PAPER

Photomagnetic molecular and extended network Langmuir–Blodgett films based on cyanide bridged molybdenum–copper complexes†

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Two types of cyanide bridged molybdenum–copper photomagnetic films have been obtained: the first one is based on a molecular [MoCu$_6$] complex, the other being a two-dimensional [MoCu$_2$] coordination network. Both systems employ surfactant functionalized ligands and films were deposited on Melinex substrates using the Langmuir–Blodgett technique. All systems, including monolayer films, showed full retention of the intrinsic photomagnetic properties known for analogous solids as demonstrated by EPR spectroscopy.

Introduction

New examples of photomagnetic compounds are attractive materials chemistry targets.[1,2] Such materials, capable of persistent photo-induced changes in their magnetization via processes such as spin crossover or charge transfer induced spin transition (CTIST), have received considerable attention in the last few years.[3–8] The ability to control the structure and morphology of these systems on the nanoscale has led to studies aimed at improving the photomagnetic properties and at better understanding photo-transformations.[9–14]

To go one step further, these light-switchable bistable compounds might be viewed as promising platforms for information storage through their integration in devices.[15–20] Among several smart photomagnetic materials being investigated, promising groups are the cobalt–iron Prussian blue analogues[21–23] as well as the molybdenum–copper octacyanometallates.[24–28] In both cases, light irradiation at low temperature induces an increase of the magnetization due to a transition from a diamagnetic to a paramagnetic or ferromagnetic state. With this in mind, photomagnetic networks and molecular analogues have been the subjects of numerous investigations. Recent attention has been devoted to the deposition of photo-switchable compounds on surfaces and whether their intrinsic properties are retained in thin films or in individual particles. Examples include studies of spin transition

compounds,[29–31] cyanometallate coordination polymers[32,33] and Prussian blue analogues on surface.[34–42] These systems sometimes exhibit significant changes of properties, such as an increase of the relaxation temperature[43] or surface induced magnetic anisoptopy.[44,45]

The main strategies for grafting discrete magnetic or photomagnetic molecules on surfaces involve functionalizing either the molecule itself or the surface[46] with anchoring linkers.[47,48] Other studies have also shown the possibility of depositing single-molecule magnets on surface using CVD[49,50] and lithographic methods.[51–59]

Langmuir–Blodgett deposition is another approach that affords a number of advantages when working with molecule-based systems.[16,60] One layer at a time deposition enables precise control of the film thickness and the ultrathin films are easily accessible by incident light sometimes leading to more efficient photo-induced processes as compared to the bulk. It is also possible to control the molecular orientation, which is of great importance when considering highly anisotropic systems; and the nature of the support can be easily changed without the need to develop new surface chemistry. Recently, examples of discrete complexes[61–65] or small clusters[66–69] have been deposited in monolayers through electrostatic association with a charged surfactant LB layer. On the other hand the more traditional approach to depositing active molecules, which is used in the current study, involves the direct functionalization of the compound so that the molecule itself is used as a surfactant to form the monolayer.[53,57,70,71]

The present study describes for the first time the deposition of molecular photomagnetic molybdenum–copper cyanometallate complexes onto a transparent support using Langmuir–Blodgett techniques. Molybdenum–copper cyanometallate complexes are generally prepared by self-assembling preformed copper complexes, [Cu–L]$^{2+}$, (L being an amino polydentate

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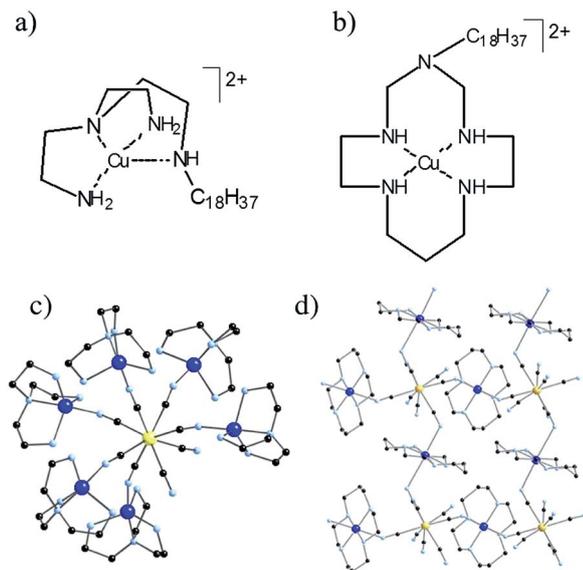
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Fig. 1 Copper complexes used as surfactant and related parent compounds (a) $[Cu-tren_{C18}]^{2+}$; (b) $[Cu-cyclam_{C18}]^{2+}$; (c) $[Mo(CN)_2(CN-Cu(tren))_6]^{8+}$; (d) 2D-$\{Mo(Cu-cyclam)_2\}_n$.

ligand) with an octacyanomolybdate complex, $[Mo(CN)_8]^{4-}$. In this study, the capping ligand of the copper ion was functionalized by an aliphatic chain, allowing the $[Cu-L_{C18}]^{2+}$ complex to act as a surfactant. Two ligands were used, the tetradentate amino ligands, $tren_{C18}$ (N,N-bis(2-aminoethyl)-N'-octadecylethane-1,2-diamine) and $cyclam_{C18}$ (N-octadecyl(1,3,6,10,13-)tetraazacyclotetradecane), which were considered because the parent ligands are known to form various stable $[MoCu_x]$ structures and examples of similar ligands forming 3d metal complexes have been reported.[72–77] In particular, the ligand $cyclam_{C18}$ has already been described in the literature as a nickel complex[78] although for different purposes. In the present work, these $[Cu-L_{C18}]^{2+}$ complexes were deposited on an aqueous sub-phase containing octacyanomolybdate-based moieties, allowing the *in situ* formation of molybdenum–copper cyanometallate complexes at the air/water interface of the Langmuir trough. Two different systems were obtained. First, the deposition of the $[Cu-tren_{C18}]^{2+}$ surfactant (Fig. 1a) on a sub-phase containing $[Mo(CN)_2(CN-Cu(tren))_6]^{8+}$ (abbreviated $[Mo(Cu-tren)_6]^{8+}$)[26] (Fig. 1c) enabled formation of discrete $[Mo(CN)_2(CN-Cu(tren))_5(CN-Cu(tren_{C18}))]^{8+}$ (abbreviated $[Mo(Cu-tren)_5(Cu-tren_{C18})]^{8+}$) species on the air/water interface (system 1). The second system used the $[Cu-cyclam_{C18}]^{2+}$ surfactant (Fig. 1b), which coupled to $[Mo(CN)_8]^{4-}$ in the sub-phase to form a network,$\{Mo(Cu-cyclam_{C18})_2\}_n$ (system 2, Fig. 1d). The photomagnetic characteristics of the parent complexes are shown to be retained in the monolayers.

Results

Formation and characterization of the films

Films were formed by condensing an octacyanomolybdate complex (either $[Mo(Cu-tren)_6]^{8+}$ or $[Mo(CN)_8]^{4-}$) with one of

the $[Cu-L]^{2+}$ surfactant. Specific design of these capping ligands allowed flexibility of the final structures. In order to deposit discrete molecular complexes, the ligand $tren_{C18}$ was synthesized from the common tren ligand (tren = tris-2-aminoethylamine), since its copper(II) complex is known to form polynuclear complexes with octacyanomolybdates, $[Mo(Cu-tren)_x]$ (x = 2, 4, 6) assemblies.[25,26] In a second experiment, the copper cyclam complex (cyclam = 1,4,8,11-tetraaza-cyclotetradecane) was used to target coordination of the octacyanomolybdate, dissolved in the sub-phase, on apical coordination sites of the Cu(II) complex, leading to a coordination network as presented on the scheme below (Fig. 2). The film formation of the two compounds is fully described in the ESI† as well as the complete characterization of system 2.

The starting $[Mo(Cu-tren)_6]^{8+}$ complex was chosen because of its remarkable photomagnetic response, a large increase of the magnetic moment after irradiation at low temperature which persists up to room temperature,[26] and because of its sufficient stability in solution. Before transferring to a solid support, the stability of the monolayer was investigated. First, a Langmuir trough sub-phase solution of $[Mo(Cu-tren)_6]^{8+}$ in 0.5 M NaCl was prepared, by either dissolving previously prepared crystals or by synthesizing the complexes *in situ*. The same results were obtained in both cases. The $[Cu-tren_{C18}]^{2+}$ complex used as a surfactant was then cautiously added on the top of the sub-phase. The surface pressure was gradually increased and the monolayer was monitored using pressure–area isotherms and Brewster angle microscopy.

System 1 is characterized in Fig. 3 with a comparison of the pressure–area isotherms of the surfactant $[Cu-tren_{C18}]$ with and without the $[Mo(Cu-tren)_6]$ complex in the 0.5 M NaCl subphase. The mononuclear complex $[Cu-tren_{C18}]$ does not form a stable monolayer on its own, collapsing below 10 mN m^{-1}. On the other hand, with the $[Mo(Cu-tren)_6]$ complex in the subphase, the monolayer is much better behaved. The pressure starts to increase at a smaller value of the surface area, 41 Å^2 per molecule instead of 45 Å^2 per molecule for the mononuclear copper complex, suggesting some preorganization, and the pressure rises more quickly. Brewster angle microscopy, Fig. 4, shows that the monolayer is fluid at low pressures, forming a continuous monolayer under applied pressures.

The monolayer can be transferred onto solid supports for characterization. Monolayer films were transferred on an ATR
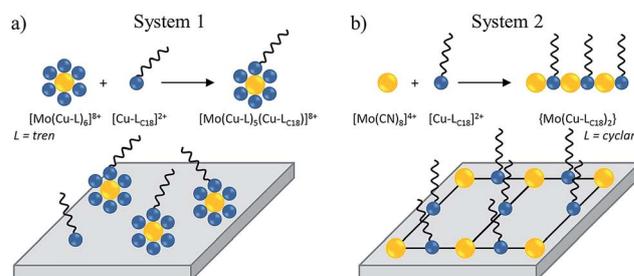

Fig. 2 Schematic formation of the films: (a) deposition of $[MoCu_6]$ entities; (b) formation of the $\{MoCu_2\}_n$ network.
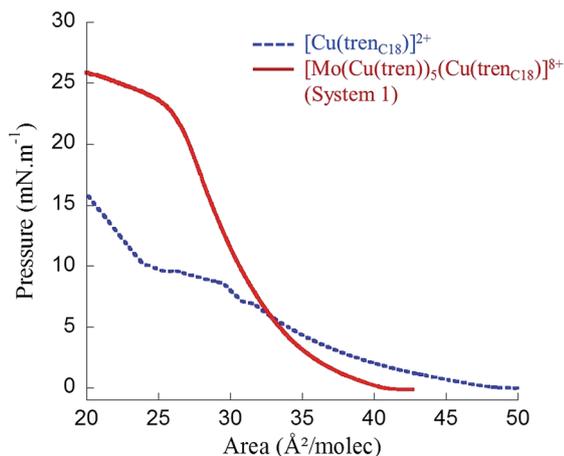
Fig. 3 Pressure−area isotherm (21 °C) for $[Cu–tren_{C18}]^{2+}$ (blue dashed line) and $[Mo(Cu–tren)_5(Cu–tren_{C18})]^{8+}$ (red line).
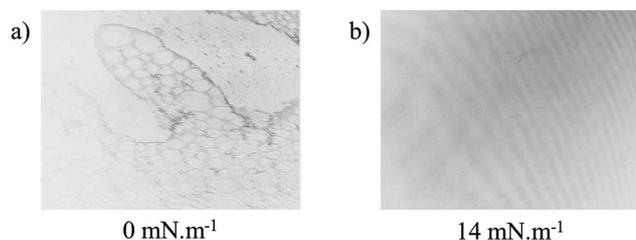

Fig. 4 Brewster angle microscopy images obtained at 24 °C for system 1: (a) with no surface pressure (b) under 14 mN m^{-1} surface pressure.

Fig. 5 Infra-red spectra (ATR) of the deposited $[MoCu_6]$ species (system 1): (a) monolayer; (b) three layers.

silicon crystal and the IR spectrum was recorded in the 3000–2000 cm^{-1} range (Fig. 5). Three narrow and intense stretches are visible at the highest wavenumbers, corresponding to alkyl chains of the surfactant: 2850 cm^{-1} (CH$_2$ symmetric elongation), 2920 cm^{-1} (CH$_2$ asymmetric elongation) and 2960 cm^{-1} (CH$_3$). The cyanide stretching modes are characteristic of the molecular cluster with two bands situated at 2111 cm^{-1} (terminal cyanides) and 2150 cm^{-1} (bridging cyanides), for which the positions and relative intensities correspond to the parent $[Mo(Cu–tren)_6]^{8+}$ complex. The same modes are present in the multilayer film as shown in Fig. 4b for three monolayers.

System 2 was prepared following similar procedures. The aqueous subphase contained the $K_4[Mo(CN)_8]$ complex, and $[Cu–cyclam_{C18}]^{2+}$ was used as the surfactant. In this case, BAM images indicate that discrete two-dimensional islands are formed at the air–water interface (Fig. 6) rather than a fluid monolayer as is normally seen for molecular films, such as it was observed in Fig. 4 for system 1. The figure shows objects with sharp edges and angles, indicating that upon interacting with the octacyanomolybdate complex, the surfactant condenses into a network. The behavior is similar to what was observed previously for cyanoferrate complexes when condensed into two-dimensional grids at the air–water interface.[33] To transfer the film, the Melinex support was then lifted
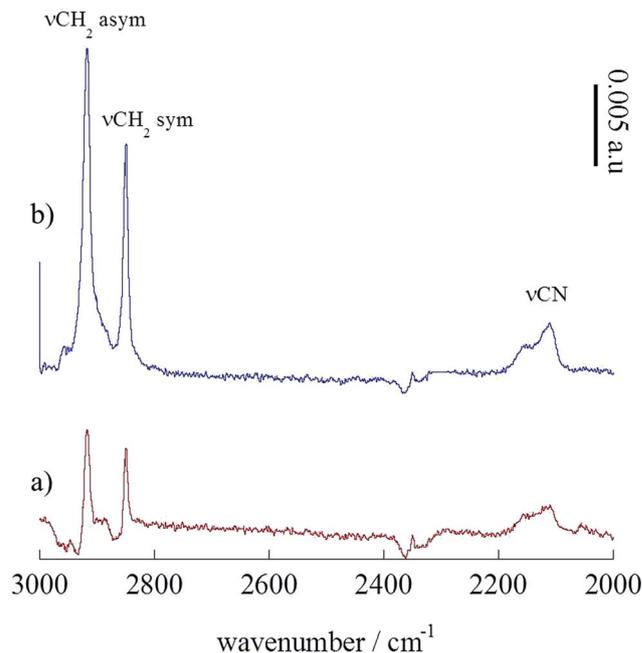
and the process iterated to get films of various thicknesses, from a monolayer up to 51-layers. Transfers took place both during the upstroke and downstroke. IR spectra on the transferred films suggest the presence of both free cyanide and bound cyanide, which is consistent with a similar Mo/Cu ratio to that of the MoCu$_2$–cyclam network compounds reported in the literature.[79,80] Together, the isotherms (Fig. S1†), BAM images (Fig. 6) and IR spectra (Fig. S2†) support formation of the $\{Mo(Cu–cyclam_{C18})_2\}_n$ network resulting from the complexation of the two precursors $[Mo(CN)_8]^{4-}$ and $[Cu–cyclam_{C18}]^{2+}$.

Photomagnetic properties

In the "molybdenum–copper" family of complexes, irradiation induces a dramatic change in the magnetization. In the case of $[Mo(Cu–tren)_6]^{8+}$, we reported[26] that before irradiation, the six coppers(II) centers are magnetically independent, as expected for diamagnetic Mo(IV) centred species. After irradiation, the
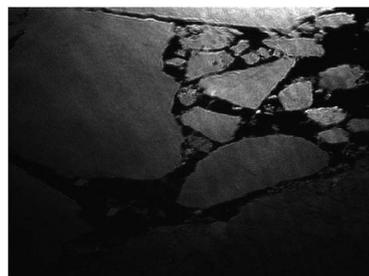

Fig. 6 Brewster angle microscopy images obtained at 24 °C for system 2 without surface pressure.

magnetic properties are found to be consistent with those of a high spin molecule with $S = 3$. This result can be explained by a spin transition located on the molybdenum center (Mo_{LS}^{IV}, $S = 0 \rightarrow Mo_{HS}^{IV}$, $S = 1/2$) associated with an electron transfer leading to a photo-induced high spin molecule, $Mo^{V}Cu^{I}Cu_5^{II}$ ($S = 3$), with ferromagnetic interaction between spin carriers. Importantly, the metastable state has a long lifetime, even at $T = 280$ K, and the phenomenon is fully reversible.

Because of its acute sensitivity, EPR spectroscopy was chosen to characterize the photomagnetic behavior of the LB films. The study was realized on films of different thickness, using Melinex as a support for its transparency. System 1 was studied on a 51 layer film (Y-type), and the results are depicted on Fig. 7. At first, the spectrum was recorded at 4 K, exhibiting an average Cu^{II} signal, symmetric and centered at $B_{res} = 3169$ Oe ($g_{iso} = 2.11$, black curve). The sharp band of smaller intensity situated at $B_{res} = 3340$ Oe corresponds to the presence of radicals formed on the Melinex substrate. Irradiation of the films was then carried out using a blue laser light ($\lambda = 405$ nm), close to the energy or the intervalence band of the previously described molecular $[Mo(Cu-tren)_6]^{8+}$ compound ($\lambda \sim 480$ nm). Upon irradiation, an immediate decrease of the signal intensity was observed, indicating that Cu^{II} ions are in a coupled state (Fig. 7, red curve). After approximately 10 min of irradiation the light was switched off and the compound was gradually warmed to 110 K, before being cooled down again. This new signal (green curve) is similar to the one recorded just after irradiation, reflecting the thermal stability of the phenomenon up to 110 K. Finally, the sample was warmed up to room temperature before being cooled again to 4 K, this time exhibiting complete relaxation of the system (the relaxation temperature is estimated at about 200 K). This photomagnetic behavior is very similar to the one observed during the EPR study of $[Mo(Cu-tren)_6]$ crystals, hence showing that the photomagnetic behavior is retained after *in situ* formation and deposition of the complexes onto a surface. The only noticeable difference between the LB film and the parent complex is that the Cu^{II} signal is not entirely quenched when irradiated. This can be explained by the presence of residual uncoupled $[Cu(tren_{C18})]^{2+}$ complexes on the surface of the films, which of course have no photo-response. However, Fig. 7 shows these species constitute a small percentage of the film sample that we have not been able to quantify.

The same experiment was performed on a monolayer film (Fig. 8). Results show an important contribution of the support, as well as a large signal attributed to residual $[Cu-tren_{C18}]^{2+}$ complexes (uncoupled to $[Mo(Cu-tren)_6]^{8+}$ species). Irradiation of the film under the same conditions as before produced a small decrease of the overall signal, which stabilized after 20 min of irradiation. Unlike the 51-layer film, only a small amount of the signal is affected by light irradiation. The difference between the two extreme signals shows the typical signal of Cu^{II} species ($g_{res} = 2.11$). This result indicates that the compound reacting to light irradiation is indeed the $[MoCu_6]$ compound grafted on the support, and not the support itself. This conclusion is supported by the fact that the signal attributed to radicals is unchanged under light irradiation.

Additional experiments were conducted using SQUID magnetometry at low temperature under irradiation, but unfortunately despite all our efforts the results significant enough due to the sensitivity of the technique.

Photomagnetic studies of the $\{Mo(Cu-cyclam_{C18})_2\}_n$ network (system 2) were carried out on films of 1, 11 and 31-layers obtained from the deposition of the monolayer on the same Melinex substrate. Evolution of the spectrum under irradiation was similar to system 1 (Fig. S3, ESI†), showing an important diminution of the Cu^{II} signal under photo-excitation, indicating the coupling of Cu^{II} through the molybdenum centers. Once again, the relaxation temperature is high (250 K). This particular result demonstrates that, once deposited on surface, the $\{Mo(Cu-cyclam_{C18})_2\}_n$ network retains its photo-magnetic properties with results similar to those obtained on the bulk material, demonstrating the feasibility of photomagnetic
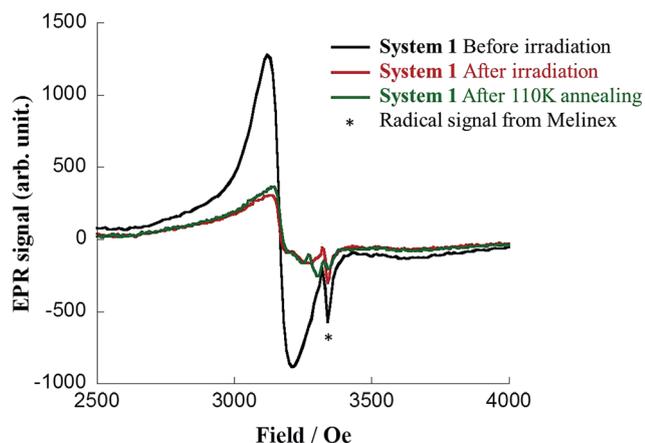

Fig. 7 Evolution of the EPR spectra of the formed films: before irradiation (black), under blue light irradiation (red) and after irradiation followed by 100 K annealing (green).
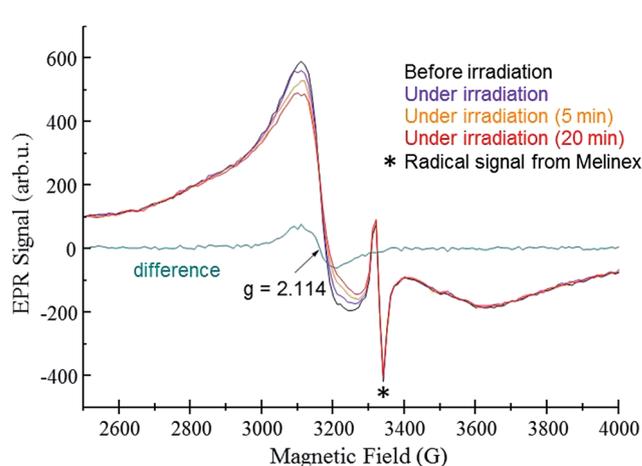

Fig. 8 Evolution of the EPR spectra of a monolayer film of [MoCu$_6$], and the resulting signal of the photoactive species.

switching in Langmuir–Blodgett thin films based on molybdenum and copper.

Conclusions

This work shows the successful deposition of molecular photomagnetic complexes [MoCu$_6$] onto a surface involving surfactant-functionalized ligands and using Langmuir–Blodgett techniques. EPR spectroscopy of the films shows the integrity of the compounds and retention of the photomagnetic properties, even at the monolayer scale. Furthermore, by changing the design of the capping ligand, a two-dimensional network, [MoCu$_2$], is formed at the air–water interface, which also exhibits photomagnetic properties. This work, that might be viewed as the first example of photo magnetic Mo–Cu Langmuir–Blodgett films, offers new prospects not only for the development of photomagnetic films but also for future applications to nanoscale magnetic devices.

Acknowledgements

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