

Hybrid Materials Based on Magnetic Layered Double Hydroxides: A Molecular Perspective

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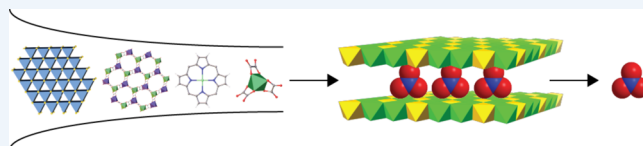
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Supporting Information

CONSPECTUS: Design of functional hybrids lies at the very core of synthetic chemistry as it has enabled the development of an unlimited number of solids displaying unprecedented or even improved properties built upon the association at the molecular level of quite disparate components by chemical design. Multifunctional hybrids are a particularly appealing case among hybrid organic/inorganic materials. Here, chemical knowledge is used to deploy molecular components bearing different functionalities within a single solid so that these properties can coexist or even interact leading to unprecedented phenomena. From a molecular perspective, this can be done either by controlled assembly of organic/inorganic molecular tectons into an extended architecture of hybrid nature or by intercalation of organic moieties within the empty channels or interlamellar space offered by inorganic solids with three-dimensional (MOFs, zeolites, and mesoporous hosts) or layered structures (phosphates, silicates, metal dichalcogenides, or anionic clays).



This Account specifically illustrates the use of layered double hydroxides (LDHs) in the preparation of magnetic hybrids, in line with the development of soft inorganic chemistry processes (also called “Chimie Douce”), which has significantly contributed to boost the preparation hybrid materials based on solid-state hosts and subsequent development of applications. Several features sustain the importance of LDHs in this context. Their magnetism can be manipulated at a molecular level by adequate choice of constituting metals and interlayer separation for tuning the nature and extent of magnetic interactions across and between planes. They display unparalleled versatility in accommodating a broad range of anionic species in their interlamellar space that encompasses not only simple anions but chemical systems of increasing dimensionality and functionalities. Their swelling characteristics allow for their exfoliation in organic solvents with high dielectric strength, to produce two-dimensional nanosheets with atomic thickness that can be used as macromolecular building blocks in the assembly of nanocomposites.

We describe how these advantageous properties turn LDHs into excellent vehicles for the preparation of multifunctional materials with increasing levels of complexity. For clarity, the reader will first find a succinct description of the most relevant aspects controlling the magnetism of LDHs followed by their use in the preparation of magnetic hybrids from a molecular perspective. This includes the intercalation anionic species of increasing nuclearity like paramagnetic mononuclear complexes, stimulus-responsive molecular guests, one- and two-dimensional coordination polymers, or even preassembled 2D networks. This approach allows us to evolve from “dual-function” materials with coexistence, for example, of magnetism and superconductivity, to smart materials in which the magnetic or structural properties of the LDH layers can be tuned by applying an external stimulus like light or temperature. We will conclude with a brief look into the promising features offered by magnetic nanocomposites based on LDHs and our views on the most promising directions to be pursued in this context.

INTRODUCTION

The design of multifunctional materials currently represents one of the most appealing topics in Materials Science. Although there are several options of choice, the so-called hybrid approach is arguably the most efficient route to chemically design this type of materials. This approach relies on the chemical combination of organic and inorganic components to render a hybrid solid. In the simplest case, the material is assembled by direct combination of two functional networks, with each network delivering a distinct physical property to the solid. When the constituting networks behave almost independently, a “dual-function” material exhibiting simple coexistence of the two properties of interest (in particular,

magnetic, electrical or optical) is anticipated. Typical examples of this kind are magnetic molecular conductors and superconductors.^{1–3} A more sophisticated case arises when both components are coupled since in that case these properties can be affected by the mutual interaction between the two components and even new properties can emerge. A relevant example in this context is achieved by introducing in a functional network, acting as a host, a guest molecule capable to respond to an external stimulus (like temperature, light, or pressure) so that the structural and/or electronic change of the

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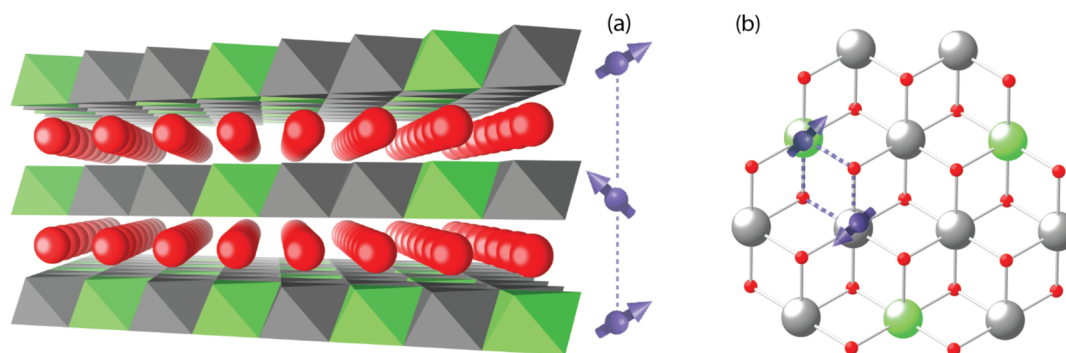


Figure 1. Structure and magnetism of layered double hydroxides. LDHs display a layered structure built from stacking of brucite-type cationic slabs interleaved with anions (red spheres) and water molecules. Grey and green octahedra stand for divalent and trivalent metals, respectively. LDHs can display a magnetic response by incorporation of paramagnetic metals to the anionic layers. Reported examples include combinations of $M(\text{II}) = \text{Ni}$, Co , and Zn , and $M(\text{III}) = \text{Al}$, Fe , Cr , Mn , and Co (See Table S1 in the Supporting Information). Magnetism in LDHs is controlled by (a) weak dipolar interactions between the net spins borne by alternating magnetic layers that can be controlled by modulating the interlayer distance and (b) stronger in-plane magnetic superexchange between neighboring paramagnetic ions through the OH^- bridges that link edge-sharing $[\text{M}(\text{OH})_6]$ octahedra across the LDH layers.

molecular component can modify the properties of the host.^{4,5} This last class of molecule-based materials is known as hybrid stimuli-responsive materials.

Layered double hydroxides (LDHs) are anionic clays built from the stacking of positively charged brucite-type inorganic layers interleaved with anions (Figure 1). They can be formulated as $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}[\text{A}^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$ (A^{n-} = organic or inorganic anions). Synthetic LDHs are quite promising based on their low cost, chemical versatility and anion exchange capabilities, which allows for tuning of their composition and properties in a wide range.^{6,7} Thanks to their layered nature, they can be also exfoliated in organic solvents by intercalation of suitable anions that minimize the interaction between layers to produce stable colloids containing single and few-layers LDHs.⁸ These positively charged nanosheets can be then used as macromolecular building blocks in the design of more complex architectures as they retain most of the properties intrinsic to the bulk host.^{8,9} Built upon these features, pristine LDHs and the mixed oxides that result from their calcination have found widespread application, even of industrial relevance.^{7,10}

■ MAGNETISM IN LAYERED DOUBLE HYDROXIDES

Regardless many of the synthetic LDHs available from the literature incorporate first row paramagnetic transition metal ions to their structure, studies on the magnetism of these systems remained very scarce.^{11–14} Magnetic LDHs have been instead generally used as precursors for metal oxides, since their thermal decomposition leads to the formation of mixed metal oxides with a high metal dispersion and high surface area.¹⁵

The first thoroughly study on the magnetic properties of LDHs was published by our group in 2002.¹⁶ In this work, we reported that NiAl- and CoAl-LDHs showed spontaneous magnetization at low temperatures as result of the ferromagnetic coupling of $M(\text{II})$ ions within the layers ($M(\text{II}) = \text{Co}$, Ni). The in-plane magnetism in LDHs is dominated by a superexchange mechanism mediated by the hydroxo (OH^-) bridges linking neighboring edge-sharing $[\text{M}(\text{OH})_6]$ octahedra (Figure 1b).¹⁷ The $M^{\text{II}}-\text{OH}-M^{\text{II}}$ angle in this case is close to 90° , favoring orthogonality of the M^{II} magnetic orbitals that results in weak ferromagnetic coupling between high-spin $\text{Co}(\text{II})$ (d^7 ; $S = 3/2$) or $\text{Ni}(\text{II})$ (d^8 ; $S = 1$) centers, responsible for the low T magnetic behavior.¹⁸ Overall, magnetism in these

solids is also controlled by much weaker dipolar interactions, which operate between magnetic layers and are strongly dependent on the magnetic moment borne by the layers and the distance separating them (Figure 1a). In following works we also showed how diamagnetic Al(III) centers occupying trivalent sites in the LDH structure can be replaced with paramagnetic ions like Fe(III) or Cr(III). This substitution results in $M^{\text{II}}-\text{OH}-M^{\text{III}}$ and $M^{\text{III}}-\text{OH}-M^{\text{III}}$ antiferromagnetically coupled pairs: overlapping between nonorthogonal magnetic orbitals like $M(\text{II}) e_g$ with $M(\text{III}) t_{2g}$. As result, these solids display richer magnetic behaviors including ferro- and ferrimagnetism at low- T ,¹⁹ as well as glassy magnetism arising from the combination of competing interactions across the layers.^{20,21} We have recently demonstrated that this last behavior originates from $M(\text{III})$ clustering, more likely for higher degrees of $M(\text{III})$ loading, that favors the occurrence of in-plane spin frustration.²² Magnetism of LDHs is also sensitive to the solid's particle size as recently demonstrated by O'Hare et al. for a family of nanosized CoAl-LDH synthesized by the reverse micelle method²³ and by us for alkoxide-intercalated CoFe-LDH nanosheets synthesized by a nonaqueous route.²⁴ See Table S1 in the Supporting Information for a summary of the properties of magnetic LDHs reported so far.

Magnetism of LDHs is typically studied by using magnetometric and calorimetric techniques. This includes the following: (a) Static susceptibility measurements (DC) to determine the nature and strength of magnetic interactions. (b) Dynamic measurements (AC) to study the presence of net spontaneous magnetization at low temperatures, which is linked to the presence of an out-of-phase signal below a given temperature (T_M). Analysis of the frequency dependence of this signal's position is generally indicative of glassy behavior. (c) Heat capacity measurements are used to ascertain the real origin of spontaneous magnetization. Whereas real magnetic ordering (long-range correlation) is associated with the appearance of a λ peak indicative of a second-order phase transition, the presence of rounded anomalies at temperatures close to T_M account for freezing of the spins at low- T typical of disordered materials showing a glassy behavior.

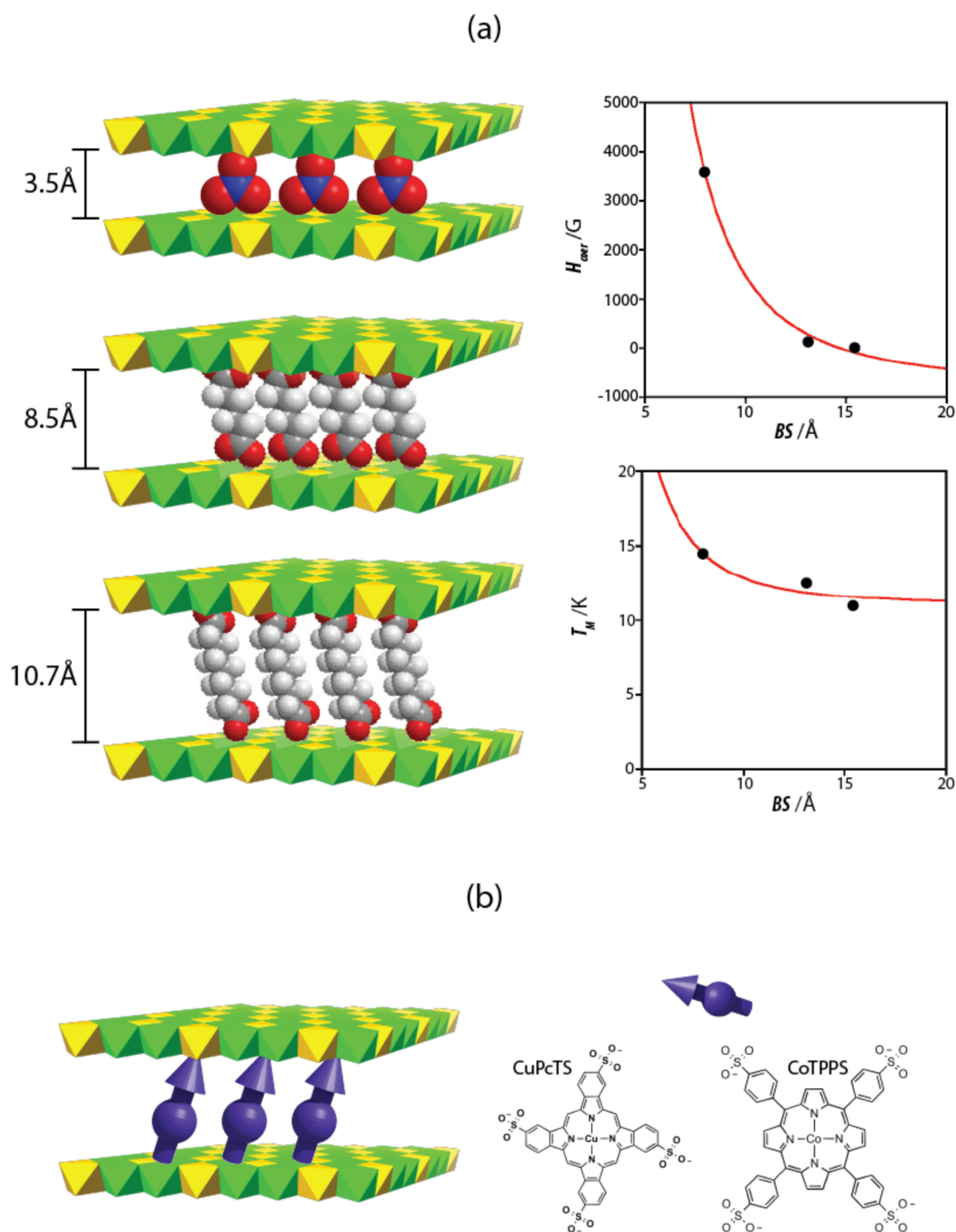


Figure 2. Magnetic multilayers obtained by intercalation of discrete molecular species. (a) Modulation of the overall magnetism of NiFe-LDHs with the interlayer separation by intercalation of diamagnetic species with increasing size (b) Hybrid magnetic multilayers by intercalation of anionic paramagnetic complexes in magnetic LDH hosts.

■ MAGNETIC MULTILAYERS OBTAINED BY INTERCALATION OF DISCRETE MOLECULAR SPECIES

Here we describe the simplest class of hybrids, built from the intercalation of anions with slight or almost negligible magnetic interaction with the LDHs. As described above, the overall magnetism of LDHs relies on the combination of (i) in-plane magnetic superexchange and (ii) through-space dipolar interactions between the magnetic layers. This scenario allows for a better understanding of the effects played by both contributions by suitable chemical manipulation. Whereas in-plane exchange is dominant and can be tuned by gradual

replacement of the M(III)/M(II) metal centers in the layers, the influence of much weaker dipolar interactions can be conveniently analyzed by intercalation of diamagnetic anions with variable size (Figure 2a). This was studied for a family of hybrid NiFe-LDHs interleaved with nitrate (NO_3^-), adipate ($\text{C}_6\text{H}_8\text{O}_4^{2-}$) and sebacate ($\text{C}_{10}\text{H}_{16}\text{O}_4^{2-}$) anions.²⁰ While the in-plane magnetism is constant for all cases, anion replacement modifies the interlayer separation (defined as the effective gap between magnetic layers) from 3.5 to 10.67 Å and controls the temperature at which spontaneous magnetization is observed (T_M), which become smaller for longer distances likely due to weaker dipolar interactions involved. This also triggers a change

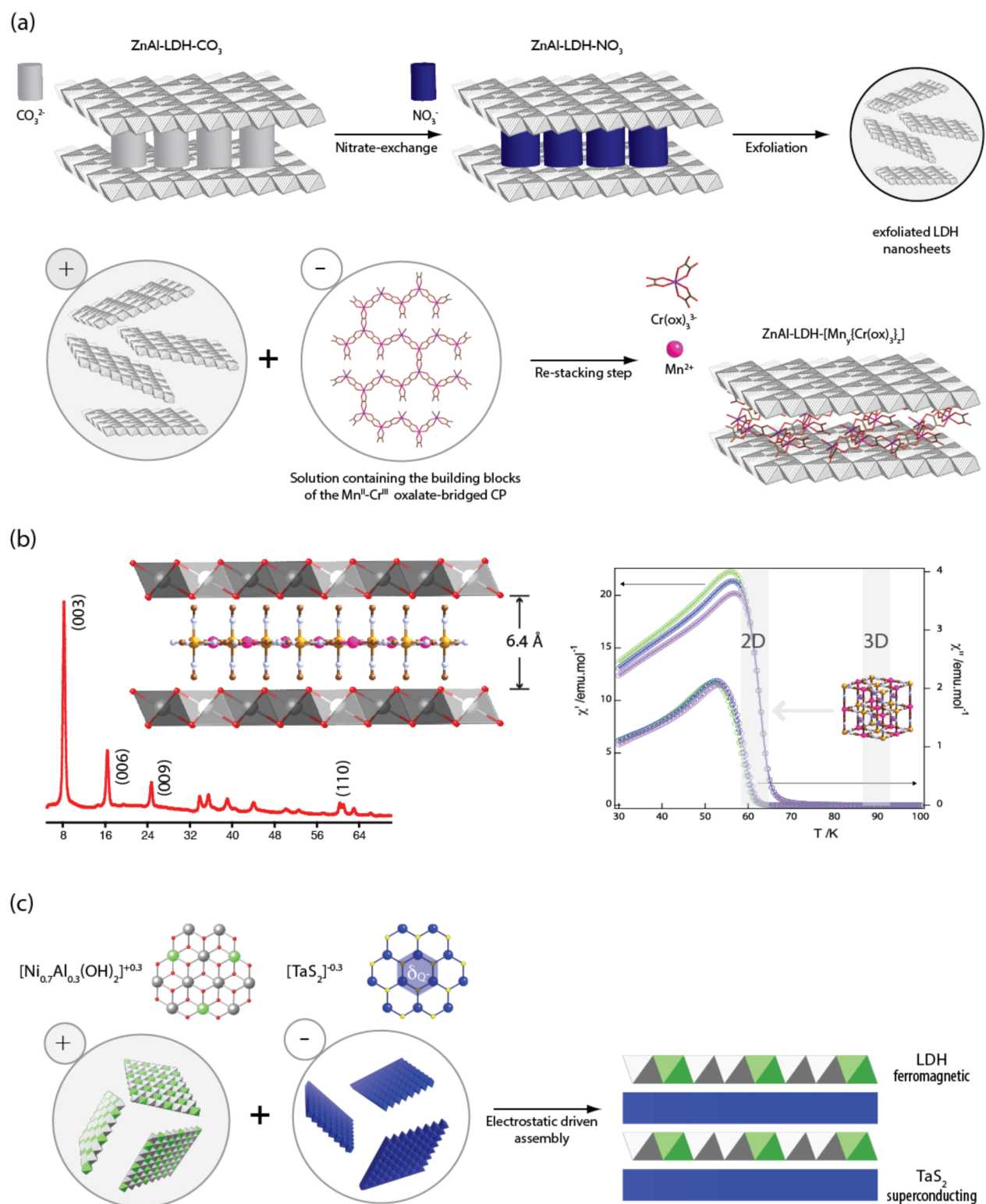


Figure 3. Magnetic hybrids obtained by intercalation of molecular entities with increasing dimensionality. (a) Scheme depicting the growth of an extended Mn(II)–Cr(III) oxalate-bridged 2D magnet using cationic nanosheets of LDH as templating host. (b) Confined growth of cyanide-based magnets in two dimensions. Magnetic measurements confirm the reduction in dimensionality with respect to the 3D analogue. (c) Chemical design of a layered hybrid displaying coexistence of ferromagnetism and superconductivity.

in the sign of the interlayer interactions, from ferro-, for large interlayer distances, to antiferromagnetic for shorter.

This strategy can be also exploited for producing magnetic multilayers by intercalation of paramagnetic anions that interact with the magnetic planes of the LDH host (Figure 2b).

Molecules like phthalocyanines (Pc)²⁵ or porphyrins (Por)²⁶ are preferred options based on their planar geometry that can be easily accommodated by these lamellae. LDH hosts, like NiAl or NiFe, provide an ideal environment for isolating paramagnetic molecules like CuPcTS (PcTS= phthalocyanine-

tetrasulfonate) or CoTPPS (TPPS = 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin)), thus minimizing intermolecular magnetic interactions in the hybrid. The incorporation of these anions has a negligible effect on the magnetism of the hybrid, with almost constant T_M values regardless the nature of the LDH host and the paramagnet intercalated. In turn, the properties of the intercalated paramagnetic molecule are somewhat modified. EPR studies for the NiAl-CuPcTS hybrid display a small g -shift in the EPR signal of the CuPcTS complex, which might originate from weak magnetic interactions between the paramagnet and the LDH layers. Nonetheless, for all hybrids reported thus far, the constituting magnetic sublattices can be considered to behave almost independently to display mere coexistence of the cooperative magnetism from the LDH with the paramagnetism from the intercalated guest molecules.

■ MAGNETIC HYBRIDS OBTAINED BY INTERCALATION OF MOLECULAR ENTITIES WITH INCREASING DIMENSIONALITY

The structural flexibility of the interlamellar space offered by LDHs and their anion-exchange ability can be also used to intercalate more complex units, which go beyond simple paramagnetic complexes in magnetic behavior and structural complexity, or even to confine their growth. This strategy is particularly appealing as it allows for combination of the intrinsic magnetism of LDHs with the properties afforded by the intercalated systems. However, this requires fine control of the synthetic conditions necessary to mediate the growth of oligomeric species or even extended coordination polymers in a nanometric confined space. Here we describe several routes that have enabled the preparation of magnetic hybrids by intercalation or controllable growth of molecule-based materials within the empty space offered by LDHs. Most of the LDHs used in this context were diamagnetic to simplify analysis of the magnetism of the interleaved moieties except for the last section that describes the assembly of magnetic/superconducting hybrids.

Intercalation of magnetic bimetallic oxalate complexes into a diamagnetic MgAl-LDH host is the first report for which the magnetic entity interleaved between planes is a polynuclear molecular complex rather than a simpler mononuclear paramagnet.²⁷ To figure out the optimum conditions for this intercalation, the nitrate salt of MgAl-LDH was immersed in either (a) an aqueous mixture of $[\text{Cr}(\text{ox})_3]^{3-}$ and MnCl_2 , simple components of the bimetallic complex $\text{Mn}_3[\text{Cr}(\text{ox})_3]_2$, or (b) the aqueous solution result of dissolving the 2D soluble magnet $[\text{K}(18\text{-crown-6})]_3[\text{Mn}_3(\text{H}_2\text{O})_4\{\text{Cr}(\text{C}_2\text{O}_4)_3\}_3]$.²⁸ The main difference between both procedures lies in the degree of association of magnetic complexes in the corresponding precursors. In light of the formulas of the hybrids, $[\text{Mg}_2\text{Al}(\text{OH})_6][\text{NO}_3]_{(1+2y-3z)}\{\text{Mn}_y[\text{Cr}(\text{ox})_3]_z\}$, with $y = 0.05$, $z = 0.17$ for (a) and $y = 0.16$, $z = 0.32$ for (b), anionic building blocks show a stronger tendency to penetrate the interlamellar space offered by the cationic host with more efficient anion exchange for protocol (b). This suggests that the use of preassembled molecular precursors is more adequate for achieving intercalation of bimetallic oxalate complexes than just the mixture of ionic components. This is likely due to the presence of $[\text{K}(18\text{-crown-6})]^+$ cations in solution (b) that stabilize big anionic oligomers that are then straightforwardly incorporated into the cationic layered framework, while the intercalation of simple moieties in (a) undergoes faster than the formation of

oligomers. From a magnetic point of view, both strategies enable formation of low-dimensional magnetic coordination structures based on bimetallic oxalate-bridged oligomers with different bridging modes.

At this stage, formation of extended coordination networks from simpler complexes was the natural step forward. This was successfully accomplished by following a completely different route to drive the formation of an oxalate-based magnet into a ZnAl-LDH.²⁹ This work beautifully illustrates how the mismatch between the charge densities born by the cationic LDH ($+0.028 \text{ q}\cdot\text{\AA}^{-2}$) and the 2D anionic polymeric network pursued $[\text{MnCr}(\text{ox})_3]^-$ (cf. $-0.014 \text{ q}\cdot\text{\AA}^{-2}$) avoids formation of the last by simple exchange reactions (Figure 3a). To circumvent this, we exfoliated the LDH in *N*-methylformamide (NMF) to produce a stable colloidal suspension of cationic nanosheets that can be then directly used as macromolecular cations to drive fast assembly of an anionic oxalate-based coordination polymer from simple anionic components like $\text{Mn}^{2+}(\text{aq})$ and $\text{Cr}[(\text{ox})_3]^{3-}$. This route can be considered equivalent to the so-called bimetallic approach in oxalate chemistry in which a bulky cation is used to template the assembly of low-dimensional anionic complexes into a layered 2D anionic network that interleaves cations to counterbalance charge.³⁰ Although the mismatch between density charges of the anionic and cationic sublattices prevents the formation of a perfect 2D anionic network, one obtains the intercalation of a bimetallic network with a Cr:Mn ratio of 1.5 that displays ferrimagnetic ordering below 3 K as a result of long-range antiferromagnetic interactions mediated by the oxalate linker, acting as a bidentate-monodentate bridge between the metal ions across the polymer (Figure 3a). This result represents a significant advance over the standard anion-exchange route as it enables intercalation of a coordination polymer.

A more elegant strategy for overcoming density charge mismatch is to analyze the multiple magnetic coordination networks available in order to define those that would be more adequate to reduce the difference between the charge born by the host and guest sublattices. This is the case of Prussian Blue analogues (PBAs) as the smaller size of cyanide compared to oxalate would render the formation of a bimetallic 2D network with charge density of $-0.024 \text{ q}\cdot\text{\AA}^{-2}$, almost identical to the cationic charge born by the LDH host (Figure 3b). This hypothesis was confirmed by using a ZnAl-LDH host to restrict the growth of a cyanide-based magnet in 2D.³¹ In this work, the NO_3^- anions present in the LDH were replaced with $[\text{Cr}(\text{CN})_6]^{3-}$ building blocks and then the resulting ZnAl- $[\text{Cr}(\text{CN})_6]$ LDH was immersed in a saturated alcoholic solution of $\text{Ni}(\text{NO}_3)_2$. Good match between charges drives rapid polymerization of the 2D PBA $[\text{NiCr}(\text{CN})_6(\text{NO}_3)_2]$ in the confined nanometric space available from the solid-state host. Reduction in dimensionality was confirmed by magnetic measurements that show how the T_c of the intercalated ferromagnet is 65 K, two-thirds of the 90 K reported for the 3D Ni-Cr PBA analogue (Figure 3b). This is quite remarkable as the formation of the 3D phase is much more favorable thermodynamically and reducing the dimensionality of this family of solids typically involves use of capping ligands to restrict their growth, while this route simply involves use of simple inorganic components. This strategy has been more recently extended to controllably grow $[\text{M}^{\text{II}}\text{Fe}(\text{CN})_6]^-$ ($\text{M}^{\text{II}} = \text{Ni}, \text{Co}$) cyano-bridged coordination polymers using dia- and ferromagnetic LDHs.³²

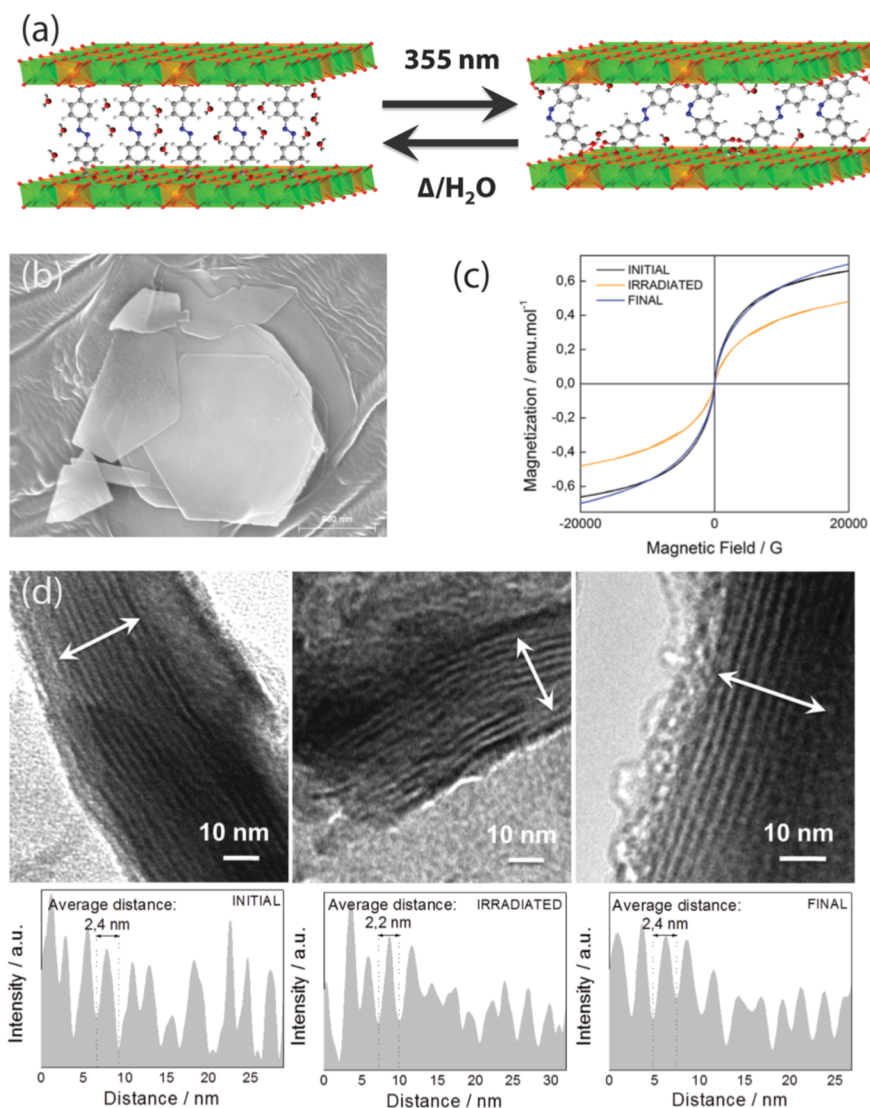


Figure 4. Switchable magnetic hybrids obtained by intercalation of photoresponsive molecules. (a) Reversible change in the structure of the hybrid after irradiation with UV light. (b) FESEM image highlighting the hexagonal morphology of the materials used in this study. (c) Hysteresis cycles for the initial CoAl-T1 (black), and the corresponding irradiated (orange) and final (blue) samples. (d) HRTEM images showing a cross view of CoAl-T1 crystals. White arrows highlight the average distance between fringes that is consistent with the basal space estimated from PXRD study of the bulk hybrids.

The versatility of this strategy has also been exploited to synthesize a family of layered materials that displayed unprecedented coexistence of cooperative magnetism and superconductivity by chemical design.³³ The molecular approach toward the synthesis of a layered solid combining both functions relies on the linkage of magnetic (M) and superconducting (SC) components from solution into an extended framework. While there are several examples of paramagnetic superconductors,² the poor association between magnetic complexes has failed to provide combination of superconductivity with long-range magnetic correlation thus far. This problem was sidestepped by using a different strategy that made use of two extended layers bearing the pursued functionalities and complementary charges so that they could be self-assembled from solution into a dual-function layered heterostructure by attractive electrostatic interactions. The M and SC building-blocks of choice were NiAl and NiFe-LDHs, that display ferro- and ferrimagnetism below 4 and 16 K, respectively, and $[\text{TaS}_2]\text{Na}_{0.33}$ that behaves as a Type-II

superconductor below 4.5 K. These inorganic graphenoids were then exfoliated in organic solvents to produce stable colloids of 2D nanosheets that retain the physical properties of the bulk solids. The perfect match between the charge densities born by the cationic M LDH ($+0.021 \text{ q}\cdot\text{\AA}^{-2}$) and the anionic SC TaS_2 (cf. $-0.022 \text{ q}\cdot\text{\AA}^{-2}$) favors the assembly of multilayered M/SC composites $[\text{Ni}^{\text{II}}_{0.66}\text{M}^{\text{III}}_{0.33}(\text{OH})_2][\text{TaS}_2]$ ($\text{M}^{\text{III}} = \text{Al, Fe}$) (Figure 3c). These can be considered chemical analogues of the technically more demanding heterostructures built by physical methods. Coexistence of both functionalities was confirmed by magnetic measurements and muon-spin rotation (μSR) experiments. The versatility of this approach has been recently exploited to produce other materials that combine the intrinsic superconductivity of $[\text{TaS}_2]^{-0.33}$ layers with single-molecule magnetism³⁴ or the bistability provided by a spin crossover complex.³⁵

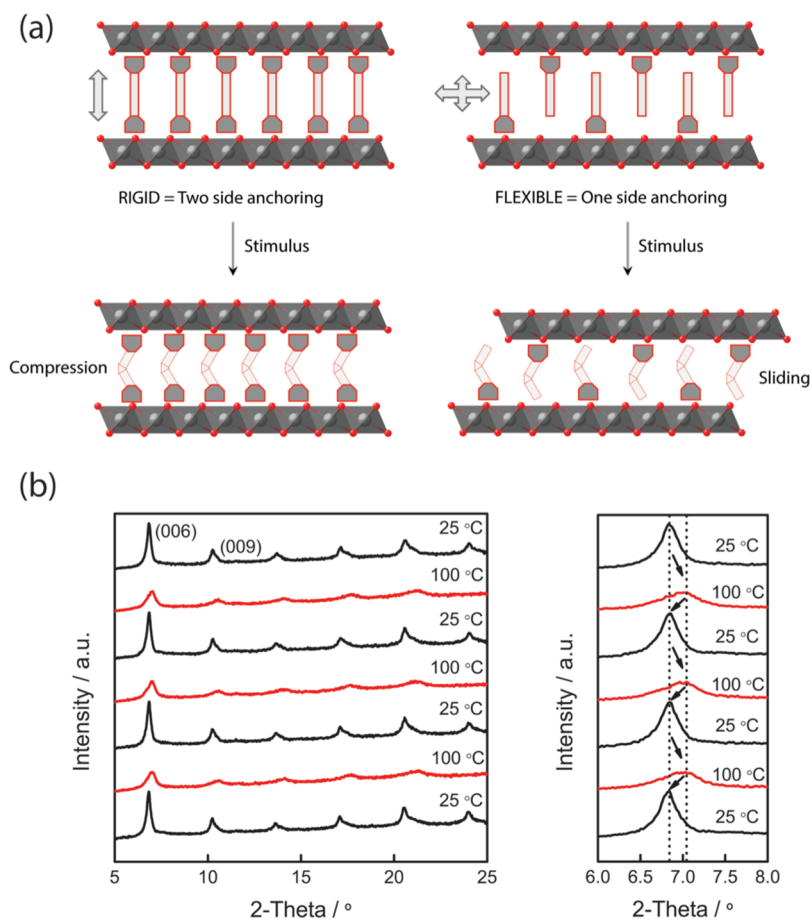


Figure 5. Switchable magnetic hybrids obtained by intercalation of thermoresponsive molecules. (a) LDH nanosheet compression/sliding movements and subsequent change in the interlayer distance by application of an external stimulus to (left) rigid system based on intercalated molecules with two anchoring groups and (right) more flexible with only one anchoring group. (b) Reversible changes in the PXRD pattern of CoAl-AOS upon heating and cooling.

■ SWITCHABLE MAGNETIC HYBRIDS

When it comes to hybrid solids, it is always difficult to go beyond simple coexistence of the properties delivered by the two networks combined. To enable mutual interaction, so that the properties of the hybrid can be affected, remains somewhat elusive. We have already described how the magnetism of LDHs can be efficiently tuned by chemical manipulation of the interlayer spacing by intercalation of diamagnetic anions with variable size. Provided the versatility of LDHs in hosting manifold anionic moieties, this same approach can be exploited for accommodating switchable guests that can modify their size with external stimuli, thus tuning the magnetism of the LDH host.

This concept was first proved in a CoAl-LDH intercalated with light-responsive azobenzene molecules (Figure 4). The magnetic properties of this hybrid solid can be reversibly switched by sequential cycles of irradiation and hydration. Here, the LDH layers are firmly linked to the two ends of azobenzene-4,4'-dicarboxylate anions³⁶ for a “rigid” system in which the *cis*–*trans* photoinduced isomerization slightly changes interlayer distances but produces an acute distortion of the internal structure of the LDH plane, as confirmed by high-resolution microscopy, and thereby the in-plane magnetism. This last must be responsible for the significant changes observed in the hybrid’s magnetism upon irradiation (i.e., drop of the magnetization at 2 K close to 27% and increase of the T_M

in ca. 1 K) as they are too dramatic to be ascribed exclusively to changes in the comparatively weaker dipolar interactions (Figure 4c).³⁷

By making use of an azobenzene molecule with only one terminal acidic group, we used this same approach to produce more flexible hybrids due to the richer conformational flexibility of the intercalated molecule that is only linked to one of the LDH layers (Figure 5a).³⁸ This is the basis for understanding the morphological changes displayed by CoAl-LDH intercalated with thermoresponsive 4-(4-anilinophenylazo) benzenesulfonate with temperature. The different molecular shape of the high- T azo and the low- T hydrazine tautomers provokes a reversible variation in the interlayer separation of the LDH host close to 1 Å, as confirmed by X-ray powder diffraction. More importantly, the diffraction peaks corresponding to the interlayer separation becomes broader upon the molecular switching, indicating that this thermal process has drastic consequences on the crystallinity of the solid (Figure 5b). This change at the nanoscale is also reflected at the microscale. Thus, upon heating a LDH crystal, it undergoes a large change in volume (up to 25% as revealed by AFM). Notice that, despite these drastic structural changes, the molecular switching leads to a very limited change in the magnetic properties (only a reduction of a 8% in the saturation of the magnetization value is observed). All these results indicate that the thermal isomerization of the guest molecules induces a significant sliding of the

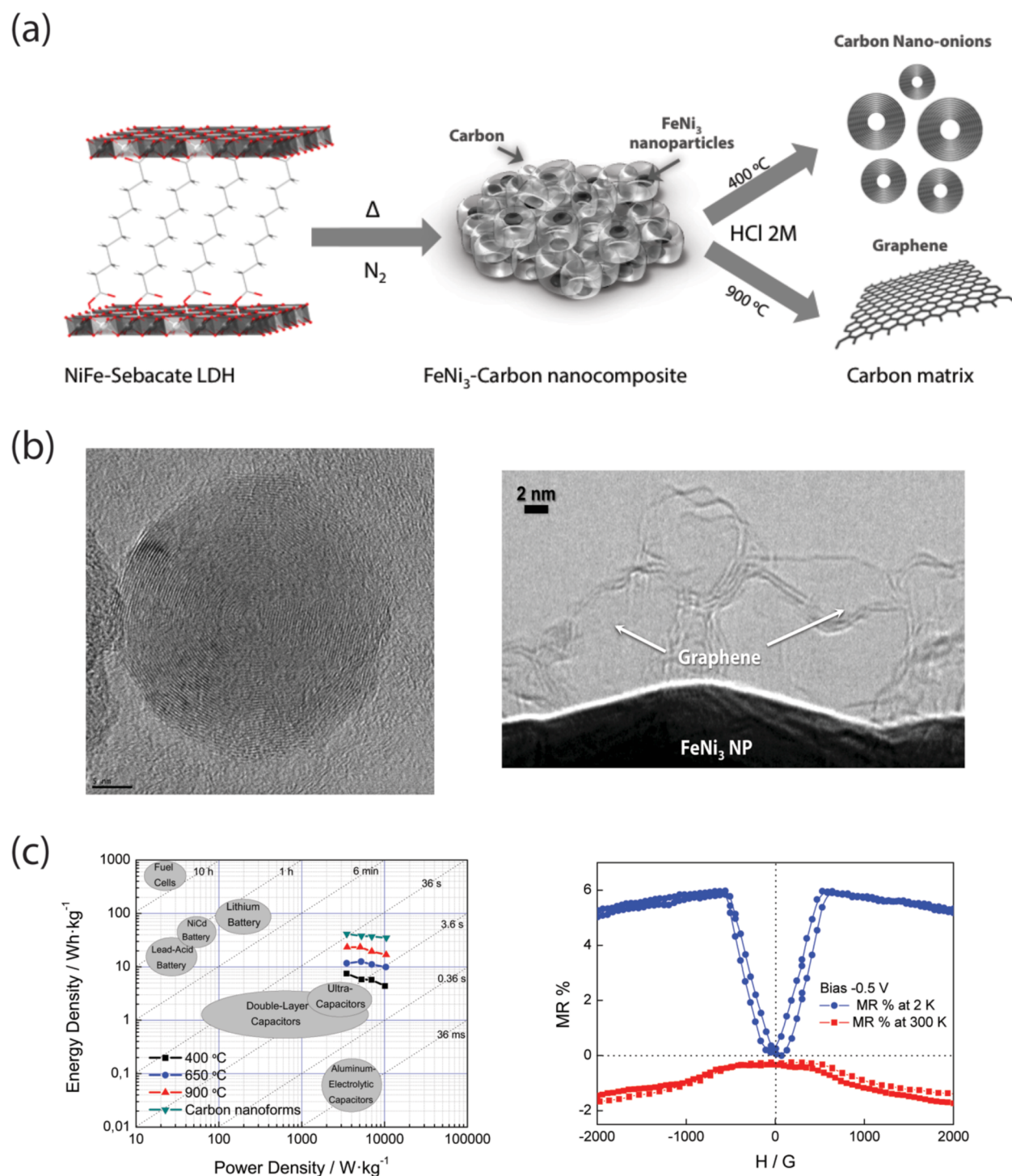


Figure 6. Magnetic nanocomposites. (a) Scheme illustrating the formation of FeNi_3 -carbon nanocomposites and the corresponding carbon nanoforms after thermal treatment (b) HRTEM images showing a carbon nano-onion and the morphology of FeNi_3 -graphene nanocomposites. (c) Ragone plot ranking the performance of LDH-derived carbon-based supercapacitive electrodes among various commercial energy-storage devices (source data from US Defense Logistics Agency) (left) and low-field plot of the field dependence of the magnetoresistance of ferromagnetic FeNi_3 NPs/G hybrids, highlighting the crossover in the MR (unpublished results).

LDH layers, while keeping the structure of these magnetic layers almost unchanged.³⁸

In conclusion, in the first example the LDH magnetic layers are rigidly connected to the intercalated molecules, as they act as bridging ligands. Hence, any structural change induced in these molecules by an external stimulus will provoke a significant change in the structure of the layers. In contrast,

in the second example the intercalated molecules are only connected by one side to the LDH layers. Hence, a molecular switching could affect the interlamellar separation as well as a sliding of the layers, but is expected to have a very limited effect on the internal structure of the LDH layers. These features explain why in the first example the changes induced in the magnetic properties by the application of an external stimulus

are more important. We believe these two examples pave the way for the development of more complex stimuli-responsive “breathing” systems based on LDHs.

■ MAGNETIC NANOCOMPOSITES

Development of functional nanocomposites by incorporation of LDHs as inorganic components are focus of extensive research nowadays due to their chemical robustness and intrinsic chemical and electrochemical properties of interest in a broad landscape of applications like magnetism, catalysis, biomedicine, sensing, corrosion-resistant coatings, electrochemical batteries, ion exchangers, absorbents, or even nanoreactors. Beyond the preparation of new materials by suitable mixing of components, researchers have now realized that their overall activity can be manipulated more efficiently by deep control over their hybridization at the nanoscale.

In line with this tendency, the synthesis of hierarchical nanocomposites built from LDH hybrids and carbon nanoforms nicely exemplifies the value of chemical design as an efficient tool to improve the applications of LDHs.³⁹ The use of magnetic organic–inorganic LDH hybrids as starting materials also enables the synthesis of carbon-based magnetic nanocomposites with physical properties and electrochemical activities that overcome those of the original solid. For example, we have reported how the liquid-phase exfoliation of a NiMn-LDH into 2D nanosheets followed by electrostatic assembly with graphene oxide (GO) produces a magnetic hybrid composite NiMn-LDH/GO that displays excellent capacitance values when used as an anode material in Li-ion batteries.⁴⁰ Even more, this hybrid can be calcined to trigger gradual GO decomposition into CO₂ coupled to controlled segregation of nickel metal nanoparticles (NPs). This collective process can be finely controlled with temperature with concomitant increase of the size of the NPs and complete decomposition of GO at higher temperatures.⁴¹

We have also demonstrated how LDH can be used as hybrid precursors for the chemical synthesis of carbon nanoforms (CNFs) at low temperatures based on the nanometric distribution of catalytic metals in the LDH layers and the intimate contact between these layers and the carbon precursors in a constricted media.^{42,43} Thermal decomposition of a NiFe-LDH intercalated with sebacate molecules, acting as carbon source, enables the low-temperature formation of carbon nano-onions (CNOs) and multiwalled nanotubes (MWNTs) through a simple reaction (Figure 6a). This process benefits from the catalytic activity of the FeNi₃ nanoparticles formed in situ, which facilitate the decomposition of the confined sebacate molecules to produce CNFs embedded into a graphitic shell via a bottom-up approach. The formation of multishelled carbon nanoforms takes place at 400 °C, a temperature way below that required for the catalytic synthesis of CNOs and related materials by using nanoparticulated Ni–Fe catalysts (cf. ≥750 °C). Our approach offers other advantages over the standard top-down physical route. This last generally requires the use of expensive equipment and leads to large amounts of amorphous carbon and starting graphite, requiring purification to isolate the nanoforms from the resulting mixture. Our method, in turn, renders mainly CNFs that can be straightforwardly isolated by removal of the metal substrate via acid leaching of the FeNi₃/C composite. This process can be also tuned to produce FeNi₃/C nanocomposites with deep control over the carbon formed that can be modulated from CNOs up to graphene (G) at higher

temperatures. While the first behave as excellent electrodes for supercapacitors offering excellent values of energy density of ca. 35 W·h·kg⁻¹ with a corresponding power density of 10 503 W·kg⁻¹ (Figure 6b),⁴⁴ FeNi₃/G hybrids display large coulombic hysteresis loops of 2.4 V and hold great potential as electrochemical multilevel memories.⁴⁵

Even more appealing is the potential interplay between magnetism and electron transport in these hybrids built from ferromagnetic FeNi₃ NPs in close contact with a conducting G matrix. Thus, they exhibit giant magnetoresistance (GMR) with temperature-dependent crossover and low-field MR operating at low fields up to 500 G, arising from the correlation of the physical properties of its initial constituents, that is, electrical conductivity and ferromagnetism (Figure 6c). These properties could be of interest for the use of these kinds of hierarchically structured hybrid nanocomposites in spintronic devices.⁴²

■ OUTLOOK AND PERSPECTIVES

In this Account, we have highlighted the emerging role that magnetic LDH hybrids are currently playing in Materials Chemistry sustained by our recent findings. These anionic clays are appealing solids provided their versatile magnetism, manipulable by in-plane chemical design, and anion exchange capabilities that afford almost unlimited hybrid architectures in which the properties intrinsic to the molecular anionic guest can be combined or even interact with the magnetism intrinsic to the LDH layers giving rise to unique examples of multifunctional layered materials with unusual combination of coexisting properties (superconductivity and magnetism, e.g.), or even to magnetic stimuli-responsive materials.

Just like other layered materials as graphite or the transition metal dichalcogenides (TMDs), LDHs can be also exfoliated in the liquid phase to produce stable emulsions of nanosheets that retain most of the properties of the pristine materials but might display novel physical and chemical properties beyond those intrinsic to the bulk provided their nanometric nature.^{9,46} From a fundamental point of view, the study of the properties of these systems in the 2D limit remains largely unexplored due to the lack of suitable examples. Exploring some fundamental issues arising from the dimensionality effects like whether a single layer can display ferromagnetism is a significant challenge. The growth of large crystals suitable for micro-mechanical exfoliation may be also of interest in this context.

These inorganic analogues of graphene hold great promise as they possess analogous morphologies, with layers of micrometric lateral size and nanometric thickness for extremely high surface area values, but exhibit enhanced thermal stability and a wider range of useful electronic properties derived from more diverse chemical compositions. In the context of magnetic LDHs, this allows for the miniaturization of magnetic devices based on ultrathin films built from the assembly or direct growth of 2D magnetic nanosheets.^{47,48} Still, successful exploitation of these advantageous features for the development of the next-generation of hybrids remains very limited by the poor degree of control we have over the way these nanometric inorganic macromolecules can be combined. We still lack the chemical tools required to functionalize LDH nanosheets and gain precise control over their assembly into hierarchical architectures.

Although application in magnetism is still limited due to the low temperature magnetism of the existing synthetic LDHs, these hybrids may find applications in other areas related with energy storage or conversion. In this context, we should

mention, for example, the development of hybrids formed by nanocarbons with LDHs or other inorganic graphenoids.⁴⁹

■ ASSOCIATED CONTENT

Supporting Information

Summary of the most relevant structural and magnetic parameters of the magnetic LDHs published to date. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.accounts.5b00033.

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