New Magnetic Thin Film Hybrid Materials Built by the Incorporation of Octanickel(II)-oxamato Clusters Between Clay Mineral Platelets

Luminita M. Toma,[†,§] Régis Y. N. Gengler,[†,§] Danielle Cangussu,[‡] Emilio Pardo,[‡] Francesc Lloret,*[‡] and Petra Rudolf*[†]

[†]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, NL-9747AG Groningen, The Netherlands

[‡]Instituto de Ciencia Molecular (ICMol)/Departament de Química Inorgànica, Universitat de València, Edificios Institutos de Paterna, Catedrático José Beltrán Martínez n° 2, 46980 Paterna, Spain

S *Supporting Information*

ABSTRACT: We report on a new method based on the combination of Langmuir—Schaefer deposition with self-assembly to insert highly anisotropic Ni_8 molecules in a hybrid organic—inorganic nanostructure. Spectroscopic, crystallographic, and magnetic data prove the successful insertion of the guest cationic molecule between templating clay platelets. These results open a new route toward the highly controlled fabrication of tailored functional organic—inorganic nanomaterials.

SECTION: Nanoparticles and Nanostructures

Hybrid film

42Å
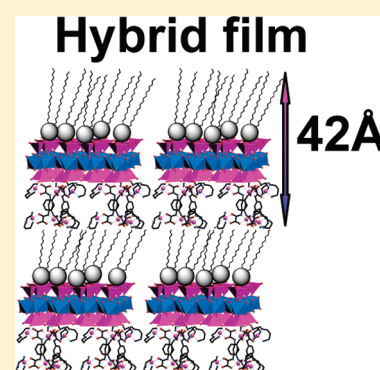
The controlled synthesis of inorganic materials with specific morphology is an important aspect in the development of new materials in many fields such as catalysis, electronics, and nanocomposites. The morphosynthesis of these novel materials into suitable ordered host systems capable of incorporating molecules with interesting physical and chemical properties is a major challenge in current materials science and nanotechnology. Our focus here is to use a new approach involving templating and self-assembly of nanoscale building blocks to prepare novel layered molecular magnet-based materials.[1−3] Among the potential magnetic guest molecules, transition metal polynuclear coordination compounds have attracted much attention since the discovery,[4,5] in 1993, of the first single-molecule magnet (SMM) with the formula $Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4$ (Mn_{12}), which exhibits slow relaxation of the magnetization below a blocking temperature (T_B) of 4.0 K. Nevertheless, the integration of such materials into actual functional devices will require morphosynthesis strategies to achieve spontaneous multilevel organization. To this purpose, heterogeneous self-assembly approaches using both inorganic and organic materials as support host systems have been used.[6] Here we present a simple synthetic strategy to prepare new magnetic thin films of preformed polynuclear building blocks through the use of single clay platelets as host template.

Montmorillonite clay is a class of layered aluminosilicate minerals with a unique combination of swelling, intercalation, and ion exchange properties. Its structure consists of two tetrahedral silica layers sandwiching a central octahedral alumina sheet. The 0.96 nm thick layers are negatively charged, and

neutrality is obtained, for example, when hydrated cations are present in the galleries. With the addition of water, the hydration shell around these cations can increase to such an extent that the clay aggregates not only swell but disintegrate into elementary clay mineral platelets. This exfoliation is an important part of our approach, which uses the Montmorillonite clay minerals as template in a combined Langmuir—Schaefer (LS) and self-assembly technique aimed at building magnetic thin films. As magnetic guest molecule, we chose the octanuclear nickel(II) oxamate complex with the formula $\{[Ni_2(mpba)_3][Ni(dpt)(H_2O)]_6\}$-$(ClO_4)_4 \cdot 12.5\ H_2O$, where mpba is the bridging ligand m-phenylenedioxamato and dpt is the terminal ligand dipropylenetriamine.[7,8] The Ni_8 cations have a dimer-of-tetramers structure with a double-propeller topology. Importantly, one coordination position of each of the six peripheral octahedral metal ions, partially blocked with the dipropylenetriamine ligand, is occupied by a labile water molecule that can be readily exchanged by anchoring and/or bridging deprotonated silanol groups from the host matrix during the ion-exchange process.[6]

To fabricate our films (for details, see the Supporting Information), we first prepared a diluted dispersion of negatively charged single clay nanosheets in water in a thermostated Langmuir—Blodgett (LB) trough at a temperature of 21 ± 0.5 °C. Then, we spread cationic amphiphilic molecules, namely, dimethyldioctadecylammonium (DODA) bromide $[CH_3(CH_2)_{17}]_2(CH_3)_2N^+Br^-$
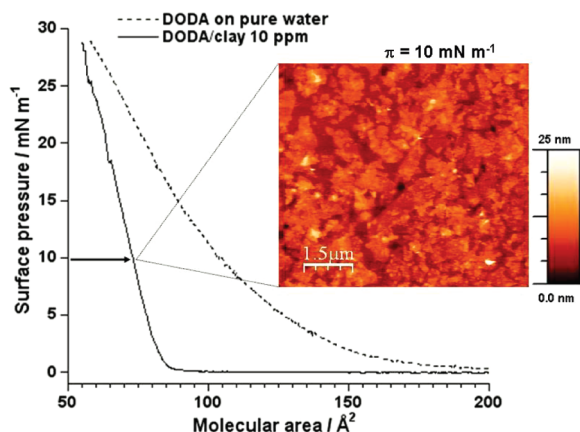
Figure 1. Π−A isotherms of DODA on pure water (dotted line) and on aqueous subphase of clay (10 ppm, solid line). The inset shows the atomic force microscopy image of the hybrid monolayer DODA-clay transferred onto a glass plate at the surface pressure of 10 mN m^{-1}.

Scheme 1. Preparation Method and Model of the Layered Structure of the Hybrid DODA-Clay-Ni$_8$ Multilayer Prepared from Clay Dispersion

dissolved in $CHCl_3$−C_2H_5OH (9:1) mixture (0.1 mg mL^{-1}), a nonaqueous volatile solvent, onto this dispersion. In contrast with a classical LB experiment, where the surfactant spreads and floats on a pure water surface, in our modified method, some of the clay sheets in the subphase are electrostatically adsorbed onto the floating surfactant monolayer, and hybrid floating DODA-clay platelet units are formed at the air−dispersion interface. Compressing the barriers of the LB trough, a hybrid DODA-clay monolayer is formed. Figure 1 shows the surface pressure−area (Π−A) isotherm of DODA spread onto pure water and onto a Montmorillonite containing subphase (clay concentration of 10 ppm). The Π−A curve for the DODA-clay monolayer is steeper and shifted toward smaller area per molecule values than the corresponding curve for DODA on pure water. This effect can be explained by the adsorption of the negatively charged clay platelets on the positively charged surfactant monolayer, which partially compensates the electrostatic repulsion between DODA head groups, allowing for a higher molecular density at a given surface pressure.[9] The molecular area of DODA in the presence of 10 ppm clay dispersion was estimated to be 82 Å^2/molecule by extrapolating to zero pressure the linear part of the isotherm where a condensed phase is formed.

The LS hybrid DODA-clay films, prepared with a clay concentration of 10 ppm in the subphase, were successfully deposited by horizontal lifting at a constant surface pressure of 10 mN m^{-1}. The AFM micrograph of one hybrid layer deposited onto a glass plate, shown as insert in Figure 1, confirms the formation of a compact hybrid monolayer at the air−dispersion interface.

The transferred film is covered on the outside with a clay layer, and some exchangeable cations (Na$^+$) remain on the outer clay surface. By dipping this clay-terminated film in a solution containing a cationic compound (in our case, Ni$_8$), the latter will naturally be adsorbed on the surface by an ion-exchange reaction and form a 2D layer of cationic molecules on top of the clay surface. As sketched in Scheme 1, this deposition sequence can be repeated as desired to create a multilayered system.

Infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and magnetic measurements all testify to the successful grafting of the Ni$_8$ species. The IR spectrum of a 40 layer thick DODA-clay-Ni$_8$ film deposited on CaF$_2$ is shown in Figure 2. It presents characteristic bands
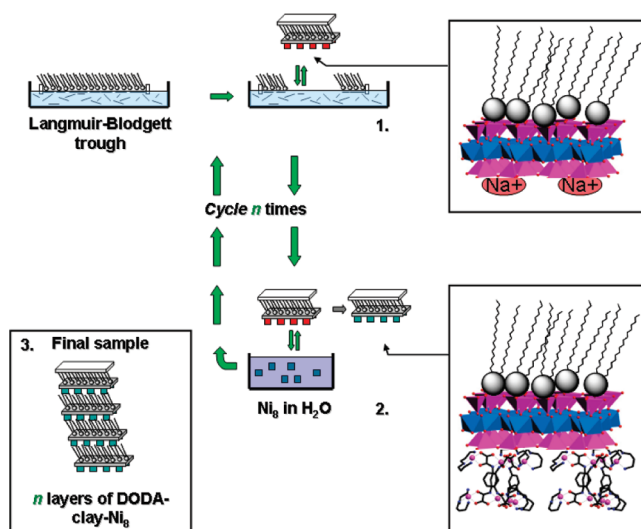
at low wavenumbers 1800−200 cm^{-1} corresponding to the Ni$_8$ cation vibrations.

XPS data were collected on a 40 layer thick film of DODA-clay-Ni$_8$ on Mylar to identify the presence of the Ni$_8$ in the hybrid structure. Figure 2 shows a survey spectrum of the synthesized compound; one can clearly identify Si, Al, C, N, O, and Ni photoemission lines, as indicated, which confirm the presence of expected components, namely, the Ni cluster, the surfactant, and the clay. A detailed scan of Ni2p core level region is displayed in the insert of Figure 2 and found to display the multiplet splitting typical of Ni^{2+} (see refs 10−12), as expected for Ni$_8$. Furthermore, the investigation of the nitrogen 1s core level spectra led to the same conclusion. Comparing the three N1s spectra (see the Supporting Information) of (i) a clay-DODA multilayer film synthesized by LS and self-assembly[9] without the Ni$_8$ adsorption step, (ii) a pure Ni$_8$ layer produced by dropcasting, and (iii) the DODA-clay-Ni$_8$ film, one observes that the N1s signal of the latter is a weighted sum of the former two. This confirms the successful integration of the Ni$_8$ compound in the layered clay structure and its integrity.

XRD data for a 40-layer DODA-clay-Ni$_8$ film (prepared with a 10 ppm clay concentration in the subphase) are shown in Figure 3. One can distinguish three broad peaks centered at $2\theta = 2.1 \pm 0.2$, 4.8 ± 0.2, and 6.7 ± 0.2. Using the Bragg formula, a corresponding $d(001)$ spacing of ∼42 ± 3 Å is deduced. This is a much larger spacing than what is observed for a pure DODA-clay- multilayer,[9] where a clay−DODA repeating unit thickness of 25 Å was found. Hence, also, XRD confirms the presence of the guest Ni$_8$ molecules in the clay stack (42 − 25 Å = 17 Å).

The direct current (dc) magnetic properties of a 110 layer DODA-clay-Ni$_8$ film in the form of the χT versus T plot, where χ is the dc magnetic susceptibility (in arbitrary units) and T is the temperature, are shown in Figure 4 and found to be qualitatively similar to those of the pure Ni$_8$ complex:[7] $\chi_M T$ for DODA-clay-Ni$_8$ exhibits a characteristic minimum at 30 K ($T_{min} = 45$ K for pure Ni$_8$; see ref 7), which is typical of two strong antiferromagnetically coupled oxamate-bridged Ni$_4$ propeller units ($J = -26.6$ cm^{-1} for pure Ni$_8$; see ref 7) that are weakly

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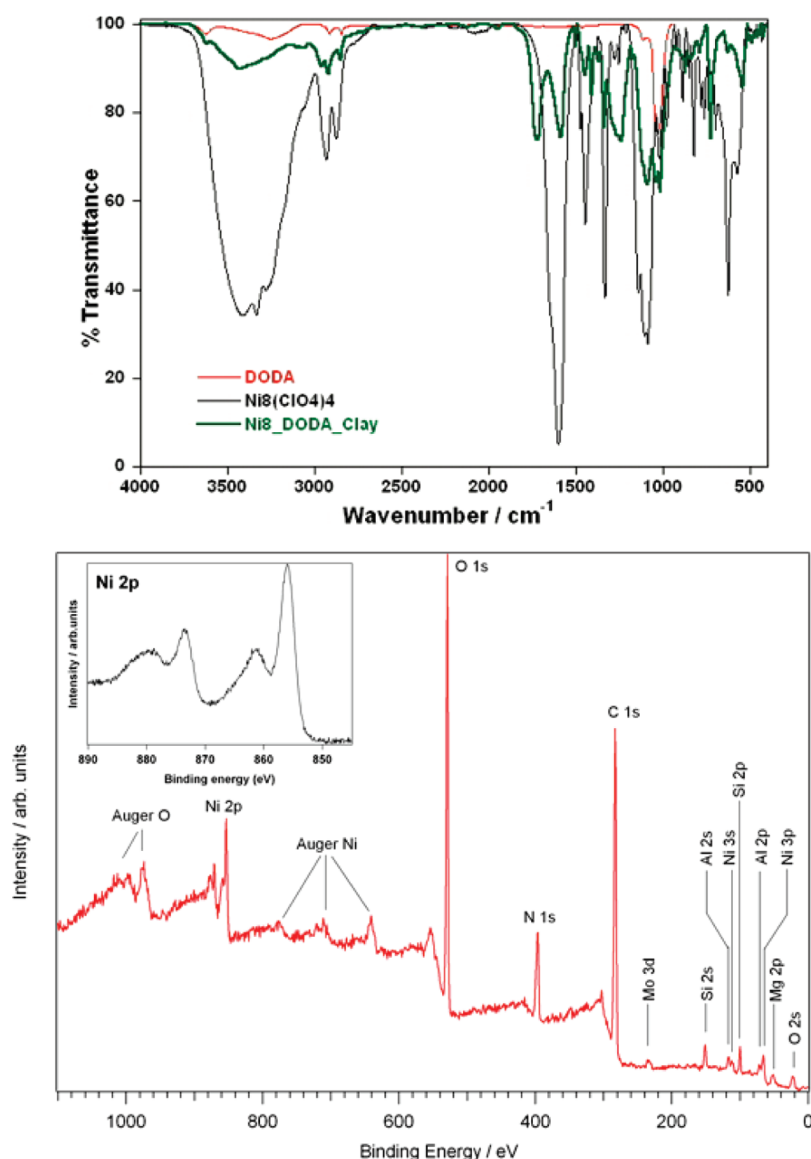dx.doi.org/10.1021/jz2007929 |J. Phys. Chem. Lett. 2011, 2, 2004–2008

Figure 2. Top panel: Infrared spectra of a 40 layer thick hybrid DODA-Montmorillonite-Ni$_8$ film (green line) and hybrid DODA-Montmorillonite film (red line) transferred onto CaF$_2$ plates at a surface pressure of 10 mN m^{-1} and for a clay concentration in the subphase of 10 mg l^{-1} and Ni$_8$(ClO$_4$)$_4$ powder (black line). Bottom panel: Wide scan X-ray photoemission spectrum of a 40-layer DODA-Montmorillonite-Ni$_8$ hybrid film on Mylar (red line) and high-resolution scan of the Ni 2p region (insert).

ferromagnetically coupled through the meta-substituted phenylenediamidate bridges ($J' = +3.1$ cm^{-1} for pure Ni$_8$, see ref 7). Upon further cooling, $\chi_M T$ of DODA-clay-Ni$_8$ shows a maximum at 7 K ($T_{max} = 3$ K for pure Ni$_8$; see ref 7) and then decreases because of the zero field splitting (ZFS) of the moderately anisotropic $S = 4$ ground spin state ($D = -0.23$ cm^{-1} for pure Ni$_8$; see ref 7), antiferromagnetic intermolecular interactions, or both. Indeed, very small distortions in the Ni$_8$ entities (supported by XPS spectra of the N1s core level region, see the Supporting Information) could be responsible for the lower values observed for the minimum and maximum of $\chi_M T$ in this material when compared with pure Ni$_8$ molecules.

The alternating current (ac) magnetic properties of DODA-clay-Ni$_8$ in the form of the χ' and χ'' versus T plot, χ' and χ'' being the in-phase and out-of-phase ac magnetic susceptibilities, respectively, show no evidence of slow magnetic relaxation effects

above 2.0 K (data not shown). This situation contrasts that of the pure Ni$_8$ complex, which shows a slow relaxation of the magnetization below $T_B = 3.0$ K that is reminiscent of SMMs. The distinct magnetic properties of DODA-clay-Ni$_8$ suggest that the Ni$_8$ molecules are not isolated but interact among each other and with their surrounding; this could trigger the loss of slow relaxation of the magnetization behavior. Alternatively, the blocking temperature could be <2 K. It is likely that the aggregation of the Ni$_8$ molecules on the surface of the tetrahedral silica layers is due to the mediating effect of the deprotonated silanolato groups. The intermolecular antiferromagnetic interactions are then propagated by the Si–O$^-$ acting as bridges between the peripheral high-spin Ni^{II} ions of neighboring Ni$_8$ molecules. Along this line, there has been a previous report on the incorporation and further aggregation of Ni$_8$ molecules in ordered mesoporous silica.[6] In that case, the silica-mediated
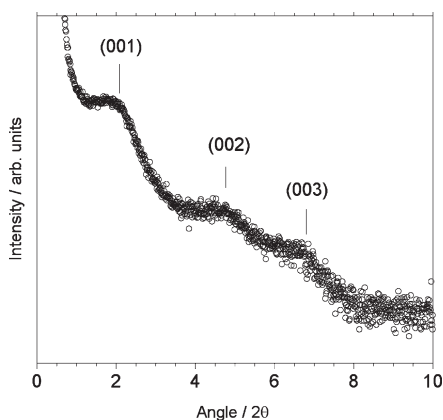
Figure 3. X-ray diffractogram of a 40 layer thick hybrid DODA-Montmorillonite-Ni$_8$ film on Mylar.
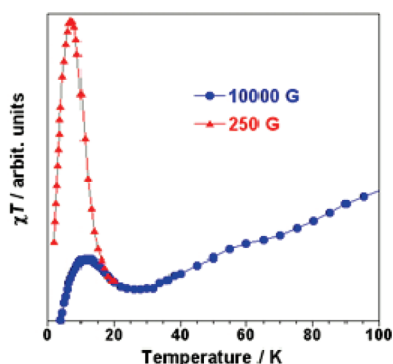

Figure 4. DC magnetic measurements of a 110 layer thick hybrid DODA-Montmorillonite-Ni$_8$ film.

surface aggregation of Ni$_8$ molecules leads to ferromagnetically coupled oligomeric $[Ni^{II}_8]_n$ aggregates with higher blocking temperatures ($T_B = 4.5-10.5$ K) than those of the crystalline material. In fact, it is well known that the nature of the magnetic coupling in related μ-hydroxo, μ-alkoxo, and μ-phenoxo nickel-(II) complexes depends critically on the Ni—O—Ni bridge angle (γ), passing from ferromagnetic to antiferromagnetic for increasing γ (for γ values close to 90°).[13−18]

In summary we have described a new method to insert highly anisotropic Ni$_8$ molecules in a hybrid organic—inorganic nanostructure. The combination of Langmuir—Schaefer deposition with self-assembly allows a control of the film growth at the molecular level. Spectroscopic, crystallographic, and magnetic data have proven the successful insertion of the guest cationic molecule between the templating clay platelets. These results open a new route toward the highly controlled fabrication of tailored functional organic—inorganic nanomaterials.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. All experimental details concerning materials employed, Langmuir—Schaefer assembly procedure, procedures/instruments for characterization of the produced films; additional XPS data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: Francisco.Lloret@uv.es; p.rudolf@rug.nl.

Author Contributions
§These authors have contributed equally to this paper.

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