

Photomagnetic molecular and extended network Langmuir-Blodgett films based on cyanide bridged Molybdenum-Copper complexes

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Supplementary Information

EXPERIMENTAL SECTION

Surfactants synthesis

The ligands syntheses were adapted from literature¹, cyclam_{C18} was already reported².

Tren_{C18}: N,N-bis(2-aminoéthyl)-N'-octadécyléthylènediamine).

7.4g of 1-bromooctadecane (22 mmol, 1 eq.) were added to a solution of tris(2-aminoethyl)amine (4.6 g, 4.75 mL), 31 mmol, 1.43 eq.) in 60 mL of anhydrous THF under an argon atmosphere. Heating the reaction mixture to reflux (80°C) for 4 hours produced a white opaque solution. After being cooled to r.t., a concentrated NaOH solution in water (1g/1mL) was added and the reaction was refluxed again overnight. Reaction was cooled down and 60 mL of distilled water were added, producing a white precipitate. The non-homogeneous mixture was solubilized with heat (60°C) enabling the quick separation of the organic phase. The aqueous phase was then extracted with diethylether (3 x 50mL) and combined with the previous organic phase which were evaporated and dried on vacuum.

¹H NMR (300 MHz, CDCl₃): δ = 0.89 ppm (t, *J* = 6.0 Hz, 3H, CH₃), 1.27 (broad s, 32H, CH₂ aliphatic chain), 2.53 (t, *J* = 6.0 Hz, 2H, N-CH₂-C₁₇H₃₅), 2.57-2.79 (m, 12H, CH₂ tren).

Film formation

For photomagnetic measurements, the monolayer was deposited onto transparent Melinex support. In order to obtain a hydrophilic surface, the support was previously treated with acid, mixture of sulfuric acid and hydrogen peroxide, and rinsed. In the case of **system 1**, the hydrophilic support was first immersed in the aqueous subphase containing [Mo(CN)₂(CN-Cu(tren))₆]⁸⁺ (abbreviated [Mo(Cu-tren)₆]⁸⁺) complexes. Then, the [Cu-tren_{C18}]²⁺ surfactant was cautiously added and the barriers were linearly compressed at a rate of 1mN/m/min with a maximum compression speed of 3 mm/min until the surface pressure corresponded to a continuous monolayer film of the desired species. Transfer ratios are close to 1, formed films are of Y-type. In the case of **system 2**, the aqueous subphase contained the K₄[Mo(CN)₈] complex, and [Cu-cyclam_{C18}]²⁺ was used as the surfactant. The support was then lifted and the process iterated to get films of various thicknesses, from the monolayer up to 51-layers films. Transfers took place both during the upstroke and downstroke.

In the case of **system 1**, different types of experiments were carried out in order to test the system. Results described in the paper reflect the most efficient and reliable system that was found during those tests.

First, the nature of the “MoCu” species present in the subphase was studied. The system 1 presented above consists in the presence of [Mo(Cu-tren)₆]⁸⁺ complexes in the subphase, obtained either by dissolution of crystals or by *in situ* synthesis from the addition of 1 eq of

$K_4[Mo(CN)_8]$ with 6 eq of $[Cu-tren](ClO_4)_2$. When varying the number of $[Cu-tren](ClO_4)_2$ equivalent, other complexes can be obtained: $[Mo(Cu-tren)_x]$ ($x=1$ to 5). Adding the $[Cu-tren_{C18}]^{2+}$ surfactant to these different subphases produced various isotherms showing only partial condensation of the precursors. However, the coupling of the $K_4[Mo(CN)_8]$ species with the $[Cu-tren_{C18}]^{2+}$ surfactant produced a very similar isotherm to the one obtained from the $\{[Mo(Cu-tren)_6]^{8+} + [Cu-tren_{C18}]^{2+}\}$ system. Only in this case IR spectra of the deposited species suggest the formation of a low nuclearity complex, probably the neutral $[Mo(Cu-tren_{C18})_2]$ species.

A different attempt consisted in trying to isolate the $[Mo(Cu-tren)_5(Cu-tren_{C18})]^{8+}$ species in order to use the molecule itself as a surfactant to be deposited on the substrate. To this end, crystals of the $[Mo(Cu-tren)_6](ClO_4)_8$ complex were synthesized and then dissolved in water, before being added to an excess of $[Cu-tren_{C18}](ClO_4)_2$ complex dissolved in chloroform. Stirring this solution for several hours produced a change of color (from blue to green) reflecting the metathesis of (most likely) one $[Cu-tren_{C18}]^{2+}$ fragment on the molecule. The organic phase was extracted and dried on magnesium sulfate, and this new $[Mo(Cu-tren)_5(Cu-tren_{C18})]^{8+}$ surfactant was spread on an aqueous phase containing 0.5M NaCl. Unfortunately, this system produced films of very poor quality that didn't allow us to go much further in the study.

INSTRUMENTATION

Monolayer films and deposition onto Melinex surface.

The aqueous sub-phase was poured on a Teflon Langmuir trough equipped with two opposing controllable barriers (KSV 2000 Langmuir-Blodgett system, KSV Instruments, max. working area 700 cm²). The temperature of the trough was controlled and set at 24 °C by a circulator imbedded in the trough. The surfactant was solubilized in chloroform and carefully deposited on the sub-phase with a Hamilton syringe, then allowed to equilibrate 15 min before compression. A paper Wilhelmy balance suspended from a microbalance (KSV Instruments) was used to record the surface pressure.

Brewster Angle Microscopy images were taken using a Nanofilm Technologie GmbH BAM2plus system with a KSV 2000 Langmuir-Blodgett system. The instrument is equipped with a polarized Nd:YAG laser (532 nm, 50 mW) and a CCD camera (572 x 758 pixels). All the experiments presented here were performed under the same conditions: objective x10; laser power: 50%; shutter speed: 1/50 s; polarizer and analyzer set at 0°.

[MoCu₂] NETWORK

Films of the MoCu₂ network was prepared by condensing the $[Cu-cyclam_{C18}]^{2+}$ complex with the $[Mo(CN)_8]^{4-}$ building-block, previously dissolved in the subphase (0.25 mM). The shape of the isotherm is dramatically different from the one obtained with the copper complexes with a NaCl solution (Figure S1). Thus, the surface pressure starts to increase for a lower value of the mean molecular area that indicates a higher condensed state that may result from the coordination network formation. The surface pressure increases linearly up to a collapse observed around 45 mN.m⁻¹. Formation of the coordination network is further evidenced by using Brewster Angle Microscopy (Figure 6 in the main paper). At zero surface pressure, the monolayer is in a liquid-expanded state. Upon compression, a continuous monolayer is formed. Consequently, the monolayer was transferred on silicon for Infra-Red. After 11 transfers, three narrows and intense stretches in the 2800-2900 range are observed and can be

ascribed to the alkyl chains of the copper complexes (Figure S2). Besides, a large band at 2100 cm^{-1} is also observed in the cyanide stretching region. This band is in very good accordance with the value observed for the bulk coordination network $[\text{Mo}(\text{CN})_8][\text{Cu}(\text{cyclam})]_2 \cdot 10.5\text{H}_2\text{O}$ and clearly indicates a coordination of the octacyanometallate moiety to the copper ion leading to the formation of a network at the air/water interface.

EPR spectroscopy was chosen to characterize the photomagnetic behavior of the LB films. The study was realized with a 31 layers film transferred onto melinex as a support (Figure S3). At 4 K, a large band is observed at $g = 2.08$, corresponding to the average Cu^{II} ions signals. A sharp band is also observed at $g = 2.00$ and can be ascribed to the presence of radicals from the melinex support. Upon irradiation, a strong decrease of the copper signal is observed as in system 1 and can be explained by a spin transition centered on the Mo^{IV} center that may eventually lead to an electron transfer between the molybdenum and the copper ions. The metastable state is at 4 K after irradiation indicating a long lifetime. The system was gradually warmed to room temperature in order to recover the original state. Based on these measurements, the relaxation temperature was found to be higher than 250 K. After warming the sample to room temperature, the EPR spectrum at 4 K is comparable to the original one before irradiation indicating an almost complete reversibility. Therefore, this indicates that the photomagnetic properties can be retained when deposited on a surface.

AFM studies performed on the 31 layers LB films show a relatively homogenous structure despite the presence of some defects (Figure S4). The thickness of the film was found to be between 25 and 30 nm which is slightly lower than the expected value.

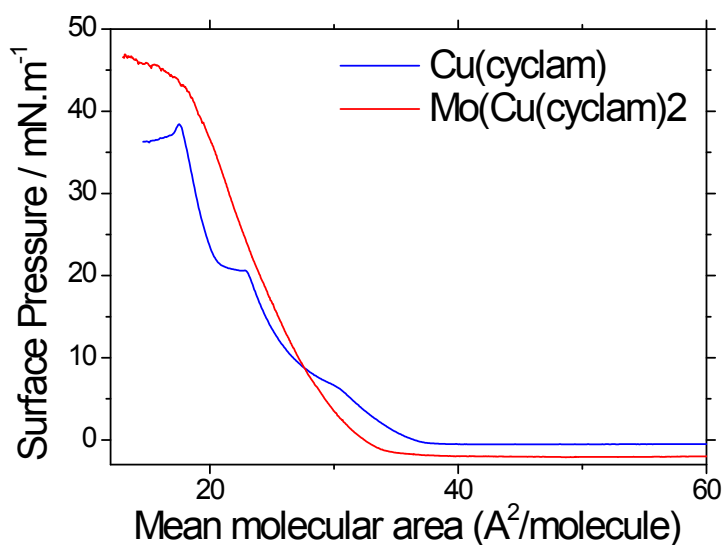


Figure S1: Pressure-area isotherm (21°C) for $[\text{Cu-cyclam}_{\text{C18}}]^{2+}$ (blue) and $[\text{Mo}(\text{Cu-cyclam}_{\text{C18}})_2]$ (red)

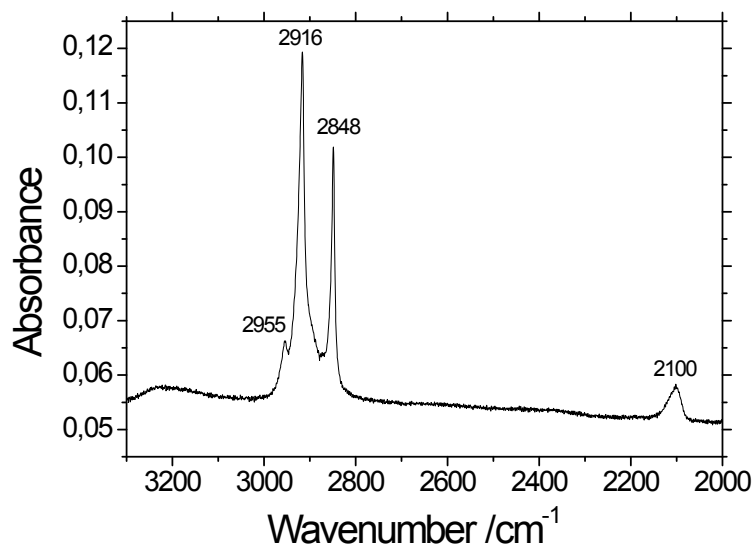


Figure S2: Infra-Red spectra (ATR) of the deposited 11 layers film of [MoCu₂-cyclam_{C18}].

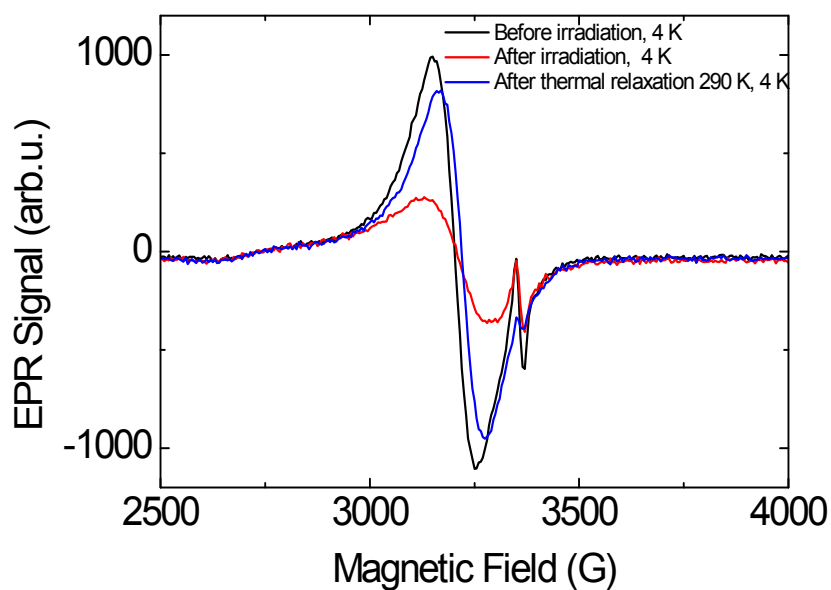


Figure S3: Evolution of the EPR spectra of a 31 layers film before irradiation (black), after irradiation (blue) and after thermal relaxation at 290 K (red).

Similar behavior was observed for the study of all samples (1, 11, 31 layer films), including the monolayer film of system 2.

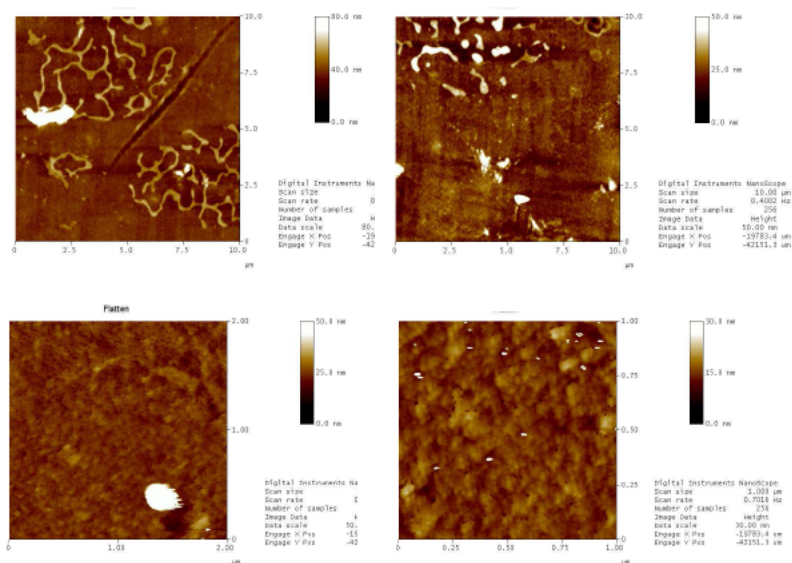


Figure S4: AFM images of the 31 layers film for two different areas ($10 \times 10 \mu\text{m}$).

The thickness of the 31 layer film of system 2 is around 25-30 nm, which is consistent with the number of layers deposited, relative to the length of the molecule ($\sim 1\text{nm}$).

¹a) Zhiming Zhang \AA Qiu Fu \AA Xiangqiu Li \AA

Xin Huang \AA Jiayun Xu \AA Jiacong Shen \AA Junqiu Liu, *J Biol Inorg Chem* (2009) 14:653–662 ; b) Anastasios Polyzos,[†] Andrew B. Hughes,* and John R. Christie, *Langmuir* **2007**, *23*, 1872-1879 ; c) ZHANG, Zhiming FU, Qiuan HUANG, Xin XU, Jiayun, LIU, Junqiu SHEN, Jiacong, *Chinese Journal of Chemistry*, **2009**, *27*, 1215–1220

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