Triazole-Based Magnetic Langmuir−Blodgett Films: Paramagnetic to Spin-Crossover Behavior

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The behavior at the air−liquid interface of a series of metal(II) metallo-organic polymers of 4-octadecyl-1,2,4-triazole has been studied. Interactions between those amphiphilic compounds and metal ions in the subphase result in the formation of stable monolayers and well-defined Langmuir−Blodgett (LB) films incorporating oligomeric metal(II)/triazole units. Infrared, X-ray Photoelectron Microscopy, and magnetic measurements show that the obtained LB films are mostly resulting from recoordination of metal ions from the subphase with triazole ligands at the air−water interface. The relative stability of the polymers and the efficiency of association with 4-octadecyl-1,2,4-triazole have been found to follow the Ni > Fe ∼ Cu > Co and Cu > Ni > Fe > Co sequences, respectively. In the iron(II) cases, partial spin-crossovers are observed, demonstrating for the first time the feasibility of triazole-based LB films possessing interesting magnetooptical properties.

Introduction

The potential use of bistable molecular materials for information storage or signal processing is receiving increasing interest.[1−3] Irrespective of the different final goals, the use of spin transition complexes seems to be particularly relevant. Indeed, such compounds can have two different electronic states depending on the value of external parameters (T, p, light).[4] In addition, the thermal spin crossover can present hysteretic phenomenon and can be adjusted to temperatures at which potential devices would function.[5] This is achieved in polymeric unidimensional complexes of Fe(II) and 4-substituted triazole ligands, in which a thermochromic effect is also associated with the spin-crossover behavior.[6] In the case of Fe(II), the two states involved in the crossover are paramagnetic ($S = 2$) and diamagnetic ($S = 0$). The formation of thin films of controlled thickness with such compounds would therefore be of great interest for device applications. Although some prototypes have been fabricated by embedding powders in polymer matrices,[6] the well-known Langmuir−Blodgett (LB) method appears better suited to achieve this goal.[7−9] Indeed, spin-crossover LB films have been obtained using monomeric complexes presenting a noncooperative conversion.[10,11] On the other hand, attempts to form LB films from polymeric spin-crossover materials based on 4-octadecyl-1,2,4-triazole (ODT) were unsuccessful, as a result of the instability of the polymeric metallo-organic materials at the air−water interface.[12] Indeed, only ODT was transferred onto solid substrates as LB films, and diffusion of Fe(II) ions into these films was performed. However, the obtained Fe(II)-containing LB films did not present any thermal spin-crossover.

Here we report the formation of LB films of a series of metal-(II) metallo-organic polymers of ODT in order to design new devices for information storage. Interactions of these polymeric materials with metal ions dissolved in the subphase allow the formation of stable Langmuir films at the air−water interface

and, more interestingly, lead to a metal-exchange mechanism. We have analyzed the formation of metal/triazole complexes after the transfer onto a solid substrate by Infra-Red (IR) spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and magnetic measurements. These experiments demonstrate that the association constant of copper with ODT is greater than for nickel, iron, and cobalt inducing strong modifications of the magnetic properties of the multilayered materials. In addition, the presence of a thermally induced spin-crossover within Fe-containing LB films is demonstrated.

Experimental Section

Materials. All reagents were purchased from Aldrich and were used without further purification. 4-Octadecyl-1,2,4-triazole (ODT) was obtained from octadecylamine and hydrazine hydrate as described previously.[13] The synthesis of the metal(II) metallo-organic polymers of ODT of formula [M(ODT)$_3$](NO$_3$)·xH$_2$O (M = Co, **1**; M = Ni, **2**; M = Cu, **3**) was achieved according to a published procedure,[13] using Co(NO$_3$)$_2$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, and Cu(NO$_3$)$_2$ as reagents, respectively. For [Fe(ODT)$_3$]-(NO$_3$)·xH$_2$O, **4**, an iron nitrate aqueous solution containing a small amount of ascorbic acid to prevent the formation of iron-(III) was prepared from FeSO$_4$·7H$_2$O and Ba(NO$_3$)$_2$, and the same procedure was applied. Infrared spectra of **1**−**4** are in agreement with a one-dimensional structure with only N1,N2-bridging ODT (see Figure 1) (i.e. the intensities of the ring torsion vibration modes of the triazoles around 670 cm^{-1} are very weak, which occurs when the local triazole ring symmetry is C_{2v}[14]). The water content was confirmed to be close to $x = 1$ by TGA experiments.

LB Films Fabrication. For LB film preparations, chloroform (HPLC grade from Prolabo) was the spreading solvent, and Millipore Q grade with a resistivity higher than 18 MΩ.cm was used for the subphase solutions. For the subphases containing metal ions, their concentration was fixed to 5×10^{-4} mol·L^{-1}. The step-by-step compression of the Langmuir films was performed 10 min after spreading in order to allow the spreading

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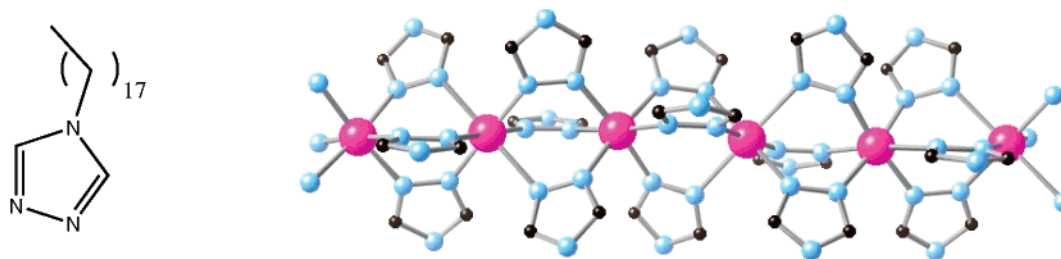
Figure 1. Representation of 4-octadecyl-1,2,4-triazole (ODT, left) and of the polymeric 1D compounds obtained by coordination of ODT to transition metal(II) ions (right).

solvent to evaporate. LB films have been obtained by the vertical lifting method using a homemade LB trough working at room temperature under a continuous dried nitrogen flow.[15] Glass plates were used as deposition substrates for X-ray diffraction and X-ray photoelectron spectroscopy (XPS), with a number of layers ranging from 15 to 100. Samples (20 layers) for infrared investigations were prepared on fluorine (CaF_2) plates. Samples (400 to 1100 layers) for magnetic studies were elaborated on Mylar substrates (Dupont). CaF_2 plates and Mylar substrates were cleaned prior to use with ethanol. When it was needed, the fluorine and glass plates were made hydrophobic by predeposition of three monolayers of arachidic acid.

Physical Methods. *Infrared (IR) spectra* were recorded on a FTIR 750 Nicolet spectrometer. *X-ray diffraction* experiments at low angles were performed on a homemade experimental setup.[16] *X-ray photoelectron spectroscopy (XPS)* measurements were performed with a VG 220 i.XL ESCALAB spectrometer. All spectra were taken using a monochromatized Al Kα source at 1486.6 eV. The spot size was approximately 25 μm. The typical operating pressure was 2×10^{-8} Pa. *Magnetic measurements* were performed with a Quantum Design MPMS-7XL SQUID magnetometer between 2 and 375 K in fields up to 70 kOe. Mylar substrates of ca. 2.5×0.5 cm^2 were cut in 4 pieces that were fit and packed parallel to the applied field within the plastic straw used for measurements. Raw magnetization data were corrected for the free Mylar substrate response.

Results and Discussion

Langmuir and Langmuir−Blodgett Film Formation. ODT and the metallo-organic polymers **1**, **2**, **3**, and **4** form a stable monolayer on a pure water subphase. Compression of the monomolecular films at room temperature produces the surface pressure (Π) versus area (A) isotherms shown in Figure 2. In the case of the ODT ligand, the mean molecular area at the onset of the pressure is close to 95 Å^2 and to 40 Å^2 at the collapse. The latter value is larger than the area per molecule expected for a solid Langmuir layer of ODT, which is approximately 25 Å^2.[12] It suggests a tilted arrangement of the ODT molecules at the surface. The area per repeating unit (M(ODT)$_3$) that was obtained for solid monomolecular layers of the polymers was around 75−85 Å^2 (values at the collapse), which is a little larger than the cross section area for three ODT molecules. This result suggests a slightly tilted arrangement of the ligands in the M(II) complexes and/or a loose packing of the polymeric chains in the monolayers. Only a slight shift toward smaller areas of the compression isotherms was observed when a 5×10^{-4} M solution of potassium nitrate was used as subphase. As expected from their electroneutrality, ODT and the metallo-organic polymers are thus poorly sensitive to changes in the ionic strength of the subphase.

The behavior of ODT, **1**, **2**, **3**, and **4** over a subphase containing metal(II) ions is markedly different from that on pure water or with K^+. Indeed, strong modifications of the isotherms were recorded (see Figure 2). The Π-A curves were shifted toward smaller areas per molecule. The mean molecular area at the collapse is around 22 Å^2 for ODT and 62−70 Å^2 for **1**, **2**, **3**, and **4**, suggesting a close packed organization of ODT molecules and of the metallo-organic polymers at the air/liquid interface. As will be demonstrated, this behavior results from a coordination or a recoordination of the metals ions to the nitrogen atoms of the ODT ligand (see Scheme 1).

To further characterize such interactions occurring at the air−liquid interface, the Langmuir films were transferred to various supports by the Langmuir−Blodgett technique. The average transfer ratio (Y-type LB films) was close to unity at a surface pressure of 16 mN/m for ODT and metallo-organic polymers over solutions containing metal ions. The transfer of ODT molecules organized over pure water or a KNO$_3$ solution required hydrophobic substrates. It was less efficient (the transfer ratio was close to 0.8) and was performed at 22 mN/m.

The structural organization of the transferred LB films was studied by X-ray diffraction experiments. In most cases, Kiessig fringes and the first Bragg peak (around $q = 0.14$ Å^{-1}) were observed, indicating well-organized lamellar films. The deduced periodicity ranges from 47 to 52 Å, which indicates that the structure of the LB films can be described as layers of metals intercalated between two layers of ODT, since the length of one ODT molecule is ∼23 Å.

Infrared Spectroscopic Characterization. LB Films of ODT. To study the binding between the nitrogen atoms of the ODT ligand and the metal ions, analysis of the triazole ring vibrations and the N−N stretching band in the infrared spectra of the LB films was performed. Figure 3 shows that the spectra of a spin-casted film of ODT and of a LB film corresponding to a pure water subphase exhibit a ν(N−N) band around 1185 cm^{-1} and two bands due to the ring stretches around 1380 and 1530 cm^{-1}, in accordance with literature.[17] When KNO$_3$ is dissolved in the subphase, a small increase of the absorbance (comparing with pure water) and a high-wavenumber displacement of 10 cm^{-1} of the 1530 cm^{-1} band are observed. These features are enhanced when metal ions are dissolved in the subphase. The absorbances of all the stretching bands markedly increase and the 1530 cm^{-1} band shifts to 1555 cm^{-1}. Moreover, the ν(N−N) band also undergoes a high-wavenumber displacement of 30 cm^{-1}, which is typical of the triazole ring being coordinated to a metal atom.[17] These results indicate that the coordination of the ODT ligand to copper, cobalt, or nickel ions occurs at the gas/liquid interface. A closer look to the intensity of the ring stretching band around 1380 cm^{-1} suggests that the complexation by copper(II) is stronger or more efficient than by cobalt or nickel ions. Indeed, a similar conclusion can be made by carefully analyzing the intensities of the shifted bands around 1215 and 1555 cm^{-1}, which are maximal when copper-
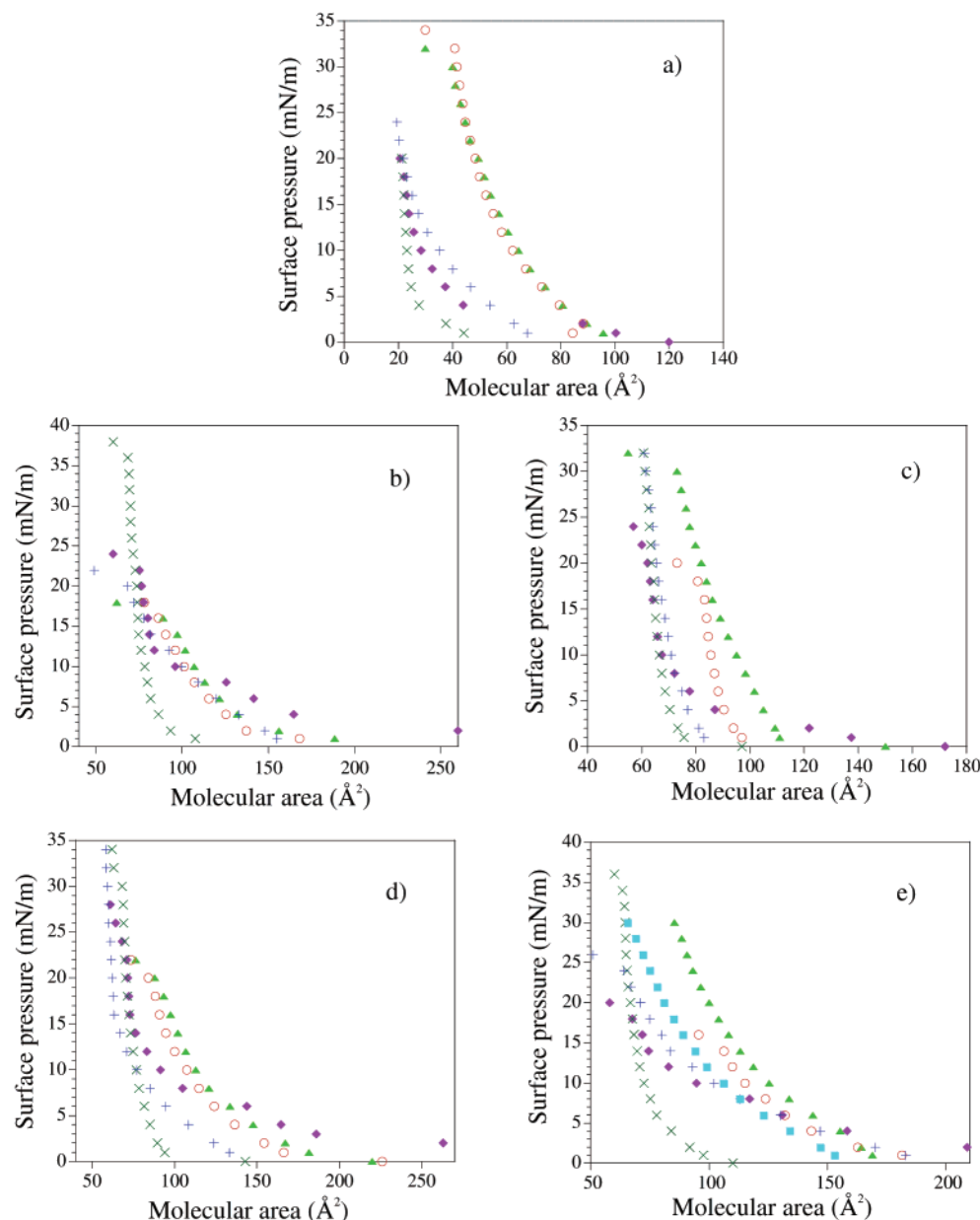
Figure 2. Room-temperature surface pressure vs mean molecular area isotherms for the following: (a) ODT; (b) **1**; (c) **2**; (d) **3**; (e) **4** over pure water (▲), 5×10^{-4} M KNO$_3$ (○), 5×10^{-4} M Co(NO$_3$)$_2$ (◆), 5×10^{-4} M Ni(NO$_3$)$_2$ (×), 5×10^{-4} M Cu(NO$_3$)$_2$ (+), and 5×10^{-4} M Fe(NO$_3$)$_2$ (■).

(II) ions are present in the subphase. Nevertheless, it has to be pointed that some uncoordinated ODT ligand remains in all cases.

LB Films of Metalloorganic Polymers. The analysis of the stretching bands in the infrared spectra of the LB films of **1**, **2**, **3**, and **4** gives similar results. As shown in Figure 4, when the metallo-organic polymers are compressed over a pure water subphase or a 5×10^{-4} M KNO$_3$ solution, typical stretching bands of the noncoordinated ring around 1530 cm^{-1} and of the exocyclic N−N bond around 1185 cm^{-1} are visible. It suggests that a depolymerization occurs, involving the formation of a monolayer of a mixture of the metallo-organic polymer and uncoordinated ODT ligand, which is in agreement with the recorded isotherms at the air/water interface. An analysis of the intensity of the bands around 1185 and 1530 cm^{-1} (see arrows in Figure 4a) shows that the depolymerization of **1** is the most efficient. The depolymerization process may also occur over solutions containing metal ions and may be followed by a recoordination process which leads to bimetallic polymers if

the metal ion dissolved in the subphase is different from the one initially present in the polymer (see Scheme 1). In fact, the displacement of the bands around 1185 and 1530 cm^{-1} observed in the spectra recorded over M(NO$_3$)$_2$ aqueous solutions clearly indicates that a recoordination process occurs. Moreover, the comparison of the intensity of the band due to the ring stretches around 1380 cm^{-1} reveals that the global amount of metal ions in all LB films is high when a Cu(NO$_3$)$_2$ solution is used as subphase. It indicates once more that the binding of triazole units with copper(II) is efficient.

X-ray Photoelectron Spectroscopy Measurements. XPS measurements have allowed a pseudoquantitative elemental analysis of the LB films. They confirm that the only elements present in the films are carbon, nitrogen, oxygen, and the metals from the polymers and the subphases e.g. K, Co, Ni, Cu, Fe (see Supporting Information). Semiquantitative analysis of C1s, N1s, O1s, K1s, and M2p^3 peak areas was performed and yielded the approximate relative molar ratios (at. % M) summarized in Table 1. The efficiency of uptake of metal ions from the

SCHEME 1: Schematic Representation of the Three Situations Encountered in the LB Films Formation Showing the Depolymerization and Recoordination Processes Occurring at the Air−Liquid Interface: (a) ODT over a Metal-Containing Subphase, (b) Metallo-Organic Polymers over Pure Water, and (c) Metallo-Organic Polymers over a Metal-Containing Subphase
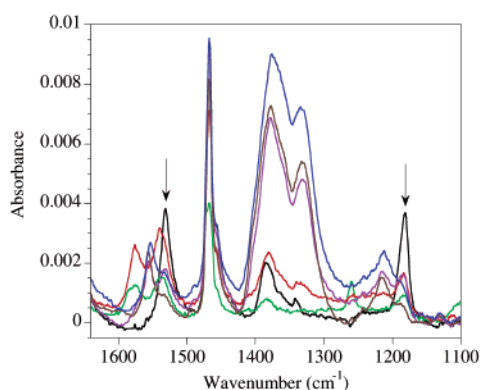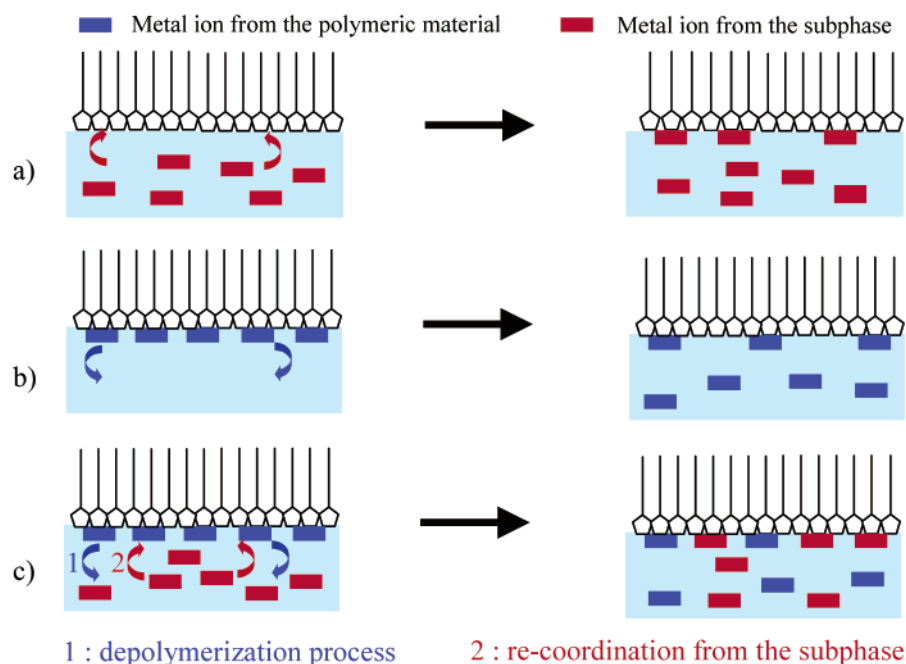

Figure 3. Infrared spectra of a spin-casted film of ODT (black curve) and of LB films (20 layers) built from a monolayer of ODT spread on the following: pure water (green), 5×10^{-4} M KNO_3 (red), 5×10^{-4} M $Co(NO_3)_2$ (violet), 5×10^{-4} M $Ni(NO_3)_2$ (brown), 5×10^{-4} M $Cu(NO_3)_2$ (blue) (arrows show the characteristic bands of the uncoordinated ODT ligand).

subphase by ODT derives directly from the metal amounts in LB films obtained from monolayers of ODT spread over metal-containing solutions. It follows the sequence Cu > Ni > Co, in agreement with the findings of the IR analysis. On the other hand, the metal content of LB films built from monolayers of metallo-organic polymers spread over pure water and a potassium nitrate solution is lower than when using metal containing subphases. This is in agreement with the ability of the metallo-organic polymers to depolymerize at the air/water and air/KNO_3 solution interfaces, already indicated by the IR analysis. Furthermore, a closer look at the data shown in Table 1 shows that the relative stability of the metallo-organic polymers follows the sequence Ni > Fe ∼ Cu ≫ Co. In cases where the subphase contains a different transition metal ion than the one present in the spread polymer, both metals are found in the LB films pointing at a metal-exchange process between the monolayer and the aqueous subphase. This confirms that the depolymer-

ization of the polymers is followed by a recoordination process at the air/liquid interface (see Scheme 1). Comparison of all the ratios at. % $M_{polymer}$/at. % $M_{subphase}$ yields the following sequence for preferred coordinated metal: Cu > Ni > Fe > Co, in agreement with the preceding findings. For example, the high Ni content of the LB film obtained from **2** over a Cu(II)-containing solution agrees with the higher stability of **2** toward depolymerization. Moreover, the very low amounts of Co in any of the obtained films arises from both the high instability of **1** toward depolymerization together with a poorer association constant of Co with ODT. Again, these findings are in perfect agreement with the results of the IR analysis. In addition, in most cases, the predominant metal ion in the LB films is that coming from the subphase. Taking into account that the metal ion concentration of the subphase and timing (∼8 h) were similar for the elaboration of all the LB films and assuming that diffusion kinetics of M(II) in aqueous solution are not likely to differ significantly, the above-mentioned sequence should correspond to the sequence of the M(II)/triazole association constants. In particular, the highest metal contents were obtained over the Cu-containing solution, in all cases, as a result of the higher association constant of that metal ion with ODT. Moreover, when spreading polymer **4** over an $Fe(NO_3)_2$ aqueous solution, the metal amount in the LB film is the highest of those determined by XPS. This is appealing in view of obtaining LB films presenting a spin conversion.

Magnetic Measurements. The temperature dependence of the $\chi_M T$ product (where χ_M is the molar magnetic susceptibility defined as M/H) of **1**, **2**, and **3** agrees well with what is expected for the molecular formula $[M(ODT)_3](NO_3)\cdot H_2O$ ($\chi_M T$ of ca. 1.98, 1.06, and 0.40 cm$^3\cdot$ mol$^{-1}\cdot$ K, respectively over the range 50−300 K, to be compared with the spin-only values of 1.875, 1, and 0.375 cm$^3\cdot$ mol$^{-1}\cdot$ K respectively). Lowering of the $\chi_M T$ product below 50 K indicates weak antiferromagnetic coupling between neighboring metal ions, already observed in such polymeric compounds of Cu.[18] On the other hand, **4** exhibits an almost complete spin-crossover in the range 210−300 K (see
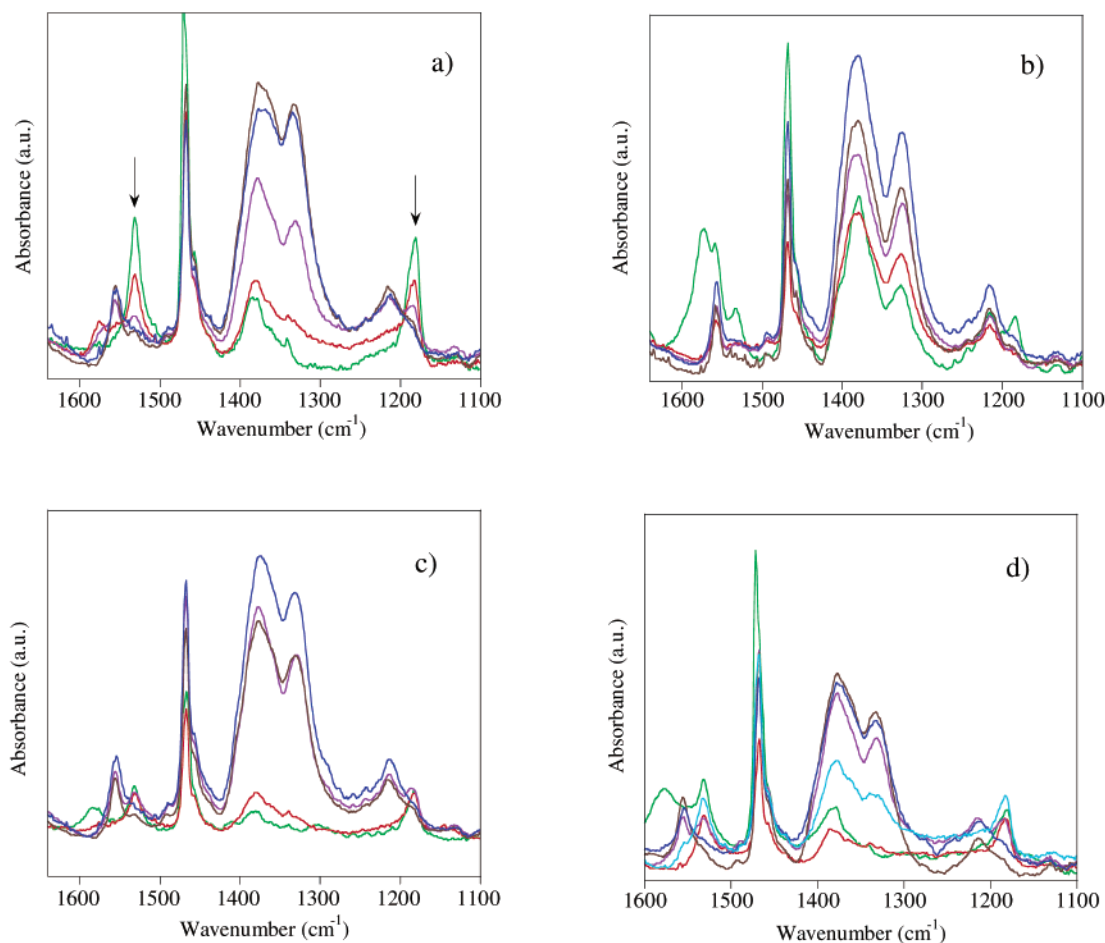
Figure 4. Infrared spectra of LB films (20 layers) built from a monolayer of the following: (a) **1**; (b) **2**; (c) **3**; (d) **4** spread on: pure water (green), 5×10^{-4} M KNO$_3$ (red), 5×10^{-4} M Co(NO$_3$)$_2$ (violet), 5×10^{-4} M Ni(NO$_3$)$_2$ (brown), 5×10^{-4} M Cu(NO$_3$)$_2$ (dark blue) and 5×10^{-4} M Fe(NO$_3$)$_2$ (light blue) (arrows show the characteristic bands of the uncoordinated ODT ligand).

Supporting Information). As for trinuclear complexes in which the outer ions do not present a thermal spin-crossover,[19,20] it is known that terminal iron(II) ions in one-dimensional systems such as **4** remain high-spin. Therefore, from the residual paramagnetism observed at low-temperature one can derive an approximate average length of the polymeric chains in **4** of ca. 60 Fe atoms (or ca. 20 nm considering an Fe—Fe distance of 3.3 Å[21]). To present a spin-crossover, the Fe-containing LB films should contain coordination entities of at minimum three Fe-(II) ions held together by bridging triazole rings of ODT.[19,20,22]

Magnetization measurement versus the applied field at 2 K of LB films deposited over Mylar substrate allows to monitor the amount of spins contained in the films. Such results can be rationalized as metal ion content if only one type of spin carrier is present in the film. Figure 5 gives the field dependence of the magnetization M normalized to M_{molar} (the saturation value of the magnetization of one mole of the corresponding spin carrier) per surface area of one layer for films containing only one type of paramagnetic transition metal ion. The amounts of spin carriers in these LB films are then corresponding to the saturation value, which was derived by adjusting experimental data to the Brillouin function (full lines in Figure 5). This represents a rude approximation since weak antiferromagnetic interactions between neighboring metal ions may be present within the entities transferred in the LB films, and in the cases of Fe(II), Co(II), and Ni(II) a significant orbital contribution is expected. These factors make the fit to the Brillouin function not very accurate, and therefore the results given together with

data from XPS spectra in Table 1 represent only a crude evaluation. Nevertheless, this evaluation is reasonable, in particular considering that the exact form of the metal-containing entities within the LB films is not known. The resulting sequence for the amount of metal ions is Cu > Fe > Ni > Co, in agreement with the XPS findings. Taking into account that the mean area of each (M(ODT)$_3$) unit is ca. 62 Å^2 at the collapse of the Langmuir films, the amount of metal ions in the LB films would be ca. 2.7×10^{-10} mole/cm^2 of layer. This value has to be taken as a maximum, reached if all (ODT)$_3$ units really coordinate a metal ion. The results given in Table 1 are of the order of this maximum value, a value that is even reached in the case of Cu(II) for which a high association constant with ODT was inferred from the IR and XPS data. This indicates that these LB films are mainly constituted by metal-coordinated ODT, proving that the recoordination process is efficient in all cases. The size of the metal-containing objects in the LB films cannot be accessed by these data, although it is unlikely that extended units of solely triple-triazole bridges would form at the air—water interface, as a result of the propeller-like arrangement of such entities (see Figure 1).

In the case of the Fe-containing films, only the metal ions in a paramagnetic $S = 2$ state are detected, and not those surrounded by 6 bridging triazole, expected to be low-spin (and thus $S = 0$) at low temperatures. Thus, the magnetic properties as a function of temperature of these films were studied in more detail. Figure 6 shows the temperature dependence of the product MT per cm^2 of a layer of the LB films built from a monolayer

Magnetic Langmuir−Blodgett Films of M(II)/Triazole Oligomers

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TABLE 1: Metal Content of the LB Films of This Study Derived from XPS and Magnetization vs Field Data (Considering $g = 2$)[a']

| LB films	at. % $M_{polymer}$	at. % $M_{subphase}$	$n_{M(II)}$ ($\times 10^{-11}$ mol/ cm^2·of layer)
1 over water	negligible		*b*
1 over K(NO$_3$)	0.2	negligible	*b*
1 over Co(NO$_3$)$_2$	1.1		4.3
1 over Ni(NO$_3$)$_2$	0.1	1.6	
1 over Cu(NO$_3$)$_2$	0.3	4.8	
2 over water	0.9		*b*
2 over K(NO$_3$)	1.7	negligible	*b*
2 over Co(NO$_3$)$_2$	1.6	negligible	
2 over Ni(NO$_3$)$_2$	1.4		5.4
2 over Cu(NO$_3$)$_2$	2.2	0.4	
3 over water	0.5		*b*
3 over Co(NO$_3$)$_2$	0.3	0.5	
3 over Ni(NO$_3$)$_2$	0.3	1.9	
3 over Cu(NO$_3$)$_2$	*b*		27.1
4 over water	0.6		1.5
4 over K(NO$_3$)	0.5	negligible	*b*
4 over Fe(NO$_3$)$_2$	3.9		8.5
4 over Co(NO$_3$)$_2$	1.0	0.7	
4 over Ni(NO$_3$)$_2$	0.7	1.5	
4 over Cu(NO$_3$)$_2$	0.5	4.6	
ODT over K(NO$_3$)		0.9	*b*
ODT over Co(NO$_3$)$_2$		0.3	*b*
ODT over Ni(NO$_3$)$_2$		1.1	*b*
ODT over Cu(NO$_3$)$_2$		2.1	*b*

a Atomic percentages (at. %) are derived from a semiquantitative evaluation of XPS spectra. The $n_{M(II)}$ are likely to be slightly overestimated since the g value is expected to be superior to 2 for these metal ions, especially Co(II). For the Fe-containing films, $n_{M(II)}$ corresponds only to the high-spin centers not showing a spin-crossover. *b* No data.
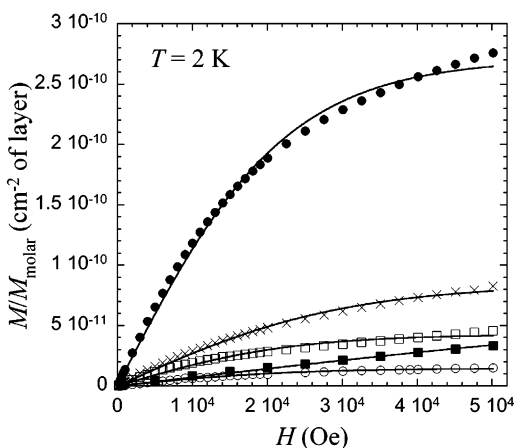
Figure 5. Normalized magnetization versus field data at 2 K of LB films of **3** over Cu(NO$_3$)$_2$ (full circles), **4** over Fe(NO$_3$)$_2$ (crosses), **1** over Co(NO$_3$)$_2$ (empty squares), **2** over Ni(NO$_3$)$_2$ (full squares), and **4** over water (empty circles). M_{molar} is the theoretical saturation value of 1 mole of the corresponding spin carriers (1 μ_B for Cu(II), 2 μ_B for Ni(II), 3 μ_B for high spin Co(II), and 4 μ_B for high spin Fe(II) with g taken equal to 2 (μ_B is a Bohr magneton)). Full lines are fit to Brillouin function, used to determine the M/M_{molar} value at saturation that directly gives the molar amount of metal ions per cm^2 of layer.

of **4** spread over pure water and an aqueous solution of iron-(II). In the case of a cobalt(II)-containing subphase, no noticeable change in the product MT is observed at temperatures where a spin-crossover would be expected (not shown). On the other hand, in the two cases shown in Figure 6 a partial thermal spin-crossover is observed between 260 and 350 K, indicating that at least trinuclear units with bridging triazole ligands are present
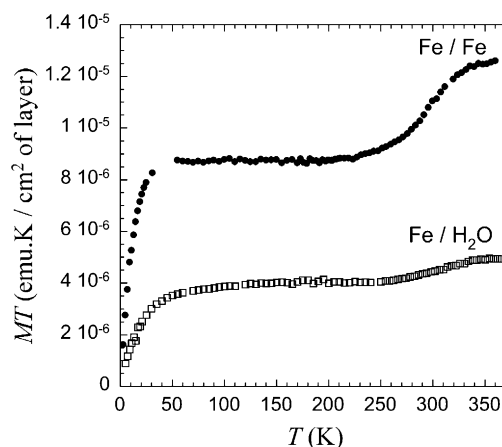
Figure 6. Temperature dependence of the product MT for iron-containing LB films at 1 kOe. Full circles and empty squares correspond to LB films built from a monolayer of **4** spread over an aqueous solution of Fe(NO$_3$)$_2$ and pure water, respectively.

in these LB films. The temperature range compares well with that of bulk **4**. The approximate percentage of iron(II) ions exhibiting the spin-crossover is 31% and 25%, respectively, for the LB films obtained from **4** over an iron nitrate solution and pure water. Thus the average size of the Fe/triazole oligomers within the LB films is comparable in both cases and is close to 3 Fe atoms. As a consequence of the enhanced stability of triple-triazole bridges,[23] trinuclear units can reasonably be formed at the air−water interface by recoordination of metal ions from the subphase. On the other hand, the presence of larger oligomers is unlikely, because the organization of the alkyl substituents of the ODT molecules in the LB films would be against the propeller arrangement of ODT molecules in polymers such as **4**. This is confirmed by the case of the Fe(II)-containing subphase: even if the iron(II) content is close to the maximum value discussed above, a large part of the Fe(II) ions still remain high spin over the whole temperature range studied, which corresponds to the behavior of small oligomeric units. The main difference between the two films exhibiting spin-crossover lies in the total amount of iron inserted in the films, which is about 4 times larger when using a subphase containing iron(II) ions. Eventually, the presence of small oligomeric units in the LB films and their formation mostly by recoordination from the subphase can be generalized to the four metal ions studied here.

Conclusions

The semiamphiphile approach has permitted the fabrication of LB films of triazole-based polymers. The three characterization techniques (IR, XPS, magnetic measurements) used here agree well with each other and give the following conclusions regarding the formation of such films that are summarized in Scheme 1. Two processes are dominating the behavior of metallo-organic polymers at the air/liquid interface, depolymerization of spread polymers, and recoordination of metal ions from the subphase. The metal ions contained in the final LB films mostly originated from the subphase. The efficiency of these two processes is cation-dependent and has been determined for the group Cu−Fe−Co−Ni. Spreading of [Fe(ODT)$_3$](NO$_3$)· H$_2$O over an Fe(NO$_3$)$_2$ aqueous solution allowed us to elaborate a LB film which exhibits spin-crossover properties, which had not been possible so far with the present system. The fact that the associated magnetooptical properties occur around ambient temperature is particularly appealing for the use of LB films in application devices.

Supporting Information Available: XPS survey and the $Fe2p^3$ area of a 20-layer LB film built from a monolayer of **4** spread over an iron nitrate subphase and $\chi_m T$ vs T for polymer **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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