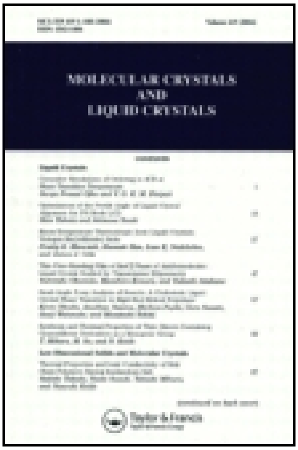

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Langmuir-Blodgett Films Based on Prussian Blue Derivatives: towards New Hybrid Magnetic Materials

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Langmuir-Blodgett Films Based on Prussian Blue Derivatives: towards New Hybrid Magnetic Materials

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The adsorption of dissolved Prussian Blue derivatives along a positively charged monolayer leads to new Langmuir-Blodgett (LB) films presenting a ferromagnetic state at low temperature. Such organic/inorganic systems containing inorganic sheets between organic amphiphilic layers constitute a new series of magnetic lamellar materials.

Keywords: Langmuir-Blodgett film; Prussian Blue; magnetism; electrochemistry; hybrid materials

INTRODUCTION

The Langmuir-Blodgett technique is one of the most powerful tool to build up molecular layered structures[1]. It has been largely used to organize amphiphilic molecules spread at the gas-water interface in order to design new materials with various properties. Instead of working with neutral molecules, another possibility is to create an ionic association along the interface: ions dissolved in the subphase are interacting with charged lipids organized at its surface and the resulting ionic pairs can be transferred onto a solid substrate. Since the early work of Langmuir[2], this so-called semi-amphiphilic strategy has been applied to organic ions[3-5] or simple metallic cations[6,7]. In particular, manganese or iron ions were used by Pomeranz et al.[8] and by Talham and coworkers[9,10] to build the first magnetic LB films.

Recently, we showed that this semi-amphiphilic technique allows the researcher to organize a large variety of inorganic complexes or entities in a multilayer architecture. In particular, polyoxometalate anions which constitute a distinctive class of inorganic compounds can be easily incorporated and organized in a LB film[11-13]. Monometallic or heterobimetallic oxalato complexes can easily be manipulated through the LB technique leading to new inorganic/organic materials[14]. Similar results have been obtained with hexacyanometalates. However, because of the average large distance and the lack of superexchange pathways between the magnetic centers, interactions between metal complexes should be negligible within those LB films. Indeed, the magnetic properties are found somewhat similar in the multilayers and in powders. To build hybrid inorganic/organic LB films presenting a cooperative magnetic behavior, a simple idea is to start from compounds having an extended character instead of molecular ions. For this point of view, the well-known Prussian Blue is an interesting basic compound of formula $Fe^{III}_4[Fe^{II}(CN)_6]_3.xH_2O$ exhibiting a 3D ferromagnetic ordering at very low temperature[15]. Recently, Verdaguer and Girolami's groups[16,17] have synthesized new cyano-bridged derivatives presenting a ferro or a ferrimagnetic order at transition temperatures as high as 315 K. In this paper, we will show that mixed-valent hexacyanometallates (i.e., Prussian Blue and copper(II) hexacyanoferrate(III)) can indeed be the starting point of new hybrid lamellar films.

EXPERIMENTAL SECTION

Dimethyldioctadecylammonium bromide (DODA) from Kodak was used without further purification. Chloroform (HPLC grade from Prolabo) was the spreading solvent. The water of the subphase was a Millipore Q-grade water with a resistivity higher than 18 MΩ.cm. Prussian blue was obtained from Aldrich. Copper(II) hexacyanoferrate (III) (noted "Cu_3Fe_2") was synthetized according to standard procedures[18]. However, in order to get a slightly more soluble product, potassium chloride was added in the pristine copper acetate solution (final concentration: 0.2 M in KCl). The magnetic properties of the compounds synthetized with or without potassium chloride are found to be identical. The chemical analysis of the commercial Prussian blue (respectively the synthetized "Cu_3Fe_2") indicates that it contains 3.5 % of sodium (respectively 1.4 % of potassium).

Built-up films have been obtained by the vertical lifting method using a home-made LB trough working at room temperature under a continuous dried nitrogen flow[11]. Infrared (IR) spectra were recorded on a FTIR 750 Nicolet spectrometer; linear dichroism was used in order to determine the molecular orientations in LB films[19]. ESR experiments were done with a Bruker ESP 300 E system working at 10 GHz (X-band) equipped with an Oxford Liquid ^{4}He temperature accessory. The magnetic susceptibility was measured with a Quantum Design MPMS-XL-5 SQUID magnetometer between 2 and 300 K. Experimental conditions were the same as those already described[12].

RESULTS AND DISCUSSION

A very diluted Prussian blue derivative solution (concentration 10^{-6}-2.10^{-5} mol.l^{-1}) is used as a subphase on which a positively charged lipid (namely dimethyldioctadecylammonium bromide, noted DODA) is spread. The compression isotherm of DODA on such a subphase is shifted when compared to that recorded on pure water. The dissolved Prussian Blue derivative is then in electrostatic interactions with the charged layer[20]. On the contrary, no interaction seems to occur when the monolayer is negatively charged.

For all the Prussian blue derivatives, the transfer of the monolayer from the interface onto a solid substrate is easily performed when the molecular density in the film is high enough[20]. The transfer is generally Y-type with a transfer ration close to unity. These multilayers were characterized by complementary techniques such as infrared spectroscopy, X-ray diffraction and magnetic measurements.

Infrared linear dichroism

Besides the bands assigned to the CH_2 stretching or scissoring vibrations of DODA alkyl chains, bands associated with the CN groups are clearly visible in the IR spectra of the LB films. Compared to the values in KBr pellet, these vibration bands in LB films are narrower and somewhat shifted. When starting from Prussian blue, the IR spectrum (see figure 1) shows that the LB films contain mainly entities based on Fe^{III}-CN-Fe^{II} bridges.

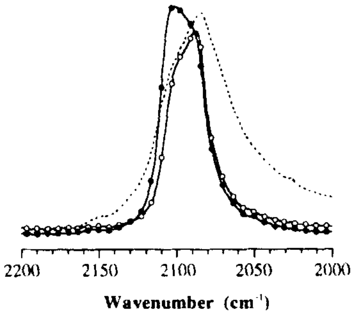

FIGURE 1 Infrared spectra of the Prussian Blue powder (dashed line) and the corresponding hybrid LB film (solid line) when the angle between the plane of the substrate and the electric field is either 0° (open circles) or 60° (full circles).

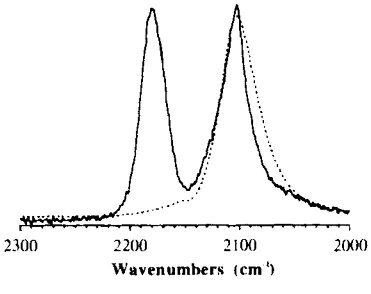

FIGURE 2 Infrared spectra of the "Cu_3Fe_2" powder (dashed line) and the corresponding hybrid LB film (solid line).

Furthermore, these CN groups are not randomly organized as in bulk. Dichroism experiments made on those LB films reveal that the CN band contains in fact two peaks at 2101 and 2086 cm^{-1} presenting different dichroic behaviors when the LB film is tilted versus the infrared beam direction: two types of CN with two different orientations exist within the LB films.

Therefore, the isotropic 3D structure of Prussian blue is certainly not maintained within the multilayers. In the case of the copper(II) hexacyanoferrate "Cu_3Fe_2", two sharp peaks are expected in the IR spectrum: one at ca 2179 cm^{-1} corresponding to the Cu-CN-Fe bridges and one at ca. 2104 cm^{-1} associated to terminal CN groups. The samples used in this work (see experimental section) have only a very weak peak associated to the bridging CN groups (this is clearly in relation with the slight solubility of the compound). However, the corresponding LB film (see figure 2) presents a strong peak at 2179 cm^{-1}. This indicates that the mixed-valent hexacyanometallate is strongly modified at the nitrogen/water interface and/or during the transfer onto a solid substrate.

X-ray diffraction

From the Kiessig fringes and Bragg peaks recorded in the diffractogram of the LB film, the lamellar structure of those hybrid materials can be characterized. In particular, the periodicity of the repetitive unit of the LB film based on Prussian Blue[20] calculated either from the fringes and the Bragg peaks is found close to 44 Å. Taking into account the length and the tilt angle of the alkyl chains, one can then estimate a thickness of about 5 Å for the inorganic layer. The structure of those LB films can then be described as layers of mixed-valent cyanometallates intercalated between two layers of organic molecules. The chemical formula of those inorganic sheets is then strongly modified when compared to the bulk Prussian blue derivative. Whatever the exact composition may be, this reproducible and well-defined material is the first organized inorganic-organic system based on such inorganic compounds.

Magnetic susceptibility

The magnetization and the susceptibility of the two LB films were then studied; their values (respectively noted M_S and χ_S) are reported per unit of surface and number of deposited layers. Upon cooling down, the product $\chi_S.T$ of the LB film based on Prussian Blue (respectively "Cu_3Fe_2") increases sharply below

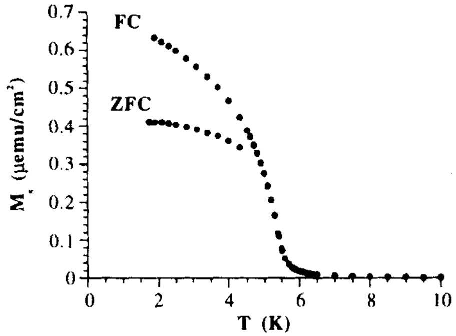

FIGURE 3 Zero-field and field-cooled (H = 10 G) magnetization versus temperature. The LB film based on Prussian Blue was 300 layer thick.

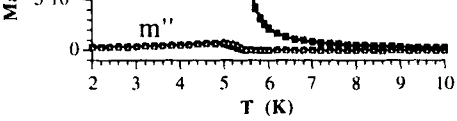

FIGURE 4 Temperature dependence of the in-phase (m') and out-of-phase (m") susceptibility of an LB film based on Prussian Blue (300 layers).

ca 6 K (respectively 30 K). At high temperature, χ_S^{-1} is linear versus the temperature and can be fitted to the Curie-Weiss law, leading to a Weiss constant $\theta = + 5.2$ K (respectively + 24.6 K). The positive values indicate ferromagnetic interactions in those materials and an associated magnetic ground state occurring at low temperature within the LB film. To verify this hypothesis, the field-cooled magnetization at H = 10 G was measured versus temperature (see figure 3). In the Prussian Blue case, it shows a clear break at $T_C = 5.7 \pm 0.1$ K which corresponds to a long-range ferromagnetic ordering. AC susceptibility measurements (performed for the first time on a LB film) confirm such a hypothesis (see figure 4). In particular, the in-phase component exhibits a peak around T_C, which is characteristic of magnetic losses in a ferromagnet.

This critical temperature is found close to that given in the literature (5.5 K[15]) and slightly higher than the 5.1 K measured experimentally for the commercial powder used in this work. In the case of the "Cu_3Fe_2", T_C is found at ca 25.1 K for the corresponding LB film, while the powder shows a ferromagnetic state below 21 K (see figure 5). This critical temperature is independent on the total thickness of the films, i.e., on the number of deposited layers (in the range 20 to 250), whereas the magnetization of the film increases linearly with the number of layers. This indicates that the amount of transferred magnetic material is constant all along this layer-by-layer deposition process.

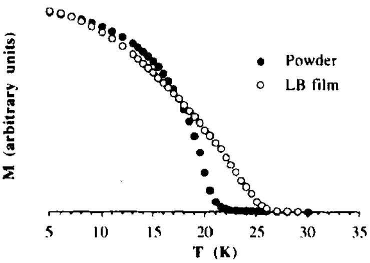

FIGURE 5 Field-cooled (H = 10 G) magnetization versus temperature of the "Cu_3Fe_2" powder (full circles) and the corresponding LB film (open circles).

When comparing the bulk mixed-valent compounds and the corresponding LB films, we observe a very slight increase of the Curie temperature. This behavior is not in agreement with the classical effect of a restricted dimensionality[21,22] on the ferromagnetism. This is clearly due, firstly, to the differences in the chemical composition between the bulk and the multilayers in which the amphiphilic quaternary ammonium plays an important role as cation. Secondly, the magnetic ordering in those systems should be related to the spin anisotropy created by the in-plane organization and only very slightly by the weak dipolar interactions between layers.

This anisotropy is indeed one of the main features of those inorganic/organic materials and is, in particular, demonstrated by ESR experiments in the case of the Prussian Blue LB film (see figure 6).

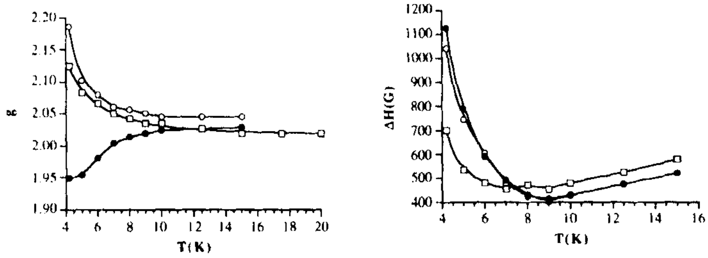

FIGURE 6 Effective g factor and linewidth (ΔH) of the ESR line versus temperature and orientation for a powder sample of Prussian Blue (open squares) and for a LB film based on Prussian Blue (100 layers) when the magnetic field is parallel (open circles) or perpendicular (full circles) to the substrate.

Thus, at 4.3 K the position of the ESR line is strongly dependent on the orientation of the film, having g values of 2.19 or 1.95 when the magnetic field is parallel or perpendicular to the layer, respectively. The linewidth of the resonance line also strongly depends on the Φ angle, defined by the normal to the substrate and the magnetic field (see figure 7). Finally, the linewidth anisotropy disappears above ca. 8 K where the g factor presents still a slight difference (2.045 and 2.027 respectively for the direction parallel and perpendicular) related to the symmetry of the iron within the LB film. All these results point out the anisotropic character of the magnetic properties of the LB film[22].

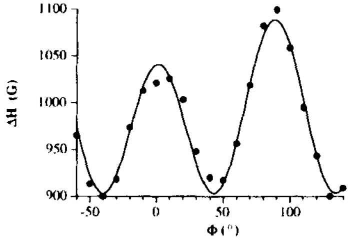

FIGURE 7 Angular dependence of the ESR linewidth versus the angle Φ between the magnetic field and the LB film plane at 4.3 K.

Electrochemistry

Besides the magnetic properties, these hybrid multilayers may have other interesting properties such as electrical or optical. Thus, using a conducting ITO substrate, electrochemistry is easily performed on this modified electrode. Electrochromism can then be observed in those LB films (see figure 8)[23]. The reduction or oxidation of the inorganic layers induces a reversible change in the optical absorption of the LB films. Therefore, those new hybrid multilayers represent new opportunities to develop original optical, magneto-optical or magneto-conducting devices.

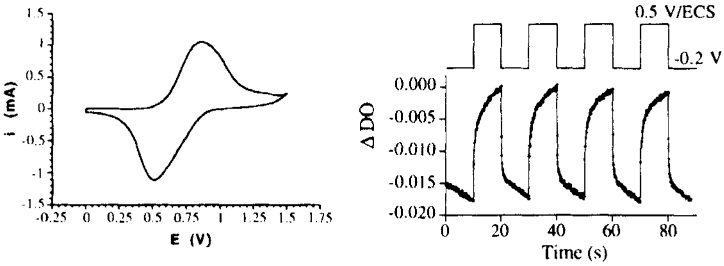

FIGURE 8 Left: Cyclic voltammogram of a 10 layer LB film based on "Cu_3Fe_2" on ITO (supporting electrolyte 0.5 M KCl, scan rate 500 mV/s, ECS reference electrode, Pt counter electrode) Right: Changes in the optical density due to electrochemical cycles of a 20 layer LB film based on Prussian Blue.

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