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## ARTICLE

# Microwave-Assisted Post-Synthesis Modification of Layered Simple Hydroxides

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A new method to functionalize Layered Simple Hydroxides, by post-synthesis modification is described. A cobalt layered hydroxide was modified with a molecule bearing a free amino group. We show here that it is possible to post functionalize the metal hydroxide layers by performing *in situ* microwave assisted reaction onto the free amino group, constituting a new appealing strategy for functionalization of layered solids. The obtained compounds are characterized by ancillary techniques and their magnetic properties were investigated, underlying the influence of the post-functionalization even though the inorganic magnetic layers are not deeply affected by the process.

## Introduction

Since the discovery of the outstanding electronic properties of the graphene derivatives,<sup>1</sup> the research in functional nanomaterials has been increasingly concerned by the conception of new multifunctional nanosheet-based systems,<sup>2, 3</sup> with an intensification of research in the field of layered materials.<sup>4, 5</sup> Among the possible chemical routes, the hybrid organic-inorganic approach is particularly well suited to promote multifunctionality within a single material. It is indeed possible to control the assembly at the nanoscale level of two components, each bearing its own property.<sup>6-8</sup> In that way, each sub-network exhibits its own properties or contributes synergistically to new physical phenomena and novel applications.<sup>9, 10</sup>

Transition metal Layered Simple Hydroxides (LSH), of general formula  $M^{II}_2(OH)_3(X)\cdot nH_2O$  ( $M = Co, Cu, Ni$  and  $X$  is an easily substitutable anion, nitrate or acetate for instance) are very well adapted to grafting reactions of various organic molecules. We and others have recently obtained hybrid compounds based on LSH functionalized with (oligo) thiophenes,<sup>11, 12</sup> azo dyes,<sup>13</sup> diarylethene,<sup>14</sup> or complexes of transition metals.<sup>15-19</sup> We have notably developed a pre-intercalation procedure which enables the insertion-grafting of large molecules due to the pre-swelling of the layered host.<sup>13</sup> However, a major drawback of the functionalization reactions of layered hydroxides lies in the fact that they proceed by anion-exchange reaction, especially effective in aqueous medium at basic pH (typically around pH = 8). The pre-intercalation strategy allows for partial stabilization of species sensitive to hydrolysis, by creating a hydrophobic environment in-between the inorganic layers.<sup>15</sup> But the ion-exchange reaction still requires the use of water, even when pre-intercalation is used. This severely limits the type of molecules that can be considered to be grafted in the interlamellar space. To overcome this difficulty, one solution is to synthesize *in*

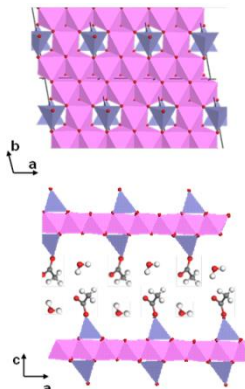
*situ* (in the interlamellar space) the desired molecules from a pre-grafted functional precursor. Thus, only the first stage (grafting the precursor) requires the use of insertion-grafting conditions by anion exchange. The following reactions may appeal to a much larger panel of conditions, including the use of non-aqueous solvents. Confinement of the reaction space may also have specific effects on the synthesis.

The post-synthesis modification strategy has been widely developed for Metal Organic Frameworks,<sup>20-27</sup> or for mesoporous silicates,<sup>28, 29</sup> Yet, to our knowledge it has seldom been used in layered materials. One noticeable example concerns the controlled 2D growth of Prussian blue analogues in the interlamellar space of Layered Double Hydroxides (LDH).<sup>30, 31</sup> In this example, Prussian blue analogue is synthesized in a two-step reaction. Hexacyanometalate is first inserted in the interlamellar space of LDH, then a M(II) salt is reacted with the hybrid, and the *in situ* reaction leads to the formation of a Prussian blue analogues in-between the inorganic layers. Another example deals with confined synthesis of pyridinic and pyrrolic nitrogen-doped graphene in layered montmorillonite.<sup>32</sup> Yet, *stricto-sensu*, these examples are not really representative of a post-synthesis modification. According to Cohen,<sup>22</sup> post-synthesis modification "can be broadly defined as a chemical derivatization of MOFs after their formation; in a more strict sense, it may refer only to those modifications involving covalent bonds,<sup>22</sup> or dative bonds<sup>25</sup> with the framework, or deprotection<sup>25</sup>". (In the present proposed extension of definition "MOFs" may be replaced by "hybrid solids".) We report in this article the post-synthesis modification of a Co LSH, functionalized by *p*-amino-benzoic acid. We show that the amine groups react *in situ* with various aldehydes (aliphatic and aromatic) to form imines (azomethine groups). Interestingly, conventional activation (heating) is inefficient in the present case, whereas microwave irradiation enables the *in situ* reaction. This

technique constitutes a new appealing strategy for functionalization of layered structures.

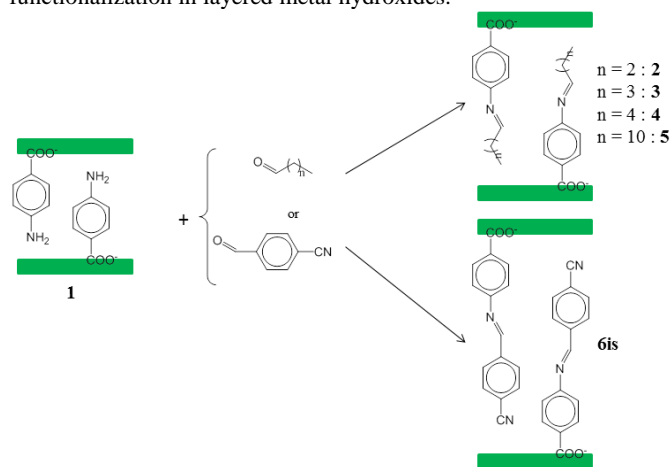
## Results and discussion

We investigated the functionalization of layered cobalt hydroxide acetate,  $\text{Co}_2(\text{OH})_3(\text{OAc})\cdot\text{H}_2\text{O}$ , the structure of which is presented in Figure 1.



**Fig. 1** Structure of  $\text{Co}_2(\text{OH})_3(\text{OAc})\cdot\text{H}_2\text{O}$  ( $R\text{-}3m$ ,  $a = 0.313$  nm,  $c = 1.27$  nm,  $\alpha\text{-Co}(\text{OH})_2$  polytype).<sup>33-36</sup> Pink and purple polyhedral hold for  $\text{Co}(\text{II})$  ions in octahedral and tetrahedral sites respectively.

The general strategy we have followed is schematized in Scheme 1. We have chosen the *in situ* formation of various alkyl or aryl imino-benzoates as a model reaction to validate the concept of post-functionalization in layered metal hydroxides.



**Scheme. 1** Post-synthesis modification strategy.

In the first step, a Co layered hydroxide was functionalized by *p*-amino-benzoic acid providing  $(4\text{-NH}_2\text{-BzAc})\text{Co}$  (**1**) by classical anion exchange. The initial pH has to be carefully settled at  $\text{pH} = 8 \pm 0.2$ . Larger values lead to a low crystallinity and to Co-oxide impurities, whereas lower values lead to a mixture of unidentified non-lamellar phases. The use of ethanol along with water (ethanol / water = 1/4 (v:v)) is also crucial, as ethanol may serve as an antioxidant.

The second step deals with the post-functionalization itself. Compound **1** is put to react with aldehydes, likely to condense with the free amino groups to give imines, sketched in Scheme 1, and

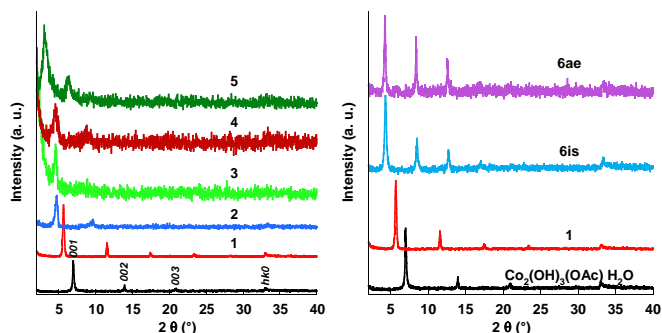
water. Yet, all attempts to perform this reaction using classical heating (up to  $80^\circ\text{C}$ ), in dry solvents (alcohols, toluene, chloroform) led to the recovery of the starting material. In order to overcome this difficulty, the reactions were then performed using microwave activation under autogeneous pressure. The best conditions were found to be: absolute ethanol as solvent (20 mL in a sealed microwave tube of 30 mL), 0.5 moles of **1**, 3 equivalents of aldehyde and a 30 W microwave irradiation during 10 min. In these conditions the pressure in the microwave tube reached typically 9 bars and the temperature increased up to  $140^\circ\text{C}$ . Microwave activation has proved to be particularly useful to accelerate reactions, to increase the yields and the purity of compounds under milder reaction conditions and to obtain products which cannot be obtained otherwise. It has essentially been used in organic chemistry,<sup>37</sup> but also in coordination chemistry<sup>38-40</sup> and in materials chemistry.<sup>41, 42</sup> It has been also used for the post-functionalization of nanoparticles,<sup>43</sup> or of MOFs,<sup>25, 44-47</sup> but to the best of our knowledge it is the first time microwave heating is used for the internal post-synthesis modification of layered hybrid solids which are stable in a reduced range of pH.

It is worth noticing here that it has not been necessary to preliminary dehydrate the starting compound  $(4\text{-NH}_2\text{-BzAc})\text{Co}$  (**1**) even though it contains 2.4 water molecules per formula unit. It was neither necessary to remove water which forms during the reaction, contrarily to what is usually done to displace the equilibrium of reactions which produce water as a by-product (using molecular sieves for instance, or Dean-Stark apparatus). The water molecules which form remain within the product, as attested by elemental analysis, and are probably engaged in H-bonds to the inorganic hydroxy network.

Two kinds of aldehyde have been chosen to react with the amino group of the pre-grafted amino-benzoate: aliphatic aldehydes, with various alkyl chain lengths (butanal, pentanal, hexanal and dodecanal), and one aromatic aldehyde (4-cyanobenzaldehyde), bearing a cyano group to serve as an IR marker.

In addition, the imine **LH** formed from the condensation of 4-aminobenzoic acid with 4-cyanobenzaldehyde, was isolated and further grafted into the interlamellar space of  $\text{Co}_2(\text{OH})_3(\text{OAc})\cdot\text{H}_2\text{O}$  by "classical" ion exchange. This compound, denoted **6ae**, served for comparison with the compound obtained by *in situ* reaction, denoted **6is**. Notably, it has not been possible to insert the other preformed imine ligands by ion-exchange. The yields of the post-synthesis modification reactions are all around 80%. The yield of formation of **6ae** is notably lower, around 60%. This underlines the relative efficiency of the microwave assisted post-synthetic modification with respect to functionalization by ion exchange. Interestingly, despite the reversible character of the imine formation reaction, it has not been possible to hydrolyze the imine formed within the interlamellar space (while keeping the integrity of the inorganic host), regardless of the activation used (classical or microwave).

The products were first characterized by powder X-ray diffraction (Fig. 2).



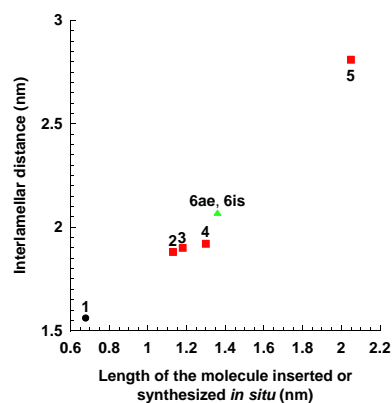
**Fig. 2** Powder X-ray diffraction patterns for compounds **1-5**, **6is**, **6ae** and the starting compound  $\text{Co}_2(\text{OH})_3(\text{OAc})\cdot\text{H}_2\text{O}$  (black).

The XRD pattern of all compounds show intense  $00l$  diffraction peaks at low angle which evidences their lamellar structure. For **1**, **6ae** and **6is**, up to four harmonics are visible, whereas for compounds **2-5**, only two harmonics are visible, which underlines their lower crystallinity. In the high angle region, all XRD patterns exhibit similar asymmetrical peaks at  $2\theta = 33^\circ$  ( $\text{Cu K}\alpha_1 = 0.1540598$  nm) corresponding to in-plane diffraction lines. The asymmetry suggests turbostratic disorder. The interlamellar distances for all compounds are collected in Table 1.

**Table 1.** Interlamellar spacing of the hybrid compounds **1-5**, **6is** and **6ae**.

Compound	Inserted molecule	Interlamellar distance (nm)
$\text{Co}_2(\text{OH})_3(\text{OAc})\cdot\text{H}_2\text{O}$	OAc	1.27
<b>1</b>	4-NH <sub>2</sub> -BzAc	1.56
<b>2</b>	AcBz-N=CH-C <sub>3</sub> H <sub>7</sub>	1.88
<b>3</b>	AcBz-N=CH-C <sub>4</sub> H <sub>9</sub>	1.90
<b>4</b>	AcBz-N=CH-C <sub>5</sub> H <sub>11</sub>	1.92
<b>5</b>	AcBz-N=CH-C <sub>11</sub> H <sub>23</sub>	2.81
<b>6is</b>	AcBz-N=CH-Bz-CN	2.07
<b>6ae</b>	AcBz-N=CH-Bz-CN	2.07

The important feature there is that the interlamellar distance increases gradually when the size of the aldehyde increases. For small alkyl chains (compounds **2**, **3** and **4**), the variation of the interlamellar spacing is linear with the number of carbon atoms of the alkyl chain. For long alkyl chain (compound **5**) a discontinuity occurs (with respect to the other aliphatic compounds) which is likely due to a change in the interdigitation of the molecules. Fig. 3 shows a clear correlation between the size of the molecule<sup>48</sup> which is supposed to form in the interlamellar space and the interlamellar distance of the hybrid compounds, which constitute further evidence for the *in situ* reaction.



**Fig. 3** Correlation between the interlamellar distance of the hybrid compounds and the size of the molecule inserted or synthesized *in situ*.

Color stands for the family of compounds (black for the starting compound **1**, red for the compounds with aliphatic chains **2-5**, and green for the compounds with the cyanobenzyl group **6is** and **6ae**).

The XRD patterns of **6is** and **6ae** are similar, but the XRD pattern of **6ae** reveals slightly broader peaks, especially at  $33^\circ$ , suggesting a lower crystallinity. Thus *in situ* post-synthesis modification leads to the same material as direct ion exchange.

Even though it is not possible to claim from elemental analysis only that the *in situ* formation of imine took place, the results of the elemental analysis confirm the presence of additional organic moieties with respect to the starting compound **1**. The post-synthesis modification procedure induces a small loss of grafted ligand: with respect to the general formula  $\text{Co}_2(\text{OH})_{4-x}(\text{L})_x$ ,  $x = 0.65$  for **1**, whereas  $x$  is slightly smaller for **2-5** and for **6is**, ranging from 0.43 to 0.53. For **6ae**  $x$  is of the same order of magnitude as for **1** ( $x = 0.62$ ). This observation underlines that despite post-synthesis modification is supposed to let the inorganic matrix untouched, the mechanism is most probably more complicated. The inorganic network probably readjusts its structure to adapt the layers to the new molecular area of the organic components, which thus leads to partial leaching of amino-benzoate molecules. This rearrangement seems different between standard anion exchange and microwave-assisted reaction.

Unfortunately, the attempts to characterize the functionalization of the samples by means of solid state <sup>13</sup>C NMR spectroscopy were unsuccessful. This is likely due to a broadening of the signal caused by the slowly relaxing paramagnetic Co<sup>II</sup> ions. Nevertheless, the compounds were further characterized by infrared spectroscopy (Fig. 4). Principal characteristic bands are collected in Table 2.

The first noticeable feature is that in all hybrid compounds **1-5**, **6is** and **6ae**, the position of the carboxylate vibration bands hardly changes. The asymmetric band corresponding to the asymmetric vibration mode is around  $1540\text{ cm}^{-1}$  whereas the one corresponding to the symmetric vibration mode is around  $1390\text{ cm}^{-1}$ . For comparison, these bands are located at  $1682\text{ cm}^{-1}$  and  $1429\text{ cm}^{-1}$  respectively for the free ligand **LH**. The position of the bands as well as the value of  $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$

indicate that the carboxylate is coordinated to the inorganic layers, in a unidentate mode.<sup>49-52</sup>

In **1**, the bending vibration of the free amine groups is visible at  $1610\text{ cm}^{-1}$  whereas their stretching vibration at higher energy is masked by the stretching vibration of the water molecules.

The similarity between the spectra of **6is** and **6ae** confirms that the two compounds are indeed identical as evidenced from elemental analysis and X-ray diffraction.

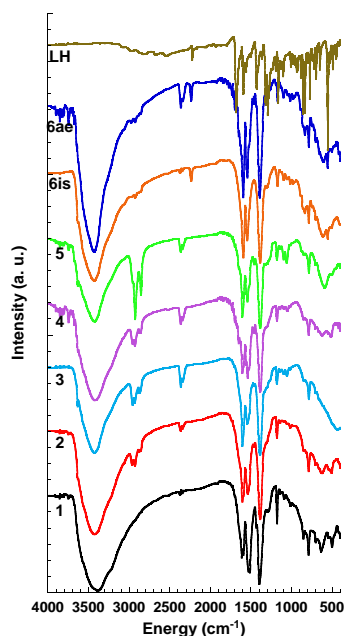
Several features confirm that additional organic moieties are present in the hybrid compounds. The  $\text{CH}_2$  and  $\text{CH}_3$  vibrations are clearly identified in the  $2850\text{-}3000\text{ cm}^{-1}$  region for compounds **2-5**. In addition, the intensity of these bands

increases with the length of the alkyl chain of the aldehyde used. For **6ae** and **6is**, the cyanide vibration band is clearly visible at  $2235\text{ cm}^{-1}$  indicating the presence of the cyanobenzene moiety.

Finally indications concerning the effectiveness of the *in situ* formation of the imine functions in the hybrid compounds **2-5** and **6is** are given by the disappearance of the  $\text{NH}_2$  bending vibration at  $1610\text{ cm}^{-1}$ , the absence of the characteristic vibration of the aldehyde group at  $1700\text{ cm}^{-1}$  and the appearance in all compounds of the imine vibration band around  $1600\text{ cm}^{-1}$ .

**Table 2.** Characteristic infrared absorption bands.

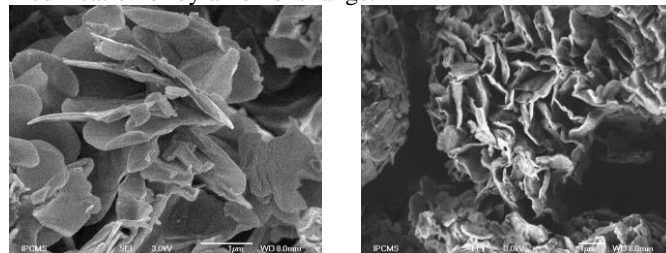
Compound	$\nu(\text{C}\equiv\text{N})$ ( $\text{cm}^{-1}$ )	$\delta(\text{NH}_2)$ ( $\text{cm}^{-1}$ )	$\nu(\text{C}=\text{N})$ ( $\text{cm}^{-1}$ )	$\nu_{\text{as}}(\text{OAc})$ ( $\text{cm}^{-1}$ )	$\nu_{\text{s}}(\text{OAc})$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )
$\text{Co}_2(\text{OH})_3(\text{OAc})\cdot\text{H}_2\text{O}$	/	/	/	1568	1403	165
<b>1</b>	/	1610	/	1528	1393	135
<b>2</b>	/	/	1606	1539	1386	153
<b>3</b>	/	/	1603	1541	1387	154
<b>4</b>	/	/	1605	1539	1385	154
<b>5</b>	/	/	1603	1543	1386	157
<b>6is</b>	2235	/	1593	1546	1385	161
<b>6ae</b>	2235	/	1594	1543	1391	152
<b>LH</b>	2222	/	1592	1682	1429	253



**Fig. 4** FTIR spectra of compounds **1-5**, **6is**, **6ae** and of the imine **LH**.

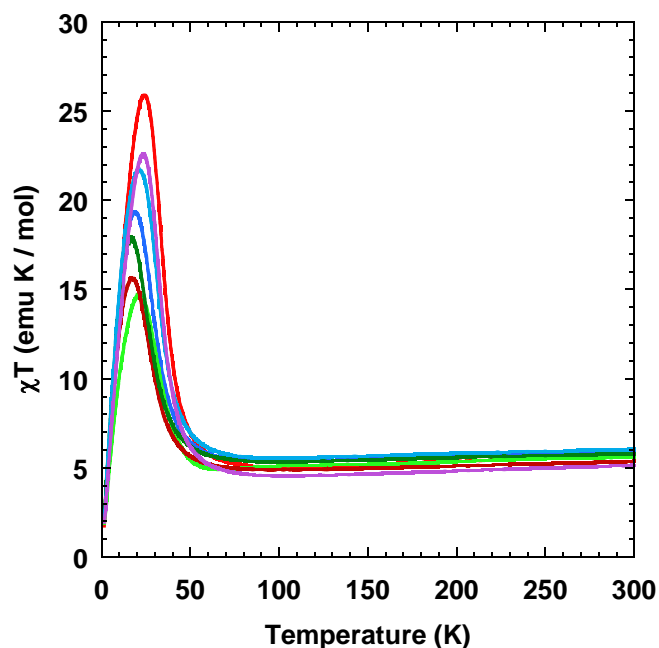
The SEM photos of compounds **1** and **4** are shown on Figure 5 and are representative of all hybrid compounds reported here (see Figure S1 ESI). They are obtained as thin platelets, in agreement with the lamellar character of their structure. No particular difference in shape, size or morphology was noticed

whether the compounds were obtained by post-synthesis modification or by anion exchange.



**Fig. 5** SEM images of compounds **1** (left) and **4** (right).

The magnetic behaviors of all compounds are much alike (Fig. 6). The Curie constants, determined from the fit of  $1/\chi = f(T)$  to the Curie-Weiss law, are all within the range  $5.69 - 6.27\text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ , in agreement with the presence of a mixture of tetrahedral and octahedral high-spin  $\text{Co}(\text{II})$  ions.<sup>53</sup> Upon cooling, the  $\chi T$  products of all compounds decrease slowly down to a minimum around 100 K. This behaviour is attributed to spin-orbit coupling for high-spin  $\text{Co}(\text{II})$  ions in octahedral sites, and / or to antiferromagnetic interactions between the spin carriers. Below this minimum, the  $\chi T$  products diverge, up to a field dependent maximum (around 20 K here under 0.5 T), which is due to saturation effect.

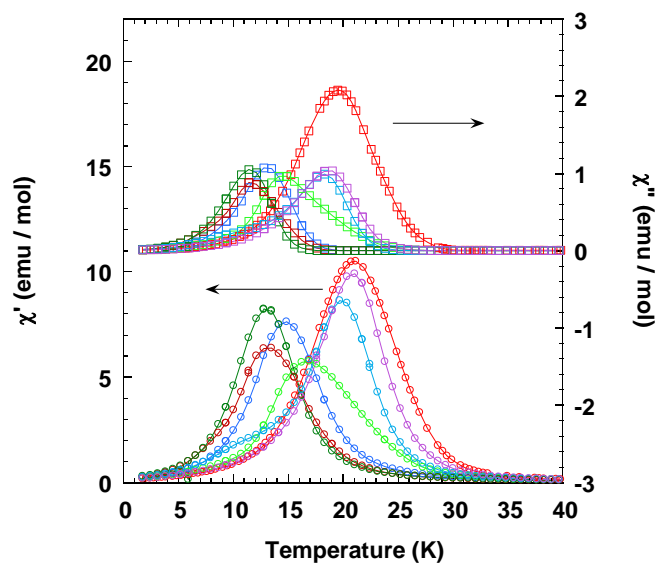


**Fig. 6**  $\chi T = f(T)$  under 0.5 T for compounds **1** (red), **2** (dark blue), **3** (light green), **4** (brown), **5** (dark green), **6is** (light blue) and **6ae** (purple).

This peculiar behaviour is attributed to the occurrence of a long range ferromagnetic-type ordering. The ordering temperatures are further determined from the maximum of the in-phase susceptibility, around 15 K for compounds **2-5**, and around 20 K for compounds **1**, **6is** and **6ae** (Fig. 7, and Table 3).

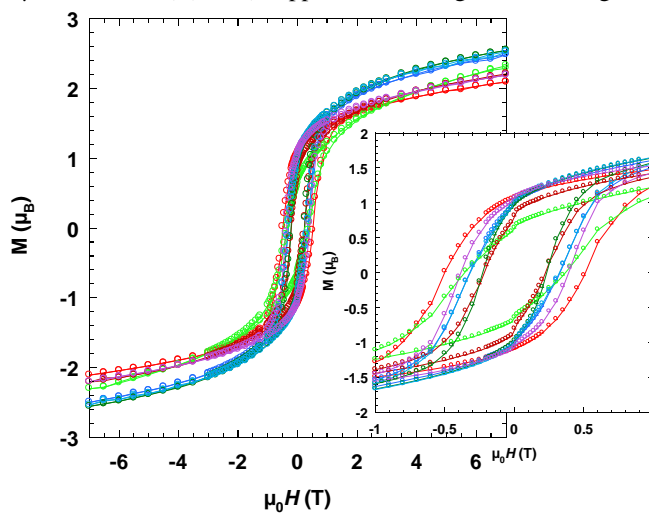
**Table 3.** Magnetic characteristics of compounds **1-5**, **6is** and **6ae**.

	C (emu·K·mol <sup>-1</sup> )	$T_N$ (K)	$\mu_0 H_c$ (T)	$M_{(7T)}$ ( $\mu_B$ )
<b>1</b>	6.29	21.0	0.50	2.1
<b>2</b>	6.27	14.9	0.32	2.5
<b>3</b>	6.11	16.7	0.36	2.3
<b>4</b>	5.87	13.2	0.22	2.2
<b>5</b>	6.20	13.0	0.23	2.6
<b>6is</b>	6.45	19.8	0.33	2.5
<b>6ae</b>	5.69	21.0	0.39	2.2



**Fig. 7** in-phase susceptibility ( $\chi'$ , bottom, open circles) and out-of-phase susceptibility ( $\chi''$ , top, open squares) for compounds **1** (red), **2** (dark blue), **3** (light green), **4** (brown), **5** (dark green), **6is** (light blue) and **6ae** (purple) (full lines are just guides for the eye).

The ferromagnetic-type behaviour is confirmed by the occurrence of out of phase signals. Accordingly, the low temperature magnetization vs. field curves (Fig. 8) show the presence of hysteresis loops, with coercive fields around 0.25 T (Table 3). The low value of the moments at high fields, much lower than expected for the total alignment of the moments (4 – 6  $\mu_B$  for two Co(II) ions) supports a ferrimagnetic ordering.<sup>18, 53</sup>



**Fig. 8**  $M = f(H)$  at 1.8 K for compounds **1** (red), **2** (dark blue), **3** (light green), **4** (brown), **5** (dark green), **6is** (light blue) and **6ae** (purple) (full lines are just guides for the eye). Inset : zoom on the -1/+1 T region.

The resemblance between the magnetic behaviours of all compounds underlines that the post-synthesis modification does not deeply alter the magnetic properties of the parent compound **1**. Yet two tendencies can be distinguished. The ordering

temperatures of compounds **1**, **6is** and **6ae** (21.0 K, 19.8 K and 21.0 K respectively) are indeed significantly larger than the ones of compounds **2-5** (14.9 K, 16.7 K, 13.2 K and 13.0 K respectively). This feature is reminiscent of what has been described in the case of layered Ni(II) organophosphonates.<sup>54</sup> In this family, the magnetic behaviour of the compounds functionalized by long alkyl chain organophosphonates is much different than that of compounds functionalized by short alkyl chain organophosphonates, or by aromatic organophosphonates. This has been ascribed to the chemical pressure induced by the long alkyl chains onto the magnetic layers.<sup>54-56</sup> The resulting distortions may cause some changes in the in-plane superexchange pathways and in the size of the 2D correlation domains.<sup>57</sup> Moreover, different magnetic dimensionalities (2D to 3D) were pointed out, highlighting the possible role of interlamellar  $\pi$ - $\pi$  interactions on the interlayer coupling. In the present series of compounds,  $\pi$ -stacking interactions (in the case of **1**, **6is**, and **6ae**) or H-bonds interactions (in the case of **1**) may be responsible of a slightly different coupling mechanism between the layers and hence of different ordering temperature.

## Conclusions

We have shown here that in addition to classical ion-exchange reactions, the functionalization of Layered Simple Hydroxide can also proceed *via* post-synthesis modification. Post-synthesis modification allows functionalizing LSH in non-aqueous solvent, which is a major advantage. Indeed, LSH may be unstable in water under too low or too high pH. Moreover, the molecules to functionalize the LSH with may be unstable under the condition of classical ion-exchange. Therefore synthesizing them *in situ* is an interesting strategy to overcome this difficulty.

In this paper we validate the feasibility of such procedure in the case of layered simple hydroxides. We underline the advantage of microwave activation, since classical thermal activation is inefficient in the present case. To the best of our knowledge, it is the first time microwave activation is used to perform post-synthesis modification of layered solids. We are currently working to extend this strategy to the *in situ* synthesis of other molecules, in order to bring new properties to layered magnetic materials, such as luminescence for instance. This strategy may further be applied to the functionalization of other kinds of layered materials (clays, LDH, layered oxalates, etc...). It thus opens very promising perspectives for the introduction of new functionalities in layered materials, unattainable with the classical functionalization processes.

## Experimental

Chemicals were of reagent grade (Alfa-Aesar, and Aldrich (cobalt acetate) and were used without further purification. Microwave syntheses were performed with a microwave synthesis reactor Monowave 300 (Anton Paar). Elemental analyses for C, H, N, Co were carried out at the Service Central d'Analyse of the CNRS

(USR-59). The powder XRD patterns were collected with a Bruker D8 diffractometer (Cu  $K\alpha_1 = 0.1540598$  nm) equipped with a SolX detector discriminating in energy. The SEM images were obtained with a JEOL 6700F (scanning electron microscope (SEM) equipped with a field emission gun, operating at 3 kV in the SEI mode). FT-IR spectra were collected on a Digilab FTS 3000 computer-driven instrument (0.1 mm thick powder samples in KBr). Solution <sup>1</sup>H NMR spectra were recorded with a Bruker AVANCE 300 (300 MHz) spectrometer. The internal references of the spectrum correspond to the peak of the non-deuteriated solvent. The magnetic studies were carried out with a SQUID magnetometer (Quantum Design Squid-VSM) covering the temperature and fields ranges 2-300 K,  $\pm 7$  T. ac susceptibility measurements were performed in a 0.20 mT alternative field (95 Hz). Magnetization measurements at different fields at room temperature confirm the absence of ferromagnetic impurities.

**Co<sub>2</sub>(OH)<sub>3</sub>(OAc)·H<sub>2</sub>O** was prepared as previously described.<sup>14, 58, 59</sup>

**LH** : the imine ligand was synthesized by mixing 4-aminobenzoic acid (1.37 g, 10 mmol) and 4-cyanobenzaldehyde (1.31 g, 10 mmol) in 60 mL of absolute ethanol. After refluxing during 2 h, the reaction was cooled to 5°C using an ice bath. The light yellow compound was collected by filtration, washed with cold absolute ethanol and dried under vacuum. Yield : 65%.

<sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 12.92 (1H, s), 8.73 (1H, s), 8.10 (2H, d,  $J$  = 8.3 Hz), 7.99 (4H, d,  $J$  = 8.3 Hz), 7.35 (2H, d,  $J$  = 8.3 Hz) ppm.

**(4-NH<sub>2</sub>-BzAc)Co (1)** : 4-aminobenzoic acid (4-NH<sub>2</sub>-BzAc) (822 mg, 6 mmol) was dissolved in water (160 mL) and the pH was adjusted to 8 using NaOH (0.2 mol·L<sup>-1</sup>). At this stage, Co<sub>2</sub>(OH)<sub>3</sub>(OAc)·H<sub>2</sub>O (496 mg, 2 mmol) was added along with 40 mL of ethanol. The mixture was stirred under argon at room temperature for 48 h. The dark green powder was collected by filtration, washed with water and ethanol, and dried under vacuum. Yield : 85%.

Anal. for Co<sub>2</sub>(OH)<sub>3.35</sub>(4-NH<sub>2</sub>-BzAc)<sub>0.65</sub>·2.4 H<sub>2</sub>O : Co<sub>2</sub>C<sub>4.55</sub>H<sub>7.25</sub>N<sub>0.65</sub>O<sub>4.65</sub>·2.4 H<sub>2</sub>O (M = 306.55 g/mol) Found (%) : Co, 37.92; C, 17.47; H, 3.29; N, 2.62; Calcd : Co, 38.45; C, 17.83; H, 3.96; N, 2.97. IR (KBr pellet, cm<sup>-1</sup>) : 3385 (s), 1610 (s), 1528 (s), 1512 (s), 1393 (s), 1177 (m) 852 (w), 789 (m), 635 (w), 501 (w).

**(AcBz-N=CH-C<sub>3</sub>H<sub>7</sub>)Co (2) : 1** (153 mg, 0.5 mmol), butyraldehyde (butanal) (108 mg, 1.5 mmol) and 20 mL of absolute ethanol were introduced in a 30 mL sealed vessel for microwave. The mixture was placed under the microwave irradiation (30 W) during 10 min. The dark green powder was collected by filtration, washed with ethanol and dried under vacuum. Yield : 80%.

Anal. for Co<sub>2</sub>(OH)<sub>3.47</sub>(AcBz-N=CH-C<sub>3</sub>H<sub>7</sub>)<sub>0.53</sub>·2.8 H<sub>2</sub>O : Co<sub>2</sub>C<sub>5.83</sub>H<sub>9.83</sub>N<sub>0.53</sub>O<sub>4.53</sub>·2.8 H<sub>2</sub>O (M = 328.13 g/mol) Found (%) : Co, 35.99; C, 21.26; H, 3.73; N, 2.04; Calcd : Co, 35.92; C, 21.34; H, 4.73; N, 2.26. IR (KBr pellet, cm<sup>-1</sup>) : 3426 (s), 2962 (m), 2928 (m), 2873 (w), 1606 (s), 1539 (s), 1386 (s), 1178 (m) 849 (w), 788 (m), 622 (w), 509 (w).

**(AcBz-N=CH-C<sub>4</sub>H<sub>9</sub>)Co (3) : 1** (153 mg, 0.5 mmol), valeraldehyde (pentanal) (129 mg, 1.5 mmol) and 20 mL of absolute

ethanol were introduced in a 30 mL sealed vessel for microwave. The mixture was placed under the microwave irradiation (30 W) during 10 min. The dark green powder was collected by filtration, washed with ethanol and dried under vacuum. Yield : 80%.

Anal. for  $\text{Co}_2(\text{OH})_{3.53}(\text{AcBz-N}=\text{CH-C}_4\text{H}_9)_{0.47}\cdot 2.9 \text{ H}_2\text{O}$  :  $\text{Co}_2\text{C}_{5.64}\text{H}_{10.11}\text{N}_{0.47}\text{O}_{4.47}\cdot 2.9 \text{ H}_2\text{O}$  (M = 326.13 g/mol) Found (%) : Co, 36.17; C, 20.76; H, 3.23; N, 1.74; Calcd : Co, 36.13; C, 20.77; H, 4.92; N, 2.02. IR (KBr pellet,  $\text{cm}^{-1}$ ) : 3426 (s), 2958 (m), 2930 (m), 2868 (w), 1603 (s), 1541 (s), 1387 (s), 1179 (m) 1056 (w), 786 (m).

(AcBz-N=CH-C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>Co (4) : **1** (153 mg, 0.5 mmol), hexanal (150 mg, 1.5 mmol) and 20 mL of absolute ethanol were introduced in a 30 mL sealed vessel for microwave. The mixture was placed under microwave irradiation (30 W) during 10 min. The dark green powder was collected by filtration, washed with ethanol and dried under vacuum. Yield : 80%.

Anal. for  $\text{Co}_2(\text{OH})_{3.57}(\text{AcBz-N}=\text{CH-C}_5\text{H}_{11})_{0.43}\cdot 2.3 \text{ H}_2\text{O}$  :  $\text{Co}_2\text{C}_{5.59}\text{H}_{10.45}\text{N}_{0.43}\text{O}_{4.43}\cdot 2.3 \text{ H}_2\text{O}$  (M = 313.87 g/mol) Found (%) : Co, 37.29; C, 21.32; H, 3.83; N, 1.95; Calcd : Co, 37.55; C, 21.39; H, 4.83; N, 1.92. IR (KBr pellet,  $\text{cm}^{-1}$ ) : 3425 (s), 2927 (m), 2858 (w), 1605 (s), 1539 (s), 1385 (s), 1179 (m), 789 (m), 618 (w), 507 (w).

(AcBz-N=CH-C<sub>11</sub>H<sub>23</sub>)<sub>2</sub>Co (5) : **1** (153 mg, 0.5 mmol), dodecanal (276 mg, 1.5 mmol) and 20 mL of absolute ethanol were introduced in a 30 mL sealed vessel for microwave. The mixture was placed under microwave irradiation (30 W) during 10 min. The dark green powder was collected by filtration, washed with ethanol and dried under vacuum. Yield : 80%.

Anal. for  $\text{Co}_2(\text{OH})_{3.49}(\text{AcBz-N}=\text{CH-C}_{11}\text{H}_{23})_{0.51}\cdot 4.2 \text{ H}_2\text{O}$  :  $\text{Co}_2\text{C}_{9.69}\text{H}_{12.67}\text{N}_{0.51}\text{O}_{4.51}\cdot 4.2 \text{ H}_2\text{O}$  (M = 407.12 g/mol) Found (%) : Co, 28.86; C, 28.35; H, 4.97; N, 1.86; Calcd : Co, 28.95; C, 28.59; H, 6.48; N, 1.75. IR (KBr pellet,  $\text{cm}^{-1}$ ) : 3426 (s), 2925 (s), 2854 (s), 1603 (s), 1543 (s), 1386 (s), 1179 (m), 1098 (w), 1060 (w), 847 (w), 786 (m), 591 (w).

(AcBz-N=CH-Bz-CN)<sub>2</sub>Co (6is) : **1** (153 mg, 0.5 mmol), 4-cyanobenzaldehyde (0.197 g, 1.5 mmol) and 20 mL of absolute ethanol were introduced in a 30 mL sealed vessel for microwave. The mixture was placed under microwave irradiation (30 W) during 10 min. The dark green powder was collected by filtration, washed with ethanol and dried in vacuum. Yield : 80%.

Anal. for  $\text{Co}_2(\text{OH})_{3.51}(\text{AcBz-N}=\text{CH-Bz-CN})_{0.49}\cdot 3.0 \text{ H}_2\text{O}$  :  $\text{Co}_2\text{C}_{7.35}\text{H}_{7.92}\text{N}_{0.98}\text{O}_{4.49}\cdot 4.2 \text{ H}_2\text{O}$  (M = 353.73 g/mol) Found (%) : Co, 33.26; C, 25.04; H, 3.02; N, 3.65; Calcd : Co, 33.32; C, 24.96; H, 3.97; N, 3.88. IR (KBr pellet,  $\text{cm}^{-1}$ ) : 3432 (s), 2235 (m), 1593 (s), 1546 (s), 1385 (s), 1171 (m), 787 (w), 613 (w), 557 (w).

(AcBz-N=CH-Bz-CN)<sub>2</sub>Co (6ae) : **LH** (750 mg, 3 mmol) was dissolved in 50 mL of water and the pH was adjusted to 8 using NaOH 0.2 M. At this stage  $\text{Co}_2(\text{OH})_3(\text{OAc})\cdot \text{H}_2\text{O}$  (248 mg, 1 mmol) was added along with 20 mL of ethanol. The mixture was stirred under argon at room temperature for 48 h. The dark green powder was collected by filtration, washed with ethanol and dried in vacuum. Yield : 60%.

Anal. for  $\text{Co}_2(\text{OH})_{3.38}(\text{AcBz-N}=\text{CH-Bz-CN})_{0.62}\cdot 1.0 \text{ H}_2\text{O}$  :  $\text{Co}_2\text{C}_{9.30}\text{H}_{8.96}\text{N}_{1.24}\text{O}_{4.62}\cdot 1.0 \text{ H}_2\text{O}$  (M = 347.89 g/mol) Found (%) : Co, 33.77; C, 32.28; H, 3.24; N, 4.68; Calcd : Co, 33.88; C, 32.11; H,

3.18; N, 4.99. IR (KBr pellet,  $\text{cm}^{-1}$ ) : 3430 (s), 2235 (m), 1594 (s), 1543 (s), 1391 (s), 1170 (m), 1100 (w), 787 (w), 605 (w), 557 (m).

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## Notes and references

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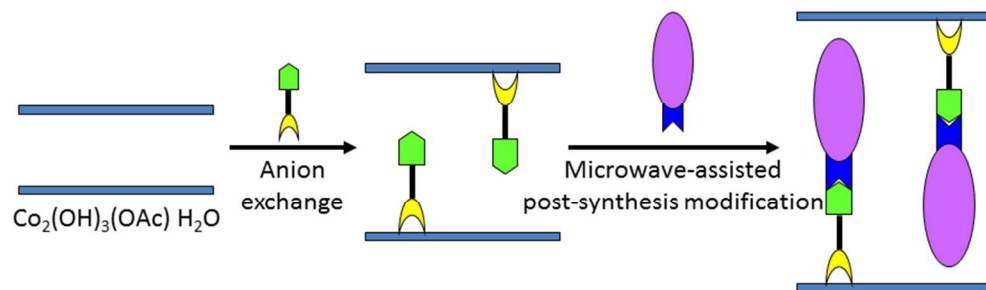
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