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Introduction

Metal–Organic Frameworks (MOFs) or Coordination Polymers (CPs) have grown from the infancy related to their general and sporadic reporting to a more adult perspective in which these compounds are now used as functional materials. Still, thousands of these new crystalline and regular compounds, obtained from the self-assembly of metal oxide clusters with organic linkers, can be found in the literature, some also based on peculiar structural architectures.^{1–5} As expected, these hybrid (organic–inorganic) materials have been pointed



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This work reports the synthesis and multifunctionality of 2D layered coordination polymers formulated as $[Ln_2(H_3nmp)_2]\cdot xH_2O$ (**1**, where Ln = Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺ and Y³⁺) (x = 1 to 4). We describe detailed synthesis of the materials using various methods [typical hydrothermal reaction (HT), microwave-assisted synthesis (MWAS) and one-pot method (OP)], while discussing the various crystal morphologies which can be fine tuned by varying systematically the conditions. We further explore the multifunctionality of this material by studying its heterogeneous catalytic activity in the ring opening of styrene oxide, its photoluminescence behaviour and its cytotoxicity. A conversion of 88%/100% yield at 4 h/24 h reaction respectively, with excellent selectivity towards 2-methoxy-2-phenylethanol product (100%) was observed. Photoluminescence properties of the optically-active [Eu₂(H₃nmp)₂]·xH₂O (**1Eu**) and the mixed-lanthanide [(Gd_{0.95}Eu_{0.5})₂(H₃nmp)₂]·xH₂O (**1GdEu**), on the other hand, show potential use for UV-to-visible light converters, with lifetimes of 2.31 ± 0.01 and 2.61 ± 0.01 ms at ambient temperature for **1Eu** and **1GdEu** samples. Preliminary cytotoxic studies showed no effects on metabolic activity of both *in vitro* human epithelial kidney (HK-2) and human hepatocellular carcinoma (HepG2) cell lines. A reduction of NR uptake was, however, observed indicating some cytotoxic effect on lysosomal activity.

out for their use in several technological fields.⁶⁻¹⁵ Even though particular attention has been devoted to gas storage and separation processes, research efforts have been spread over different fields: biomedicine,¹⁶⁻¹⁹ magnetism,^{14,20,21} in the fabrication of membranes²²⁻²⁵ or thin films,²⁶⁻²⁹ catalysis,³⁰⁻³² ion exchange,³³ electrodes for batteries,^{34,35} or even in the preparation of light-conversion devices (using their peculiar photoluminescent properties as optical sensors).^{6,11,36}

Our research group focused in the last decade on the preparation of MOFs and CPs based lanthanides self-assembled with organic linkers bearing phosphonic acid groups. By fine tuning the experimental conditions and designing new organic linkers we were able to obtain a myriad of 1-, 2- and 3-dimensional materials with interesting properties. In fact, we were able to obtain materials with potential application in heterogeneous catalysis,37 photoluminescence38,39 and more recently as excellent proton conductors.40 One of these materials, a positively charged 2D layered material based on Gd^{3+} and the H₆nmp organic linker [H₆nmp = nitrilo(trimethylphosphonic)acid], [Gd(H₄nmp)(H₂O)₂]Cl·2H₂O,³⁷ presented an interesting single-crystal to single-crystal transformation into another 2D layered material. This transformation is followed by a considerable increase of proton conduction reaching 0.51 S cm⁻¹, being one of the best reported materials up to date.41 While in that work we solely focused on the



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Fig. 1 Schematic representation of the crystal packing of $[Gd_2(H_3nmp)_2] \cdot xH_2O$ (1Gd) (x = 1 to 4).⁴¹

conduction herein proton process, present we а detailed characterization of the transformed material, $[Ln_2(H_3nmp)_2] \cdot xH_2O$ (x = 1 to 4) (1, where Ln = Sm³⁺, Eu³⁺, Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} and Y^{3+}) (Fig. 1), in terms of synthesis optimization. In fact, this new crystalline 2D structure has been prepared by alternative synthetic methods based on typical hydrothermal reaction (HT), microwave-assisted synthesis (MWAS) and one-pot method (OP), either using the respective lanthanide chloride salt or its oxide precursor. This optimization allowed us to synthesize 1 in just 1 minute (using MWAS), which is an important improvement for the rapid preparation of potential functional MOF compounds. This paper further explores the potential multifunctionality of this material as a heterogeneous catalyst in the ring opening of styrene oxide and as a light-converting compound. We have also evaluated its cytotoxic effect in human epithelial kidney (HK-2) and human hepatocellular carcinoma (HepG2) cell lines.

Results and discussion

Synthesis optimization

Optimization of the synthetic conditions revealed that $[Ln_2(H_3nmp)_2]\cdot xH_2O(1)$ (x = 1 to 4) could readily be isolated using various synthetic approaches: static hydrothermal synthesis (HS) based on convection heating, microwave-assisted synthesis (MWAS) and one-pot procedures (OP) at atmospheric pressure (Fig. S1†). It was additionally found that the material can also be isolated using a wide range of composition for the reactive mixtures. We note that throughout this manuscript each sample can be identified as $T_mP_nt_p$ (with *T* standing for temperature, *P* for pressure, and *t* for reaction time) with the subscripts indicating each set of specifically employed experimental conditions.

Several conclusions can be drawn (please note: all prepared materials have been inspected using a combination of various characterisation techniques):

(i) Isotypical materials are preferentially isolated for lanthanide cations with small atomic radius (Sm^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} and Y^{3+}). The use of Yb^{3+} promotes the formation of an amorphous compound.

(ii) HS leads to "poorly" crystalline **1** that could be isolated after just a few hours of reaction (*e.g.*, 2 h at 140 °C or 1 h at 190 °C); crystallinity could be slightly improved using longer reaction periods (*e.g.*, 4 days at 140 °C or 2 days at 190 °C).

(iii) Using HS, the molar ratio composition of the initial reaction mixture does not influence neither the isolated product nor its overall crystallinity.

(iv) Using MWAS, for temperatures lower than *ca.* 100 °C amorphous materials are typically isolated; at *ca.* 140 °C and 100 W of power, physical mixtures of **1** with another (known) layered material, $[Gd(H_3nmp)]$,⁴² are isolated. For this latter temperature, decreasing the irradiation power to, *e.g.* 50 W, **1** is isolated as a pure phase (please note: a careful combination of irradiation power and the time for the heating ramp needs to be adjusted).

(v) Contrasting with HS, in the MWAS the reaction time plays a decisive role in the isolation of **1**. Mixtures with either $[Gd(H_3nmp)]\cdot 1.5H_2O^{43}$ or $[Gd(H_3nmp)]^{42}$ are easily obtained: the optimal conditions to isolate **1** within just 10 minutes correspond to a temperature of *ca.* 100–120 °C and an irradiation power of *ca.* 100 W.

(vi) The one-pot method (OP) produces again "poorly" crystalline **1** at lower temperatures (*e.g.*, refluxing at 80 °C for 12 h). Slightly larger crystals (isolated as aggregated) of **1** were obtained using the OP method by replacing the metal source (chloride for the oxide) and including HCl in the reaction medium. The optimal conditions were found to be: 100 °C for

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12 h using a volume ratio of HCl/H₂O of about 1/9, or 120 °C for 48 h and HCl/H₂O of about 1/1. Please note: with the increase of acid concentration we can observe the formation of yet another 2D layered material also previously reported by us: $[Gd(H_4nmp)(H_2O)_2]Cl\cdot2H_2O.^{37}$

Crystal morphology and particle size

Crystals of $[Ln_2(H_3nmp)_2] \cdot xH_2O(1)$ (x = 1 to 4) present a platelike morphology for a wide range of synthetic conditions, with individual crystallites being stacked into aggregates with different shapes (Fig. 2 and 3). Crystals are, thus, very regular thin (in the nanometer range) plates which grow uniformly without the presence of precipitates (or other defects). This was observed using TEM studies, but because of the sensitivity of 1 towards the electron beam (most likely due to the presence of a large amount of water molecules), more detailed highresolution TEM studies could not be performed.

Considering the average particle size, we observed variations according to the employed reaction conditions, specifically the heating method. A significant decrease in the particle



Fig. 2 SEM images of bulk $[Ln_2(H_3nmp)_2]\cdot xH_2O$ (1) (x = 1 to 4) obtained using hydrothermal reaction conditions. The effect on the crystallite morphology and size when varying the reaction time and the temperature is emphasised.



Fig. 3 SEM images of the bulk material $[Ln_2(H_3nmp)_2]\cdot xH_2O$ (1) (x = 1 to 4) obtained using microwave-assisted hydrothermal synthesis. The effect on the crystallite morphology and size when varying the reaction time and the temperature is shown.

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size happens when we change from the typical hydrothermal approach to the microwave-assisted synthesis (Fig. 3). This effect was expected considering that microcrystalline powders or nano-sized crystals are most often isolated under microwave heating due to the fast kinetics of crystal nucleation and growth.⁴⁴ The particle size is, thus, a feature which can be somehow controlled by changing the synthesis approach between microwave heating and typical hydrothermal conditions.

For the case of the hydrothermal approach the increase in temperature yielded plate-like units with larger thickness and overall size, while no differences were observed when increasing the reaction time. Furthermore, the differences that occasionally could be observed in the dimension of the aggregates when increasing the time of reaction are not significant and similar sizes have been found for a wide range of experimental conditions. Noteworthy, the aggregation of crystallites usually gave rise to well defined spherical agglomerates (Fig. 2).

Using MWAS it is possible to note a similar increase on the average particle size when increasing the temperature, though this behaviour is not so clear as before. For this case, and unlike the typical hydrothermal reaction, the agglomeration of particles gave rise to clusters with irregular shapes (Fig. 3).

The one-pot method was the one that showed more overall differences. Even when the purity of the final product has not been compromised for different experimental conditions, this method was able to yield particles with distinct sizes and shapes. In fact, when using the same molar ratio of the reactants, the increase in temperature (from 100 °C to 120 °C), in reaction time (from 12 h to 48 h) and in ratio of solvent mixture (from HCl/H₂O 1/10 to 1/1) resulted in a significant increase on the crystallite dimensions (Fig. 4). The reactions in which the quantity of water was much higher than that of hydrochloric acid, resulted in 1 having particle morphology alike to that previously observed in the first two synthetic methods. Nevertheless, the agglomeration of the crystallites is rather similar to that obtained from MWAS, though the crystallite size can have in some cases a slightly smaller size. On the other hand, and for higher contents of HCl we observed the presence of rectangular and larger particles of 1 (with length

having dozens of micrometres), in addition to the concomitant increase in the crystallite thickness.

Having in mind the latter result, we have transposed the knowledge of using HCl in this chemical system to the typical hydrothermal conditions in order to unveil if large crystals of **1** could be obtained by this route. Despite this objective was readily achieved, unlike before, the purity of the final product is dependent on the cooling rate of the reaction mixture. For this case, when quenching the reaction vessel **1** was always obtained as a phase-pure compound, while mixtures of **1** with the aforementioned unknown material were observed when slow cooling was used.

Solid-state structural characterization

Solid-state NMR. Fig. S2 (in the ESI[†]) shows the ³¹P MAS solid-state NMR spectrum of the isotypical $[Y_2(H_3nmp)_2] \cdot xH_2O$ material (**1Y**) (x = 1 to 4). The isotropic region of the spectrum is composed of two main sets of resonances. One is formed of three convoluted resonances peaking at *ca.* -1.10, -0.50 and -0.17 ppm, and a more resolved peak at *ca.* 1.35 ppm. The more deshielded resolved peak is, in fact, composed of two resonances peaking at *ca.* 9.07 and 9.44 ppm. Peak deconvolution and integration, including the spinning sidebands, yields a ratio of *ca.* 1:1:1:1:1 for the six resonances, which agrees well with the presence of six crystallographically independent ³¹P sites composing the asymmetric unit of **1Y**.

FT-IR. Vibrational spectroscopy studies also support the structural features unveiled by the X-ray diffraction studies. Fig. S3[†] presents the FT-IR spectra of $[Gd_2(H_3nmp)_2]\cdot xH_2O$ (**1Gd**) (x = 1 to 4), in the 3800–400 cm⁻¹ region, including assignments for each main observed band. **1Gd** contains a broad band centred at about 3500 cm⁻¹ attributed to the ν (O–H) stretching vibrational modes from water molecules. The typical ν (N–H) and ν (C–H) stretching vibrational modes of the N–C–H group appear in the 3100–2600 cm⁻¹ region. In the 1500–1300 cm⁻¹ range, a number of very weak bands can be attributed to ν (C–H) modes characteristic of P–CH₂ moieties. The typical P–OH stretching modes were also observed between 2500 and 2200 cm⁻¹, as very faint and broad bands. In the range of 1500–600 cm⁻¹, it is possible to notice the



Fig. 4 SEM images of the bulk material $[Ln_2(H_3nmp)_2] \cdot xH_2O$ (1) (x = 1 to 4) obtained using the one-pot method. The effect on the crystallite morphology and size when varying the temperature, the reaction time and the molar ratio of the HCl/H₂O mixture is emphasised.

typical ν (C–N) stretching vibrational modes of tertiary amines assigned to the intense bands pointing at about 1099 and 1070 cm⁻¹. Also, in this region, the stretching modes of ν (P=O) are noticed from *ca.* 1250 to 1150 cm⁻¹, and those of ν (P=O) from *ca.* 1080 to 900 cm⁻¹. We observe as well the ν (P-C) stretching vibrational modes, in particular between *ca.* 770–600 cm^{-1.45}

Thermal stability. The thermal stability of bulk $[Gd_2(H_3nmp)_2] \cdot xH_2O$ (1Gd) (x = 1 to 4) was investigated between ambient temperature and ca. 800 °C providing additional information on the overall hydration level of the compound (Fig. 5). Thermogravimetric analysis revealed three main weight losses, with the first occurring between ambient temperature and ca. 140 °C attributed to the early release of crystallization water molecules. Indeed, in this temperature range, the compound loses approximately 4.7% of total weight, which agrees with the release of 1.4 water molecules per formula unit (calculated 3.6% for the release of a single water molecule). We note that thermogravimetric analysis of samples obtained with different experimental conditions can lead to slightly different, ultimately corresponding to the release between one and up to four water molecules (which also induces to changes in elemental analysis). More details of the structure are explained elsewhere.⁴¹

Thermodiffractometry shows that the overall crystalline structure of the material only remains intact up to ca. 50 °C

(Fig. 5 - inset). With the increase in temperature and the early release of the water moieties, the first reflection [corresponding to the (001) plane] of the material is shifted to higher 2theta values while getting significantly broader. This observation suggests a reduction of the unit cell dimensions, particularly along the [001] direction, which further indicates a closer proximity between the 2D layers. The thermodiffractometry study clearly shows a decrease in the overall crystallinity of the bulk material. Between 140 °C and 350 °C no additional weight losses are observed, including changes of the crystalline phase or overall crystallinity. At higher temperatures (above ca. 350 °C) we may consider three subsequent weight losses, globally corresponding to ca. 1.6% (350-425 °C range), ca. 4.4% (425-620 °C range) and ca. 3.3% (620-800 °C range), respectively. These latter three weight losses are attributed to the full decomposition of the organic component, with the thermodiffractometry indicating the existence of an almost amorphous residue at the end. Even though the final residue could not be identified using powder X-ray diffraction, it is reasonable to assume that it is composed of a mixture of phosphonate and oxides of the corresponding lanthanide employed.

Heterogeneous catalysis

 $[Gd_2(H_3nmp)_2] \cdot xH_2O$ (**1Gd**) (x = 1 to 4) was investigated as a heterogeneous catalyst in the reaction of the ring opening of styrene oxide. 2-Methoxy-2-phenylethanol was the sole product



Fig. 5 Thermogram and variable-temperature powder X-ray diffraction studies of $[Gd_2(H_3nmp)_2] \cdot xH_2O$ (1Gd) (x = 1 to 4).

Table 1 Ring opening of styrene oxide with methanol, at 55 °C ^a

Sample	Reaction time (h)	Conversion ^{b} (%)	Selectivity ^c (%)
None	$4 \\ 4/24 \\ 4/24 \\ 1^d$	2	100
1 Gd		88/100	100/100
GdCl₃·6H₂O		65/94	75/82
H ₆ nmp		100	100

^{*a*} Reaction conditions: Styrene oxide (0.83 mmol), catalyst (36.5 mg **1Gd**, or 0.08 mmol of GdCl₃ or H₆nmp), methanol (2 mL), in a closed batch reactor at 55 °C. ^{*b*} Conversion of styrene oxide. ^{*c*} Selectivity to 2-methoxy-2-phenylethanol. ^{*d*} The same catalytic results were obtained using 100 times less initial amount of H₆nmp.

formed in 88%/100% yield at 4 h/24 h reaction, respectively, exhibiting excellent regioselectivity towards 2-methoxy-2-phenylethanol. Under similar experimental conditions, but in the absence of the catalyst, the conversion of styrene oxide was only of *ca.* 2%/10% at 4 h/24 h of reaction, respectively (Table 1).

The primary building units of **1Gd**, *i.e.*, the ligand (H_6 nmp) and the lanthanide source (GdCl₃·6H₂O), were also tested as catalysts in the methanolysis of styrene oxide at 55 °C (using equivalent molar quantities as to those found in 1Gd). For the two precursors the reaction mixture was homogeneous in nature. In the case of H₆nmp, 2-methoxy-2-phenylethanol was formed in quantitative yields within 1 h of reaction, which indicates that this molecule is a highly active and selective homogeneous Brønsted acid organocatalyst (Table 1). A hundred-fold decrease in the initial amount of H₆nmp gives 100% conversion at 1 h of reaction, further strengthening the high catalytic activity of the ligand precursor. In the case of the lanthanide precursor, GdCl₃·6H₂O, the reaction of styrene oxide with methanol gives 2-methoxy-2-phenylethanol in 86% yield at 48 h reaction (89% selectivity). In addition, two minor products were also detected and identified as the α -(chloromethyl)-benzyl alcohol and (chlorophenyl)ethanol isomers, formed in ca. 3% and 8% selectivity, at 98% conversion. A major limitation of these homogeneous catalysts is their difficult recyclability which makes their potential application unattractive.

The recyclability of catalyst 1Gd was investigated in three consecutive batch runs. Prior to reuse, the solid catalyst was separated from the reaction mixture by centrifugation, washed with *n*-hexane and dried at ambient temperature overnight. 2-Methoxy-2-phenylethanol remained as the sole reaction product. A comparison of the kinetic curves for consecutive batch runs shows a significant decrease in the reaction rate from the 1st to the 2nd run; this is less pronounced from the 2nd to the 3rd run (Fig. 6). Leaching tests performed for the as-prepared material gave $\Delta LT(1-4 h)$ of 5%, which is minor in comparison to 33% conversion for the same interval of reaction time in the presence of 1Gd. Leaching tests performed for the solid catalysts recovered from the 1st and 3rd runs also gave negligible values of $\Delta LT(1-4 h)$. These results suggest that the catalytic reaction is heterogeneous in nature.



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Fig. 6 Catalytic reaction of the ring opening of styrene oxide with methanol, at 55 °C and three different reuse runs, in the presence of the heterogeneous catalyst $[Gd_2(H_3nmp)_2] \cdot xH_2O$ (**1Gd**) (x = 1 to 4).

The catalysts recovered from the 1st and 3rd runs were characterized in the solid state by FTIR spectroscopy, PXRD and microscopy imaging (Fig. S4–S6 in the ESI†). The FTIR spectra of the re-used catalysts are similar to that of the as-prepared material, with only a handful of small differences in the bands assigned to the P–O and P–OH vibrational modes (Fig. S5†). The PXRD data show a small decrease in crystallinity, with SEM images further revealing a gradual disaggregation of the crystallites. We thus infer that the small decrease in catalytic activity may be attributed to the destruction of some active sites. Nevertheless, TEM investigations also showed that after catalysis **1Gd** retains its uniform nature with no precipitates (or other defects) being observed in the crystal faces (Fig. S4†).

Photoluminescence

The isotypical pure Eu³⁺ material, $[Eu_2(H_3nmp)_2]\cdot xH_2O$ (1Eu) (x = 1 to 4) emits the characteristic red colour when irradiated under UV light. A mixed-lanthanide phase was also prepared in which a stoichiometric amount of Eu³⁺ was dispersed in the Gd³⁺-based matrix of the network: $[(Gd_{0.95}Eu_{0.05})_2(H_3nmp)_2]\cdot xH_2O$ (1GdEu) (x = 1 to 4). Both materials were characterized by SEM microscopy and EDS mapping showing unequivocally the presence of Eu³⁺ in the mixed-lanthanide matrix, being distributed in a homogenous way (Fig. S7 and S8 in the ESI†).

The excitation spectrum of **1Eu** recorded at ambient temperature (298 K) and 12 K (Fig. 7) displays the characteristic sharp lines of the Eu³⁺ intra-4f⁶ transitions, namely ${}^{7}F_{0,1} \rightarrow {}^{5}D_{4-1}$, ${}^{5}L_{6}$, ${}^{5}G_{2-6}$, ${}^{5}H_{3-7}$ and ${}^{5}F_{1-5}$. In the high energy region the spectra exhibits at ambient temperature a broad band attributable to a ligand-to-Eu³⁺ (O²⁻ \rightarrow Eu³⁺) charge transfer (CT),



Fig. 7 Excitation spectra of $[Eu_2(H_3nmp)_2]\cdot xH_2O$ (x = 1 to 4) (**1Eu**, bottom) and $[(Gd_{0.95}Eu_{0.05})_2(H_3nmp)_2]\cdot xH_2O$ (x = 1 to 4) (**1GdEu**, top) recorded at ambient temperature (black line) and at 12 K (red line), while monitoring the emission at 611 nm. The intensity is comparable for the variation of the temperature in each sample, but not between different samples.

peaking at 249 nm (4.98 eV; FWHM of 0.34 eV), which agrees well with reported values for related materials.⁴⁶ At low temperature (12 K) an additional and more complex broad band appears with, at least, two peaks at *ca.* 275 and 282 nm. This temperature-dependent broad band is partially superimposed with some of the Eu³⁺ intra-4f⁶ sharp lines. For **1GdEu** the excitation spectra are dominated by the Gd³⁺ intra-4f⁷ lines, such as, the ${}^{8}S_{7/2} \rightarrow {}^{6}I_{7/2-11/2}$ and ${}^{6}P_{3/2-7/2}$ (Fig. 7), showing the occurrence of an energy transfer from the Gd³⁺ to the Eu³⁺ ions, which is more effective at ambient temperature.

Fig. 8 shows the emission spectra of 1Eu (bottom) and 1GdEu (top) excited at 393 nm as a function of pressure and temperature. The sharp lines are assigned to transitions between the first excited non-degenerate ⁵D₀ state and the $^7\mathrm{F}_{\mathrm{0-4}}$ levels of the fundamental Eu^{3+} septet. Except for the $^5D_0 \rightarrow \ ^7F_1$ lines, which have a predominant magnetic-dipole character independent of the Eu³⁺ crystal site, the observed transitions are mainly of electric-dipole nature. The ${}^{7}F_{0-2}$ levels have a local-field splitting into one, three and, at least, six Stark sublevels, respectively. Considering the maximum splitting by the crystal-field effect in 2J + 1 Stark sublevel for a unique Ln³⁺ local site, the identification of at least six components for the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition in both 1Eu and 1GdEu samples is a clear indication of the presence of more than one single Eu³⁺ environment in the materials. Additionally, the third Stark component of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ do not has a symmetrical shape which can be due to the superposition of multiple levels. The time-resolved emission spectra of 1Eu (Fig. S9 in the ESI[†]) for very distinct resolution times gives almost identical results. Also, the ⁵D₀ lifetime of Eu³⁺ of the pure and diluted (5%) Eu³⁺ samples (Fig. S10 in the ESI⁺), independently of the selected excitation and emission wavelengths, are always well fitted by single exponential functions, yielding life-



Fig. 8 Emission spectra of (bottom) $[Eu_2(H_3nmp)_2] \cdot xH_2O$ (x = 1 to 4) (**1Eu**) and (top) $[(Gd_{0.95}Eu_{0.05})_2(H_3nmp)_2] \cdot xH_2O$ (x = 1 to 4) (**1GdEu**), with excitation at 393, recorded at ambient conditions (black line; 298 K and pressure of *ca*. 1 bar), with a high vacuum (blue line; 298 K and pressure of *ca*. 5 × 10⁻⁶ mbar), and at 12 K (red line; pressure of *ca*. 5 × 10⁻⁶ mbar). Please note: the intensity is only comparable for the variation of the temperature and pressure in each sample, not between different samples.

times of 2.31 ± 0.01 and 2.61 ± 0.01 ms, at ambient temperature and 12 K, and 2.61 ± 0.01 and 2.63 ± 0.01 ms, at ambient temperature and 12 K, respectively, for the **1Eu** and **1GdEu** materials, respectively. Assuming the presence of two distinct Eu³⁺ environments, as called by the crystallographic determination and model of the material,⁴¹ the time-resolved emission spectra and the decay curves indicates that the two Eu³⁺ local sites must be very similar, almost identical. In the present case, the emission spectra of both **1Eu** and **1GdEu** samples are similar, even with distinct excitation wavelengths (data not shown).

Assuming that the two Eu³⁺ sites have identical emission properties (they cannot be distinguished), we can follow the small modifications on the first Eu³⁺ coordination sphere, such as those promoted by high vacuum exposure, analysing the changes observed in the emission spectra. The ratio between the integrated intensities of the ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow$ ${}^{7}F_{1}$ transitions, $I_{({}^{5}D_{0} \rightarrow {}^{7}F_{2})}/I_{({}^{5}D_{0} \rightarrow {}^{7}F_{1})}$, known as the asymmetric ratio (R), gives values at ambient pressure and high vacuum of 2.24 and 2.34, and 2.30 and 2.43 for 1Eu and 1GdEu, respectively. These values, typical of moderately symmetrical local environments, point to a slightly more distorted environment of the Eu³⁺ coordination polyhedron with the vacuum exposure in both samples (a low value indicates a lower distortion of Eu³⁺ local environment, approaching to the ideal case of an inversion centre for which the ${}^5D_0 \rightarrow \, {}^7F_2$ transition is absent). This is probably due to the release of some solvent water molecules. The small distortion on the Eu³⁺ coordination polyhedron also justifies the decrease of the associated Eu³⁺ emission lifetime from 2.31 \pm 0.01 to 2.01 \pm 0.01 ms, when the 1Eu sample is exposed to the high vacuum at ambient temperature (Fig. S9 in the ESI[†]).

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In vitro cytotoxicity studies

The multifunctionality of MOFs and CPs, as well as the continuous change from academic research to a more industrial approach, gives arguments to the growing concern regarding both the potential environmental and health impact. Although most of these compounds are not meant to be used in biomedical applications, the increase use of MOFs and CPs can lead to bioaccumulation through contamination of, for example, water sources. For this reason, we believe that is necessary to further investigate the potential cytotoxicity of such materials.⁴⁷

The cytotoxic profile of $[Gd_2(H_3nmp)_2]\cdot xH_2O$ (x = 1 to 4) (**1Gd**) in human epithelial kidney (HK-2) and human hepatocellular carcinoma (HepG2) cell lines was evaluated in order to estimate the potential harmful effects of bioaccumulation of this material in cells that play a crucial role in metabolism and excretion.^{48,49} For that, both cell lines were exposed to **1Gd** at concentrations of 100, 200 and 400 µg mL⁻¹ for 24 hours. Cell viability was assessed by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) and neutral red (NR) assays (Fig. 9). The organic linker (H₆nmp) and the gadolinium metallic course (Gd₂O₃) were also tested at concentrations calculated by the amount of each component in the CP structure. The organic linker (H₆nmp) and the gadolinium metallic course (Gd₂O₃) were also tested at concentrations calculated by the amount of each component in the CP structure. Cell viability was assessed by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) and neutral red (NR) assays. The results are presented in Fig. 8 and expressed as mean (% of control) \pm SEM of three independent experiments (n = 3).

After 24 hours of exposure, it was observed a slight (but significant) decrease in metabolic activity of HK-2 cells when treated with **1Gd**, the H₆nmp ligand and Gd₂O₃ at the lowest concentration. The treatment of HepG2 cells with **1Gd** (all tested concentrations), H₆nmp ligand (5.2 and 10.4 μ M) and Gd₂O₃ (12.4 μ M) also led to a slight decreasing of formazan formation. However, in both cell lines, metabolic activity was higher than 88.2%, which is not considered as a cytotoxic effect of materials.⁵⁰

The treatment of cells with Gd_2O_3 caused a decrease in NR dye uptake in HK-2 cells (10.4 $\mu M,$ 84.8 \pm 3.4%; 20.8 $\mu M,$ 77.2 \pm



Fig. 9 Cytotoxicity evaluation of $[Gd_2(H_3nmp)_2]\cdot xH_2O$ (x = 1 to 4) (**1Gd**) (black data; 100, 200 and 400 µg mL⁻¹), H₆nmp ligand (red data; 5.2, 10.4 and 20.8 µM) and Gd_2O_3 (blue data; 3.1, 6.2 and 12.4 µM) in HepG2 and HK-2 cell lines after 24 hours of exposure determined by MTT reduction and the NR uptake assays. Results are expressed as mean % cell viability \pm SEM (n = 3) Statistical comparisons were made using two-way ANOVA and in all cases, p values lower than 0.05 were considered significant (*p < 0.05, **p < 0.01, ***p < 0.001, ****p < 0.0001 vs. control data). Legend: M – **1Gd**, L – H₆nmp, G – Gd₂O₃.

3.0%) and in HepG2 cells (20.8 μ M, 82.1 \pm 3.4%). These harmful effects were also observed for the highest concentration tested after treatment with **1Gd**, which led to a decrease of NR uptake percentage to 71.8 \pm 2.1% and 72.7 \pm 4.5% for HK-2 and HepG2 cells, respectively.

The data from cytotoxicity evaluation suggested that 1Gd, as well as the H₆nmp ligand and Gd₂O₃, did not exert any cytotoxic effects in metabolic activity of the two types of in vitro cell models. However, 1Gd and Gd₂O₃ caused a reduction of NR uptake in both cell lines. Despite the lack of information in the literature related with a typical MOF cytotoxic profile, Tamames-Tabar et al. reported that after cellular internalization, the MOF particles are localised mainly in cytoplasmatic organelles, such as lysosomes.⁵¹ They further suggested that lysosomal enzymes might degrade the polymeric structure of MOF releasing the content, which in our case contains Gd³⁺ ions. In the alignment of this, materials containing gadolinium could led to lysosomal rupture in concentration and time-dependent manners.⁵² This combined information allow us to suggest that both 1Gd and Gd₂O₃ presented cytotoxic effects in lysosomal activity of the cells in a concentrationdependent manner.

Conclusions

In this work we report the synthesis and multifunctionality of the 2D layered coordination polymer $[Ln_2(H_3nmp)_2]\cdot xH_2O$ (1, where $Ln = Sm^{3+}$, Eu^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} and Y^{3+}) (x = 1 to 4). This material was recently obtained by us during a single-crystal to single-crystal transformation of $[Gd(H_4nmp)(H_2O)_2]$ $Cl\cdot 2H_2O$ at high temperature and relative humidity. The transformation lead to an increase in proton conductivity, reaching values never reported for other MOF materials (up to 0.51 S cm⁻¹). Here, the heterogeneous catalytic activity, photoluminescent behaviour and cytotoxicity of 1 is reported.

1 showed good catalytic activity in the ring opening of styrene oxide, with the formation of 2-methoxy-2-phenylethanol as the sole product with 88%/100% yield at 4 h/24 h of reaction. The recyclability was also tested in three different runs, showing a decrease in the reaction rate from the 1st to the 2nd run, being less pronounced from the 2nd to the 3rd run. This may be attributed to the destruction of some active sites, since we observe a small loss in crystallinity and the crystals reveal a gradual disaggregation of the crystallites. The inclusion of optically active lanthanide centers, on the other hand, yielded photoluminescent materials. Clearly, the absence of aromatic component of the organic linker accounts for lower emission of the Eu³⁺ and the mixed-lanthanidebased material. Nonetheless, 1 has proved to be effective in transferring energy to Eu^{3+} with lifetimes of 2.31 \pm 0.01 and 2.61 \pm 0.01 ms, at ambient temperature and 12 K, and 2.61 \pm 0.01 and 2.63 \pm 0.01 ms, at ambient temperature and 12 K, respectively, for the 1Eu and 1GdEu samples.

A preliminary cytotoxic study was also performed for **1**. While MOFs and CPs, especially lanthanide-based materials,

are regarded as potentially toxic and harmful compounds, **1** showed no cytotoxic effects in metabolic activity of both *in vitro* human epithelial kidney (HK-2) and human hepatocellular carcinoma (HepG2) cell lines. It caused, however, a reduction of NR uptake suggesting a cytotoxic effect in lysosomal activity of the cells. The data obtained in this study reflects the importance of understand the MOF cytotoxic profile as well as the mechanisms that led to cell viability decrease, since due to their inherent insolubility, MOFs might be subject to bioaccumulated in organisms. Further studies are currently being carried out.

Conflicts of interest

There are no conflicts to declare.

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