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# Introduction

Porphyrins are a well-known class of naturally occurring compounds that represent many important enzymes including hemes, chlorophylls and horseradish peroxidase.<sup>1,2</sup> The combination of porphyrins and appropriate host materials produces the regulated structure and excellent functionality in biological systems.<sup>3</sup> For example, in enzymes, the structures of the proteins surrounding the porphyrin derivatives are crucial for their functions. As a result, functional hybrids have been prepared by immobilization of porphyrin derivatives in various organic and inorganic host materials (polymers,<sup>4</sup> clays,<sup>5,6</sup> layered semiconductors,<sup>7–10</sup> *etc.*) with potential applications in many fields such as photochemistry, electrochemistry and catalysis.

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, form a class of anionic clay. The general

# Facile assembly for fast construction of intercalation hybrids of layered double hydroxides with anionic metalloporphyrin<sup>†</sup>

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Anionic manganese tetrasulfonatophenyl porphyrin (MnTSPP) has been intercalated into the interlamellar space of Mg–Al and Ni–Al layered double hydroxides (LDHs) through the exfoliation/restacking approach by using exfoliated LDH nanosheets and guest molecules as building blocks. The obtained hybrids were characterized by a variety of analytical techniques such as CHN analysis, XRD, FTIR, SEM, HRTEM, UV-vis spectroscopy and thermal analysis. Interlayer spacings determined from XRD patterns reveal a perpendicular orientation of the MnTSPP anions between the hyroxylated layers of both LDHs. The results of zeta potential measurements give information about the surface charge change of LDH nanoparticles associated with the spontaneous coassembly process. The catalytic performance of the heterogeneous catalysts MnTSPP/Mg–Al LDH<sub>2.0</sub> and MnTSPP/Ni–Al LDH<sub>1.0</sub> for the epoxidation of cyclohexene was investigated using molecular oxygen as an oxidant and isobutylaldehyde as a co-reductant. The intercalated hybrids appear to be promising catalysts owing to their good catalytic activity and selectivity.

formula of LDHs is  $[M_{1-x}^{II}M_{x}^{III}(OH)_{2}]^{x+}(A^{n-})_{x/n} \cdot mH_{2}O$ , with  $M^{II}$ and M<sup>III</sup> representing the metal cations octahedrally coordinated by hydroxyl groups and  $A^{n-}$  representing a hydrated counterion situated between the layers.<sup>11,12</sup> The highly tunable intralayer composition coupled with the widest possible choice of anionic organic moieties makes LDHs a promising building block for hybrid materials. There has been growing interest in the intercalation compounds LDH-porphyrin and LDHphthalocyanine due to their technological importance in catalysis, sensors and optics development.13-16 Several approaches (coprecipitation, ion-exchange reaction and reconstruction methods) have been applied to introduce porphyrin molecules between the hydroxide layers.<sup>17-19</sup> However, these methods suffer from one or more drawbacks such as long reaction times, low yield of the products and tedious work-up. Thus, the development of a simple, efficient and rapid procedure is in demand.

Delamination of LDHs, defined as their segregation into single entities through soft chemistry methods,<sup>20–22</sup> is an interesting route for producing positively charged thin platelets with the thickness of a few atomic layers. The development of inorganic–inorganic or organic–inorganic multifunctional nanocomposites based on exfoliated LDH nanosheets has attracted increasing attention during the past few years. Various techniques have been used to fabricate these hybrids such as electrostatic sequential deposition, flocculation or layer-by-layer (LBL) methods.<sup>23–27</sup> Among them, flocculation is



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Fig. 1 Schematic illustration of the preparation process for metalloporphyrin intercalated LDH nanocomposites *via* the exfoliation/ restacking route.

most convenient. Furthermore, since the interlayer of the LDH is completely open, there is no steric restriction for the immobilization of bulky guest moieties. As reported, inorganic nano-colloids such as graphene oxide,<sup>28</sup> Au nanoparticles,<sup>29</sup> CdSe quantum dots<sup>30</sup> and transition metal oxide nanosheets<sup>31–33</sup> have been assembled with LDH nanosheets *via* spontaneous flocculation, forming sandwich-structured hybrids. In contrast, reports on the combination of LDH nanosheets and organic molecules *via* flocculation are quite limited.<sup>34</sup>

Herein, we have reported the direct coassembly of LDH nanosheets and Mn porphyrin anions to fabricate sandwichstructured nanocomposites for the first time (Fig. 1). The generality of this protocol was examined by choosing LDHs with different lateral sizes, Mg-Al LDH (lateral size in micrometres) and Ni-Al LDH (lateral size in hundreds of nanometers). The preparation method is as follows: synthesis of highly crystalline  $M(\pi)$ -Al-CO<sub>3</sub> LDHs (M( $\pi$ ) = Mg, Ni); conversion of the interlayer CO<sub>3</sub><sup>2-</sup> to NO<sub>3</sub><sup>-</sup> by means of salt-acid treatment; exfoliation of these M(II)-Al-NO3 LDHs in formamide; and finally fabrication of metalloporphyrin/LDH lamellar nanocomposites by adding metalloporphyrin aqueous solution into the colloidal dispersion of LDH nanosheets. The positively charged LDH nanosheets have been employed as macrocationic templates to direct the self-assembly of metalloporphyrin anions in solution resulting in the precipitation of MnTSPP/M(II)-Al LDH hybrids. The assembly of metalloporphyrin anions into the interlamellar space of the LDH host can be finished in 20 minutes at room temperature without complicated instruments. This assembly system will pave the way for further applications of the diverse co-assemblies with novel functionalities.

## **Experimental section**

# Preparation of exfoliated $M(\pi)$ -Al LDH ( $M(\pi)$ = Mg, Ni) nanosheets

Highly crystalline particles of M(II)-Al-CO<sub>3</sub> LDH were synthesized according to a previous report. Typically,  $M(II)(NO_3)_2$ ,

Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and urea were dissolved in 80 mL of deionized water to give the final concentrations of 0.1, 0.05 and 0.245 M, respectively. The mixture was transferred to a Teflon-lined autoclave and placed in a preheated oven at 140 °C for 24 h. The resulting precipitate was collected by centrifugation and washed with deionized water and anhydrous ethanol several times. Anal. calc. for  $[Mg_{0.66}Al_{0.34}(OH)_2](CO_3)_{0.17}\cdot 0.63H_2O$ : C, 2.53; H, 4.07; found: C, 2.58; H, 4.11. Anal. calc. for  $[Ni_{0.68}Al_{0.32}(OH)_2](CO_3)_{0.16}\cdot 0.57H_2O$ : C, 1.88; H, 3.09; found: C, 1.84; H, 3.06.

0.2 g of M( $\pi$ )-Al-CO<sub>3</sub> LDH was further treated with 200 mL of an aqueous solution containing 1.5 M NaNO<sub>3</sub> and 5 mM HNO<sub>3</sub> and stirred under a nitrogen atmosphere at ambient temperature for 24 h. The exchanged product was recovered using the same procedure as that described for the pristine material.<sup>35,36</sup>

To perform the delamination of M(n)-Al-NO<sub>3</sub> layered structure and access to a colloidal suspension, 0.1 g of the LDH sample was dispersed into 100 mL of formamide and stirred vigorously for 2 days under a nitrogen atmosphere. The resulting translucent colloidal suspension was then centrifuged at 2000 rpm for 10 min to remove the unexfoliated particles.

#### Fabrication of MnTSPP/M(II)-Al LDH intercalation hybrids

The colloidal dispersion of LDH nanosheets has been purged with nitrogen gas to eliminate interference from atmospheric carbon dioxide. Then, 2.5, 5.0, or 10.0 mL of 1.26 mmol  $L^{-1}$  MnTSPP aqueous solution were added to the delaminated LDH suspension, corresponding respectively to a MnTSPP/LDH volume ratio of 0.5, 1.0, and 2.0, denoted hereafter as MnTSPP/LDH<sub>0.5</sub>, MnTSPP/LDH<sub>1.0</sub>, and MnTSPP/LDH<sub>2.0</sub>. The precipitation was centrifuged under 8000 rpm for 5 min, followed by washing with deionized water and anhydrous ethanol repeatedly to remove water and formamide completely. The quantity of Mn porphyrins in the final hybrids has been listed in ESI.†

#### Sample characterization

X-ray diffraction patterns were obtained with a RINT 2000 diffractometer (Rigaku), using Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) with  $2\theta$  from  $2^{\circ}$  to  $70^{\circ}$ . The metal contents of LDH samples were determined by inductively coupled plasma (ICP) emission spectroscopy on a Shimadzu ICPS-7500 instrument. Carbon, hydrogen and nitrogen analysis data were obtained with a Perkin-Elmer 2400 CHN elemental analyzer. Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrometer with the use of KBr pellets. Zeta potential of LDH colloids was measured using a Malvern Zetasizer Nano instrument. The morphology of the samples was investigated by a field-emission scanning electron microscope (FESEM; FEI Quanta 600) and a high-resolution transmission electron microscope (HRTEM; JEOL JEM-2100F). Samples for HRTEM measurements were prepared by sonicating the products in ethanol for 30 min and evaporating a drop of the resulting suspension onto a copper grid. UV-Vis absorption spectra were recorded on a Thermo Fisher spectrometer (Evolution 220). Thermogravimetry (TG) and differential scanning calorimetry (DSC) measurements were carried out simultaneously using a Netzsch STA449F3 apparatus at a heating rate of 10  $^{\circ}$ C min<sup>-1</sup> under a nitrogen atmosphere.

#### Catalytic oxidation reaction

The oxidation reactions were carried out at room temperature under 1 atm of oxygen with constant stirring. Cyclohexene (2 mmol), the solid catalyst (in a MnTSPP/substrate molar ratio of 1:1000) and isobutylaldehyde (6 mmol) were suspended in 4 mL of acetonitrile.<sup>37</sup> The consumption of the substrate and formation of oxidized products were monitored by GC-MS (Shimadzu GCMS-QP2010) using naphthalene as an internal standard substance. For the recycling experiments, the catalyst was exhaustively washed with acetonitrile to remove the occluded reactants and products. The recycled catalysts were then dried at room temperature and reused using the same experimental conditions as those described above.

### **Results and discussion**

#### Preparation of LDH nanosheets

The XRD patterns (Fig. 2) of M(n)-Al-CO<sub>3</sub> LDH samples showed very intense basal reflection series, indicative of the highly crystalline nature of these products. The (003) reflections of both LDHs were located on almost the same  $2\theta$  angle



**Fig. 2** XRD patterns of carbonated, nitrated Mg–Al and Ni–Al LDHs and MnTSPP/LDH hybrids obtained at different volume ratios of MnTSPP solution to colloidal suspension of LDH nanosheets.

of ~11.7°, indicating a basal spacing of ~0.76 nm. And the (110) diffraction peaks of Mg–Al and Ni–Al LDH are at about 60.8° and 61.1°, respectively. From the diffraction peaks of (110) and (003), unit cell values of *a* and *c* can be calculated as 0.3048 and 2.2838 nm for Mg–Al LDH, and 0.3034 and 2.2760 nm for Ni–Al LDH. The unit cell areas of Mg–Al and Ni–Al LDH nanosheets are 8.046 and 7.972 Å<sup>2</sup>. Chemical analysis gives a Mg/Al ratio of 1.94 and a Ni/Al ratio of 2.13 in the two carbonated LDH samples, respectively. Accordingly, the layered charge density of Mg–Al and Ni–Al LDHs can be obtained as 0.0423 and 0.0401 e<sup>+</sup> per Å<sup>2</sup>, respectively (Table S1†).<sup>38</sup>

After the decarbonation and anion exchange with  $NO_3^-$ , the basal spacings of Mg-Al and Ni-Al LDH samples increased to 0.89 and 0.88 nm, respectively. The interlayer expansions are consistent with that in previous work.<sup>39</sup> Through treating the as-prepared nitrated LDHs with formamide at room temperature for 2 days, colorless and light green transparent colloidal suspensions were yielded for MgAl- and NiAl-LDH samples respectively. Clear Tyndall light scattering was discerned for both suspensions and no sediment was observed upon standing, demonstrating the collapse of layered structure and the presence of abundant exfoliated nanosheets dispersed in formamide. The delamination mechanism has been proposed by Hibino<sup>40</sup> and Li<sup>41</sup> et al. The carbonyl group of formamide has a strong interaction with the LDH hydroxyl slabs, whereas the other end (-NH<sub>2</sub>) bonds weakly with NO<sub>3</sub><sup>-</sup>. Therefore, once the replacement of water by formamide takes place, this weakens the interlayer attraction force through the destruction of the strong hydrogen-bonding network and promotes delamination.

#### Coassembly of LDH nanosheets and MnTSPP

Fig. 2a and b show the XRD patterns of the samples prepared by mixing MnTSPP aqueous solution with a colloidal suspension of Mg–Al and Ni–Al LDHs in formamide. In comparison with the corresponding precursors, the (00*l*) diffraction peaks shift to lower angles, evidencing the stacking of LDHs with large metalloporphyrin molecules in the interlayer. The decrease in crystallinity after the restacking process is indicated by not only the weaker intensity and broader profile of the (00*l*) reflection lines, but also by the absence of many (10*n*) and (01*n*) in-plane lines at high angle values. The structural disorganization of the obtained composites probably arises from the rapid precipitation and nature of the materials, which is one of the main drawbacks of the exfoliation/restacking method.<sup>24</sup>

Furthermore, it is interesting to note that the diffraction peak shape of the resulting hybrids varies according to the respective proportions of each component involved initially in the restacking process. XRD patterns of MnTSPP/Mg–Al LDH<sub>1.0</sub>, MnTSPP/Mg–Al LDH<sub>2.0</sub> and MnTSPP/Ni–Al LDH<sub>1.0</sub> give a series of symmetric and well-defined peaks corresponding to 00*l* reflections, while in other cases, relatively broader and less symmetric reflections were obtained, implying a bigger number of stacking faults. The gallery heights of MnTSPP/Mg– Al LDH<sub>2.0</sub> and MnTSPP/Ni–Al LDH<sub>1.0</sub> were estimated to be 2.32

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and 2.36 nm. By subtracting the thickness of the brucite-like LDH layer (~0.48 nm), the net interlayer height of 1.84 and 1.88 nm for metalloporphyrin intercalated MgAl- and NiAl-LDH could be obtained, respectively. Considering the molecular dimension of the MnTSPP macrocycle (18.0 × 18.0 × 4.3 Å, as obtained from steric energy minimization using the MM2 method), a perpendicular orientation of the macrocycles to the layers with the four anionic groups interacting with the hydroxylated sheets can be speculated. Thus, the surface area per unit charge ( $S_0$ ) for MnTSPP equals 19.4 Å<sup>2</sup> per e<sup>-</sup>. The comparison with  $S_0$  values of Mg–Al (23.6 Å<sup>2</sup> per e<sup>+</sup>) and Ni–Al (24.9 Å<sup>2</sup> per e<sup>+</sup>) LDH hosts indicates a good surface compatibility. Such a perpendicular arrangement has also been described by Taviot-Guého *et al.*<sup>42</sup> for ZnTSPP and FeTSPP and Abellán *et al.*<sup>43,44</sup> for CoTSPP.

The IR spectra of carbonated LDHs, nitrated LDHs and the restacked materials are shown in Fig. S1.† MnTSPP/Mg-Al LDH<sub>2.0</sub> exhibits characteristic absorption bands associated with the intercalated manganese porphyrin: 856, 877, and 1008 cm<sup>-1</sup> (C-H pyrrole bending); 1349 and 1416 cm<sup>-1</sup> (C-N stretching); 1491 and 1574 cm<sup>-1</sup> (C-C phenyl and pyrrole stretching, respectively); 1039, 1126, 1187 and 1221 cm<sup>-1</sup> (sulfonic groups).<sup>45</sup> The bands in the range of 450–800 cm<sup>-1</sup> arise from the vibrations of the hydroxyl-based octahedral metallic complexes belonging to the LDH slabs. Similar vibration bands are also observed in the IR spectrum of MnTSPP/Ni-Al LDH<sub>1.0</sub>. These results further confirm the incorporation of the metalloporphyrin complex into the LDH interlamellar space. Additionally, the sharp, strong absorption peak at 1356  $\text{cm}^{-1}$ in pristine carbonated LDHs belongs to the v3 stretching mode of CO<sub>3</sub><sup>2-</sup>. Although less intense, this peak can also be observed in nitrated LDHs and the restacked materials, indicating the residual presence of non-exchanged  $CO_3^{2-}$  anions.

As observed in situ from Fig. 3, dark brown flocculent precipitates were formed and they settled down to the bottom of the container quickly after MnTSPP aqueous solution was added to the M(II)-Al LDH nanosheet suspension. The reaction is extremely fast, and is complete within 20 minutes. To get better insight into the restacking process, the surface charge changes were traced through zeta potential measurements. The zeta potentials of Mg-Al and Ni-Al LDH nanosheet dispersions are 35.9 and 32.3 mV, respectively, which shows that both dispersions are stable and well-dispersed. For the samples with addition of MnTSPP, supernatant liquid was collected and measured. As shown in Fig. 3c, a progressive increase of MnTSPP volume reduces the zeta potential of LDH nanosheets gradually. When 2-fold volume of MnTSPP is introduced, zeta potential absolute values for both nanoparticles approach zero, suggesting extremely unstable suspensions. In the case of MnTSPP/Ni-Al LDH<sub>2.0</sub>, coassembly of positively charged LDH nanosheets with MnTSPP even converts the surface properties of LDHs from positive to negative. The larger the MnTSPP volume involved, the better the destabilization of the colloidal solution is.

Scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) images of the flocculated MnTSPP/LDH nanocomposites are displayed in Fig. 4. For comparison, the morphologies of the pristine carbonated LDHs are shown in Fig. S2.<sup>†</sup> The SEM image of Mg–Al–CO<sub>3</sub> LDHs reveals hexagonal platelets with an average particle size of about 2–4  $\mu$ m. Ni–Al–CO<sub>3</sub> LDHs are crystallized into irregular plate crystals with the lateral dimension of about 200–400 nm, which is smaller than that of Mg–Al–CO<sub>3</sub> LDHs. For MnTSPP/LDH nanocomposites, the aggregation of platelike particles is formed as expected. This result clearly evidences that after the coassembly of exfoliated M( $\pi$ )–Al LDH nanosheets with MnTSPP anions, a two-dimensional layered structure is reconstructed. Additionally, this process also leads



Fig. 3 Digital photographs of colloidal suspensions of Mg–Al (a) and Ni–Al (b) LDHs in formamide (left), MnTSPP aqueous solution (middle) and the corresponding mixture of LDHs and MnTSPP (right). (c) The relationship between zeta potential and MnTSPP/LDH volume ratio.



Fig. 4 SEM and HRTEM images of MnTSPP/Mg–Al LDH<sub>2.0</sub> (a, b) and MnTSPP/Ni–Al LDH<sub>1.0</sub> (c, d).



**Fig. 5** UV-visible absorption spectra of (a) MnTSPP aqueous solution, (b) MnTSPP/Mg–Al LDH and (c) MnTSPP/Ni–Al LDH hybrid.

to a reduction in the size of particles with respect to the precursors, indicating the breakage or fracture of sheets during the delamination process. The lamellar fringe was not completely parallel but slightly twisted in some areas, which may be due to the high flexibility of the nanosheets. Our research demonstrates that both LDHs can be used to fabricate MnTSPP/LDH intercalation hybrids whatever the lateral size of LDH crystals is.

Fig. 5 shows UV-Vis absorption spectra of free MnTSPP in aqueous solution and intercalation hybrids. For the MnTSPP aqueous solution, the Soret band at 467 nm and two weaker Q bands between 550 and 650 nm can be observed. The absorption spectra of the hybrids suggest that no demetallation occurred (characterized by a blue shift of the Soret band associated with a significant amount of free base porphyrin).<sup>46-48</sup> The insertion of MnTSPP anions into the Mg-Al and Ni-Al interlayers led to a 6 nm and a 10 nm red shift in the Soret band, respectively. A similar phenomenon has been repeatedly observed by many groups who have worked with this kind of immobilization reaction (metalloporphyrin immobilized in inorganic supports).49-51 And the spectral change of metalloporphyrin is mostly attributed to the steric constraints caused by the support, which modifies the manganese porphyrin structure substantially in the hybrid. Moreover, a broadening of the Soret band is also observed for the intercalation hybrids, which is generally attributed to some degree of aggregation and stacking of the metalloporphyrin molecules.<sup>15</sup>

#### Thermal analysis

Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses have been carried out for the samples (pure metalloporphyrin, pristine LDHs and intercalation hybrids) under a nitrogen atmosphere in the 25–800 °C range, as shown in Fig. 6. The decomposition of pure metalloporphyrin seems to occur in two steps. The first and sharp one at about 307 °C is attributed to the loss of chains of the porphyrin ring and the second and broader one at about 566 °C corresponds to collapse of the porphyrin skeleton (Fig. 6a). TG-DSC curves of carbonated LDHs presented in Fig. 6b and d show two main weight loss steps. The first step that occurs at the 25–210 °C



Fig. 6 TG (solid line) and DSC (dashed line) curves for MnTSPP (a), Mg–Al–CO<sub>3</sub> LDH (b), MnTSPP/Mg–Al LDH<sub>2.0</sub> (c), Ni–Al–CO<sub>3</sub> LDH (d) and MnTSPP/Ni–Al LDH<sub>1.0</sub> (e).

interval can be attributed to the evaporation of physically adsorbed and interlayer water. The water content for LDHs has been extracted from this first step (see ESI, Table S1†). The following steps of weight loss, with two endothermic peaks at 290 and 429 °C for Mg–Al and at 273 and 337 °C for Ni–Al, are produced by the removal of hydroxyl groups from the layers and the decarbonation (Fig. 6b and d).<sup>52</sup>

In contrast, metalloporphyrin-containing LDH samples present more complicated thermal decomposition behaviors (Fig. 6c and e). Besides the same decomposition steps as those of the pristine LDHs discussed above, the weight loss above 320 °C could be related to the degradation of MnTSPP intercalated in the interlayer. The extent of intercalated MnTSPP in the LDH host is also reflected in the residue obtained. MnTSPP/Mg–Al LDH<sub>2.0</sub> yields a lower amount of residue (38.2%) at 800 °C compared with that for Mg–Al LDH (55.6%) at the same temperature. Similarly, the residue of MnTSPP/

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Ni–Al LDH<sub>1.0</sub> (49.5%) is also lower than that of Ni–Al LDH (66.8%). This is another proof for the successful coassembly of LDH nanosheets with metalloporphyrin molecules *via* the exfoliation/restacking route. Moreover, pure MnTSPP starts to decompose at *ca*. 260 °C and the onset is shifted to about 325 °C and 340 °C after the direct assembly with Mg–Al and Ni–Al LDH nanosheets. This result indicates that host–guest interactions thermally stabilize the porphyrin molecules similarly to other intercalated molecules.<sup>23,43</sup>

# Catalytic performance of the intercalated manganese porphyrin

Epoxidation of cyclohexene was studied in order to investigate the efficiency and stability of manganese porphyrin as a catalyst for alkene oxidation and also to have an idea of the accessibility of the substrate and of the oxidant to the manganese(m) sites in the intercalated catalysts. The results from cyclohexene epoxidation by molecular oxygen catalyzed by the MnTSPP either in solution or immobilized in matrixes are presented in Table 1.

In the control reaction, only 20% cyclohexene is converted after 5 h. As for MnTSPP, 95% cyclohexene is converted within 2 h, demonstrating that the metalloporphyrin catalyst is crucial for the aerobic oxidation system. However unsatisfactory selectivity for the epoxidation product is observed in the homogeneous system. Substantially better yields are obtained with the heterogeneous catalysts under the same reaction conditions. Here we can recall that the net interlayer height of the synthesized MnTSPP/Mg-Al LDH2.0 and MnTSPP/Ni-Al LDH1.0 were 1.84 and 1.88 nm, respectively. Thus, they seem to provide sufficient space for cyclohexene of which the size is about 0.45 nm to approach the central metal of porphyrin.<sup>6</sup> The good catalytic capability of the intercalated porphyrin may be attributed to the better distribution of the intercalated manganese porphyrin than the aggregated form of porphyrin in organic solution and the prevention of inactive µ-oxo dimers.53

 
 Table 1
 Epoxidation of cyclohexene by molecular oxygen in the presence of various catalysts and isobutyraldehyde<sup>a</sup>

Catalyst	Reaction		
	time (h)	Conv. (%)	Yield (%)
MnTSPP	2.0	95	64
MnTSPP/Mg-Al LDH <sub>2.0</sub>	2.0	>99	91
1st reutilization	2.0	99	90
2nd reutilization	2.0	92	83
MnTSPP/Ni-Al LDH1.0	2.0	97	88
1st reutilization	2.0	95	86
2nd reutilization	2.0	89	80
Mg-Al-CO <sub>3</sub> LDH <sup>b</sup>	5.0	21	17
$Ni-Al-CO_3 LDH^b$	5.0	21	17
No catalyst <sup>b</sup>	5.0	20	15

<sup>*a*</sup> Conditions: cyclohexene (2 mmol), isobutyraldehyde (6 mmol), catalyst (2  $\times$  10<sup>-3</sup> mmol), CH<sub>3</sub>CN (4 mL), O<sub>2</sub> bubbling, room temperature. <sup>*b*</sup> Control reaction performed under the same conditions as the oxidation reaction described in (a).

The reuse of both heterogeneous catalysts gives a similar selectivity (about 90%) and slightly lower yields with respect to the first use. This can also be indicative of the resistance of manganese porphyrin to the harsh oxidative reaction conditions and strong interaction between the manganese porphyrin and LDH supports. LDHs seem to contribute to the stabilization of the metalloporphyrin complex, and also play a role in constructing a two-dimensional nanoreactor. The oxidation can proceed selectively in the molecule size of the substrate by means of this reaction field.

# Conclusions

In summary, we have reported a simple and rapid exfoliation/ restacking synthetic route for preparing the intercalation hybrids of layered double hydroxides with metalloporphyrin. Based on XRD analysis, a perpendicular arrangement of the porphyrin ring with respect to the LDH layers has been proposed. The intercalation of MnTSPP into the LDH changes the crystallinity and morphology of the resulting nanocomposites substantially in relation to the LDH-CO<sub>3</sub> precursor. Spectroscopic studies reveal that the intercalation hybrids display a red-shift in the Soret-band of metalloporphyrin. Furthermore, the thermal degradation temperature of MnTSPP in the nanocomposites is raised, implying that the host-guest interactions thermally stabilize the porphyrin molecules between the LDH nanosheets. Preliminary results demonstrate that the intercalation hybrids present good catalytic properties in the cyclohexene epoxidation. It can be expected that a wide variety of functional bulky anions can be introduced into the interlayer spacing of LDHs in a similar manner. By virtue of the highly tunable compositions for both inorganic LDH hosts and organic guest molecules, these hybrid composites can be tailored with potential technological applications in numerous fields, including catalysts, sensors and optoelectronic devices.

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