODA LB film recorded at 2 K with the magnetic field (H) parallel (open circles) and perpendicular (filled circles) to the LB layers (adapted from ref. 64).](image)

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Later on, different strategies were introduced to prepare LB films of PBAs. Culp et al.\textsuperscript{65-68} included one of the metal sites in an amphiphilic complex (figure 3.8 (a); 17). Reaction of this Langmuir film with the metal ions present in the subphase results in a 2-dimensional metal cyanide grid network at the air/water interface. This network can be deposited onto a substrate to obtain monolayer, bilayer or multilayer LB films, whose structure is schematically illustrated in figure 3.8. The magnetic response of the 2-dimensional magnetic network is determined by the in-plane, interplane and long range dipolar interactions as show in figure 3.9. The coercive field of the deposited film increases with increasing number of layers. Since the reactants combine at the air/water interface, the film formation process discriminates against the formation of higher-dimensionality products and provides elegant control of the structures at early stages of growth. The resulting films were ferromagnetic at low temperature.

Figure 3.8. a) Chemical structure of the pentacyanoferrate amphiphilic molecule used to form Langmuir films. b) Schematic structure of two-dimensional Fe\textsuperscript{3+}-Ni\textsuperscript{2+} cyanide grid networks assembled at the air/water interface and transferred as monolayer, bilayer and multilayer using the Langmuir-Blodgett technique (adapted from ref. 68).
Figure 3.9. Magnetization vs applied magnetic field (B) for monolayer (light blue), bilayer (red) and multilayer (dark blue) Langmuir-Blodgett films shown in Figure 3.8. The hysteresis increases with increasing number of layers (adapted from ref. 68).

Another strategy reported for the ‘on surface’ synthesis of PBA-based LB films involves the use of clay platelets along with amphiphilic molecules. Figure 3.10 depicts the deposition scheme of a DODA-clay-PBA multilayer film. The cross-sectional high resolution TEM and high-angle annular dark-field scanning electron transmission microscopy analysis, shown in figure 3.11, confirmed the formation of a layered structure where a low dimensional PBA network is sandwiched between clay layers. The brighter contrast in Figure 3.11 (b) is due to atoms with high atomic number (metal ions) contained in PBA. These films showed magnetic properties in between superparamagnetic and spin-glass behaviour with high blocking glass temperatures above 65 K.
Figure 3.10. Deposition procedure adapted from ref. 69. Amphiphilic DODA absorbs clay platelets when spread on aqueous clay dispersion. This DODA-clay layer is deposited on a hydrophobic substrate and sequentially dipped into aqueous solutions of metal ions and hexacyanometallate ions to obtain DODA-clay-PBA film.

Figure 3.11. High-resolution TEM and high-angle annular dark-field scanning electron transmission microscopy (HAADF-STEM) analysis performed on the 120-layer-thick hybrid films of DODA-clay-PBA (adapted from ref. 69)
3.3.2. Polyoxometalate complexes

Polyoxometalate anions (POMs) represent a diversified class of molecular inorganic compounds with the general formula $X_aM_bO_c^{n-}$ ($M = Mo, W, V$ etc. and $X = P, Si, B, Co$ etc.). Their versatile nature in terms of composition, size, structure and charge distribution provides access to a huge library of functional building blocks\(^70\) which can be interconnected with other functional molecules to construct tailored molecular framework materials. M. Clemente-Leon et al.\(^71\)-\(^74\) incorporated a series of magnetic POM clusters with varying nuclerities into LB films as counterions to cationic surfactants such as DODA. X-ray diffraction and spectroscopic analysis indicated that the POMs are organized in monolayers within these LB films. Magnetic measurements on these LB assemblies indicated that the clusters are magnetically isolated\(^72\).

3.3.3. Single-molecule nanomagnets

M. Clemente-Leon et al.\(^75\)-\(^76\) also explored the use of LB technique to organize single molecule magnets in a way to achieve molecular bi-stability suitable for information storage at the molecular level. Initial experiments were performed with mixed valence manganese clusters $[\text{Mn}_{12}\text{O}_{12}(\text{carboxylato})_{16}]$ (carboxylato = acetate, benzoate), referred to as $\text{Mn}_{12}$ (figure 3.12 (a)). To obtain a stable Langmuir film from these clusters, behenic acid (BA) was used as the co-surfactant. The organization of the $\text{Mn}_{12}$ clusters within the Langmuir film showed a strong dependence on the BA:$\text{Mn}_{12}$ ratio as illustrated in figure 3.12 (b). A bi-dimensional molecular system resulted for ratios near 1:5 while partial monolayers of clusters were obtained at lower concentrations of clusters. These films showed marked hysteresis loops at 2 K, with coercive fields of 0.1 T for the benzoate derivative and 0.06 T for the acetate derivative.

In another effort to arrange the magnetic clusters into a well-organized multilayered film, L. M. Toma et al.\(^77\) combined the Langmuir-Schaefer method with self-assembly to deposit thin magnetic films of highly anisotropic $\text{Ni}_8$ molecules. Figure 3.13 (a) displays the XRD pattern of a multilayer film which confirmed the proposed layered structure shown in Figure 3.13 (b).
Figure 3.12. a) Schematic view of the chemical structure of a Mn$_{12}$O$_{12}$(carboxylato)$_{16}$ cluster. The large circles, white circles and small black circles represent Mn ions, oxygen atoms and carbon atoms, respectively. b) Schematic representation of the structure of a BA-Mn$_{12}$ LB film for different concentrations of Mn$_{12}$ clusters (adapted from ref. 76).

Figure 3.13. (a) X-ray diffraction pattern of a 40-layer-thick hybrid DODA-clay-Ni$_8$ film on Mylar testifying to the layered structure schematically shown in (b) (adapted from ref. 77).
3.3.4. Magnetic nanocrystals

Recently, M. Pauly demonstrated a strategy to fabricate controlled assemblies of ligand-coated iron oxide nanoparticles using the Langmuir-Blodgett technique\textsuperscript{78}. Figure 3.14 shows a schematic representation of the structure of such a multilayer LB film. The films were homogeneous and dense over large areas as shown by the SEM, AFM and TEM images shown in Figure 3.14. The thickness of the 10-layer-thick film was well defined in the AFM images with a root-mean-square (rms) roughness of 5 nm, half of the nanoparticles diameter. The dipolar interactions were found to be stronger for particles assembled in a thin film compared to a powder sample\textsuperscript{79}.

![Figure 3.14](image)

**Figure 3.14.** (a) Schematic representation of the structure of a multilayer LB film deposited from coated iron oxide nanoparticles. (b) Top and (c) section view of 10 layer-thick LB film in SEM. (d) AFM results and (e) TEM cross-section. (Adapted from ref. 78)

3.4. Langmuir-Blodgett films with mixed functionalities

The Langmuir-Blodgett technique utilizes the amphiphilic nature of the surfactant molecules and the layer-by-layer deposition protocol to grow supramolecular architectures on surfaces. Both aspects make Langmuir-Blodgett deposition a superior method for combining multiple functions into one film. Changing the surfactant molecules from one layer to the next, ordered heterostructures can be created with well-defined smooth junctions (interfaces). Each layer in the resulting heterostructures not only contributes a separate property, providing a film with composite properties, but can also couple to
adjacent layers to produce new phenomena. Examples of such structures are the conducting and magnetic films involving molecular layers of photoactive or electroactive components\textsuperscript{21,80} which are introduced to switch the magnetic or conducting properties with external stimulus. Films where conductivity and magnetism coexistent have also been targeted. Such organic-inorganic hybrids have been found to exhibit several interesting phenomena arising from the coupling between individual building blocks as illustrated in a review by T. Sugimoto \textit{et al}.\textsuperscript{81} Here, discussion is limited to the class of LB films that are both conducting and magnetic.

M. Clemente-Leon \textit{et al}.\textsuperscript{82} used magnetic POM clusters in combination with semi-fluorinated TTF derivatives (SF-EDT shown in figure 3.15) to prepare hybrid LB films. In a first step POM clusters were transferred from the air/water interface to a substrate with the help of a DODA layer. This results in a hydrophobic surface because the alkyl chains of the DODA arrange at the film/air interface. Onto this hydrophobic surface a molecular layer of TTF derivatives was deposited in a second LB deposition step. As confirmed by X-ray diffraction and IR linear-dichroism experiments\textsuperscript{82}, a multilayer LB film with the structure schematically presented in figure 3.15 could be obtained by repeating this two-step cycle several times. The as-deposited films were treated with iodine vapours to oxidize the TTF moieties. However, the macroscopic conductivity remained very low even after oxidation treatment, although charge delocalization was observed in the IR spectra\textsuperscript{82}.

Another type of hybrid LB film in which the polar network was the manganese phosphonate lattice and the organic network was composed of substituted TTF moieties (18 in figure 3.16) was prepared by M. A. Petruska \textit{et al}.\textsuperscript{83-84}. These authors determined that these films were canted antiferromagnets below 11.5 K. Post-oxidation treatment of the as-deposited film with iodine vapours resulted in an unstable phase. However, a manganese phosphonate-based hybrid LB film, when prepared with a different TTF moiety (19 in figure 3.16), was found to form a stable phase upon photo-oxidation in the presence of \text{CCl}_4.\textsuperscript{85} The oxidation procedures have been described by B. A. Scott \textit{et al}.\textsuperscript{86} Spectroscopic studies of the photo-oxidized manganese phosphonate LB films with donor (19) confirmed the presence of a conducting organic network, albeit with a very low macroscopic conductivity.
3.5. Concluding remarks

The results obtained to date have significantly advanced towards the goal of Langmuir-Blodgett films displaying both conductivity and magnetism. Several types of surfactant and charge donating molecules have been tested to improve the cooperative properties, which however remain limited by structural defects. The effects of structural defects are magnified in low-dimensional systems and responsible for the type of ergodicity breaking exhibited. As a result, the macroscopic conductivities in the conducting films are lower than those of the related crystalline solids. Similarly, limited structural coherence can result in glassy
behaviour in magnetic LB films. However, wise strategies based on thorough understanding of the correlation between physical properties and film structure could lead to some of tomorrow’s great discoveries of new functional materials. The future looks bright for the hybrid Langmuir-Blodgett method in this regard because this technique not only produces molecular thin layers with precise control but also provides the opportunity to combine different functionalities in a single thin film assembly.

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