

Crystallization of Prussian Blue Analogs beneath Langmuir Films

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The preparation of organized nanoscopic or microscopic inorganic material is of importance in electronics, catalysis, magnetism, and sensory devices. For such a reason, biominerization has been extensively investigated and three important processes pointed out: supramolecular pre-organization, interfacial molecular recognition (templating), and cellular processing.¹ This demonstrates the paramount influence of interfaces between media in crystal nucleation and crystal growth occurring in such systems. Crystal morphology and orientation may indeed be tuned and controlled by optimization of the structure and chemistry of those surfaces.²

To obtain a better understanding of these processes, one may use model interfaces such as Langmuir films. Monolayers spread at the gas–water interface have already been used as templates for *in situ* growth of crystals.³ For example, nucleation and oriented growth of α -glycine beneath floating monolayers have been studied.⁴ This approach has been applied to simple inorganic systems such as calcium carbonate,⁵ barium sulfate,⁶ or calcium oxalate.⁷ However, this strategy has not yet been extended to molecular materials, in particular, to metallic cyanide systems. The cyanometalates are very often used as molecular bricks to elaborate mixed valence bimetallic materials. For example, Prussian Blue (PB) and analogues constitute a large family of interesting compounds having the general formula $M'_p[M(CN)_6]_q \cdot xH_2O$ where M' occupies all the summits and all the centers of the faces of a cubic structure and

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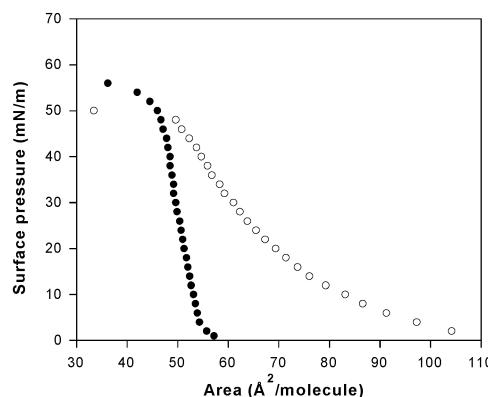


Figure 1. Compression isotherms of DODA on pure water (open circles) and on a solution of $\{\text{Fe}(\text{CN}_6)^{3-} + \text{Cu}^{2+}\} \times 10^4 \text{ M}$ (solid circles) at 21°C .

the $[\text{M}(\text{CN})_6]^-$'s are located at the octahedral sites.⁸ Despite the fact that PB is the oldest known coordination compound, new properties in the field of magnetism and photomagnetism are still under study in this series of compounds.^{8,9} But since few attempts¹⁰ have been made toward the control of the morphology of the PB crystals, we have tried to induce the crystallization of Prussian Blue analogues beneath a Langmuir film by the so-called ionotropic effect¹¹ due to the electrostatic accumulation of ionic charges at specific sites on the organic substrate.

In our experiences, a compressed monolayer of a positively charged surfactant (dimethyldioctadecylammonium bromide, DODA) was used as a template for the formation of bimetallic cyanides by introducing equimolar solutions of $\{\text{K}_3\text{M}(\text{CN})_6 + \text{M}'(\text{ClO}_4)_2\} \times 10^{-4} \text{ M}$ ($\text{M} = \text{Fe, Co, Cr}$ and $\text{M}' = \text{Cu, Ni}$) in the subphase. The idea was to induce a locally high concentration of $\text{M}(\text{CN})_6^{3-}$ by electrostatic interactions with the densely packed cationic monolayer to facilitate the subsequent coordination of the M'^{2+} and therefore the formation of the bimetallic cyanides.

When one solution of $\{\text{K}_3\text{Fe}(\text{CN})_6 + \text{Cu}(\text{ClO}_4)_2\} \times 10^{-4} \text{ M}$ is used as a subphase, the DODA isotherm is shifted toward smaller areas per molecule, when compared to a pure water subphase (see Figure 1).

This effect clearly indicates the adsorption of anions along the interface, which counterbalances, at least partially, the repulsions between the headgroups.¹² Similar results were obtained with the other mixtures $\{\text{M}(\text{CN})_6^{3-} + \text{M}'^{2+}\} \times 10^{-4} \text{ M}$ ($\text{M} = \text{Fe, Co, Cr}$ and $\text{M}' = \text{Cu, Ni}$).

Right after compression (ca. 70 min after spreading), the monolayer was partially recovered onto grids (by

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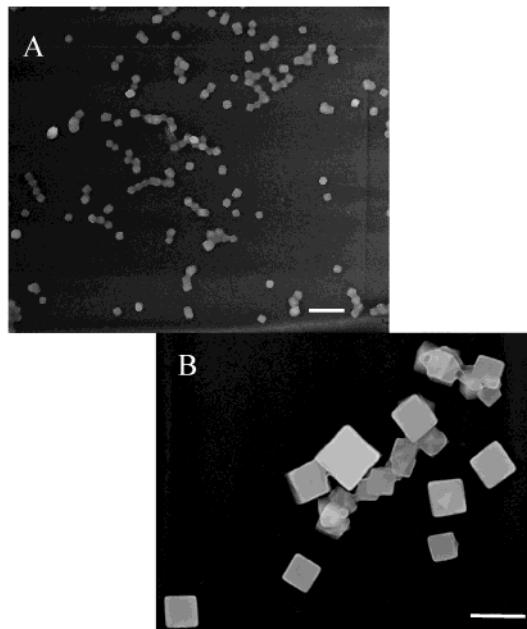


Figure 2. TEM images obtained from a Langmuir film over a solution in the subphase containing a mixture of (A) $\text{Fe}(\text{CN})_6^{3-}$ and Ni^{2+} and (B) $\text{Cr}(\text{CN})_6^{3-}$ and Cu^{2+} (scale bars 200 nm).

horizontal touching) and analyzed by transmission electron microscopy (TEM) (Figure 2) and X-ray energy-dispersive spectrometry (XEDS). Those samples show well-defined nanocubes having a size between 40 and 60 nm in the case of the $\{\text{K}_3\text{Fe}(\text{CN})_6 + \text{Ni}(\text{ClO}_4)_2\} \times 10^{-4}$ M subphase and between 50 and 200 nm for the $\{\text{K}_3\text{Cr}(\text{CN})_6 + \text{Cu}(\text{ClO}_4)_2\} \times 10^{-4}$ M subphase.

Some of those nanocubes have fused together but they are all oriented with one of the cube faces parallel to the surface, as expected, to maximize the electrostatic interactions between the positively charged monolayer and the surface of the nanocubes. XEDS analysis demonstrates that these crystallites contain the two metal ions dissolved in the subphase.

The nanocubes have been observed for all types of subphases and suggest that crystallization occurs along the Langmuir film. When a negatively charged monolayer (made of dihexadecyl phosphate) or a ionizable layer of behenic acid is used instead of the DODA film, no nanocube formation is observed. Therefore, the positively charged layer is necessary to obtain such nanocubes.

However, these crystallites may be formed either in the subphase and then adsorbed along the positively charged monolayer or during the partial recovering of the monolayer onto the TEM grid (due to the evaporation of subphase droplets dragged with the monolayer onto the grid). To check that the drying of the grid is not entirely responsible for the crystal growth, transfer of the Langmuir film by the Langmuir–Blodgett (LB) technique has been performed. Figure 3 shows that the same nanocubes in Figure 1 are observed by TEM, except that the perfect orientation (parallel to the substrate) is lost during the transfer. Therefore, those nanocrystals should be present under the DODA monolayer.

Analysis of the inorganic entities transferred onto the solid substrate was also performed using infrared

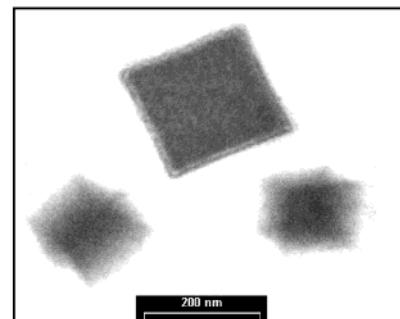


Figure 3. Nanocubes observed by TEM in a Langmuir–Blodgett film (one transferred layer) elaborated from a DODA monolayer spread over a mixture of $\text{Cr}(\text{CN})_6^{3-}$ and Cu^{2+} .

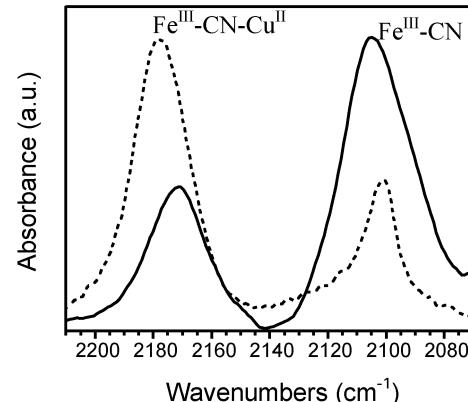


Figure 4. Infrared spectra of the powder obtained from a solution of $\{\text{Fe}(\text{CN})_6^{3-} + \text{Cu}^{2+}\} \times 10^{-2}$ M (solid line, Nujol dispersion), compared to the one of the LB film elaborated from a DODA monolayer spread on a solution $\{\text{Fe}(\text{CN})_6^{3-} + \text{Cu}^{2+}\} \times 10^{-4}$ M in the subphase (dashed line, CaF_2 substrate).

spectroscopy. Indeed, the elongation of the CN groups $\nu(\text{CN})$ gives rise to a very thin and intense band between 2000 and 2200 cm^{-1} .¹³ When the M–CN–M' bridges are formed, the $\nu(\text{CN})$ is shifted to a higher frequency. Following this band associated to bridging CN groups allows one to evaluate easily the formation of the PB derivatives.

The LB film obtained from a mixture of $[\text{Fe}(\text{CN})_6^{3-} + \text{Cu}^{2+}] \times 10^{-4}$ M in the subphase shows formation of $\text{Fe}^{3+}\text{–CN–Cu}^{2+}$ binding by the band at 2178 cm^{-1} (Figure 4). This spectrum presents one other band less intense at 2100 cm^{-1} , which corresponds to the $\text{Fe}^{3+}\text{–CN}$ stretching mode, compared to the one obtained of a film that contains only $\text{Fe}(\text{CN})_6^{3-}$. Such a result confirms the observation made by TEM, which is the formation/adsorption of the Prussian Blue analogue under the Langmuir film. IR spectra of the other mixtures $\{\text{M}(\text{CN})_6^{3-} + \text{M}'^{2+}\} \times 10^{-4}$ M (M = Fe, Co, Cr and M' = Cu, Ni) give similar results under the same conditions. Lower concentrations of ions in the subphase induce a relative decrease of the IR peak associated to bridging CN groups versus the band linked to nonbridging CN functions.

To compare those results with the bulk, we extracted the ions from aqueous solutions equivalent to the subphase by a phase transfer using a chloroform solution of DODA (see Experimental Section). After evapo-

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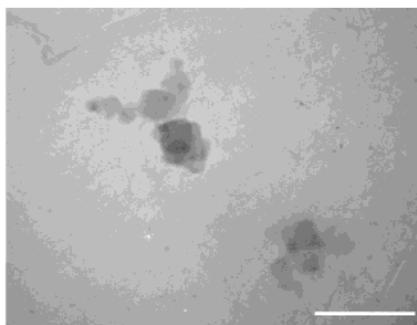


Figure 5. TEM image of the powder obtained by extraction of a $\{\text{Fe}(\text{CN})_6^{3-} \text{ and } \text{Cu}^{2+}\} \times 10^{-2} \text{ M}$ solution (see Experimental Section). This powder was redissolved in chloroform and spread on the TEM grid (scale bar 200 nm).

ration of the organic solvent, IR spectra were recorded to analyze the CN bands. The IR spectra have been recorded showing that, for the concentration of 10^{-4} M (with a delay between the preparation of the subphase and extraction equivalent to the one between the preparation of the subphase and the end of the LB transfer), the bridging cyanide band is very weak compared to the nonbridging CN peak. In fact, solutions 100 times more concentrated (10^{-2} M) than those in the Langmuir film experiments should be used to have clearly the band of the bridging CN groups (see Figure 4). Even for such a higher concentration, the IR band related to nonbridging CN groups is still the most important one, in contrast to the LB film. Therefore, the formation of the Prussian Blue analogue appears to be easier (or faster) along the Langmuir film than in the bulk.

Furthermore, observations (see Figure 5) by TEM of the extracted solid spread onto a grid by dissolution in chloroform suggest that the crystallization occurring in the bulk (in those experimental conditions) leads mainly to poorly defined crystals (even if few nanocubes are observed).

These results demonstrate, for the first time, that a Langmuir film can be used to induce the crystallization of molecular materials. This interfacial crystal nucleation appears at much lower concentrations of the precursor ions than in bulk, leading to nanocubes oriented parallel to the interface, which can be finally trapped in a thin film using the Langmuir–Blodgett technique, leading to new interesting hybrid materials. For example, preliminary magnetic measurements performed on LB films obtained from a mixture of $[\text{Fe}(\text{CN})_6^{3-} + \text{Cu}^{2+}] \times 10^{-4} \text{ M}$ in the subphase have

shown that a spontaneous magnetization appears at a Curie point of $22.5 \pm 1 \text{ K}$. This demonstrates that a ferromagnetic ground state is still present in those particular systems as in bulk material.⁸ Therefore, such experiments open new opportunities for selecting the crystalline phases of various molecular materials and therefore for controlling their physical properties.

Experimental Section

The cyanometalates, metal salts, and hydrogen dihexadecyl phosphate were obtained from Aldrich, behenic acid from Fluka, and dimethyldioctadecylammonium bromide from Kodak. All commercial compounds were used without further purification. Chloroform (HPLC grade from Prolabo) was used as a spreading solvent and the lipid solution (concentration ca. 10^{-3} M) was kept at $-18 \text{ }^{\circ}\text{C}$ during experiments to limit solvent evaporation.

Langmuir films were studied in a homemade trough already described.¹² The barrier is moved by a dc motor to perform a stepwise compression of the monolayer. After each increase of the surface pressure, a waiting time (5 min average) allows the system to reach its equilibrium. Steps of 2 mN/m were usually chosen and the temperature was maintained at $21 \pm 1 \text{ }^{\circ}\text{C}$. Millipore Q-grade water with a resistivity higher than $18 \text{ m}\Omega\text{-cm}$ was used for the subphases.

Langmuir–Blodgett films have been built up by the vertical lifting method with a dipping speed of ca. 0.5 cm/min . Films were transferred at a pressure of 30 mN/m onto optically polished calcium fluoride (precoated with three layers of behenic acid if necessary) to record the infrared spectra or onto copper grids previously stuck onto glass substrate for TEM analysis.

For the analysis of PB analogues formation in bulk, aqueous solutions of $\{\text{K}_3\text{M}(\text{CN})_6 + \text{M}'(\text{ClO}_4)_2\}$ at different concentrations (10^{-2} – 10^{-4} M) are maintained under agitation for 2 h (period corresponding to the delay between the preparation of the subphase and the elaboration of the LB film used for comparison between bulk and interfacial processes). Then a chloroform solution of DODA (from 10^{-2} to $5 \times 10^{-2} \text{ M}$) is added and the mixture is vigorously agitated for ca. 2 h . After separation of both phases (at this stage, the aqueous solution is colorless), the solvent of the organic solution is evaporated under reduced pressure until a solid product, which consists of surfactant encapsulating the inorganic ions, is obtained. The IR spectra of these powders are recorded in Nujol dispersions.

Transmission electronic microscopy has been carried out with a JEOL JEM 2000 FX. FTIR has been performed on a Nicolet 750 spectrometer.

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