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Review

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Hybrid interfaces in layered hydroxides: magnetic and multifunctional superstructures by design

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Abstract: This article is a critical review on layered hybrid organic-inorganic functional structures. We specially discuss a series of results concerning the design of magnetic and multiproperty systems derived from hybridization of layered transition metal hydroxides. A series of hybrid materials showing original magnetic properties are reviewed, which were prepared by functionalization of layered simple hydroxides (LSH) of the general formula $M_2(OH)_3A$ (M=Co, Cu, Ni, Zn, … and A=NO_3^-, OAc^-, alkylcarboxylates, peptides, metal complexes…). To make the point on this vast family of hybrid compounds, we present first the work investigating the mechanism of interaction and the structural factors influencing the magnetic properties of hybrid materials based on LSH. Then, we detail how even more complex anions can be immobilized and grafted into the interlamellar space giving rise to new functionalities. These systems are very good models for understanding the correlations between the structure of hybrid systems and the physical properties brought by the inorganic host and by the molecular moieties grafted onto the inorganic metal network. The interface between the organic and inorganic components, i.e. chemical bonding, charge density, or local pressure, is essential for the control of the properties of multifunctional hybrid systems. Some conclusions are drawn on the future of this approach, useful for developing new two-dimensional functional systems.

Keywords: hybrid interfaces; layered materials; magnetism; multifunctional nanostructures; synergy.

1 Introduction

Today, there is a great interest for the rational design of new materials with increasingly varied applications from electronics, catalysis, to biology, and healthcare. The development of new multiproperty devices led to explore new tracks for designing materials combining very different functional blocks within the same phase. One speaks, for instance, of the generalization to hybrid materials of the Lego-like chemistry [1], which was first proposed for the dispersion of inorganic nano-objects (oxo-clusters, oligosilsesquioxanes, …) in polymer matrices [2–5] or for the design of metal organic frameworks [6], and which might be extended to crystal chemistry of oxides [7]. The definition and the association of various functional bricks call on the expertise of solid state chemists, molecular chemists, biochemists, … and also physicists and materials engineers. This is particularly clear in the field of multifunctional hybrid materials. Indeed, today we are witnessing an increasing activity in the controlled synthesis of hybrid materials, [1, 8–11] combining concepts from several disciplines to obtain new materials with specific chemical [12–20], physical [12, 13, 16, 21, 22], or biological properties [23–25]. In particular, the insertion of organic or organometallic species in lamellar compounds gives rise to functional organic/inorganic [26–36], inorganic/inorganic [37–42], or bioorganic/inorganic [43–46] structures organized at the nanoscale. Thanks to the multiscale organization of their components and synergistic effects, such structures may have novel properties and behave as “multimaterial”, that is to say, a unique material simultaneously answering several specifications. The lamellar compounds, in which the properties of each subnetwork and their interaction can be modulated by the topology and the chemical bond between constituents can present remarkable combinations of properties such as magneto-optics [47–52], or magnetism and

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superconductivity [51, 53]. Chemistry plays an important role in improving the interactions between organic and inorganic networks. It is also essential to control the structural characteristics and the physical mechanisms influencing the properties of such new hierarchical nanostructures [1, 8, 9, 54, 55].

In many of the lamellar systems explored in the literature, such as bimetallic trioxalatometalates $A[M^{II}M^{III}(ox)_3]$ [50–53, 56–59], hexathiohypodiphosphate MPS_3 [47–49, 60, 61], or layered double hydroxides (LDH) $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2][A^{n-}_{(x/n)}(H_2O)]$ [29, 37, 45, 62–71], the bond between organic species and inorganic network is weak (electrostatic interactions, hydrogen bonds). Therefore, interactions between properties are low, and little synergy is obtained between electronic properties. We and others have chosen to develop a similar approach, but favoring more synergy, by hybridization of layered simple hydroxides (LSH) $M_x(OH)_{2x-yn}(X^{n-})_y$ (divalent cation M(II)=Co, Cu, Ni, Mn, Zn, and anion X^{n-}=carboxylate, sulfate, or sulfonate) [72]. These lamellar anion exchangeable hydroxides are adapted to promote a strong bond between the components, as the anions are bound to the transition metal forming the structure of the crystal lattice. We discuss hereafter the results on the synthesis of these hybrid systems, their flexibility and their properties to make a point on this approach toward hybrid multifunctional materials.

Basically, the structures of LSH, with the general formula $M_2(OH)_3X$ (M(II)=Co, Cu, Ni, Mn, Zn and X^-=NO_3^-, $CH_3CO_2^-$, Cl^-), derive from that of Botallackite, as shown in Figure 1 for the copper hydroxyacetate [72, 73]. It consists of a quasi-planar triangular array of octahedral metal(II) ions separated by anions coordinating the metal atoms and water molecules [73, 74]. Small variations may occur [75], essentially because of the necessary adaptation of the molecular area of each divalent metal to the molecular area of the grafted anions. In the case of cobalt or zinc LSHs, the structure of the inorganic layer may exhibit a triple deck arrangement similar to that of the $Zn_5(OH)_8(NO_3)_2\cdot 2H_2O$ or $Co_7(OH)_{12}(C_2H_4S_2O_6)(H_2O)_2$ analogs [76, 77]. It is formed of a monolayer of octahedral M(II) hydroxide, with metal vacancies that are counterbalanced by tetrahedral Co(II) or Zn(II) sites on both sides of the octahedral monolayer (see Figure 1). In this kind of structure, it is generally assumed that each non-hydroxyl anion (carboxylate, sulfate, sulfonate) is linked to one metal ion in a tetrahedral environment [77–80]. Therefore, the number of coordinating groups corresponds to the number of tetrahedral Co(II) or Zn(II) ions. The presence of short metal-metal distances (ca. 0.3 nm), brought about by the μ_3 coordination mode of the OH^- moieties within the hydroxide layers, results in an extended metal framework. For example, effective magnetic interactions may occur by exchange coupling along the metal-oxygen-metal pathways, leading to a ferromagnetic, antiferromagnetic, or ferrimagnetic 2D behavior. Moreover, the structure and, hence, the properties of these layered transition metal hydroxides is influenced by

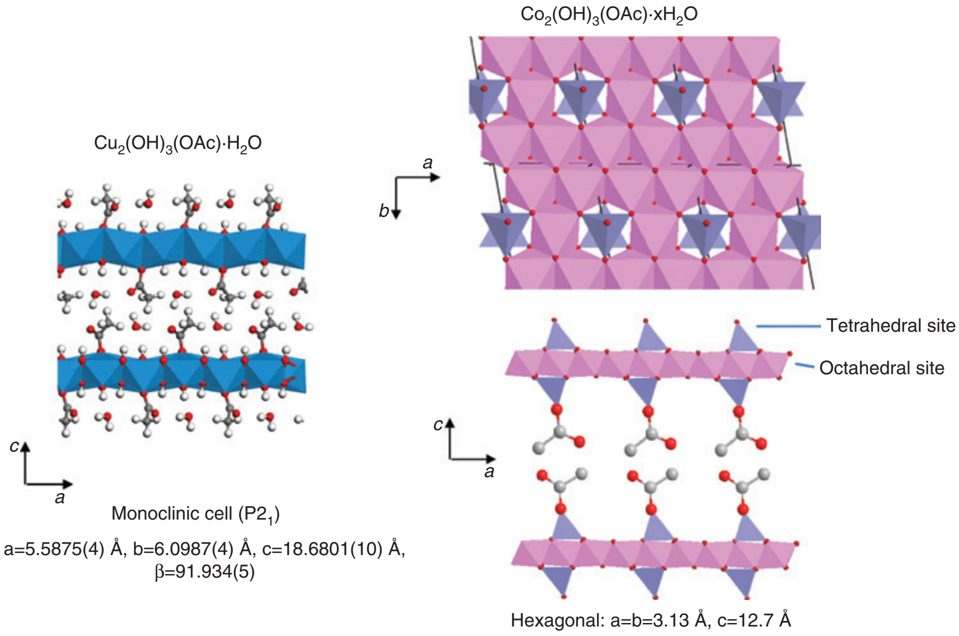


Figure 1: Structure of the acetate hydroxides $Cu_2(OH)_3(OAc)\cdot H_2O$ (left) [73, 74] and $Co_2(OH)_3(OAc)\cdot H_2O$ (right) [79, 80, 81]. In the latter case, hydrogen atoms are not represented in the model.

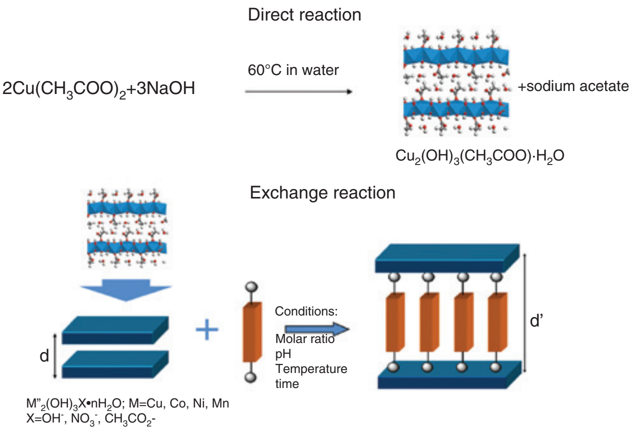


Figure 2: Summary of the main types of reaction routes used for synthesizing hybrid transition metal hydroxides. Direct reaction of a metal salt in aqueous solution with an alkaline base leads to metal hydroxide by precipitation. Direct reaction can be carried out under hydrothermal conditions. Another route consists in starting from a pre-formed layered hydroxide, which is further hybridized by anion exchange reaction.

the functionalization of the layers. Three reaction methods were explored to synthesize the layered transition metal hydroxide hybrids, which are summarized in Figure 2.

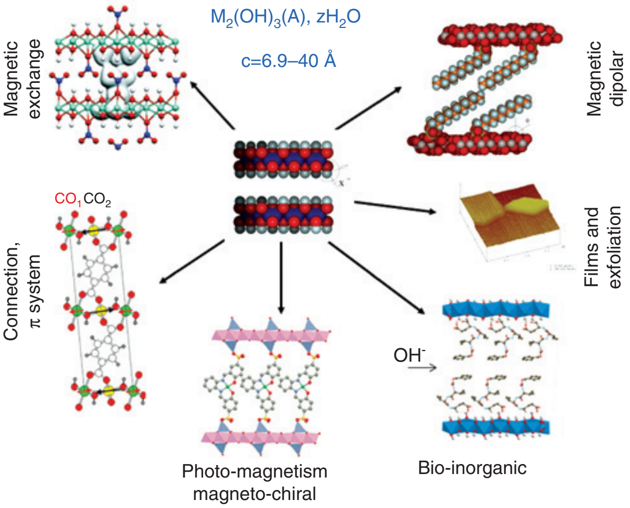
The first one consists in reacting directly transition metal salts in aqueous solution with an alkaline agent, precipitating the hydroxide phase. It is well adapted and widely used in the case of small anions like chloride, nitrate, or acetate leading to nice crystalline powders, which allows often the determination of their crystal structure.

For larger or more complex anions to be grafted onto hydroxide layers, it is often necessary to proceed in hydrothermal conditions in Teflon-walled autoclaves in the range 100–250°C, similar to the synthesis of metal organic frameworks (MOF). Remarkable results were obtained in hydroxo compounds build from terephthalate or thiophene-carboxylate anions (see below). The crystal structure could be investigated by using single crystal or powder X-Ray diffraction, showing great versatility and interesting relations between 1D, 2D, and 3D parent structures. In addition to their peculiar properties, all these compounds, whose structure is known, constitute structural models that can be used for comparison with less crystalline parent derivatives.

Finally, the X^- anion located in the interlayer space may be substituted by a large variety of organic molecules or molecular metal complexes via anionic exchange reactions. New layered M(II) derivatives are usually obtained from the metal hydroxyacetate, $M_2(OH)_3(CH_3COO)\cdot xH_2O$ (M=Cu, Co), substituting acetate moieties by various anionic function like n-alkylcarboxylates, sulfonates, or sulfates. Mixing the starting compound into a solution of the anion to graft at appropriate temperature, concentration, and pH, the acetate anions are totally exchanged after a few hours. The new products give powder X-Ray diffraction patterns with intense *00l* reflections, characteristic of layered structures. The other reflections, *hkl* with *h* or *k*≠0, are much weaker and exhibit usual asymmetrical enlargement for disordered pillared compounds.

The interleaved species can be used as a pillar or as a connector between the magnetic layers for monitoring the interlayer interactions as a function of the size and electronic characteristic of the exchanged anion [72, 75, 78, 79, 82–89].

New hybrid materials with original magnetic properties were prepared by anion exchange reaction from preformed lamellar compounds, essentially $M_2(OH)_3A$ (M=Co, Cu), in which the anion A to be substituted is NO_3^- or OAc^- [78, 81, 90–96]. As illustrated by Scheme 1, the grafting of many types of ligands changes the electron density or the distance between the magnetic layers and, thus, influences the magnetic coupling between layers. We can also produce multilayers alternating organic (radicals) and inorganic (hydroxides) magnetic layers. Finally, we looked at the connection between layers via π electron molecules and realization of bifunctional systems by grafting of photosensitive molecules. These hydroxide-based compounds are characterized by the nature of the links between subnetworks. The organic anion A is linked to the transition metal sheet and plays an important role on the magnetic properties leading to a variety of ferro- or ferrimagnetic hybrids systems.



Scheme 1: Schematic summary of our approach for the realization of magnetic and bifunctional lamellar hybrid materials based on simple hydroxides of transition metals [35, 72].

2 Structure-property relationship and magnetic interaction mechanisms in layered hybrid systems

2.1 Influence of the interplane distance

Various hybrid lamellar compounds grafted with n-alkyl chains were synthesized having the general formula $M_2(OH)_{4-x}A^{n-}{}_{x/n}$, mH_2O (M=Co(II), Cu(II), $A^{n-}=C_nH_{2n+1}SO_4^-$, $C_nH_{2n+1}COO^-$, $OOC(CH_2)_nCOO^{2-}$), where the A^{n-} anions act as spacers between brucite-type layers. The copper compounds are synthesized by anionic exchange in the copper hydroxyacetate $Cu_2(OH)_3(CH_3COO)$, H_2O. The acetate ions were, thus, replaced by the long-alkyl chain anions by dispersing the starting material in an aqueous solution of the corresponding sodium salt. Cobalt salts were obtained similarly starting from the hydroxynitrate $Co_2(OH)_3(NO_3)$.

This substitution induces a change in the coordination sphere of the metal influencing the magnetic exchange interaction in the planes (ferromagnetic or antiferromagnetic). It also allows a significant modulation of the distance interplane (between 4.6 Å and 40 Å) and, consequently, the coupling between magnetic planes.

Structural studies have shown that the interlayer distance, *d*, is linearly related to the number of carbon atoms n (Figure 3), and its variation is characteristic of the arrangement of the alkyl chain. For copper(II) compounds with n-alkyl carboxylate anions, the alkyl chains form a bilayer with a tilt angle of 30° (Figure 4), whereas for n-alkyl sulfates anions for instance, the chains are stacked in monolayer, orthogonal to the sheets (Figure 4).

From the structural point of view, the results are very similar for the cobalt or copper salts. For the latter, however, depending on the exchange reaction time with carboxylates, two series of compounds (denoted α and β) were isolated, which correspond to two interplanar spacings for the same aliphatic chain (Figure 3).

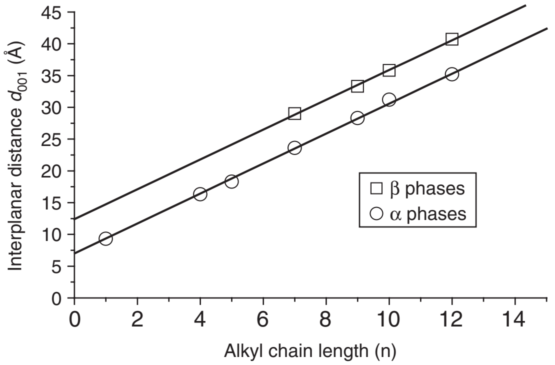


Figure 3: Variation of the interplanar distance (d_{001}) for copper hydroxycarboxylates in the α or β form (see text).

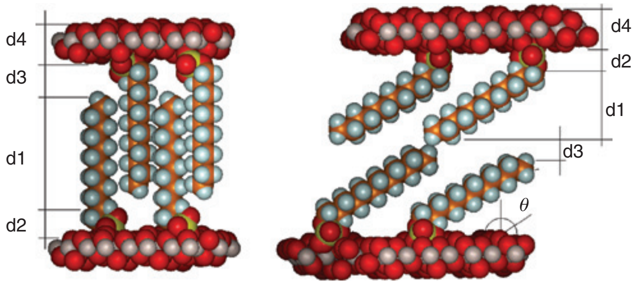


Figure 4: Examples of alkyl chain arrangement after exchange reaction in copper(II) or cobalt(II) basic salts (see text). Distances d_i and the tilt angle θ are directly related to the characteristic distance of the layer stacking (basal spacing) as deduced from powder X-ray diffraction patterns. Adapted with permission from [81]. Copyright 1999 Royal Society of Chemistry.

These two series are differentiated by the distance between the terminal methyl group and by the thickness of the inorganic layer $[Cu_2(OH)_3]^+$. The compounds of the α series present an antiferromagnetic behavior over the entire temperature range between room temperature and 4.2 K. In contrast, the β compounds are characterized by the existence of a 3D ferromagnetic order at low temperature (Figure 5). This difference in behavior is explained by the modification of the Cu-O-Cu bond angles, related to the arrangement of the carboxylate groups coordinating the metal, which leads to a drastic change in the magnetic behavior [78, 93].

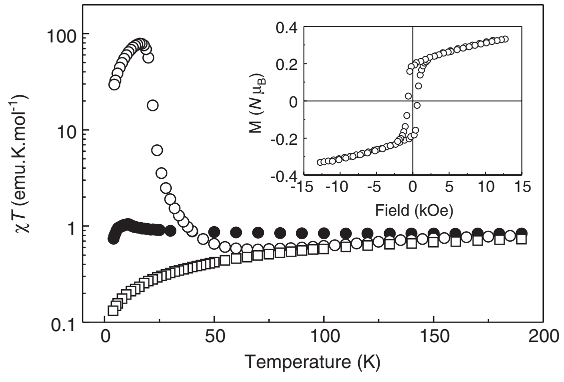


Figure 5: Temperature variation of the χT product for copper compounds exchanged with n-alkyl-carboxylates of different carbon chain lengths. ●) n=1, acetate (metamagnetic), ❑) n=7, α (antiferromagnetic), ❍) n=7, β (ferrimagnetic). Insert shows the magnetization vs. field curve at 4 K of the β phase. Adapted with permission from [81]. Copyright 1999 Royal Society of Chemistry.

The study of the cobalt(II) compounds also highlighted new layered architectures with cobalt atoms in octahedral and tetrahedral sites [78]. Then, the behavior of the planes is ferro- or ferrimagnetic. At low temperatures, the long-chain systems exhibit a 3D ferromagnetic long-range order.

The correlations between structure and properties of these series of lamellar magnetic compounds made possible the setting of some general rules [72, 81, 87, 90, 97]. Thus, when the anion is a simple spacer (aliphatic chain), and ferromagnetic interactions dominate in the sheets, the situation depends on the distance, *d*, between layers. For small gaps (<10 Å), a 3D antiferromagnetic order is established at low temperature, by an exchange-coupling mechanism (orbital overlap, hydrogen bonding). In contrast, large spacings favor the development of a spontaneous magnetization even for $d \approx 40$ Å, which is explained by a dipole interaction mechanism between the giant moments developing in the sheets at low temperature. The magnetic behavior of these series of compounds was analyzed by a scaling law model approach in the framework of the theory of phase transitions [98, 99]. A high-temperature a 2D regime followed by a transition to a 3D regime was well identified. This validates the semi-classical model proposed by P. Panissod and M. Drillon, and application to our compounds described the special action of dipole interactions in stabilizing ferromagnetic order at a large distance [100]. This model is widely used today to explain the long-range coupling in 2D and 1D structures involving distant magnetic entities [40, 101–103].

It should, however, be pointed out here that the critical distance of 10 Å established for these series of hydroxides and the F or AF character of the 3D magnetic order may depend on the nature of the species present in the interlayer space. This was shown, for example, by a recent analysis of the magnetic behavior of layered nickel hydroxides, including halogen ions in the interlayer space [104]. A series of hydroxy-nickel(II) halides LHS-Ni-X (X=Cl, Br, I) was prepared by the anion exchange reaction starting from the nickel hydroxyacetate obtained by hydrolysis in polyol reaction medium. These compounds, characterized by FTIR spectroscopy and X-ray diffraction (XRD), have a brucite-type structure with turbostratic disorder. Their interlamellar distance varies linearly with the radius of the halide ions between 7.9 and 8.7 Å, while the distance of the starting hydroxyacetate is 10.53 Å. In contrast with the replacement of acetate anions or hydroxyl groups in brucite structures, as in the hydroxy carboxylates, sulfates, or sulfonates described above, the EXAFS and XRD studies showed that the halide ions are intercalated in the interlamellar space with water molecules, without covalent bonding to the nickel ions. All compounds have similar structures and can be described as α-$Ni(OH)_2$ type nickel hydroxides (Figure 6).

These compounds are ferromagnetic in keeping with recent reports on α-Ni(OH)2 analogs [105, 106]. This behavior has been discussed on the basis of the Drillon-Panissod model for the magnetic layers interacting via dipolar interactions [100] and taking into account the structural features determined by XANES and XRD, as well as the intrinsic properties of the halide ions. Despite the low interlamellar distance, the hydroxy-halides, like other α-$Ni(OH)_2$ analogs [105–107], present a 3D ferromagnetic order, unlike hydroxides of the β-$M(OH)_2$ form [108]. The fact that T_C varies with anions could be explained by the nature and the structural arrangement of the anions inserted between the magnetic layers and considering a competition between the through-space dipolar interaction and through-anion interaction. We shall return to this type of competition further for other examples, especially compounds involving conjugated bridges.

2.2 Magnetic metal-radical multilayers

Imino nitroxide radicals (meta and para forms) have also been grafted by anion exchange reaction on inorganic sheets made of cobalt(II) hydroxide (Figure 7), giving the new hybrid ferromagnetic compounds $Co_2(OH)_{3,5}(IMB)_{0,5}\cdot 2H_2O$ (IMB=imino-nitroxide benzoate anion) [91, 95]. In these systems, the cobalt(II)-based sheets are separated by radical anion, and the two sub-entities are strongly linked by ionocovalent bonds. The distance between the ferrimagnetic cobalt(II) layers becomes >20 Å.

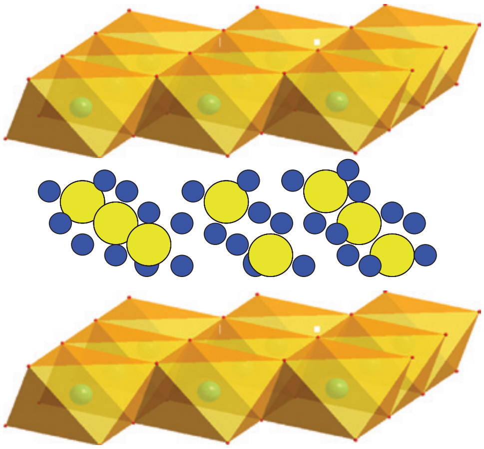


Figure 6: Structural model proposed for the halide-hydroxy series of nickel(II). The yellow and blue spheres hold for halogen and water molecules, respectively. Adapted with permission from [104]. Copyright 2014 American Chemical Society.

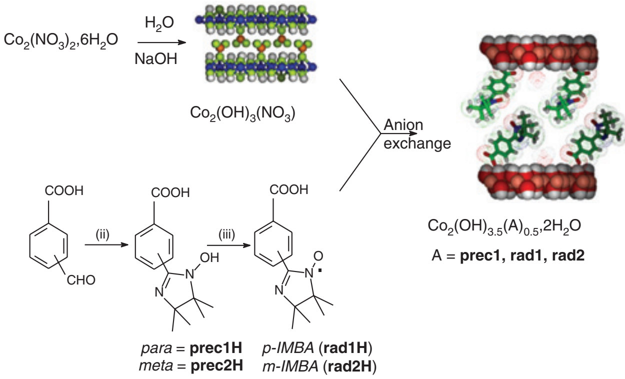


Figure 7: Grafting benzoate nitroxide radicals by anion exchange in cobalt(II) hydroxy nitrate and structural model. Adapted with permission from [91]. Copyright 1998 Wiley.

Both radical compounds, Co-rad1 and Co-rad2, show a 3D ferromagnetic order with Curie temperatures of 6.0 K and 7.2 K for the radical in para or meta position, respectively (Figure 7). Compounds equivalent to Co-rad1 and Co-rad2 were obtained by grafting the nonmagnetic precursor of the radical anion (hydroxyl radical precursors, prec1H and prec2H in Figure 7). Their investigation shows that the transition temperature is strongly correlated with the nature of the organic species as T_C increases by 8 K in the case of the precursor (Figure 8B). By comparison with the exchange product with the non-radical molecule, and after EPR analysis, the behavior of the metal-radical hybrid compounds has been linked to strong interactions between 3d and π electrons [91].

These results reflect the existence of a genuine exchange interaction between sub-networks, i.e. the metal one and the radical one, through bridging anions. The study by EPR shows that this interaction is antiferromagnetic and is opposed to the ferromagnetic coupling of dipolar origin between cobalt(II) layers. This was among the first examples of metal-radical multilayer systems with coupled magnetic properties.

2.3 Connection between spin layers – influence of π electrons

To better control the coupling between the spin layers formed by the hydroxide sheets, we then proceeded to use bifunctional bridging molecules to establish a real connection between the inorganic sheets. Exchange reactions were conducted with alkane-α,ω-dioate anions, $(CH_2)_n(CO)_2^{2-}$, n=1 to 8 [109]. The inter-sheet distance shows a linear variation dependent on the parity of n. The results for the full copper series give an inclination angle of 25.7° of the aliphatic chains for n even and 42.9° for odd n. This was explained by the difference of mutual orientation of the carboxylate end groups. Actually, the crystallographic structure of these compounds, obtained as poorly crystallized powder, could not be resolved. Nevertheless, an EPR study (electron paramagnetic resonance spectroscopy) performed at high field (LCMI, Grenoble, France) has established a great similarity of the local structure of this series of compounds with that of the hydroxy Cu(II) terephthalate, isotype to its Co(II) counterpart described below [110, 111].

The magnetic behavior is closely related to the dimension of the spacers and to the nature of the bonds along the carbon chain. An outstanding result was obtained in the case of six carbon atom bridges (n=4), namely, adipate anion (**4_0**) with saturated bonds, trans-hexene dioate anion (**4_1**) with an unsaturated bond, and the muconate anion (**4_2**), conjugated with two double C=C bonds. In all three

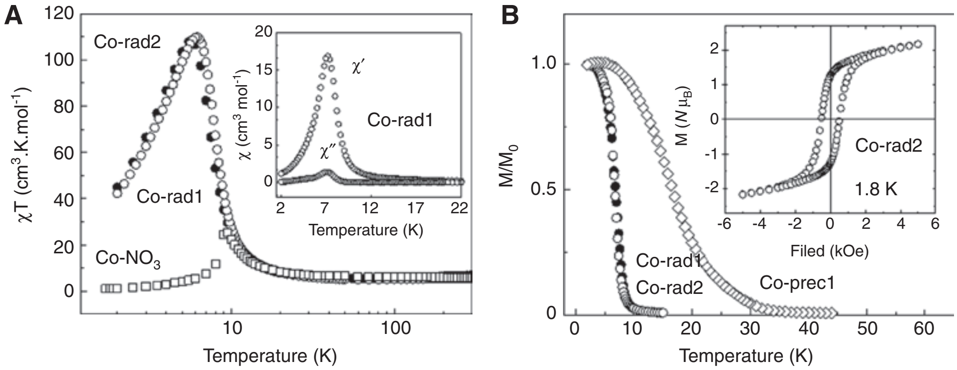


Figure 8: Substitution with benzoate radical anion (A) comparison of the magnetic susceptibility of the starting cobalt hydroxynitrate (metamagnetic) and exchanged products Co-rad1 and Co-rad2 (ferromagnetic) with the variation of the alternative susceptibility of Co-rad1 in insert; (B) T_C changes related to the presence or absence of the radical. Adapted with permission from [91]. Copyright 1998 Wiley.

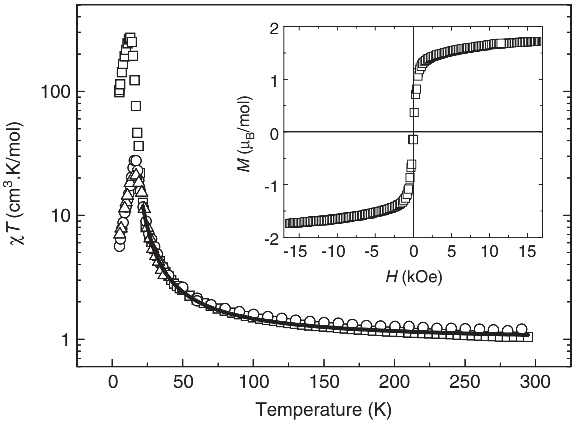


Figure 9: Magnetic behavior of the copper(II) compounds with bridging dicarboxylate anions with n=4 alkane chains: (○) metamagnetic compound **4**$_0$, (□) ferromagnetic compound **4**$_1$, (△) metamagnetic compound **4**$_2$. The magnetization at 4 K of **4**$_1$ is given in the insert. The solid line corresponds to the fit to the S=½ Heisenberg model described in the text.

cases, the interplane distance is similar (d=10.34±0.12 Å). The magnetic behavior is shown in Figure 9. The three compounds are remarkably alike at high temperature indicating a similar ferromagnetic behavior of the inorganic layers, corresponding to an exchange interaction of 27 K. The latter was deduced from the fit of the experimental data with a high temperature series expansion model for S=1/2 Heisenberg planar triangular systems [112]. At low temperatures, the compound **4**$_0$ exhibits an antiferromagnetic (AF) order between layers and a metamagnetic transition below T_N. The compound **4**$_1$, on the other hand, is characterized by a 3D ferromagnetic order below 12.8 K and the conjugated compound **4**$_2$ orders antiferromagnetically as in the first case.

This changing magnetic behavior was attributed to π electrons from bridging anion and providing magnetic coupling with polarization effect [109]. NMR measurements showed that 13C spin density along the carbon chain is zero in the case of adipate (**4**$_0$) and significant in other cases. These results show that it is possible to change the coupling between magnetic layers using bridging anions having only partial electron delocalization within their π system and that conjugation can have a strong influence [98, 113]. This assertion was further supported by Kojima et al., who succeeded in grafting diarylethene (DAE) di-sulfonates molecules in the interlayer space of cobalt hydroxide [89, 114, 115]. Actually, the hybrid compounds obtained with the open form (un-conjugated) or the closed form (fully conjugated) of DAE exhibit ordering temperatures of 9 K and 20 K, respectively.

2.4 The hydroxyterephthalates: hydrothermal synthesis, magnetic structure, giant coercivity, and dimensionality

Despite significant achievements, the major disadvantage of anion exchange reactions is they often lead to poorly crystallized systems. Lack of knowledge of the detailed structure of the inorganic layers substantially limits the structure-property relationship. That is why the synthesis of these hybrid compounds was developed using the hydrothermal reaction of a metal salt (nitrate) with the desired carboxylic acid and a base (sodium or potassium hydroxide) in aqueous solution. The syntheses were carried out in Teflon-lined autoclaves under autogenous pressure in the temperature range 100–200°C.

A striking result was obtained in the case of cobalt(II) hydroxyterephthalate, $Co_2(OH)_2(C_8H_4O_4)$, which was synthesized in the form of well-crystallized powder and whose structure was solved *ab initio* by powder diffraction X-ray, by Masciocchi et al. (Figure 10) [86]. The magnetic structure under field could be solved on a deuterated sample [116]. This compound can be described as the stack of layers of cobalt(II) ions in compressed octahedral sites formed by the oxygen atoms of the hydroxyl and carboxylate groups and forming a triangular network.

The short axes of the octahedral sites form a strong angle between cobalt(II) neighbors. The layers are connected by

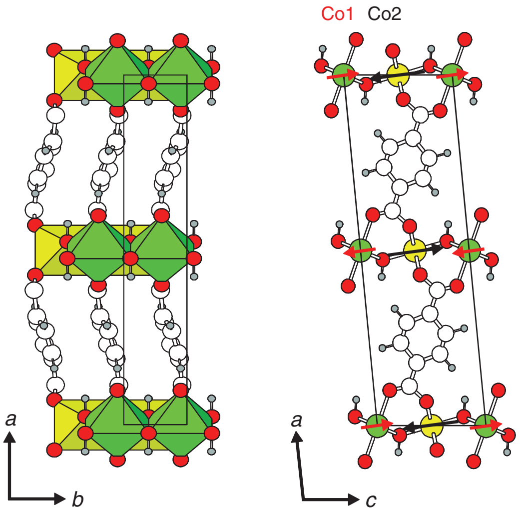


Figure 10: Crystallographic structure of $Co_2(OH)_2(C_8H_4O_4)$ along *c* (left) and *b* (right) axis. At right also, the antiferromagnetic structure below 48 K, on the basis of a collinear arrangement. Ordered moments held by the two non-equivalent Co(II) are different. A small canting between moments, at the origin of the low ferromagnetism, is not taken into account. Adapted with permission from [116]. Copyright 2003 Elsevier.

terephthalate anions and separated by a distance of about 10 Å. The observed magnetic behavior is relatively complex. Interactions are antiferromagnetic between Co(II) ions in the layers, but the moments carried by the inequivalent cobalt atoms are different. This leads to ferrimagnetism and divergence of the χT product at low temperatures (Figure 11).

Ferrimagnetic layers are coupled antiferromagnetically through the organic anions with an ordering temperature T_N=48 K. The magnetization curves below T_N are characteristic of a metamagnetic compound. However, below 44 K, a ferromagnetic order appears, characterized by the occurrence of a peak in the imaginary part of the ac susceptibility and low remanent magnetization. Despite the opening of the cycle, the magnetization keeps the S shape characteristic of metamagnetic systems. This was explained by the existence of a canting between moments in adjacent ferrimagnetic layers. The S shape fades away to the low temperatures. The situation is summarized in the phase diagram shown in Figure 12A. At low temperatures, under strong field, a highly canted phase is stabilized, and the hysteresis loop (Figure 11) shows a giant coercive field of nearly 6T.

The study by neutron diffraction of $Co_2(OH)_2(C_8H_4O_4)$ in a magnetic field indicates that the ground state of the system at low temperatures is the weakly canted structure (WCA), while the strong canting phase (SCA) is metastable and appears only under a magnetic field. These results highlight the effects of a large anisotropy related to the structure and to the Co(II) ions. The complex phase diagram is the result of a competition between anisotropy fields and AF exchange coupling (Figure 12).

The analogous copper(II) compound has a ferromagnetic behavior over the entire temperature range. Copper(II) ions are weakly anisotropic, and very low coercivity was observed [110, 117].

Nickel terephthalates exhibit high structural diversity. However, it should be noted that the anhydrous nickel analog of the previous cobalt or copper compounds could never be obtained by direct reaction. A series of nickel compounds was obtained by François et al. by dehydration of the hybrid compound $[Ni_3(OH)_2(tp)_2(H_2O)_4]$ (**1**) [118], whose structure is isotype to that of cobalt or nickel thiophene dicarboxylates described elsewhere [119, 120]. Heating this compound led to sequential departure of coordinated

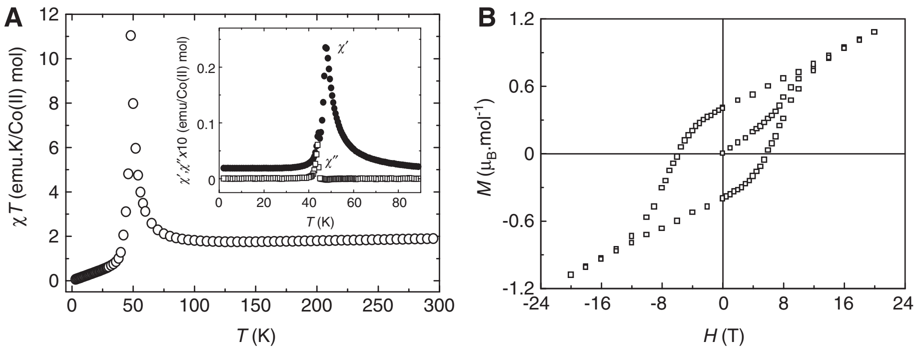


Figure 11: (A) Magnetic susceptibility of $Co_2(OH)_2(C_8H_4O_4)$ and (B) hysteresis cycle of magnetization at 4.2 K. Adapted with permission from [86, 87]. Copyright 2000 American Chemical Society and 2003 Wiley, respectively.

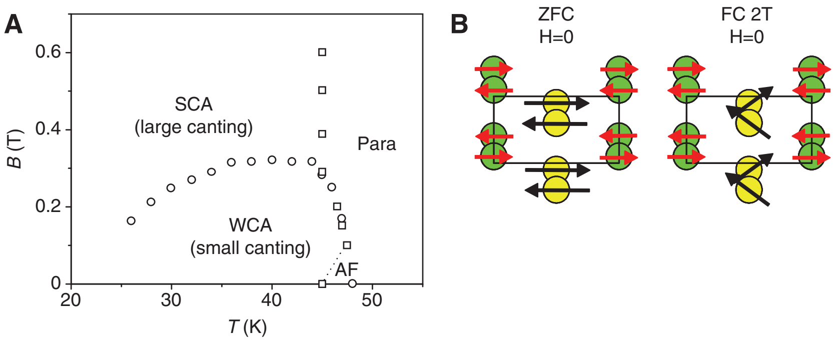


Figure 12: (A) Magnetic phase diagram of $Co_2(OH)_2(C_8H_4O_4)$ and (B) comparison of magnetic structures at zero field observed at 10 K after cooling with zero field (left) and cooling under 20 kOe. The view, along a, shows two adjacent Co planes, at x=0 and x=½, whose moments are aligned in the AF ZFC case. Adapted with permission from [116]. Copyright 2003 Elsevier.

water molecules to yield [$Ni_3(OH)_2(tp)_2(H_2O)_2$] (**2**) at T_1=433 K and then the anhydrous compound [$Ni_2(OH)_2(tp)$] (**3**) at T_2=483 K. These two successive structural transformations have been fully characterized by X-ray powder diffraction coupled to modeling using a DFT approach (DFT for density functional theory). The crystal structure of the two new compounds was determined. Thus, at T_1=433 K, the infinite chains of nickel atoms linked by oxo bridges built from the [$Ni_3(\mu_3\text{-}OH)_2]^{4+}$ units in **1** collapse and form infinite porous layers in **2**. The second transformation at T_2=483 K leads to the expected anhydrous compound **3**, which is isostructural with $Co_2(OH)_2(tp)$ presented above (Figure 13).

These irreversible changes directly affect the magnetic behavior of each phase. Thus, **1** is antiferromagnetic with the order at T_N=4.11 K and exhibits a metamagnetic behavior with a threshold field Hc about 0.6 T at 2 K. Compound **2** has a canted antiferromagnetic state below T_N=3.19 K, and **3** is ferromagnetic below T_C=4.5 K. In addition, the magnetic exchange couplings were evaluated in compound **1** on the basis of an S=1 Heisenberg chain model consisting of the interconnection of dimers Ni1-Ni1 connected by Ni2 center forming butterfly motifs [120]. The numerical resolution of the corresponding spin Hamiltonian has allowed a very good fit of the experimental data (Ni1-Ni1 interaction, J_1/k_B=+26.6 K and Ni1-Ni2 interaction, J_2/k_B=−2.8 K, with g=2.1). Similarly, the behavior of the compound **3** with dense sheets was analyzed by a scaling law approach. Intra-layer interaction was evaluated by parameterization of the magnetic susceptibility with high-temperature series expansions in the approximation of a planar triangular system (g=2.18 and J/k_B=-1.48 K). The analysis of the correlation length suggests the contribution of interactions between planes to the magnetic order. These interactions occur through the ligands, associated to the spin polarization of the π system along the terephthalates bridges [87, 121, 122].

2.5 Flexible and adaptive magnetic lamellar structures

As stated earlier, most copper lamellar derivatives were obtained by the exchange reaction from the hydroxyacetate, $Cu_2(OH)_3(CH_3COO)\cdot H_2O$, by the substitution of the acetate anions by n-alkyl carboxylates, sulfonates, or sulfates. As the magnetic properties of the hybrids obtained by anion exchange were particularly investigated, it seemed important to conduct a detailed magnetic study on the starting hydroxyacetate, which has a rather complex structure and an intermediate behavior between antiferromagnetism and ferromagnetism [123].

The pressure dependence of the magnetic behavior of the copper hydroxyacetate is summarized in Figure 14. At ambient pressure, the compound is antiferromagnetic, the ferromagnetic layers being antiferromagnetically coupled. The weak antiferromagnetic coupling results in a metamagnetic system below T_N. Under a pressure of 1.2 GPa, a transition to a metastable ferromagnetic state was observed. This transition is reversible and has been correlated with a reversible distortion of the inorganic network. A study of the structure (lattice parameters and Cu-O-Cu angles) was conducted by X-ray powder diffraction as a

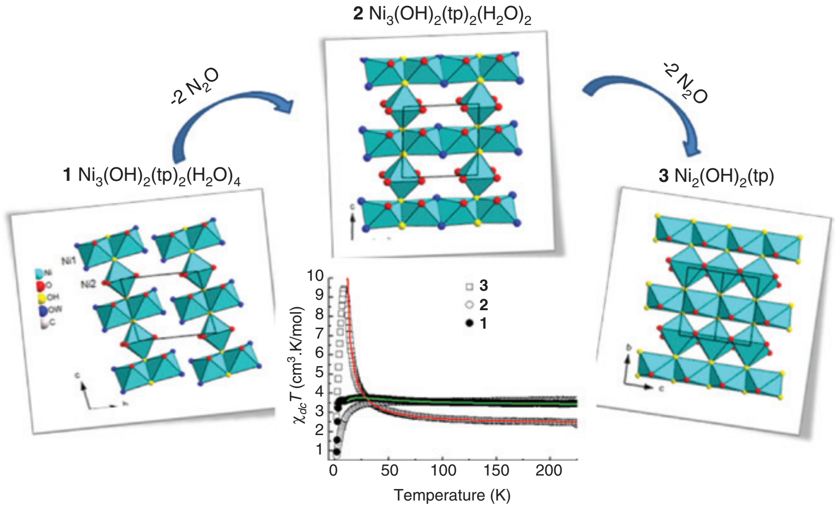


Figure 13: Processing inorganic metal-oxygen subunits of Ni hydroxy-teraphthalates from **1** to **3** by loss of coordination of water molecules and temperature dependence of χT for the three compounds. The solid curves correspond to the parameterization of the experimental data using appropriate models. Reprinted with permission from [118]. Copyright 2014 American Society of Chemistry.

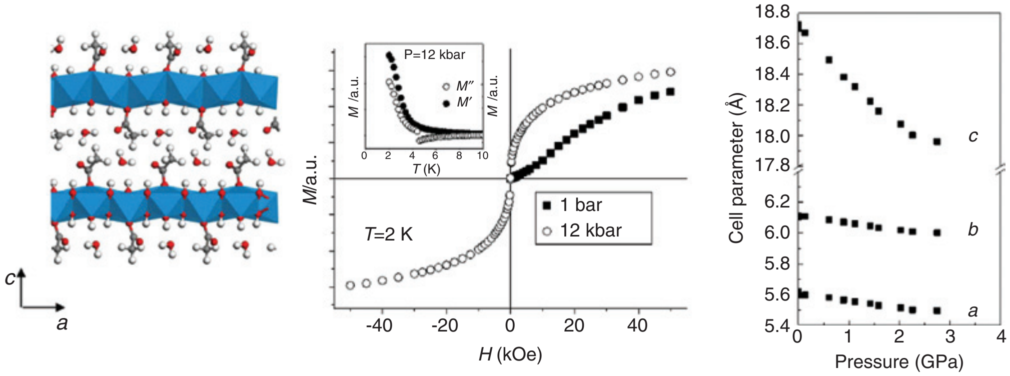


Figure 14: Left: representation of the structure of $Cu_2(OH)_3(CH_3COO)\cdot H_2O$ showing the stacking according to c of the copper(II) hydroxide layers separated by (OAc) groups and water molecules. Middle: magnetization curves as a function of magnetic field of the copper hydroxy-acetate at isostatic pressure of ambient pressure (squares) and 1.2 GPa (circles); the insert shows real and imaginary parts, *M′* and *M″*, of the ac magnetic moment under 12 kbar. Right: pressure dependence of the lattice parameters *a*, *b*, *c*. Adapted with permission from [123]. Copyright 2008 American Society of Chemistry.

function of external pressure. It was deduced that the pressure significantly alter the relative values of the magnetic interactions within the layers, predominantly antiferromagnetic, and in competition. This experimental result provides information on the mechanisms responsible for the magnetic behavior observed in these lamellar systems and more generally in complex systems with competing interactions, whose fundamental magnetic state is difficult to predict *a priori*. Also, one understands better how the insertion grafting may influence the magnetism. The flexibility of these organic-inorganic hybrid systems is remarkable, and the AF/F transition induced by the pressure is original. Further study validated also the use of DFT modeling to calculate the structural, electronic, and magnetic properties of relatively large systems (in terms of number of atoms) and having atoms with open shell structure, as proposed by Massobrio et coll [124–127].

3 Toward an engineering of complex multifunctional hybrid materials

3.1 Magnetic and photo active hybrid materials: the synergy issue

3.1.1 Magnetic hybrid materials comprising photo luminescent organic molecules

The basic idea is to create new compounds combining different functionalities provided by each sub-entity, the inorganic one (magnetism) and the organic one (luminescence, nonlinear optics, photo-induced effect …). In a way, this relatively simple idea consists in synthesizing, by chemical routes, systems similar to metal or oxide multilayer-based nanostructures that were produced otherwise by using physical techniques such as sputtering or pulse laser deposition, for instance [128–133].

As for luminescence, simple candidate molecules to be used to functionalize layered magnetic hydroxides are conjugated systems, like (poly)thiophene carboxylate, [134, 135] or oligophenylenevinylene (OPV) [136, 137]. The latter is well known for a high yield of luminescence with relatively short life time of the excited state. For instance, OPV molecules functionalized with four carboxylate “arms” were grafted on Ni(II)-based layered hydroxide layers (Figure 15). The hybrid compound is a ferromagnet. A striking feature is that the maximum of luminescence of the compound, arising from the OPV moieties, is shifted at the magnetic ordering temperature, T_C=11 K. Moreover, this shift was more pronounced when approaching a permanent magnet (ca. 100 Oe) near the sample. This shows the possible influence of the magnetic order on the luminescence [34]. These results allow considering multifunctional systems with synergy between properties.

Other functional organic molecules have been studied. Thus, oligothiophene dicarboxylates were used as connectors between magnetic layers. Oligothiophenes are indeed of a major interest by their electronic properties (luminescence and conduction) and excellent chemical stability. First, we have succeeded in synthesizing a wide variety of lamellar compounds with monothiophenecarboxylates and in developing the most effective experimental protocols (Figure 16) [83, 138].

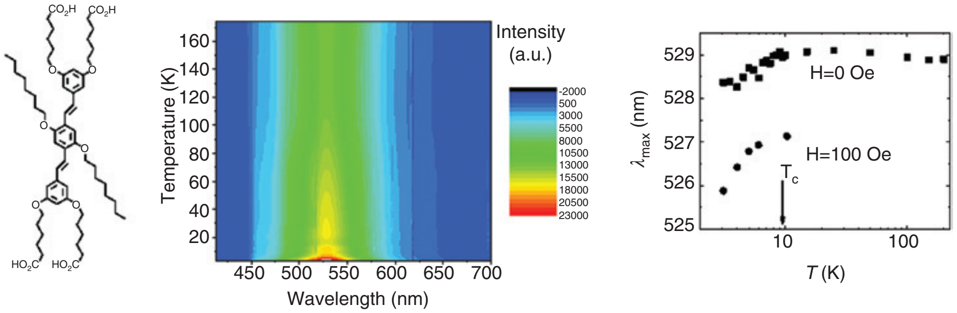


Figure 15: The OPV-tetracarboxylate molecule inserted between the Ni(II) planes of $Ni_2(OH)_{0.4}(OPV)_{0.9}\cdot 2.6H_2O$ and temperature dependence of the luminescence of the ligand in the hybrid compound. The figure on the right indicates the variation of the maximum of luminescence as a function of temperature at zero field and under a magnetic field of 100 Oe, with a shift at the magnetic ordering temperature T_c.

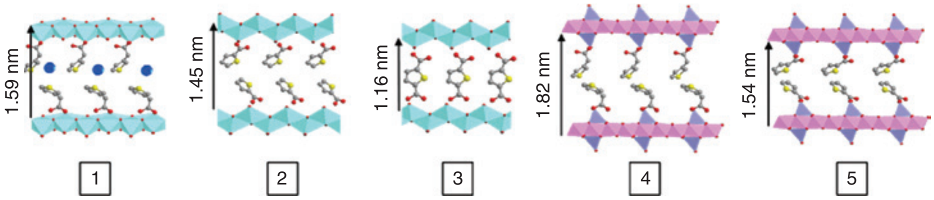


Figure 16: Schematic representations of the structures of hybrid compounds deduced from the structural, thermal, and spectroscopic analyses, based on the known structures of the parent compounds $Cu_2(OH)_3(CH_3CO_2)\cdot H_2O$(1), $Cu(OH)_2$ (2) and (3), $Co_7(OH)_{12}(C_2H_4S_2O_6)(H_2O)_2$ (4), and (5) [83, 139].

Oligothiophenedicarboxylates (Figure 17) were inserted between the layers of hydroxides of copper, nickel, and cobalt.

Different synthesis methods have been explored to the insertion of these oligothiophenes, i) by anion exchange from a preformed hydroxyacetate or hydroxynitrate lamellar structure, in which acetate or nitrate ions are exchanged by the desired functional anions [83], ii) hydrothermal synthesis using transition metal salts and the given carboxylic acid [139]. Thus, many hybrid multilayer compounds based on Cu(II), Ni(II), and Co(II) could be prepared by inserting oligothiophene comprising one to four thiophene rings (Figure 18).

Control of the synthesis led to the lamellar compounds M-Tn (M=Cu, Ni, Co, n=1–4) in which the metals are all in octahedral site, as in the brucite-type hydroxides, β-$M(OH)_2$. All these compounds have a wide range of magnetic behavior, i.e. ferromagnetism (F), antiferromagnetism (AF), AF canted, metamagnetic transition ferrimagnetism, field-induced ferromagnetism, giant coercive fields (3–6 T) [139]. All ligands are fluorescent. In the hybrid, we find the characteristic absorption bands of $\pi-\pi^*$ transitions, but there is a quenching of luminescence explained by the proximity of paramagnetic centers, contrary to what is observed in OPV-based systems [34]. Moreover, no electron delocalization was detected in these materials despite the presence of oligothiophenes. Attempts to oxidize it *in-situ* with iodide were unsuccessful.

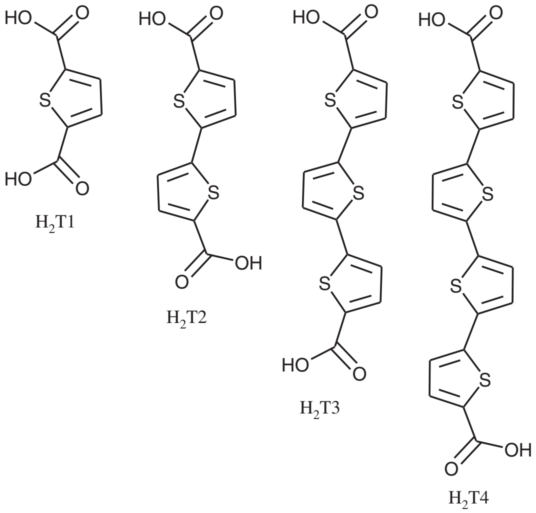


Figure 17: Chemical structure of the oligothiophene acids inserted in the dioate form into layered transition metal hydroxides, H_2T1, 2,5-thiophenedicarboxylic acid, H_2T2, 2,2′-bithiophene-5,5′-dicarboxylique acid, H_2T3, 2,2′:5′,2″-terthiophene-5,5″-dicarboxylic acid and H_2T4, 2,2′:5′,2″:5″,2‴-quaterthiophene-5,5‴-dicarboxylic acid.

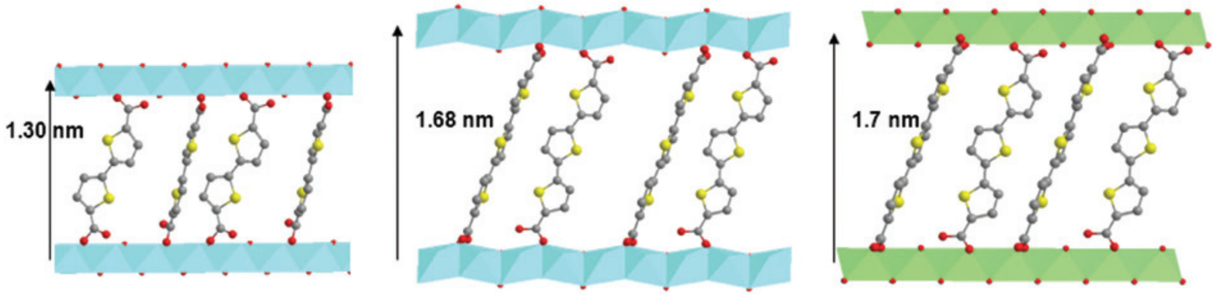
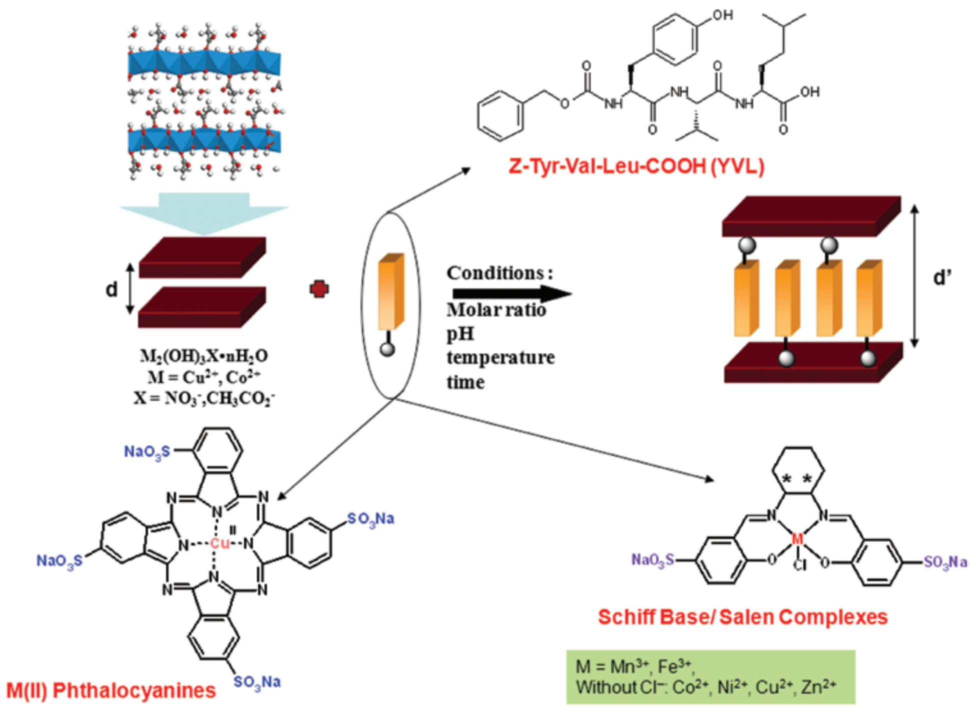


Figure 18: Schematic representation of the compounds Cu-T2 (derived from the Brucite structure), Cu-T3 (derived from the structure of $Cu_2(OH)_3NO_3$) and Ni-T3 or Co-T3 (derived from the Brucite structure). Water molecules are omitted.

3.1.2 Hybrid materials including photoswitching molecules

More recently, works in the field aimed to explore the anion exchange reactions for the insertion of luminescent molecules with various anchoring functions (carboxylate, sulfonate, phosphate) and transition metal complexes that may present relatively long-lasting photoexcited state, as illustrated in Scheme 2 [140].

A first work concerned inserting stilbazolium dyes carboxylate and/or sulfonate as described in Figure 19. New hybrid systems have been obtained by anionic exchange reaction: the cobalt compounds, $Co_2(OH)_{3.57}(MR)_{0.43}$, 1.88 H_2O, $Co_2(OH)_{3.27}(MO)_{0.73}$, 2.94 H_2O, $Co_2(OH)_{3.45}(OrangeIV)_{0.55}$, 2.92 H_2O and $Co_2(OH)_{3.46}(MY10)_{0.27}$, 2.34 H_2O starting from the cobalt hydroxyacetate $Co_2(OH)_3(OAc)$, H_2O, the copper compounds $Cu_2(OH)_{3.23}(MR)_{0.77}$, 2.92 H_2O, $Cu_2(OH)_{3.29}(MO)_{0.71}$, 2.31 H_2O, and $Cu_2(OH)_{3.39}(OrangeIV)_{0.61}$, 1.80 H_2O starting in that case from pre-intercalated $Cu_2(OH)_3(DS)$ (DS: dodecyl-sulfate). Concerning the latter, this pre-intercalation strategy of the lamellar structure, necessary to obtain pure intercalated phases, has been developed for the first time in this type of hydroxides. This opens interesting prospects for the insertion of molecules



Scheme 2: Synopsis of exchange reactions performed in lamellar hydroxides from functional molecules, as metal complexes or bio-inspired molecules with optical properties.

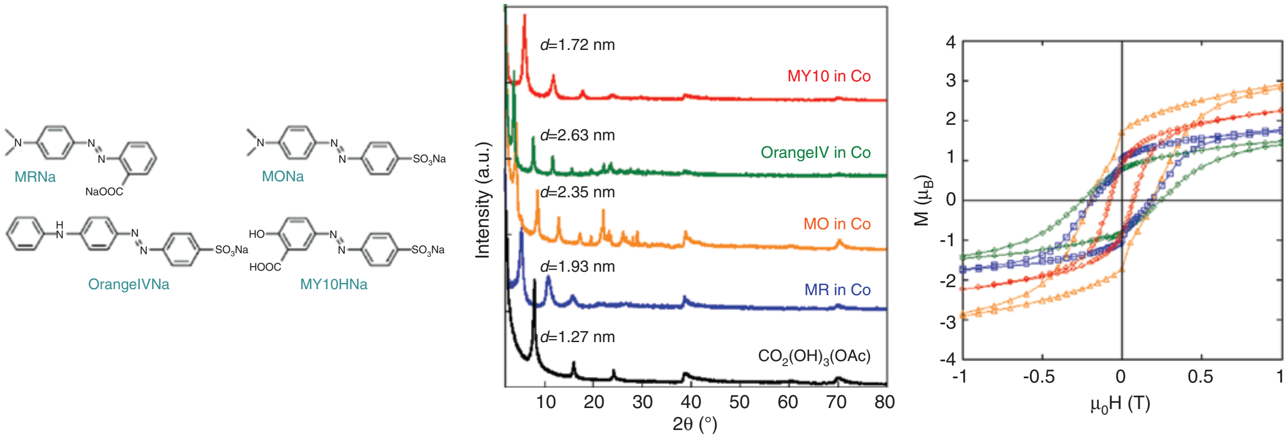


Figure 19: Azo dyes used for anion exchange reaction and X-ray powder diffraction patterns of the corresponding hybrid multilayer compounds. Right, magnetization cycles at 1.8 K of the Co(II) compounds MR@Co (blue), MO@Co (orange), OrangeIV@Co (green) and MY10@Co (red). Adapted with permission from [141]. Copyright 2009 Royal Society of Chemistry.

difficult to insert due to their size or hydrophobicity, for example. Hybrid layered compounds have a ferrimagnetic behavior. The cobalt derivatives order between 6.9 K and 18 K. All of these compounds are fluorescent magnets [141]. It is worth noting here that, despite the presence of azo moieties, it was not possible to photoisomerize efficiently the dyes after intercalation. At least, no photomagnetic effect was observed in this series of compounds. This was likely explained by the fact that the azo dyes are coordinated to the metal layers. This coordination is thought to hinder the change of conformation of the molecules. Moreover, the photo-excited state might be quite difficult to stabilize. The group of Coronado reported recently on the insertion of azo dyes into layered double hydroxides (LDH). In that case, the dyes act as counter anions toward the metal(II)/metal(III) positively charge hydroxide layers. The dyes are not coordinated to the layers, and photomagnetic and thermomagnetic effects were observed [142, 143].

3.2 Multilayer alternating hydroxide layers and transition metal complexes

A second component relates to the insertion grafting of transition metal complexes. One of the encountered difficulties (now overcome) is the possible low stability of the complexes during the anionic exchange reactions, with respect to the aqueous medium, or to transition metal in the hydroxide sheets. Besides the chemical challenge it represents, insertion grafting of transition metal complexes is promising. The observed properties are

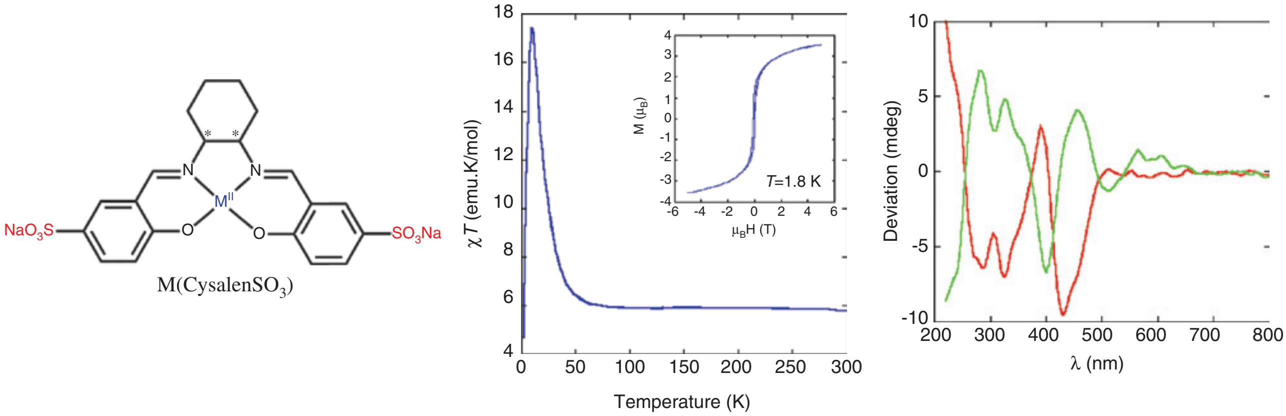


Figure 20: Salen complexes derived from hexane diamine bridge (M=Co(II), Ni(II), Cu(II), Zn(II)). Magnetic behavior as a function of the temperature of the compound Ni(SalenSO$_3$)@Co. Circular dichroism spectra (solid phase) for compounds Ni(CysalenSO$_3$(*RR*))@Cu (green) and Ni(CysalenSO$_3$(*SS*))@Cu (red). Adapted with permission from [140]. Copyright 2010 Société Chimique de France.

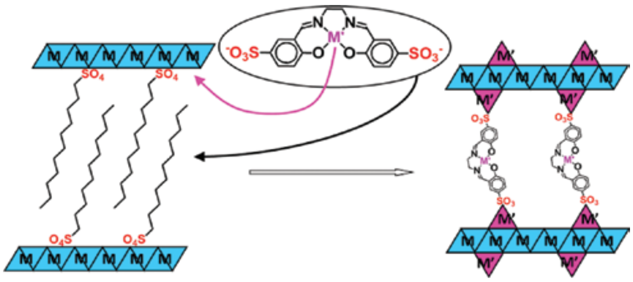


Figure 21: The insertion grafting of Salen-type complexes within lamellar copper or cobalt hydroxides leads to a drastic change in the structure and composition of the inorganic layers due to possible dual exchange mechanism, i.e. anionic and cationic. Reprinted with permission from [145]. Copyright 2012 Wiley.

diverse and *a priori* easily adjustable depending on the metal cation. The results illustrate the versatility of this approach for obtaining multifunctional materials with unique properties associated with the presence of two distinct subnetworks.

A first family was synthesized by insertion of Schiff base complexes (salen) comprising sulfonate group as anchoring functions on magnetic inorganic layers (Figure 20) and involving different diamine bridges [140, 144, 145].

The insertion of such complexes generates specific difficulties due to their possible hydrolysis during the exchange reaction [144]. This difficulty has been overcome by working from compounds pre-intercalated with dodecyl sulfate or dodecylsulfonate in a water-ethanol mixture (50:50 v/v). A major result concerns the insertion of chiral cysalen complexes (Figure 20), which leads to chiral magnets, with the formula $Co_2(OH)_{3,32}(Ni(SalenSO_3))_{0,34}$·4,4 H_2O. A transfer of chirality from the complex to the hybrid compound has been detected by optical circular dichroïsm [146].

However, the insertion of di-sulfonate complexes of different transition metals presented additional difficulties [145]. Thus, two series of compounds were obtained from the complexes $M(SalenSO_3)Na_2$ (M=Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+}) and copper and cobalt hydroxides pre-intercalated with alkyl chains $Cu_2(OH)_3(DS)$ and $Co_2(OH)_3(DS_0)$ ($SalenSO_3Na_2$: N,N′-bis(5-sulfonatosalicylidene)-1,2-diaminoethanedisodium, DS^-: dodecylsulfate and DS_0^-: dodecylsulfonate). The reaction of $M(SalenSO_3)Na_2$ with the copper hydroxide led by anionic exchange to the compounds $Cu_2(OH)_{3.00}(CuSalenSO_3)_{0.50}$·0.20 H_2O and $Cu_2(OH)_{3.24}(NiSalenSO_3)_{0.38}$·2.6 H_2O if M=Cu^{2+} or Ni^{2+}. Similarly, reaction with the layered cobalt hydroxide gave the exchanged products $Co_2(OH)_{3.18}(NiSalenSO_3)_{0.41}$·4.0 H_2O and $Co_2(OH)_{3.44}(CoSalenSO_3)_{0.28}$·3.7 H_2O if M=Ni^{2+} or Co^{2+}. In other cases, the reaction of $M(SalenSO_3)Na_2$ with copper hydroxide when M=Co^{2+} or Zn^{2+} and reaction with the lamellar cobalt hydroxide when M=Cu^{2+} or Zn^{2+} induce a change in the host structure due to a concomitant partial cation exchange between the salen complex and the inorganic layers (Figure 21) [145]. Mixed exchanged compounds were thus obtained, $Cu_{1.16}Co_{0.84}(OH)_{3.28}(Co(SalenSO_3))_{0.36}$, 6.4 H_2O, $Cu_{0.7}Zn_{1.30}(OH)_{3.20}(ZnSalenSO_3)_{0.40}$, 2.11 H_2O, $Co_{1.72}Cu_{0.28}(OH)_{3.28}(CuSalenSO_3)_{0.36}$, 3.20 H_2O et $Co_{0.80}Zn_{1.20}(OH)_{3.20}(ZnSalenSO)_{0.40}$, 2.25 H_2O (Figure 21).

This dual exchange mechanism (anionic/cationic) was characterized by XPS studies, in particular. The magnetic behaviors are strongly modified by the functionalization of the sheets and partial cation exchange. The situation approaches the case of layered double hydroxides (LDH), in which the sheets may contain paramagnetic divalent or trivalent cations. The nature of the cations and their distribution, related to the synthesis conditions and to the distribution of counter anions between the layers, greatly influence the magnetic

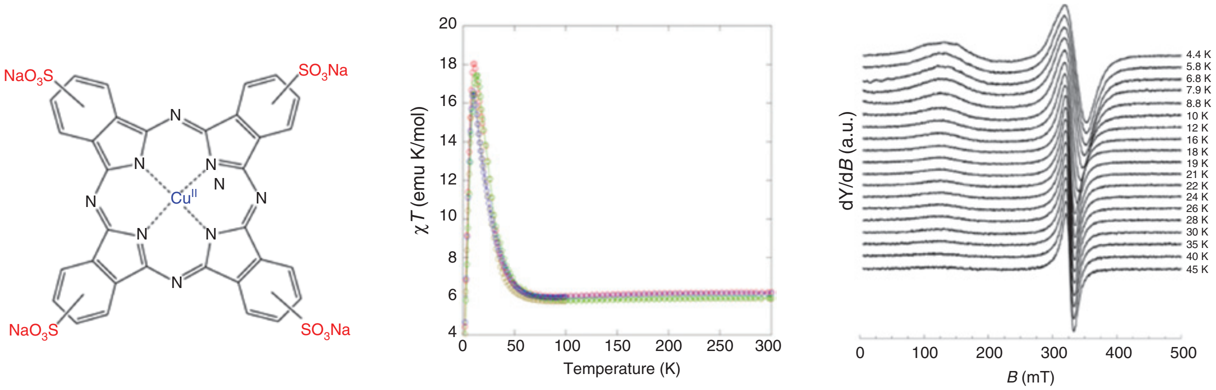


Figure 22: Left: phthalocyanines tetrasulfonates sketch [M=Co(II), Ni(II),Cu(II)]. Middle: magnetic behavior as function of temperature for $CuPcTS_0$@Co (red), $CoPcTS_0$@Co (blue), and NiPcTS0@Co (green). Right: thermal variation of the X band EPR spectrum of $CuPcTS_0$@Co. Adapted with permission from [101]. Copyright 2014 American Chemical Society.

properties [147]. In the present case of LSH, however, all cations remain divalent.

The particular reactivity of salen sulfonate complexes was explained by the inductive attractor effect of the sulfonates, which destabilizes the complex. This phenomenon could be circumvented by the use of similar complexes but with carboxylate functions. In this case, hybrid compounds were obtained with Mn, Fe, Co, Ni, Cu, and Al complexes without cation exchange [148]. Furthermore, while the magnetic ordering temperatures do not vary with the metal complexed by the sulfonate ligands, metal was found to have a significant influence when complexed by carboxylate ligands. The carboxylate moieties transmit better the exchange interaction to the functionalized hydroxide layers. Varying the nature of the metal complex that is inserted opens thus interesting perspectives in modulating either magnetic or optical properties (luminescence or nonlinear optical chirality) of the hybrid compounds formed.

Another approach consisted in grafting robust macrocyclic complexes, namely, phthalocyanine tetrasulfonates MPc, M=Cu, Co, Ni (Figure 22) [101, 140]. A detailed study of the synthesis process helped to better understand the exchange reactions with the identification of co-inserted phases. Again, the indirect pathway starting from the pre-intercalated structures $Cu_2(OH)_3(DS)$ and $Co_2(OH)_3(DS_0)\cdot H_2O$ (DS=dodecyl-sulfate, DS_0=dodecyl-sulfonate) proved to be relevant for functionalizing hybrid compounds showing good crystallinity. The formula of the final products was $M_2(OH)_{4-4x}(M'PcTS_0)_x\cdot y\ H_2O$ (with M=Co(II) or Cu(II), M′=Co(II), Ni(II), or Cu(II), 0.1<x<0.2 and 2<y<3). The cobalt compounds, noted $MPcTS_0$@Co, have a ferrimagnetic behavior (Figure 22) with ordering temperatures of 5.8, 6.8, and 7.8 K for the compounds functionalized by the Co, Ni, and Cu phthalocyanine, respectively. The ordering temperature is changed with respect to that of the unsubstituted compound, T_N=19.5 K. Electron paramagnetic resonance (EPR) spectroscopy was used to follow the shift of the EPR signal of the copper phthalocyanine inserted into cobalt hydroxide, as a function of temperature. This shift reflects the evolution of the internal dipole field arising from the increase in the magnetic correlation length within the cobalt layers [101]. Thanks to a precise X-band and Q-band EPR study, the value of a purely dipolar internal field developing in between magnetic layered simple hydroxides was determined from the shift of $g_\perp$ between 90 and 5 K: $B_{\text{dipolar}}\approx 30$ mT. A similar feature was also observed in the case of $CuPcTS_0$ inserted into the ferromagnetic NiAl-LDH [149]. In that case, however, it is likely that the too low resolution of X-band EPR spectroscopy prevented the precise study of the evolution of the parallel and perpendicular components of the transition. These results reinforce the validity of the

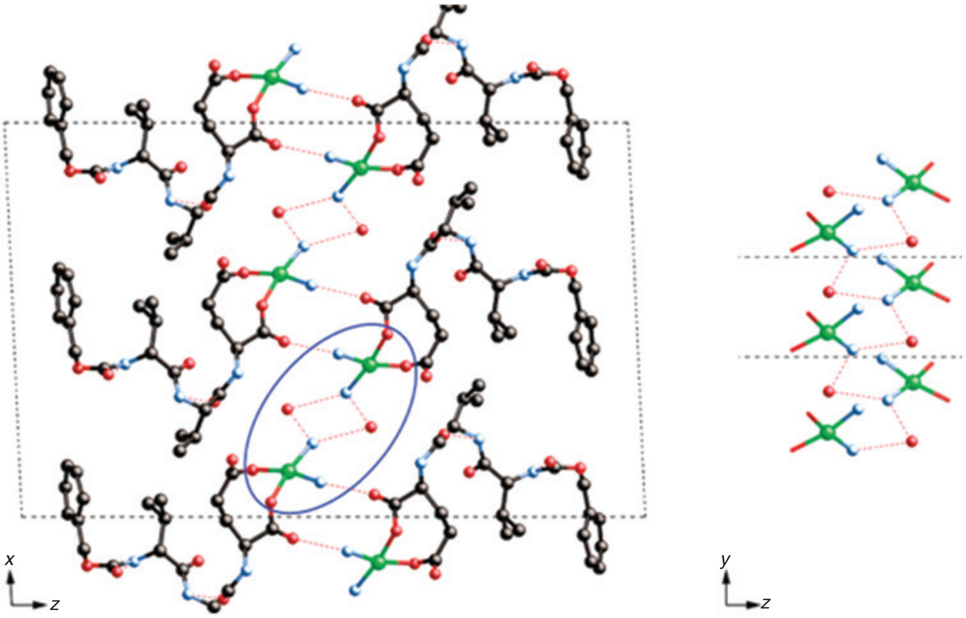


Figure 23: Hydrogen bonding network in the ac plane (left) and perpendicular view to the helical pathway between water molecules and ammonia according to [010] (right). The hydrogen atoms are omitted. Reprinted with permission from [167]. Copyright 2008 American Chemical Society.

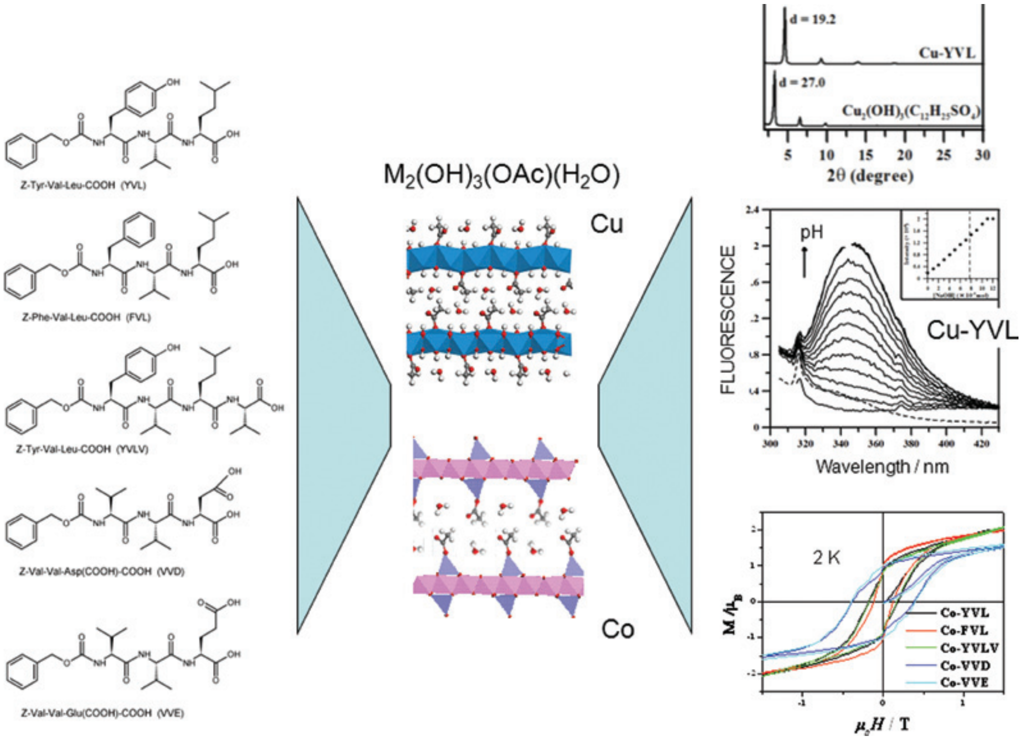


Figure 24: Carboxylate grafted peptides in lamellar hydroxides; structure and physicochemical properties.

interplanar dipole interaction model proposed by Drillon and Panissod [100].

In addition to magnetism or electronic aspects of these multilayer hybrid systems, additional properties can be explored to be brought by this functionalization, such as conductivity, luminescence, redox properties, or catalysis.

3.3 Structuring and functionalization of solid

Let us look further at the nanostructuring of functional solids (platelet-like nanoparticles) by molecules having optical, electronic, or self-assembly properties. The main challenge is to help in the design by chemical pathways of new multifunctional nanomaterials providing opportunities, for example, in the field of sensors or imaging [46, 150–155]. Thus, inorganic, supramolecular, or biomimetic systems were inserted within lamellar hydroxide-based hybrids [46, 153, 156–159]. Here, it is important to evaluate the effect of confinement on the structure or properties of the inserted compounds and their sensitivity to external stimuli. To generalize our approach to the integration of the most diverse systems in lamellar structures, new synthetic routes have been developed.

3.3.1 Synthesis and grafting of peptides in the lamellar hydroxides

Biological or bio-related molecules can be used to construct supramolecular assemblies or coordination networks [129, 160–164]. These include the “Metal Peptide Frameworks” (MPFs) [165–168], initially reported by Taubert et al. and Marsh et al. [165]. In MPFs, the metal ions are coordinated by the carboxylate functions of short peptides organized under the influence of supramolecular interactions (H-bonding, hydrophobic-hydrophobic) shown in Figure 23 [167].

Since the pioneering works, the porosity and connectivity of the metal framework was improved by using short peptides [166, 168]. Yet, the metal centers are usually diluted in MPFs, and magnetic interactions are weak, especially in the case of oligopeptide-based frameworks as shown in Figure 23. We have, therefore, undertaken to stabilize a peptide assembly between the layers of transition metal hydroxides forming an expanded magnetic array. New hybrid materials were synthesized by grafting synthetic peptides in the interlayer space of Cu(II) and Co(II) simple lamellar hydroxides (LSH) [44]. Our results are summarized in Figure 24.

To recapitulate the main results, the interplane distance of the hybrids obtained depends on the length of

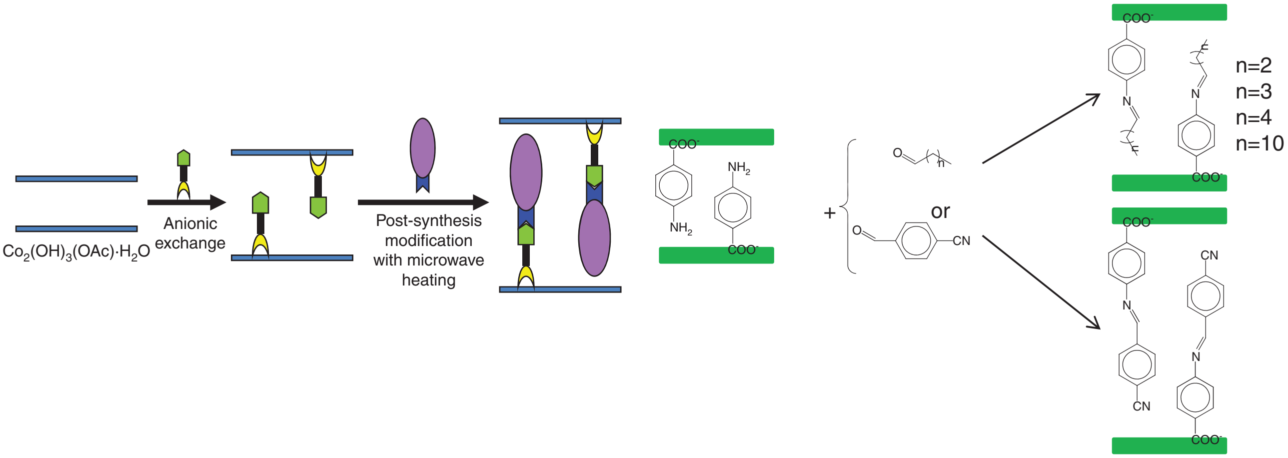


Figure 25: Scheme of the postsynthesis modification strategy in lamellar hydroxides (left) and specific examples obtained (right) [171].

the peptide chain; this dependency is specific for the compounds with copper or cobalt, which suggests a metal-dependent interaction of the peptides with the inorganic layers. When tyrosine is present in the oligopeptide, its fluorescence is quenched after grafting into the hybrid structure. Studies of the fluorescence as a function of pH indicate deprotonation of the tyrosine functions into tyrosinate at high pH. This deprotonation is accompanied by the appearance of fluorescence. The luminescence increases with the concentration of OH^- ions. Thus, the hybrid acts as a stable chemical sensor in a basic medium. Moreover, the variation of the luminescence with pH indicates that the tyrosine functions located inside the interlayer space are accessible to the ions present in the solution. In addition, the presence of peptides influences the magnetic properties. Copper-based compounds have an antiferromagnetic behavior; those based on cobalt are ferrimagnetic.

3.3.2 Development of new synthetic routes by post-functionalization of hydroxides

The chemical and structural versatility of the layered simple hydroxides allows to envisage the insertion grafting of many types of functional molecules or metal complexes. Conceptually, several pathways have been opened such that the insertion grafting of transition metal complexes which is really promising for generating multifunctionality. Many properties can be exploited such as conductivity, luminescence, chirality, magnetism, electroactivity catalyst, etc. Moreover, these features can be easily modulated by modifying the host species. However, the insertion and grafting of diverse chemical species is not trivial. The above results have shown, in particular, that the stability of the inserted species toward that of the host matrix, in the appropriate reaction conditions, is a limiting factor for the anion exchange reactions. Therefore, it is necessary to focus on developing new approaches. Particularly post-functionalization or *in situ* molecular synthesis is appealing. This approach consists in pre-grafting simple molecules providing reaction sites on which it is possible to build the entire molecule one wills to graft onto the inorganic host. This postsynthesis modification strategy has been developed for many metal organic frameworks, [169] or mesoporous silica [170]. To our knowledge, it has been little used for layered materials.

Recently, we were able to show the validity of the postsynthesis modification approach by synthesizing an organic molecule *in situ*, that is to say in the interlayer space of the hydroxide hosts [171]. To this end, we functionalized the interlamellar space of a cobalt hydroxide with para-aminobenzoic acid. We tried to use the amine, *a priori* free in the interlamellar space, for reaction with aliphatic and aromatic aldehydes. However, to our surprise, the "classical" reaction conditions – reaction to reflux in dry methanol or ethanol or in dry toluene with a Dean-Stark setup to drive the water formed and thus shift the equilibrium – do not allow the post-functionalization of the compound. Moreover, conventional heating in solvothermal conditions led to a degradation of the compound. We then used less conventional heating methods. Hence, the microwave activation has led to the desired result, namely, the postsynthesis modification of the starting compound. The general outline of the strategy followed is given in Figure 25.

This approach represents a promising new strategy for the functionalization of lamellar structures.

4 Conclusions

In recent years, a true engineering of multifunctional hybrid compounds was born, and the development of hybrid lamellar magnetic model compounds, by hydrothermal or anion exchange reaction, is an example. A significant part of this activity is the study of the magnetic behavior of transition metal compounds with a particular emphasis on the effects of anisotropy (spin-orbit coupling, structural anisotropy), dimensionality, and the coupling between magnetic and optical properties (luminescence, chirality). In these current developments, it comes to suggest hybrid systems whose properties are controlled by the choice of suitable organic, organometallic, and inorganic bricks. Transition metal-layered hydroxides have been functionalized with photoactive or photoreactive molecules. This was possible due to the chemical and structural flexibility of hydroxides. A significant breakthrough was the insertion of transition metal complexes. Besides the chemical challenge, which was pointed, this gives access to multilayer magnetic subnetworks with multiplet levels sensitive to internal magnetic field, to optical properties involving long-lasting excited states, and this allows an opening to other properties such as catalysis or electrochemistry. Remarkable results are the change in the luminescence of OPV by magnetic ordering and the chirality transfer obtained with the chiral Schiff base complexes.

The most recent work has focused on the development of anion exchange as a synthetic route. This way is relatively versatile, and we could get multifunctional compounds with organic or organometallic magnetic, fluorescent chiral, or bio-inspired anions. The coupling between properties is at the heart of our current concerns. Results regarding the coupling between magnetic and optical properties, including fluorescence or chirality, were obtained. In the case of hydroxides functionalized with oligopeptides, we studied the effect of the presence of redox and fluorescent groups as well as the nature of the pendant chains on the overall properties of the final hybrid material. Some rules may be enounced for the synergy occurs between magnetism and optical property. Pertinent parameters are the grafting mode, the luminescence efficiency, $\lambda_{abs}/\lambda_{em}$, and life time of the excited state. This approach to the bifunctional materials is advantageous as the grafting of photoactive molecules in a crystalline structure provides an organized array of molecules capable of creating a cooperative effect. Complex or organic molecules may play a structural role or act as an electronic coupler (conjugated systems), and the existence of an iono-covalent bond between subnetworks promotes synergy between the properties of each entity.

We examined the adaptability of these systems to physical or chemical external factors. A study under pressure demonstrated the existence of competing magnetic interactions within the metal(II) layers. The balance between interactions can be modulated by structural deformation inducing a drastic change in magnetic behavior. For the chemical aspect, the grafting of synthetic oligopeptides in layered transition metal hydroxides is particularly instructive. The resulting hybrid materials combine magnetism and fluorescence. This result opens the possibility of the use of our systems. Indeed, hydrophobic interactions in the supramolecular assemblies can modulate the properties, especially the magnetic properties, of layered systems. In addition, by grafting luminescent peptides as YVVL, pH sensors can be obtained. It is important to note here that the reactivity of tyrosine in confined interlayer space demonstrated the accessibility of the functions confined to external species present in solution. The field is not limited to transition metal hydroxides. Actually, layered lanthanide hydroxides are also appealing for providing magnetic layers with strong anisotropy effects [172, 173]. At present, new synthetic methods are being explored to expand the scope of the functionalization of lamellar structures or nanosheets. The goal is designing new complex adaptive systems. In particular, exfoliation and re-stacking processes are very appealing to provide new layered devices with possible application in a wide range of domains as electronics, energy, coatings, photocatalysis, or environment [24, 36, 39–42, 45, 151, 174–185]. In all cases, the hybrid interfaces between components is of crucial importance for the control of the properties. We hope that the knowledge gained with model materials such as hydroxides will help to progress faster in the realization of unprecedented devices.

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