Langmuir–Blodgett films based on inorganic molecular complexes with magnetic or optical properties

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Abstract

Langmuir and Langmuir–Blodgett (LB) films of a great variety of molecular metal complexes with interesting magnetic or optical properties have been prepared in the last few years. Some of the results obtained by our group and others are summarized in this article.

(i) LB films of polyoxometalates (POM) were first prepared taking advantage of the adsorption properties of these cluster anions along a positively charged monolayer of an organic surfactant spread in water. A correct choice of the POM allowed the preparation of LB films with magnetic, electrochromic, or luminescent properties. Besides this semiampiphilic method, two new methods to prepare LB films of POMs have been developed by other groups: one is based on the replacement of the charge-balancing counter-ions of the POMs salts by cationic surfactants. With this method luminescent LB films have been prepared. The other method is based on the synthesis of a bis(alkyl) substituted amphiphilic POM.

(ii) LB films of the Mn12 single-molecule magnets were prepared from mixtures of the benzoate and acetate derivatives of Mn12 with behenic acid. These magnetic films showed a marked hysteresis loop in the magnetization below 5 K.

(iii) Magnetic LB multilayers of two ferritin molecules, containing 4220 and 3062 Fe atoms have been prepared. Magnetic measurements have shown that the superparamagnetic properties of these molecules are preserved. Thus, a marked hysteresis loop of magnetization has been observed in these films below 15 K.

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1. Introduction

In the last few years many novel molecule-based materials have been developed which exhibit useful solid-state properties usually associated to inorganic materials, such as ferromagnetism, superconductivity or non-linear optics [1]. One of the advantages of these materials with respect to the inorganic materials is that they are formed by molecular building blocks that can be organized in the solid state to design novel materials with predictable properties. A current trend that illustrates this “building block” concept is that of obtaining multifunctional materials combining two or more physical (or chemical) properties in the same crystal lattice through a wise choice of the starting molecular fragments [2]. So far however most of the existing materials have been obtained as crystals. These have shown to be very useful as model systems to study and even to tune the properties, but very limited from the point of view of the applications. The development of processing techniques is required to make these materials more suitable for applications. This would allow to prepare these materials as films or nanoparticles, or to incorporate them into organic or inorganic matrices.

An elegant approach to arrange molecules into well-organized multilayered films is the Langmuir–Blodgett (LB) technique [3]. Compared to other processing techniques, this approach offers several advantages. First of all, the LB method allows the processing of molecules in the form of thin films, which are preferred for many applications. Second, it permits to control at the molecular-level the two-dimensional structure of these films. In fact, it provides a level of control over the orientation and placement of the molecules that is not available with other techniques. For this reason, the LB technique has been widely applied to create ultrathin films with a specific architecture which can be used as chemical sensors, modified electrodes or to incorporate them into organic or inorganic matrices.

2. LB films of polyoxometalates

Polyoxometalate anions (POMs) represent a wide 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 [5]. Their structures can be depicted as molecular fragments of close-packed metal-oxides of formula $X_nM_yO_{z+n}$ ($M=Mo, W, V, \ldots; X=P, As, Ge, B, Co, Fe, \ldots$) [6]. One of the most important electronic properties of these metal-oxide clusters is that of acting as electron reservoirs. In fact, they are readily reversibly reduced by 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 of the heteropoly framework. This produces complexes having a magnetic character. These abilities, together with their solubility and chemical stability in both aqueous and non-aqueous solvents, make them very useful as inorganic component of functional molecular materials.

The processing of POMs as films has been developed using different techniques. One possibility has been that of embedding these molecular metal-oxides into conducting polymers (polypyrrole or polyaniline for example). This approach has led to the preparation of hybrid conducting films which can be of interest as electrodes in batteries [7].

Hybrid inorganic–organic films of polyoxometalates and organic polymers have also been reported using the layer-by-layer method [8]. This molecular self-assembly method relies on the electrostatic interaction between alternated layers of charged materials to produce multilayer films [9]. This method has been used to prepare thin films of polyoxometalates of different sizes and charges [10]. Some possible applications of these kinds of multicomposite films have been presented. Thus, the polyoxometalate $[\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{12}\text{O}_{40})]^{16-}$ has been incorporated within multicomposite materials that can act as pH-sensitive probes [11] or NO sensors [12], and photoluminescent and electrochromic multilayer films of the rare-earth containing polyoxometalates have also been prepared [13].

To obtain multilayer films of POMs in a more controlled manner we have used the LB technique. In 1997 we showed that this technique could be used to organize polyoxometalate Keggin POMs $[X^{n-}W_{12}O_{40}]^{(8-n)-}$ ($X^{n+}=2(H^+), P^V, S^IV, B^{III}, Cu^{2+}$) (see Fig. 1 a) by a semiamphiphilic method [14]. Afterwards our group and others have extended this method for a large variety of POMs with different sizes, charges and shapes [15]. A correct choice of the POM allowed the preparation of LB films with magnetic, electrochromic, or luminescent properties. Besides this
semiamphiphilic method, two new methods to prepare LB films of POMs have been developed by other groups in the last years. A brief summary of the most important results is given in the following lines.

2.1. LB films of polyoxometalates prepared by the semiamphiphilic method

2.1.1. General preparation

The general procedure to prepare LB films of POMs using the semiamphiphilic method consists of forming a positively charged Langmuir monolayer of the cationic surfactant dimethyl dioctadecylammonium (DODA) (Fig. 2) by spreading an organic solution containing this amphiphilic cation onto a dilute aqueous solution of POMs. In the presence of such a solution, the DODA isotherm is shifted towards smaller areas per molecule when compared to pure water. 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 [14,15]. This effect is general for all the POMs studied, 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 along the positively charged monolayers is given by Brewster angle microscopy (BAM) [16] and ellipsometry [17]. The higher packing of the DODA monolayers spread on the POM solutions allows us to effectively transfer the Langmuir film onto a hydrophilic substrate. This is not possible for DODA monolayers spread on pure water.

2.1.2. Structure

The lamellar structure of the hybrid DODA/POM LB films is clearly demonstrated by low-angle X-ray diffraction experiments. The periodicity of the layers can be calculated from the observed Bragg peaks (see Fig. 3a). With these values and taking into account the DODA length [18] and the calculated tilt angle of the alkyl tails calculated from IR linear dichroism, one can evaluate the thickness of the inorganic layer within the LB film. A value of ca. 10 Å is obtained for the smaller and more isotropic polyanions [14b,15]. Interestingly, this indicates that each inorganic layer is a monolayer of polyanions. Therefore, in these organized lamellar structures the monolayers of POMs are alternating with bilayers of DODA to afford centrosymmetrical LB films (see Fig. 3b). The thickness of the inorganic layer for LB films of the bigger and more anisotropic POM is too small even for a monolayer. This suggests that the organization of these POMs within the LB films is not so good as for the smaller ones. The lamellar structure of the films is distorted by the presence of these big polyanions [15].

![Fig. 1. Molecular structure of the polyoxometalates used to construct Langmuir and LB films.](image1)

![Fig. 2. Molecular structure of the amphiphilic molecules used to construct Langmuir and LB films of inorganic molecular complexes.](image2)
2.1.3. Properties

2.1.3.1. Electrochromic films of polyoxometalates. Cyclic voltammetric response of LB films of POM deposited onto ITO (Indium Tin Oxide) electrodes can be obtained. Two different examples have been reported so far. The group of S. Dong studied the voltammetric behavior of hybrid DODA/[P₂Co(H₂O)W₁₇O₆₁]₈⁻ LB films immobilized on ITO glass obtained by the semiamphiphilic method. This POM shows two prominent two-electron reductions in aqueous solution. LB films show also two reversible, two-electron waves that are slightly shifted toward negative potential in comparison to that observed in solution [19]. More recently, we have used another POM, [P₂Mo₁₈O₆₂]₆⁻ (Fig. 1c), to study the voltammetric behavior of hybrid DODA/POM LB films. This POM shows three prominent two-electron reductions in solution that occur at relatively high potentials. Cyclic voltammetric response of LB films of this polyanion deposited onto ITO electrodes shows also three well-defined sets of reversible peaks that are close to those exhibited by the POM in solution (Fig. 4a).

The intense absorbance of the reduced forms of this POM that is 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 POM within the LB film were determined by spectroelectrochemical potential-step experiments. Thus, we observed that it is possible to induce absorbance changes of an LB film of the polyanion at 700 nm.

Fig. 3. (a) Low-angle X-ray diffractogram of a DODA/CoW₁₂ LB film with 100 monolayers deposited on glass. (b) Schematic representation of the Y-type LB films with different polyanions; DODA/CoW₁₂ and DODA/Co₂P₂W₁₅.

Fig. 4. (a) Cyclic voltammograms of DODA/[P₂Mo₁₈O₆₂]₆⁻ LB films with 1, 3 and 9 monolayers in aqueous 0.5 M NaHSO₄. Scan rate 0.5 V/s. (b) Absorbance changes of a DODA/[P₂Mo₁₈O₆₂]₆⁻ LB film with 5 monolayers at 700 nm after step potential changes between −0.3 and 0.5 V.
nm by repeated switching of the applied potential (Fig. 4b). 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 forms of the polyanion. Coloration and bleaching of the LB film occur very quickly and are reversible [15]. Electrochromic thin films of (NH₄)₁₁.₅K₀.₅[Eu(OH)₂P₅W₁₀O₄₁]·2H₂O have also been obtained by the Layer-by-Layer method [13c]. These films present higher changes of absorbance and a better reversibility than the LB films of the [P₂Mo₁₈O₆₂]⁶⁻ anion. Two possible explanations can be given: (i) the higher number of monolayers deposited for the Layer-by-Layer films and (ii) the more flexible and porous structure of these films that could make easier the adsorption or release of ions during the red/ox cycles.

2.1.3.2. Magnetic LB films of polyoxometalates. Magnetic properties of LB films of POMs that contain magnetic ions or magnetic clusters were measured [15]. We started with simple compounds such as the Keggin anions, [Co₁₂W₁₂O₴₀]⁶⁻ (Co₁₂W₁₂) [14a] and [SiMn(OH)₂W₁₁O₃₉]⁶⁻ (SiMnW₁₁) that contain isolated magnetic ions, and then we passed to POMs that contain magnetic clusters of increasing nuclearities such as [Co₄(H₂O)₂(PW₉O₃₄)₂]¹⁰⁻ (Co₄PW₉) and [Co₄(H₂O)₂(P₁₅S₅O₅₀)₂]¹ⁱ⁻ (Co₄P₂W₁₅) that encapsulate a Co₄O₁₆ ferromagnetic cluster, and [Co₉(OH)₃(H₂O)₆(HPO₄)₂(PW₉O₃₄)₃]¹⁰⁻ (Co₉) and [Ni₉(OH)₃(H₂O)₆(HPO₄)₂(PW₉O₃₄)₃]¹⁰⁻ (Ni₉) that encapsulate a nonanuclear Mo₉O₃₆ cluster (Fig. 1). Magnetic properties of LB films of the giant heteropolyoxomolybdate [Mo₅₇Fe₆(NO)₆O₁₇₄(OH)₃(H₂O)₂₄]¹₅⁻ (Mo₅₇, Fig. 1) were also measured [15]. Magnetism of the LB assemblies indicates that the clusters are magnetically isolated and gives similar results to powder measurements for all the compounds. Thus, magnetic behavior of LB films containing POMs that encapsulate a Co₄O₁₆ ferromagnetic cluster (Co₄PW₉ and Co₄P₂W₁₅) is completely analogous to that observed in the potassium salt of the corresponding POMs (Fig. 5). In the magnetic cluster, the ions are ferromagnetically coupled giving rise to a highly magnetic ground state [21]. Thus, γT product shows a sharp increase below 50 K upon cooling, and a maximum at ca. 6.5 K. Below this temperature, γT product shows a decrease due to the magnetic anisotropy of the cluster. EPR measurements of these two LB films showed that the EPR signal depends on the orientation of the LB film with respect to the external magnetic field [15]. The observation of such anisotropy is in agreement with the restricted orientation of the cluster within the monolayer suggested by IR linear dichroism and X-ray diffraction studies. The magnetic properties of the LB films of the higher nuclearity clusters Co₉ and Ni₉ are again similar to powder measurements (Fig. 6). Magnetic properties of Co₉ and Ni₉ can be explained by the coexistence of ferromagnetic interactions and antiferromagnetic interactions within the clusters. In the case of the Ni₉, the increase of γT down to 25 K indicates the presence of dominant ferromagnetic intra-triangle interactions, while the sharp decrease at lower temperatures is a consequence of the antiferromagnetic inter-triangle interactions that give rise to a non-magnetic ground state [22]. Co₉ also shows a similar coexistence but in this case the former interactions are dominant giving rise to a continuous decrease in γT [23]. Finally, the magnetic properties of LB films of the giant
polyanion Mo$_{57}$ are also very similar to those of the powders (Fig. 7). In this case, a decrease of $\chi T$ with decreasing $T$ is observed due to weak antiferromagnetic interactions between the Fe(III) ions [24].

2.1.3.3. Luminescent LB films of polyoxometalates. In the last 3 years luminescent LB films of rare-earth containing POMs have been successfully fabricated by Wang et al. [25] using the semiamphiphilic method, with DODA or ODA (octadecylamine; Fig. 2) as cationic surfactants. The POMs appropriate to prepare such luminescent films are [XW$_{10}$O$_{36}$]$^9^-$ (X = Eu, Sm and Dy), [Eu(MW$_{11}$O$_{30}$)$_2$]$^{13^-}$ (M = Si and Ge) and [Eu(BW$_{11}$O$_{30}$)$_2$]$^{15^-}$ (Fig. 1g and h). X-ray diffraction experiments of DODA-containing LB films show the lamellar structure of these films which are formed by monolayers of POMs alternating with bilayers of the surfactant, in a similar way to that described above for the LB films containing magnetic POMs. However, structure of ODA LB films is determined by a Z-type transfer that gives rise to a lamellar structure formed by alternating monolayers of ODA and POM [25]. The average thickness per monolayer of the LB films obtained from (DODA)$_{20}$(NH$_4$)[H$_3$Mo$_{57}$V$_6$(NO)$_6$O$_{183}$(H$_2$O)$_{18}$] is very close to that obtained for LB films of the similar heteropolyoxomolybdate, [Mo$_{57}$Fe$_6$(NO)$_6$O$_{174}$(OH)$_3$(H$_2$O)$_{24}$]$^{15^-}$ prepared by the semiamphiphilic method (see above). These differences can be caused for the different structural organization of this POM within the LB films obtained by the two methods even if the periodicity of the lamellar structure is the same for both films (4.9 nm) [25c,29].

More recently, Bu et al. have prepared Langmuir and LB films of SECs of the following POMs: [Cu$_4$(H$_2$O)$_2$ (As$_5$W$_{15}$O$_{56}$)$_2$]$^{16^-}$ [28], [Eu(SiW$_{11}$O$_{30}$)$_2$]$^{13^-}$ [29], [H$_2$Mo$_{57}$V$_6$(NO)$_6$O$_{189}$(H$_2$O)$_{12}$(VO)$_6$]$^{15^-}$ and [Eu(H$_2$O)$_2$P$_2$W$_{30}$O$_{110}$]$^{12^-}$ [30]. Luminescence properties of the LB film obtained from [Eu(SiW$_{11}$O$_{30}$)$_2$]$^{13^-}$ SEC are different to those of the same POM prepared by the semiamphiphilic method. These differences can be caused for the different structural organization of this POM within the LB films obtained by the two methods even if the periodicity of the lamellar structure is the same for both films (4.9 nm) [25c,29].

2.2. LB films of polyoxometalates prepared from surfactant-encapsulated cluster complexes

This method, developed by Kurth et al. [26], is based on the replacement of the charge-balancing counter-ions of the POMs salts by cationic surfactants. This strategy is equivalent to the one used years ago to prepare conducting LB films of metal dithiolate complexes (M(dmit)$_2$) [27]. The first examples of this kind where the DODA salts of the high nuclearity heteropolyoxomolybdates [H$_3$Mo$_{57}$V$_6$(NO)$_6$O$_{183}$(H$_2$O)$_{18}$]$^{21^-}$ and [Mo$_{132}$O$_{372}$(CH$_3$ COO)$_{10}$(H$_2$O)$_{72}$]$^{12^-}$ (Fig. 1i and j). These surfactant-encapsulated clusters (SECs) are formed by single POMs cores encapsulated by a shell of DODA molecules (Fig. 8). They were dissolved in organic solvents and subsequently spread on pure water to study the Langmuir and LB film formation [26]. Analysis of the X-ray reflectance data proves in a quantitative way that the core-shell structure of the SEC is preserved upon LB transfer and that the alkyl chains are completely disordered [26c].

A promising new method to prepare Langmuir monolayers and LB films of POM without the use of any additional surfactant molecule has been developed by Chambers et al. [31]. It relies on the synthesis of a bis(alkyl) substituted amphiphilic POM that is subsequently spread on pure water to form Langmuir monolayers and LB films. An asymmetric amphiphilic derivative of Keggin anion of formula [{[CH$_3$(CH$_2$)$_1$Si]$_2$OSiW$_{11}$O$_{30}$}]$^{4^-}$ was used for the preparation of these LB films. The transfer ratios of the down stroke decreased after successive dipping cycles leading finally to an X-type LB film.

2.4. Hybrid multifunctional films based on polyoxometalates

The electronic properties of POM LB films presented before are those coming from the POMs, as the cationic surfactant plays only a structural role. Another possibility is that of creating novel hybrid LB films that combine two properties, one coming from the inorganic entities and the other one from the organic part of the film. With this idea in mind, the tetraphiafulvalene (TTF) semi-fluorinated derivative, SF-EDT (Fig. 2), that can introduce electronic delocalization within the LB film, has been combined with the magnetic POMs [Co$_4$(H$_2$O)$_2$(P$_2$W$_{15}$O$_{56}$)$_2$]$^{16^-}$ (Co$_4$P$_2$W$_{15}$) to prepare hybrid organic/inorganic LB films.
The cluster Co₄P₂W₁₅ was transferred with a monolayer of DODA as discussed above. A monolayer of SF-EDT was then transferred onto the hydrophobic surface provided by DODA layer. This process was repeated several times giving rise to alternating DODA/Co₄P₂W₁₅/SF-EDT LB films with the structure shown in Fig. 9. X-ray diffraction and IR linear-dichroism experiments are consistent with the layered structure proposed in Fig. 9. Oxidation of these films with iodine vapour leads to the appearance of a charge-transfer band in the IR spectra consistent with charge delocalization within the SF-EDT monolayer. However, the macroscopic conductivity remains very low, suggesting that the structure of the film do not permit long-range delocalization.

Fig. 9. Proposed structure of a DODA/Co₄P₂W₁₅/SF-EDT LB film.
3. LB films of single-molecule nanomagnets

In view of the interesting results obtained in the building-up of LB films of POMs, we have explored in a further step the use of the LB technique to organize other inorganic clusters presenting more interesting magnetic properties. Our first choice was the mixed-valence manganese clusters \[\text{[Mn}_{12}\text{O}_{12}\text{(carboxylato)}_{16}]\] (carboxylato = acetate, benzoate), referred to as Mn\(_{12}\) (Fig. 10). These clusters are motivating a current excitement in molecular magnetism as they can act below 4 K as single-molecule magnets of nanometer size \[33,34\]. Thus, at 2 K they show large magnetic hysteresis comparable to that observed in hard magnets opening the way to store information at the molecular level. On the other hand, these nanomagnets provide unique examples to observe the quantum tunneling of an electron spin through a potential barrier from one orientation to another, which is a fundamental question in physics \[35–37\]. Extension of the Langmuir–Blodgett technique to the Mn\(_{12}\) clusters appears very desirable to explore the fabrication of organized films of the aforementioned single-molecule magnets. Notice that other techniques are also being used in the attempt to attach these magnetic clusters as monolayers and other nano-structures on metal surfaces \[38\].

The acetate and the benzoate derivatives (\[\text{[Mn}_{12}\text{O}_{12}\text{(CH}_3\text{COO)}_{16}(\text{H}_2\text{O})_4]\), Mn\(_{12}\)Ac and \[\text{[Mn}_{12}\text{O}_{12}\text{(C}_6\text{H}_5\text{COO)}_{16}(\text{H}_2\text{O})_4]\], Mn\(_{12}\)Bz) were used to prepare the LB films. When chloroform solutions of the two clusters are spread pure at the gas–water interface, a stable Langmuir film is not formed. For this reason, mixture between these complexes and a lipid is needed in order to get a monolayer. Behenic acid (BA) was then used as matrix, (\(\text{CH}_3\text{(CH}_2\text{)}_{20}\text{COOH}\)). The compression isotherms of mixtures of behenic acid and Mn\(_{12}\) acetate allowed us to conclude that there is no phase separation of both molecules. There is a real mixture in the water–gas interface that causes important changes in the isotherm of behenic acid. Brewster angle microscopy measurements of Mn\(_{12}\)Ac/BA and Mn\(_{12}\)Bz/BA Langmuir film with a 1/10 ratio suggest that a homogeneous monolayer is formed. The resulting molecular system is clearly bidimensional at the gas–water interface. The Langmuir films of Mn\(_{12}\) clusters and BA are perfectly stable vs. time if the ratio lipid/cluster is high enough (typically higher or equal to 5).

The structure of the corresponding Y-type LB films was investigated by IR-linear dichroism and X-ray diffraction at different cluster/BA ratios. From the structural characterization we concluded that the degree of organization of the clusters within the films is strongly dependent on the concentration of clusters in the LB film. For low concentrations, isolated clusters or partial monolayers of clusters are obtained, while for the higher concentrations (typically in the range 1/10 to 1/5 Mn\(_{12}/\)BA) lamellar structures with the clusters organized in well-defined monolayers are obtained (Fig. 11).

The magnetic study has been focused on the 1/10 and 1/5 films which are those containing monolayers of clusters. The magnetic properties are measured with the film parallel or perpendicular to the magnetic field direction. A remarkable magnetic result comes from the magnetization data vs. the applied magnetic field performed at temperatures below 2 K.
and above the blocking temperature of the cluster of 3.8 K (Fig. 12). As for the parent crystalline salt, the LB films of the two Mn$_{12}$ clusters show at 2 K a marked hysteresis loop with coercive field of ca. 0.1 T (benzoate derivative) or 0.06 T (acetate derivative), which vanishes as the temperature is increased to 5 K (see inset of Fig. 12). We also observe that in the benzoate derivative the shape of the loop depends on the orientation of the film with respect to the applied magnetic field $H$. Thus, when $H$ is parallel to the plane of the magnetic monolayer the loop is softer than when $H$ is perpendicular. Such an anisotropy indicates a preferential orientation of these anisotropic clusters within the layers. This effect is not observed for the acetate film that seems to be less oriented within the layer. A possible explanation is the larger shape of the benzoate derivative that makes more difficult an out-of-plane orientation of the cluster. The coercive field at 2 K is strongly reduced by an order of magnitude when comparing the film to the crystal. This is surely related to the different spin dynamics of the Mn$_{12}$ cluster in these two media, as it is submitted to different environments and packings. In fact, it is well known that the magnetic relaxation in the Mn$_{12}$ cluster can be strongly affected by its surroundings [39].

Monolayers of another cluster, [Cr$_8$O$_4$(O$_2$CPh)$_{16}$], at the air–water interface have been structurally characterized with GIXD and X-ray reflectivity [40]. In contrast to the Mn$_{12}$ case described above, this cluster forms monolayers at low surface pressure. At higher pressures, the film becomes less compressible, but a second monolayer begins to form on the first. Transfer of this cluster onto solid substrates has not been studied.

4. LB films of ferritin

A second choice, which can be of interest to generate magnetic LB films with a memory effect, consists of using the ferritin molecule as it contains a much higher number of magnetic ions and exhibits superparamagnetic behavior at blocking temperatures higher than those observed in the Mn$_{12}$ clusters. This approach has been attempted very recently [41].
Natural ferritin is the iron-storage protein of animals, plants and bacteria [42]. It is a roughly spherical protein about 12 nm in diameter composed of 24 subunits arranged around a 7.5 nm diameter iron ferrihydrite-like capable to accommodate up to 4500 iron atoms (Fig. 13). Studies of ferritin in solution have shown a superparamagnetic behavior with frequency dependent ac susceptibility peaks between 15 and 20 K and a marked hysteresis loop of magnetization below 15 K.

To prepare LB films of this magnetic protein we have used the same conditions described by Britt et al. to prepare monolayers of ferritin [43]. This method is based on the adsorption properties of ferritin dissolved in an aqueous subphase onto a mixed monolayer of dioctadecyldimethylammonium bromide (DODABr) and methyl stearate (SME) in a 6:1 ratio. This mixture of cationic DODA and non-ionic SME molecules has shown to enhance the adsorption properties of ferritin which, at the pH of the water subphase (5.5), is negatively charged. LB films of two ferritins with different Fe loading, containing, respectively, 4220 and 3062 Fe atoms have been obtained by the vertical lifting method. Transfer ratios close to unity are reached giving rise to LB films with a strong red color. Infrared and UV–Vis spectroscopy indicates that ferritin molecules are incorporated within the LB films [41].

The iron antiferromagnetic oxohydride core of ferritin presents a net magnetic moment arising from uncompensated iron spins largely at the surface of the core [44]. Magnetic properties of LB films of 80 monolayers of the two ferritins deposited onto mylar substrates have been measured. A marked hysteresis loop of magnetization is obtained for both LB films at 2 K with a coercive field of 3400 G for the ferritin containing 4220 Fe atoms and 2400 G for the ferritin containing 3062 Fe atoms. The hysteresis loop of magnetization (Fig. 14) is a clear evidence of the presence of ferritin molecules within the LB films. The shape of the curve is very similar to that found on powder measurements. LB films of ferritin show several advantages compared to the previous work with Mn$_{12}$ (see above). They present a higher coercive field (3400 G vs. 1000 G) and an increase of the temperature at which the hysteresis loop of magnetization is observed (15 K vs. 5 K).

5. Conclusion

In this short review we have demonstrated that it is possible to organize as monolayers several polynuclear metal complexes of nanometric size having magnetic or optical functionalities using the LB technique. An extensive class of complexes that has been described is the polyoxometalate complexes. We have shown that an appropriate choice of the polyoxometalate has allowed the preparation of LB films having magnetic, electrochromic or luminescent properties.

The use of other inorganic complexes of magnetic interest such as the Mn$_{12}$ magnetic clusters or the iron-oxide nanoparticles encapsulated by ferritin protein has allowed the preparation of magnetic thin films with magnetic hysteresis. The main advantage of this molecular approach is that is not necessary to prepare monolayers formed by extended ferromagnetic 2D structures to observe magnetic memory effects, as these last polymeric structures are much more difficult to generate using the LB technique. Monolayers formed by discrete magnetic units of ferritin showing superparamagnetism also show magnetic effects. The main problem associated with the molecular approach to the magnetic LB films is that the blocking temperatures are still too low. We have shown that ferritin-containing films provide a way to increase the blocking temperatures from 5 (in Mn$_{12}$ films) to 15 K. Further increases in these values will be obtained in the future playing with the possibility of replacing the iron oxohydride core of natural ferritin by other magnetic nanoparticles (nanoparticles of metals like cobalt, or ferrite nanoparticles, for example). Other interesting issue not yet investigated could be the use of photoactive amphiphilic molecules that could influence the magnetic properties of the LB film after irradiation.

![Fig. 14. Hysteresis loops of magnetization at 2 K of an LB film of ferritin containing 4220 Fe atoms (a) and 3062 Fe atoms (b).](image-url)
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