Polyoxometalate Monolayers in Langmuir–Blodgett Films

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Abstract: Langmuir and Langmuir–Blodgett (LB) films of a variety of polyoxometalates of different shapes, sizes, and charges were prepared by taking advantage of the adsorption properties of these polyanions on a positively charged monolayer of an organic surfactant spread on water. Three different aspects were investigated. 1) The electrochemical and electrochromic properties of LB films containing the easily reducible polyoxoanion $[P_2Mo_{18}O_{62}]^{6-}$. Absorbance changes of these LB films deposited onto an ITO substrate have been induced by repeated switching of the applied potential. These changes are due to the formation of the colored reduced forms of the polyanion. Coloration and bleaching of the LB film occur very quickly and are reversible. 2) The preparation of LB films based on magnetic polyoxometalates, such as the Keggin anions, $[CoW_{12}O_{40}]^{6-}$ and $[SiMn(OH_2)W_{11}O_{39}]^{6-}$, or containing magnetic clusters of increasing nuclearities such as $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Co_4(H_2O)_2(P_2W_{15}O_{62})_2]^{16-}$ based on a Co_4O_{16} ferromagnetic cluster, and the polyoxometalates $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ and $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ based on a nonanuclear M_9O_{36} cluster. 3) The preparation of LB films of the giant heteropolyoxomolybdate, $[Na_3(NH_4)_{12}][Mo_{57}Fe_6(NO)_6O_{174}(OH)_3(H_2O)_{24}]\cdot 76\,H_2O$.

Keywords: electrochromism · Langmuir–Blodgett films · magnetic properties · monolayers · polyoxometalates

Introduction

Polyoxometalate anions (POMs) represent a large class of inorganic compounds that, thanks to their topological and electronic versatilities, have found applications in fields as diverse as catalysis, biology, medicine, and materials science.[1] Their structures can be depicted as molecular fragments of close-packed metal oxides of formula $X_aM_bO_c^{n-}$ (M = Mo, W, V, etc.; X = P, As, Si, Ge, B, Co, Fe, etc.).[2] One of the most important electronic properties of these metal oxide clusters is that they act as electron reservoirs. In fact, they are readily reversibly reduced by the addition of various specific numbers of electrons. The reduction products are mixed-valence species with a characteristically deep blue color ("heteropoly blues"). Another property of POMs is that of accommodating one or more paramagnetic d-transition metals at specific sites in the heteropoly framework. This produces complexes that have a magnetic character. These abilities, together with their solubility and chemical stability in both aqueous and nonaqueous solvents, make them very useful as the inorganic components of functional molecular materials. For instance, they have been combined with conducting radical salts based upon organic π-electron donors such as tetrathiafulvalene (TTF) and its derivatives to produce molecular materials, which show the coexistence of localized magnetic moments and itinerant electrons.[3] They have also been embedded in organic conductive polymers such as polypyrrole,[4] polyaniline,[5] polythiophene,[6]

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or poly(3-methylthiophene)[7] to afford hybrid materials of interest in electrocatalysis or as battery electrodes.

More recently the layer-by-layer method has been used to build hybrid inorganic–organic films of polyoxometalates and organic polymers.[8] This molecular self-assembly method relies on the electrostatic interaction between alternate layers of charged materials to produce multilayer films.[9] Some possible applications of these kind of multicomposite films have been presented. Thus, the polyoxometalate $[Co_4(H_2O)_2(P_2W_{15}O_{61})_2]^{16-}$ has been incorporated within multicomposite materials that can act as pH-sensitive probes or NO sensors.[10] Photoluminescent multilayer films of rare-earth-containing polyoxometalates have been prepared.[11]

A useful experimental tool to obtain multilayer films in a more controlled manner is the Langmuir–Blodgett (LB) technique. Indeed, this technique has been widely applied to create ultrathin films with a specific architecture that can be used as chemical sensors, modified electrodes, or molecular electronic devices.[12] In 1997 we discovered that the LB technique could also be used to organize polyoxometalate clusters. Thus, taking advantage of the adsorption properties of these anionic species along a positively charged monolayer of an organic surfactant spread in water, such as the dimethyldioctadecylammonium cation (DODA), we showed that LB films of Keggin POMs $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ (X^{n+} = $2(H^+)$, P^V, Si^{IV}, B^{III}, Co^{II}) can be obtained.[13] The monolayers of POMs alternate with bilayers of DODA in these organized lamellar structures to afford centrosymmetrical LB films. Similar results were obtained by Dong et al. two years later with the Dawson-Wells POM of formula $[Co^{II}(H_2O)P_2W_{17}O_{61}]^{8-}$, using the same method.[14] Afterwards, Kurth et al. combined DODA molecules with the high nuclearity heteropolyoxomolybdates $[H_3Mo_{57}V_6(NO)_6O_{183}(H_2O)_{18}]^{21-}$ and $[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$ to construct surfactant-encapsulated clusters that were subsequently spread on pure water to study the Langmuir and LB film formation.[15] In the last two years the group of Zhang has prepared LB films of rare-earth-containing polyxometalates to study their luminescence properties.[16] More recently, the synthesis of a bis(alkyl)-substituted amphiphilic polyoxometalate has allowed the preparation of LB films of polyoxometalates without using other amphiphilic molecules.[17]

In the present work we have extended the above semiamphiphilic method to insert a variety of polyoxometalates of different shapes, sizes, and charges between the organic layers. Three different aspects will be investigated, namely 1) the electrochemical and 2) electrochromic properties of LB films containing the easily reducible polyoxoanion $[P_2Mo_{18}O_{62}]^{6-}$ (**P_2Mo_{18}**, Figure 1c), and 3) the magnetic properties of LB films based on polyoxometalates of increasing nuclearities. Thus, polyoxometalates containing magnetic ions, such as the Keggin anions, $[CoW_{12}O_{40}]^{6-}$ (**CoW_{12}**, Figure 1a) and $[SiMn(OH_2)W_{11}O_{39}]^{6-}$, (**$SiMnW_{11}$**, Figure 1b), or magnetic clusters of increasing nuclearities, such as $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (**Co_4PW_9**, Figure 1d) and $[Co_4(H_2O)_2(P_2W_{15}O_{62})_2]^{16-}$ (**$Co_4P_2W_{15}$**, Figure 1e) that encapsulate a

Abstract in Spanish: *Se han preparado películas de Langmuir y Langmuir-Blodgett (LB) de una gran variedad de polioxometalatos de diferentes formas, tamaños y cargas. Se ha aprovechado las propiedades de adsorción de estos polianiones sobre una monocapa cargada positivamente de un surfactante orgánico dispersado en agua. Tres aspectos diferentes han sido investigados: 1) Las propiedades electroquímicas y electrocrómicas de películas LB de un polioxoanión fácilmente reducible como el* $[P_2Mo_{18}O_{62}]^{6-}$. *Se ha inducido cambios reversibles de la absorbancia de estas películas LB depositadas en ITO mediante la aplicación de un potencial de forma cíclica. Estos cambios son debidos a la formación de las especies reducidas fuertemente coloreadas del polianión. La coloración y decoloración de la película ocurren rápidamente y de forma reversible. 2) La preparación de películas LB basadas en los polioxometalatos magnéticos, como los aniones de Keggin,* $[CoW_{12}O_{40}]^{6-}$ *y* $[SiMn(OH_2)W_{11}O_{39}]^{6-}$, *o los que contienen clusters magnéticos de nuclearidad creciente como* $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ *y* $[Co_4(H_2O)_2(P_2W_{15}O_{62})_2]^{16-}$ *basados en el cluster ferromagnético* Co_4O_{16}, *y los polioxometalatos* $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ *y* $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ *basados en el cluster nonanuclear* M_9O_{36}. *3) La preparación de películas LB del heteropolioxomolibdato gigante,* $[Na_3(NH_4)_{12}][Mo_{57}Fe_6(NO)_6O_{174}(OH)_3(H_2O)_{24}]\cdot 76\,H_2O$.

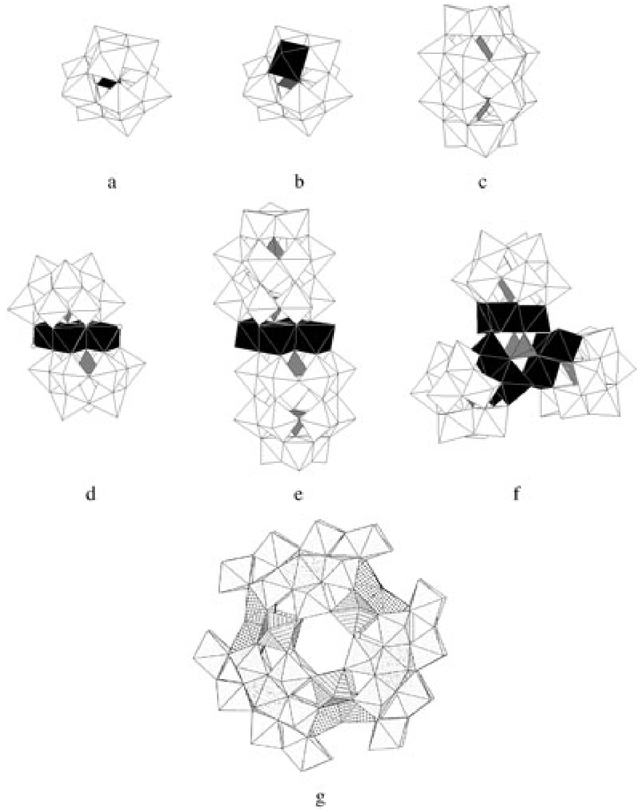

Figure 1. Molecular structures of the polyoxometalates used in this work.

Co_4O_{16} ferromagnetic cluster,[18] and $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ (**Co₉**) and $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ (**Ni₉**) that encapsulate a nonanuclear M_9O_{36} cluster (Figure 1f), were organized in LB films. Finally, we have used the giant heteropolyoxomolybdate $[Mo_{57}Fe_6(NO)_6O_{174}(OH)_3(H_2O)_{24}]^{15-}$ (**Mo₅₇**), which has a similar structure to the $[H_3Mo_{57}V_6(NO)_6O_{183}(H_2O)_{18}]^{21-}$ polyanion used by Kurth et al. to form Langmuir and LB films (see above) by a different strategy.[15a] This cluster is composed of three negatively charged $\{Mo_{15}(MoNO)_2O_{58}(H_2O)_2\}^{20-}$ units acting as bridging ligands for the cationic centers, which are six $\{Fe(H_2O)_6\}^{3+}$ and three dinuclear $\{Mo^V(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo^V\}^{9+}$ species (Figure 1g).[19]

Results and Discussion

Preparation and structural characterization: Whatever the exact nature of the polyoxometalate may be, a solution of the POM in water with a concentration in the range 10^{-5}–10^{-6} M was used as the subphase. On such a solution, the DODA isotherm is shifted towards smaller areas per molecule when compared with pure water. The isotherm recorded on a solution of $[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ (**Co₉**) in water is presented as a representative example in Figure 2. It shows a steep increase at the end of the compression that corresponds to a more dense packing of the DODA molecules than on pure water. This effect is general, even if the exact shape of the compression curves depends on the nature of the used polyanions, and arises from the adsorption of the polyoxometalate along the positively charged monolayers. Indeed, the interaction of the polyanions with the layer compensates the electrostatic repulsion occurring between DODA head groups, permitting a higher molecular density for a given surface pressure. Direct evidence of the adsorption of the POM on the positively charged monolayers is given by Brewster angle microscopy (BAM)[20] or by ellipsometry.[21]

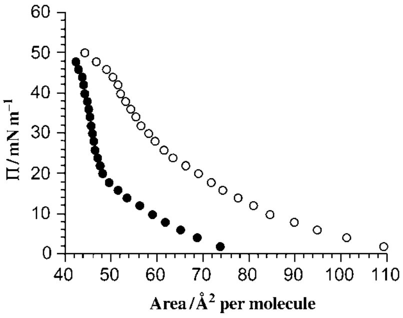

Figure 2. Compression isotherm of DODA on pure water (open circles) and on a solution **$Co_4P_2W_{15}$** in water (10^{-6} M; full circles) at room temperature.

The closer packing of the DODA monolayers spread on the POM solutions allows us to effectively transfer the Langmuir film onto a hydrophilic substrate with a maximum transfer ratio between 0.9 and 1 for a surface pressure of 30 mN m^{-1} and a dipping speed of 0.5 cm min^{-1}. Again, these experimental parameters appear to be independent of the exact nature of the dissolved anions. In all cases, the built-up LB film have no optical defects and common organization features, as demonstrated by infrared linear dichroism and X-ray diffraction experiments.

The infrared spectra of DODA/POM LB films are characterized by very strong bands below 1200 cm^{-1}, due to the presence of the polyanions (see the Supporting Information). These bands are narrower and generally slightly shifted in the LB films with respect to the spectra of polyanions in KBr pellets. This is due to the different organization of the polyanions in the LB films and to the lower hydration of the POMs in the multilayers. Indeed, whereas strong bands around 3300–3500 cm^{-1} and 1600–1650 cm^{-1} associated with the stretching and bending modes of water are observed for the pristine POMs in a KBr pellet, those bands are missing in the LB films, except for those that contain the giant polyanion $[Mo_{57}Fe_6(NO)_6O_{174}(OH)_3(H_2O)_{24}]^{15-}$ (**Mo₅₇**). In this last case the presence of coordinated water in the polyanion leads to a broad and weak band centered at 2900 cm^{-1}. The infrared spectrum of the DODA/**Mo₅₇** LB films also has a band at 1635 cm^{-1} that can be attributed to the ν(NO) stretching vibration of the $\{Mo(NO)\}^{3+}$ moiety. This band is narrower in the LB film and is shifted toward higher frequencies relative to the band observed for the NH_4^+ salt of the polyoxoanion at 1611 cm^{-1}. On the other hand, since the bands of the NH_4^+ counterions at 1400 cm^{-1} are missing in the IR spectra of the LB films, we can conclude that they are substituted by DODA molecules in the monolayers.

Another striking feature of the infrared spectra of the DODA/POM LB films is the strong out-of-plane dichroism. As an example, Figure 3 shows infrared spectra of a DODA/**Co₉** LB film. When the infrared electrical field is not parallel to the plane of the substrate, the intensities of the IR peaks are strongly modified and even new peaks clearly appear (see peaks in the range 900–1000 cm^{-1} and 750–850 cm^{-1}). This result shows that some transition dipoles associated with vibrations of the polyanions are oriented with respect to the normal of the substrate. The polyanions there-

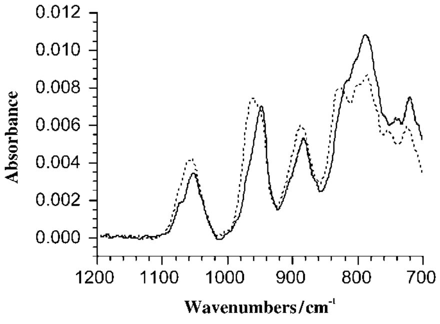

Figure 3. Infrared spectra of a DODA/**Co₉** LB film (20 layers) on zinc selenide. The angle between the plane of the substrate and the electric field is either 0° (solid line) or 60° (dashed line).

fore have a well-defined orientation within the LB film. The electrostatic interaction with the charged lipids should be responsible for such a particular organization within the multilayers. Finally, the position of the bands associated with the alkyl chains (at approximately 2920 and 2850 cm^{-1}) suggests that these chains adopt a fully extended all-*trans* conformation. The tilt angle of these hydrophobic tails with respect to the substrate normal can therefore be evaluated for various DODA/polyanion LB films (see Table 1). Small differences in the tilt angles of the alkyl chains appear between the smaller and less-charged Keggin anions and the other polyoxometalates. In the this case, angles of around 30° can be calculated,[13b] while for the larger polyanions used in this study these angles are in the range of 20–26° (see Table 1). Such a difference may be due either to the higher negative charge of these polyanions, or to their anisotropic shape.

Table 1. Tilt angle (ϕ; ±5°) of alkyl chains (determined by infrared dichroism), and periodicities (d, ±1 Å) of the layers (deduced from X-ray diffraction experiments) in DODA/polyoxometalate LB films.[a]

	$\mathbf{CoW_{12}}$	$\mathbf{Co_4PW_9}$	$\mathbf{Co_4P_2W_{15}}$	$\mathbf{Co_9}$	$\mathbf{Mo_{57}}$
ϕ [°]	34	20	24	23	26
d [Å]	48	52	43	43	45
max negative charge	6	10	16	16	15
ratio POM/DODA	5±1	10±1	20±2	20±2	16±2

[a] The ratio POM/DODA was calculated by comparing the amount of paramagnetic polyanions trapped within the LB film (calculated comparing magnetization of the LB film with magnetization of the parent polyoxometalate salt measured in powder) with the number of DODA molecules in the LB film (easily evaluated from the size of the substrate, transfer ratio and molecular area at the deposition surface pressure).

The lamellar structure of the hybrid DODA/POM LB films is clearly demonstrated by low-angle X-ray diffraction experiments. As an example, four Bragg peaks are identified in the X-ray diffractogram of a 100 monolayers $\mathbf{CoW_{12}}$-based LB film (Figure 4). Both Kiessig fringes and one Bragg peak corresponding to the (001) reflection are observed for samples with a lower number of monolayers (see the Supporting Information). The periodicity of the layers (d) calculated from the Bragg peaks leads to similar values for all the smaller polyoxometalates (close to 45 Å, see Table 1). From these results and taking into account the DODA length[22] and the calculated tilt angle of the alkyl tails, one can evaluate the thickness of the inorganic layer within the LB film (Δd). A value of approximately 10 Å is obtained for the smaller and more isotropic polyanions, such as the polyanions with the Keggin structure or the $\mathbf{Co_4PW_9}$ polyanion (Table 1).[13b] This value roughly corresponds to the thickness of the Keggin anion. Interestingly, this indicates that each inorganic layer is a monolayer of polyanions and not a bilayer as supposed for a Y-type transfer. The transfer occurring during the upper stroke should involve large changes concerning the polyanions adsorbed along the last monolayer deposited onto the solid substrate. This reorganization could be explained by the instability of a bilayer of negatively charged polyoxometalates. In fact, such a structure (based on inorganic layers trapped in between alkyl bilayers) has been recently found in a synthesized crystal of DODA and Lindqvist hexamolybdate anions.[23] As the $\mathbf{Co_4PW_9}$ polyanion has an anisotropic shape, this result also shows that this anion lies flat along the charged organic layers (Figure 5). Such organization favors stronger electrostatic interactions between the DODA layers and the polyanions. The calculated thicknesses for the inorganic layers of the LB films of the bigger and more anisotropic polyanions, $\mathbf{Co_4P_2W_{15}}$, $\mathbf{Co_9}$, and $\mathbf{Mo_{57}}$ are 5, 4, and 7 Å respectively. These values are too small with respect to the thickness of these polyanions (ca. 10 Å). This suggests the X-ray data are representative only of organized parts within the film that do not contain POM species. The lamellar structure of the LB films could be distorted by the presence of such big

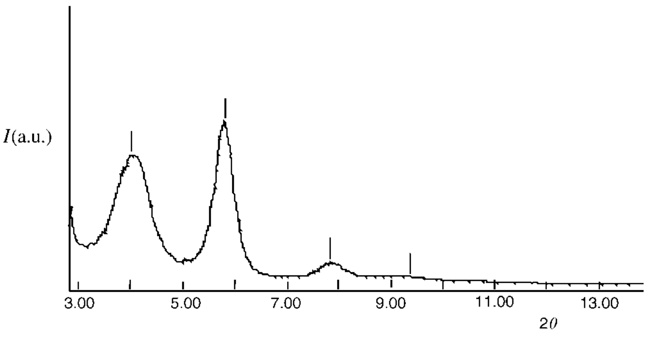

Figure 4. Low-angle X-ray diffractogram of a DODA/$\mathbf{CoW_{12}}$ LB film with 100 monolayers deposited on glass.

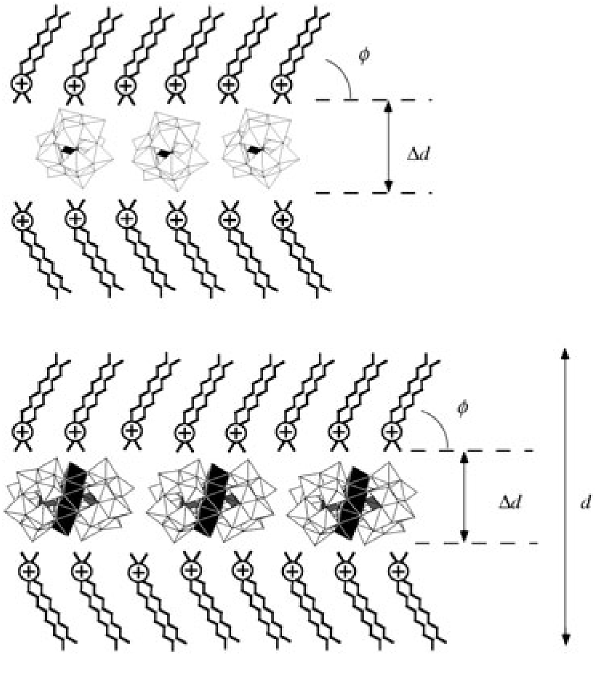

Figure 5. Schematic representation of the Y-type LB films with different polyanions; DODA/$\mathbf{CoW_{12}}$ (top) and DODA/$\mathbf{Co_4P_2W_{15}}$ (bottom).

polyanions. The organization of these DODA/POM LB films is therefore not as good as for the smaller POMs.

Finally, we can compare the structure of the LB films of **Mo$_{57}$** obtained by us with the semiamphiphilic method to that of the LB films of a similar POM $[H_3Mo_{57}V_6(NO)_6O_{183}(H_2O)_{18}]^{21-}$ prepared by Kurth by spreading a DODA salt of the POM on pure water.[15a] The average thickness of a monolayer of this LB film, as calculated from ellipsometry measurements, is 23 Å. This value is very similar to the periodicity, corresponding to a bilayer, obtained by us (45 Å). We can conclude, therefore, that both methods lead to similar results.

Electrochemistry and electrochromism: We have chosen the $[P_2Mo_{18}O_{62}]^{6-}$ ion as a representative example of the electrochemical properties of hybrid DODA/POM LB films, because the electrochemical properties of this polyanion have been studied extensively, both in solution[24] and absorbed on many substrate surfaces.[25] In solution it shows three prominent two-electron reductions that occur at relatively high potentials, at which the reduction of protons does not occur.

The cyclic voltammetric response of LB films of the polyanion deposited onto ITO electrodes is shown in Figure 6. Three well-defined sets of reversible peaks are observed. The potentials of these three peaks are close to those exhibited by the polyanion in solution. The voltammetric response remained unchanged after dozens of potential cycles. Therefore, desorption of the polyoxometalates from the multilayer assembly is excluded. The response of the cathodic peak current around 350 mV versus SCE on the number of deposited layers shows a linear dependence. This indicates that the transfer of polyanions is homogeneous during the all LB film preparation. Furthermore, it shows that the reduction of the polyanions occurs even in the presence of the insulating DODA layers. This feature has already been observed in the LB films of DODA and prussian blue and was explained by the presence of defects in the DODA layers.[26]

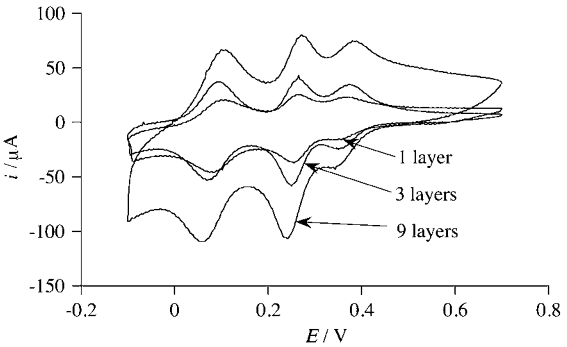

Figure 6. Cyclic voltammograms of DODA/$[P_2Mo_{18}O_{62})]^{6-}$ LB films with 1, 3, and 9 monolayers in aqueous 0.5 M $NaHSO_4$. Scan rate 0.5 V s^{-1}.

The intense absorbance of the reduced forms of the polyanion, responsible for its blue color, is well known. This property gives rise to electrochromism. The reversibility and stability of the electrochromic properties associated with the reduction of the polyoxometalates have been determined by spectroelectrochemical potential step experiments. We report the absorbance changes of a five-layer LB film of the polyanion at 700 nm induced by repeated switching of the applied potential (Figure 7). On increasing the potential from −0.3 V to 0.5 V, the absorption at 700 nm increases due to the formation of the colored reduced form of the polyanion, as reported for deposited films of this polyanion.[25] As one can see, coloration and bleaching of the LB film occur very quickly and are reversible. Electrochromic thin films of $(NH_4)_{11.5}K_{0.5}[Eu(OH_2)P_5W_{30}O_{110}]\cdot 24H_2O$ were also obtained by the layer-by-layer method.[8e] These films have larger changes in absorbance and a better reversibility than the LB films of the $[P_2Mo_{18}O_{62}]^{6-}$ ion. Two possible explanations can be given: 1) the higher number of monolayers deposited for the layer-by-layer films and 2) the more flexible and porous structure of these films which could facilitate the adsorption or release of ions during the redox cycles.

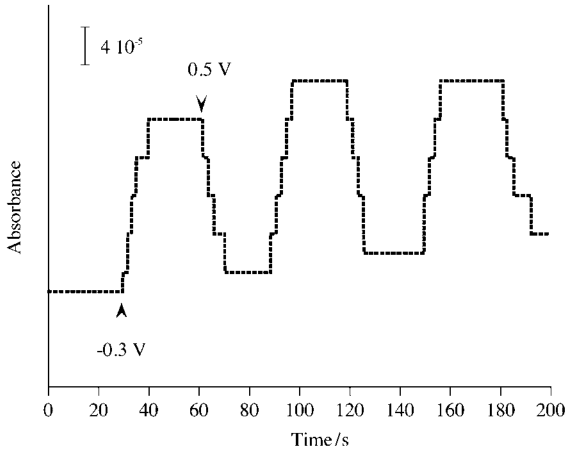

Figure 7. Absorbance changes of a DODA/$[P_2Mo_{18}O_{62})]^{6-}$ LB film with five monolayers at 700 nm after step potential changes between −0.3 and 0.5 V.

Magnetic properties: Magnetic LB films have been constructed by using polyoxometalates with a Keggin structure encapsulating magnetic ions in the tetrahedral site in a first step. A representative example is provided by $[CoW_{12}O_{40}]^{6-}$, which contains high-spin Co^{II} in the tetrahedral site.[13a] The magnetization of the LB film was measured after deposition onto a diamagnetic substrate. The magnetization of the DODA/$CoW_{12}O_{40}$ LB film is, within the experimental error, identical to that reported for the $K_5H[CoW_{12}O_{40}]$ salt (Figure 8 top). Thus, it exhibits Curie law behavior until approximately 20 K and, at low temperature the magnetic moment decreases due to the zero-field splitting of Co^{II} in a

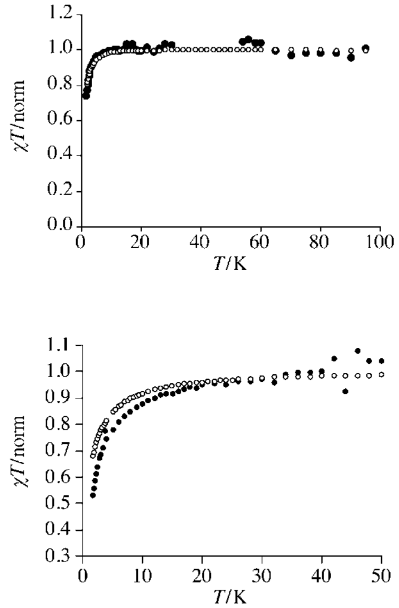

Figure 8. Top: Plot of χT (normalized value) versus T for the $K_5H[CoW_{12}O_{40}]$ polyanion in powder (empty circles) and for the DODA/**CoW_{12}** LB film (full circles). Bottom: Plot of χT (normalized value) versus T for the $K_6[SiMn(OH_2)W_{11}O_{39}]$ polyanion in powder (open circles) and for the DODA/**$SiMnW_{11}$** LB film (full circles). All data concerning the LB film are corrected from the substrate diamagnetism and points around 40 K associated with adsorbed oxygen were deleted.

tetrahedral environment.[27] From such experiments it appears that the magnetic site of such polyanions encapsulated in the LB film is insensitive to the surrounding charge associated with the DODA molecules. On the other hand, these measurements are useful to calculate the amount of paramagnetic polyanions trapped within the LB film. The number of DODA molecules in the LB film is easily evaluated from the size of the substrate, transfer ratio, and molecular area at the deposition surface pressure. By comparing these two values, the ratio between the number of DODA molecules and polyanions in the LB film is found close to 5 ± 1. Such a value is close to the maximum charge of the $K_5H[CoW_{12}O_{40}]$ polyanion (i.e., −6).

In a second step, Keggin polyanions that contain coordinating 3d-transition-metal ions in the octahedral sites located at the surface of the cluster were used. These monosubstituted anions can be considered as being derived from the nonsubstituted Keggin anions $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ by simple replacement of one of the external constituent atoms and its terminal oxygen atom by a 3d-transition-metal atom (Z) and a water molecule, respectively. The polyanion used to construct the corresponding paramagnetic LB film was the $[SiMn(OH_2)W_{11}O_{39}]^{6-}$ ion (in short **$SiMnW_{11}$**). The magnetic behavior of the DODA/$SiMnW_{11}$ LB film is slightly different from that of the $K_6[SiMn(OH_2)W_{11}O_{39}]$ powder. Thus, below 20 K, the decrease of χT appears to be more important in the LB film (Figure 8 bottom), suggesting the presence of stronger antiferromagnetic interactions in the LB film. This result is in contrast to what is observed in the $[CoW_{12}O_{40}]^{6-}$ case, and may be due to less magnetic insulation provided by the polyoxometalate framework in the Mn derivative.

In a third step, the above method was extended to polyanions of higher nuclearity and more interesting magnetic properties. Thus, the magnetic polyoxoanions $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ were used to construct magnetic LB films.[28] These polyoxoanions are of magnetic interest, since they contain the magnetic Co_4O_{16} cluster encapsulated between two polyoxotungstate moieties $[PW_9O_{34}]^{9-}$ and $[P_2W_{15}O_{56}]^{12-}$ (Figure 1). The ions are ferromagnetically coupled in the magnetic cluster, giving rise to a highly magnetic ground state.[29] The magnetic properties of the corresponding LB films are plotted in Figure 9. In both cases the χT product shows a sharp increase below 50 K upon cooling, and a maximum at approximately 6.5 K. Below this temperature, the χT product shows a decrease due to the magnetic anisotropy of the cluster. Such behavior is completely analogous to that observed in the potassium salt of the corresponding polyanions and demonstrates that the ferromagnetic cluster is maintained within the LB film. From such measurements, and by comparison with the potassium salt, the amount of magnetic polyanions trapped within the LB film was calculated. Again the calculated ratio DODA/polyanions is close to the charge of the polyanion (see Table 1). Interestingly, these two films also show magnetic anisotropy in their EPR properties. The study of the low-temperature EPR behavior of the LB films of both polyanions ($[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$) deposited onto a quartz substrate is shown in Figure 10 for two different orientations of the applied magnetic field (perpendicular or parallel to the normal of the substrate). A signal centered at 500 G is observed, in close coincidence with powder measurements. This signal depends slightly on the orientation of the LB film with respect to the external magnetic field. Thus, when the magnetic field is perpendicular to the normal of the substrate, the intensity of the signal is lower and the signal is displaced towards higher fields. This effect is more pronounced in the Dawson–Wells derivative $[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$. To un-

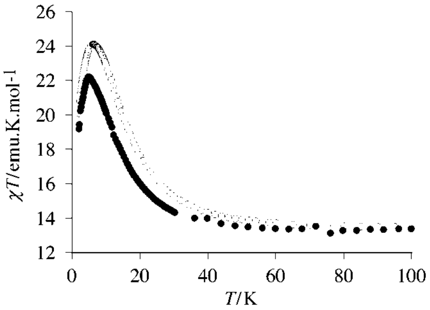

Figure 9. Plot of χT versus T for the $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$ polyanion (empty circles) and for the DODA/**Co_4PW_9** LB film (full circles). The magnetization of the LB film was normalized to the powder measurement.

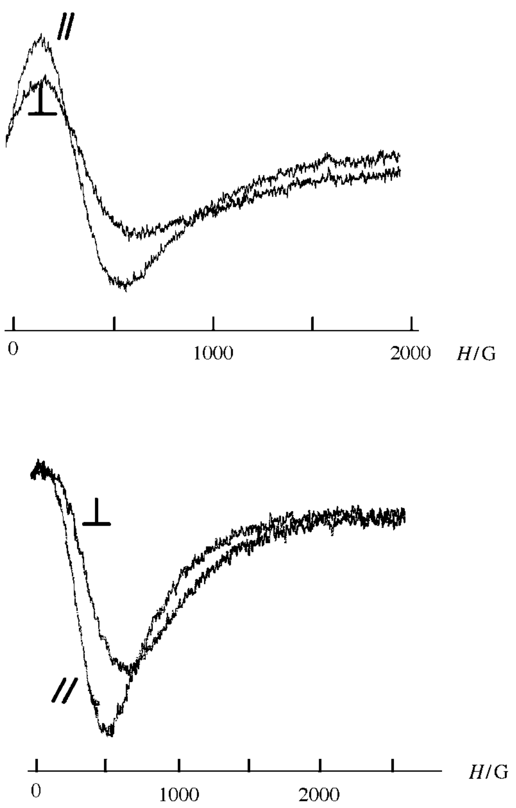

Figure 10. EPR spectra of DODA/$\mathbf{Co_4PW_9}$ (top) and DODA/$\mathbf{Co_4P_2W_{15}}$ (bottom) LB films.

derstand these results we have to take into account that, although the clusters can be randomly oriented within the plane, the interlayer spacing is fixed and prevents the cluster to be oriented with their longer axis perpendicular to the plane of the monolayer. This restricted orientation of the magnetic clusters also explains why the magnetic anisotropy is more pronounced in the $[Co_4(H_2O)_2(P_2W_{15}O_{56})]^{16-}$ ion. As this anion is much longer than the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ ion, the out-of-plane orientation of this cluster is more difficult to achieve. In conclusion, the presence of anisotropy supports the restricted orientation of these anions within the monolayer, as was also suggested from IR linear dichroism and X-ray diffraction studies.

It is possible to increase the nuclearity of the polyanions by using the $[M_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ (M_9, M=Ni, Co) ions. These polyanions contain a central M_9O_{36} cluster formed by three triangular M_3O_{13} edge-sharing units. These triangles are connected to each other by three OH^- bridging groups and two central HPO_4^{2-} moieties (Figure 1). The magnetic properties of these clusters can be explained by the coexistence of ferromagnetic interactions within the triangles and antiferromagnetic intertriangle interactions. In the case of the Ni_9, the increase of χT down to 25 K indicates the presence of dominant ferromagnetic interactions, while the sharp decrease at lower temperatures is a consequence of the antiferromagnetic intertriangle interactions that give rise to a nonmagnetic ground state.[30] The $\mathbf{Co_9}$ ion also shows a similar coexistence but, in this case, the former interactions are dominant, giving rise to a continuous decrease in χT.[31] The magnetic properties of the LB films of both clusters are similar to powder measurements of the salts $K_5Na_{11}[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]\cdot 52\,H_2O$ and $K_{11}Na_5[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]\cdot 30\,H_2O$ (Figure 11). The calculated ratio between DODA molecules and polyanions is again close to the charge of the polyanions (−16).

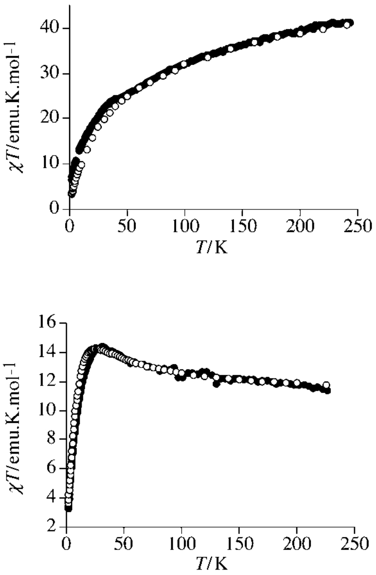

Figure 11. Top: Plot of χT versus T for the $K_{11}Na_5[Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]\cdot 30\,H_2O$ polyanion (empty circles) and for the DODA/$\mathbf{Co_9}$ LB film (full circles). Bottom: Plot of χT versus T for the $K_5Na_{11}[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]\cdot 52\,H_2O$ polyanion (empty circles) and for the DODA/$\mathbf{Ni_9}$ LB film (full circles). The magnetization of the LB films was normalized to the powder measurement.

We have also studied the magnetic properties of LB films of the giant polyanion $[Mo_{57}Fe_6(NO)_6O_{174}(OH)_3(H_2O)_{24}]^{15-}$ ($\mathbf{Mo_{57}}$). This polyanion contains three $\{Mo^{VI}_{15}(MoNO)_2O_{58}(H_2O)_2\}^{20-}$ units that are diamagnetic, six paramagnetic $\{Fe^{III}(H_2O)_6\}^{3+}$ units and three dinuclear $\{Mo^V(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo^V\}^{9+}$ units that are diamagnetic due to a strong antiferromagnetic coupling. Therefore, the χT value of the $[Na_3(NH_4)_{12}][Mo_{57}Fe_6(NO)_6O_{174}(OH)_3(H_2O)_{24}]\cdot 76\,H_2O$ salt is close to the expected value at high temperatures for six high-spin Fe^{III} units, and decreases sharply below 100 K due to weak antiferromagnetic interactions between the Fe^{III} ions.[32] The magnetic properties of the LB film are very similar to powder measurements (see Figure 12). The calculated ratio between DODA molecules and polyanions is again close to the charge of the polyanions (see Table 1).

Conclusion

After our first communication showing that Keggin polyoxometalate anions can be organized as monolayers using the LB technique,[13a] we have shown here that this approach is

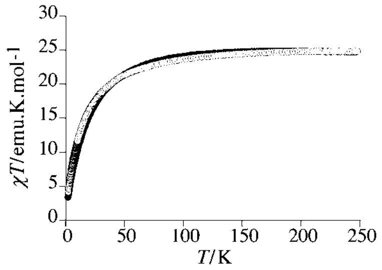

Figure 12. Plot of χT versus T for the $[Na_3(NH_4)_{12}][Mo_{57}Fe_6(NO)_6O_{174}(OH)_3(H_2O)_{24}]\cdot 76\,H_2O$ polyanion (empty circles) and for the DODA/**Mo_{57}** LB film (full circles). The magnetization of the LB films was normalized to the powder measurement.

general for many polyoxometalates. Thus, we have used the adsorption properties of polyoxometalates on a positively charged monolayer of DODA to construct new organic–inorganic LB films. We have demonstrated that through use of the LB technique it is possible to organize polyoxometalates of different sizes, shapes and charges in monolayers. The lamellar structure of the hybrid DODA/POM LB films is clearly demonstrated by low-angle X-ray diffraction experiments. The structure of the LB films of the smaller polyoxometalates is constituted of monolayers of polyoxometalates intercalated between bilayers of DODA. Interestingly, each inorganic layer is a monolayer of polyanions and not a bilayer as supposed for a Y-type transfer. The thickness of the inorganic layer of the biggest and more anistropic POM is too small even for a monolayer. This suggests that the organization of these larger POMs within the LB films is not as good as for the smaller ones. The lamellar structure of the films is distorted by the presence of such big polyanions. X-ray data are representative only of those organized parts of the film that are far from the POMs.

An appropriate choice of the polyoxometalate has allowed the preparation of LB films that exhibit electrochromic or magnetic properties. Thus, the heteropolymolybdate, $[P_2Mo_{18}O_{62}]^{6-}$, which can accept electrons reversibly to give rise to colored "heteropolyblues", has been used to build an electrochromic film in which coloration and bleaching occur very quickly and reversibly. On the other hand, we have reported the first example of organized LB films formed by alternating monolayers of polyoxometalate clusters that possess high magnetic moments. Due to the good magnetic isolation of the magnetic ions, the magnetic properties of the clusters are not affected, or only weakly affected by their organization in monolayers. EPR measurements of LB films of two anisotropically shaped polyoxometalates containing ferromagnetic Co_4 clusters have shown that the EPR signal depends on the orientation of the LB film with respect to the external magnetic field. The observation of such anisotropy is in agreement with the restricted orientation of the clusters within the monolayer suggested by IR linear dichroism and X-ray diffraction studies. Finally, we have extended this method to prepare LB films of the giant heteropolyoxomolybdate, $[Mo_{57}Fe_6(NO)_6O_{174}(OH)_3(H_2O)_{24}]^{15-}$. This proves that the semiamphiphilic method developed by us to build-up LB films of POMs is a general method that is not limited by the size or the charge of these inorganic anions.

Experimental Section

The following heteropolyoxometalate salts were used. They were synthesized according to previously reported procedures:[19,30,31,33] $K_5H[CoW_{12}O_{40}]\cdot 15\,H_2O$,[33a] $K_6[SiMn(OH_2)W_{11}O_{39}]$,[33b] $Na_6[P_2Mo_{18}O_{62}]\cdot 24\,H_2O$,[33c] $K_6[P_2W_{18}O_{62}]$,[33d] $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot 22\,H_2O$,[33d] $Na_{16}[Co_4(H_2O)_2(P_2W_{15}O_{56})_2]$,[33d] $K_{11}Na_5[Co_9(H_2O)_6(OH)_3(HPO_4)_2(PW_9O_{34})_3]\cdot 30\,H_2O$,[31] $K_5Na_{11}[Ni_9(H_2O)_6(OH)_3(HPO_4)_2(PW_9O_{34})_3]\cdot 52\,H_2O$,[30] and $[Na_3(NH_4)_{12}][Mo_{57}Fe_6(NO)_6O_{174}(OH)_3(H_2O)_{24}]\cdot 76\,H_2O$.[19]

Chloroform (HPLC grade from Prolabo) was used as spreading solvent and the lipid solutions (concentration approximately 10^{-3} M) were kept at −18 °C during experiments in order to prevent solvent evaporation.

Built-up films were obtained by the vertical lifting method using a custom-made LB trough at room temperature under a continuous dry-nitrogen flow.[13b] A step-by-step compression of the monolayer (steps of $2\,mN\,m^{-1}$ were chosen) was performed in order to reach the transfer surface pressure. A waiting time (20 to 30 minutes on average, after each increase of the surface pressure) allowed the system to reach its equilibrium. The subphase was Millipore Q-grade water with a resistivity higher than 18 MΩcm. Dipping speed was set to $0.5\,cm\,min^{-1}$. Films were transferred onto optically polished calcium fluoride (precoated with three layers of behenic acid if necessary) or zinc selenide for infrared measurements and onto optically polished glass substrate (treated with dichlorodimethylsilane) for low-angle X-ray experiments.

Infrared (IR) spectra were recorded on a FTIR 750 Nicolet spectrometer. To determine the orientation of the molecules in the LB films, linear infrared dichroism was used. Two spectra were recorded: one with the incident light parallel to the substrate normal and a second one with the incident IR beam forming an angle of 60° with the substrate normal. The out-of-plane dichroic ratio β for each band was then defined as the ratio between both spectra: $\beta(60°) = A_{\parallel}(60°)/A_{\parallel}(0°)$in which A is the absorption of the IR band with the electrical field perpendicular to the rotation axis of the sample. The angle ϕ between the substrate normal and a transition dipole moment of a particular vibration can then be evaluated (with a precision of ca. 5°) from the β value using a model already published.[34]

X-ray diffraction patterns were obtained by using a conventional generator (Kristalloflex Siemens Ltd) delivering non-monochromatized line-focused $Cu_{K\alpha}$ radiation. This beam passes through the sample (100 layers deposited on glass, mounted vertically and oscillated during exposure). The integrated intensities of the Bragg reflections were collected by an INEL CPS 120 curved position-sensitive detector (with a resolution of 0.1° in 2θ) associated with an IBM computer for peak assignments. A Philips X'Pert PRO MRD diffractometer, equipped with a curved graded multilayer mirror and a four-crystal Bartels-type Ge (220) monochromator, with $Cu_{K\alpha}$ radiation was used for DODA/**$Co_4P_2W_{15}$** and DODA/**Co_9** LB films. EPR experiments were performed on a Bruker system working at 10 GHz (X-band) equipped with a liquid ^4He temperature accessory. The magnetic susceptibility of LB films was measured with a SQUID magnetometer Quantum Design MPMS-5 between 1.7 and 300 K, and 300 monolayers were deposited on mylar substrates to measure the magnetic properties. Two experiments (substrate and LB film, then substrate alone) were carried out successively under the same experimental conditions (applied magnetic field parallel to the substrate). By difference, the intrinsic LB film magnetization was obtained.

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