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Layered exfoliable crystalline materials based on Sm-, Eu- and Eu/Gd- 2-phenylsuccinate frameworks. Crystal structure, topology and luminescence properties


ABSTRACT Three new layered metal-organic frameworks (MOFs) based on 2-phenylsuccinic acid (H$_2$psa) and lanthanide ions, with formula [Ln$_2$(C$_{10}$H$_8$O$_4$)(H$_2$O)] (Ln= Eu, Sm and Eu-Gd) have been synthesized under solvothermal conditions and fully characterized by single-crystal X-ray diffraction, thermal and vibrational analysis. The compounds are isostructural featuring 2D frameworks that consist of infinite zig-zag chains composed by [LnO$_8$] and [LnO$_8$(H$_2$O)] edge-sharing polyhedra linked by psa ligands leading to layers further connected by weak π-π interactions in an edge orientation. Moreover, a topological study was carried out to obtain the simplified net for better comparison with structurally related compounds. The Eu-psa crystals were exfoliated into nanolayers after miniaturization by addition of sodium acetate as capping agent in the reaction medium. Scanning electron microscopy was applied to characterize the miniaturized samples whereas the exfoliated hybrid nanosheets were studied by atomic force microscopy. The photoluminescence (PL) properties of the bulk compounds as well as the miniaturized and exfoliated materials were investigated and compared with other related ones. An exhaustive study of the Eu(III)-based MOFs was performed on the basis of the obtained PL parameters (excitation and emission spectra, $k_e$, $k_{nr}$, intrinsic quantum yields and lifetimes) to explore the underlying structure-property relationships.

1. Introduction

In recent years, the design and synthesis of lanthanide-containing coordination polymers have developed into a significant area of research on the basis of their intriguing frameworks and potential applications in several fields. Particularly, their luminescence properties that enable these materials to be employed as sensors, optical fiber lasers and amplifiers, molecular thermometers and electroluminescent materials have received increasing attention. MOFs offer a unique platform and methodology for the development of luminescent lanthanide materials not only because of some well described synthesis methods and resulting porosities, but also for certain degree of structural tenability. The structures of the resulting MOFs can be tailored through variations of the linkers, templates and growth conditions. Regarding the selection of the linkers, the variety of available aliphatic and aromatic dicarboxylate ligands offers the possibility to develop diverse architectures with specific structure-properties relationships. For example, 1D or 2D MOFs exhibiting properties such as luminescence, magnetism or mechanic-elastic properties are suitable to be studied by “top-down” approaches as precursors for creating continuous thin films or to be integrated with other matrices (e.g., polymers) to form robust composite materials. Furthermore, MOFs having only weak inter-layer interactions in their structures can be exfoliated in nanosheets by simple methods such as ultrasonication, opening the possibility to obtain functional thin films by controlled deposition. Succinic acid (H$_2$suc) is a symmetrical and flexible dicarboxylic acid that has been widely combined with transition metal (TM) and rare earth (REE) ions giving rise to numerous
pure inorganic matrices. Furthermore, focusing on the second phenylsuccinate ligand (psa) and Sm(III) or Eu(III) ions, as preferred among the whole lanthanide ions for optical devices bulky substituent, seems to be a good candidate to develop low bulky groups are both located on the same carbon atom.

Regarding the inorganic component, Eu(III) and Tb(III) are the characteristic offered by the MOF approach that enable the incorporation chromophores either as linkers or guest molecules as antennas for light absorption. However, it is a well-known fact that Ln(III) centers cannot efficiently absorb light due to forbidden 4f-4f transitions (the extinction coefficient for such trivalent cations is about 1-10 M⁻¹ cm⁻¹). One strategy to sensitize Ln-MOF luminescence is to incorporate chromophores either as linkers or guest molecules that act as antennas for light absorption. The luminescence intensity can also be enhanced by energy transfer from one lanthanide to another lanthanide ion and several heterolanthanide MOFs based mainly on Eu(III) or Tb(III) have been reported. TM alo4ng with lanthanide ions have also been probed in the construction of luminescent heterometal-organic frameworks (HMOFs) because the coexistence of heterometallic ions not only contributes to obtaining fascinating structures but can in some cases also tune the energy levels of the MOFs.

Finally, nanoscale processability is another attractive characteristic offered by the MOF approach that enable the application of luminescent MOFs, particularly in the fields of biology, drug delivery, and biomedical imaging in which the nanoscale materials are essential for their internalization into cells. Furthermore, nano-MOFs (NMOFs) display higher surface areas than their macroscopic counterparts and unique size-dependent properties.

With all these design concepts in mind, we have continued our studies on REE-MOFs selecting the system containing the 2-phenylsuccinate ligand (psa) and Sm(III) or Eu(III) ions, as pure inorganic matrices. Furthermore, focusing on the second and most interesting ion, two strategies were carried out to optimize the obtaining of MOFs with improved photoluminescence (PL) properties. On the one hand, the synthesis conditions were modified to reduce the particle size and a post-synthetic treatment was applied later to exfoliate the MOF particles to achieve nanoscale dimensions. On the other hand, the Eu(III) content in the framework was significantly reduced by incorporation of Gd(III) ion.

Here we report the synthesis, single-crystal structure determination, topological analysis, characterization by thermal analysis and powder thermoporometry of three novel compounds based on psa, with formula [Ln₅(C₁₀H₁₆O₈)(H₂O)] with Ln(III) = Sm, Eu, Eu-Gd. The PL properties of these compounds are presented and discussed in comparison with those of other related REE-MOFs. The characterization by Scanning Electronic Microscopy (SEM) and Atomic Force Microscopy (AFM) of samples resulting from miniaturization-exfoliation assays along with the corresponding luminescence activity are also reported.

2. Experimental Section

2.1. Synthesis

2.1.1. General Procedures for Synthesis of [Sm₃(C₁₀H₁₆O₈)(H₂O)] (Sm-psa) and [Eu₂(C₁₀H₁₆O₈)(H₂O)] (Eu-psa). Both compounds were synthesized under identical solvothermal conditions, by dissolving 2-phenylsuccinic acid (1 mmol) and the lanthanide chlorides (1 mmol) in a mixture of 30 mL of distilled water and 30 mL of ethanol. The pH value was adjusted to 3-4.5 with 1 mmol of 4,4′-bipyridine. The resultant mixtures were heated at 160 °C in a 120 mL Teflon-lined Parr bomb during three days and then, the reactor was immediately cooled to room temperature (42% and 39% yields based on Sm and Eu, respectively). Anal. Calcd. for Sm-psa: C, 40.26; H, 2.9; O, 23.23. Found: C, 40.11; H, 2.7; O, 23.30. Anal. Calcd. for Eu-psa: C, 40.12; H, 2.89; O, 23.14. Found: C, 40.11; H, 2.69; O, 23.22.

2.1.2. General Procedure for Synthesis of [Eu₁.₁₁Gd₂₄(C₁₀H₁₆O₈)(H₂O)] (Eu,Gd-psa). The compound was prepared under the same solvothermal conditions (temperature, reaction time, pH value and solvent mixture) as Eu-psa and Sm-psa, by dissolving 2-phenylsuccinic acid (2 mmol) and the lanthanide chlorides with a 0.75:0.75 molar ratio. The molar ratio of Eu(III)/Gd(III) in the mixed compound was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (45% yield based on Eu). Anal. Calcd. for Eu,Gd-psa: C, 39.91; H, 2.88; O, 23.02. Found: C, 39.84; H, 2.81; O, 22.92.

Colorless rhombic single crystals suitable for X-ray diffraction were obtained for all the compounds.

2.1.3. Miniaturization-Exfoliation Assays. The Eu-psa samples with reduced particle size were obtained by the same synthesis route employed for Eu-psa with the addition of different amounts of sodium acetate (NaOAc). Eu-psa-1, Eu-
psa-2, Eu-psa-3 and Eu-psa-10 samples were obtained with 1 mmol, 2 mmol, 3 mmol and 10 mmol of NaOAc, respectively. The liquid exfoliation experiments of Eu-psa-10 consisted in ultrasonication of suspensions prepared with two different concentrations; i.e. 5.46 mg or 0.28 mg of the crystalline sample in 1 mL ethanol, for a period of 60 minutes. The most concentrated mixture resulted in a milky white suspension, while an almost transparent colloidal solution was obtained with the most diluted one. The purity of the samples was confirmed by comparison of the experimental and simulated PXRD patterns (see Figure S1). Detailed information about the synthetic procedure and characterization is available in the Electronic Supplementary Information (ESI).

2.2. Single-Crystal Structure Determination. Single crystal of Sm-psa compound was mounted on a Bruker four circle kappa-diffractometer equipped with a Cu INCOATEC microsource operated at 30 W power (45 kV, 0.60 mA) to generate Cu Kα radiation (λ = 1.54178 Å), and a Bruker AXIOM area detector (microcap technology). Diffraction data were collected over a hemisphere of reciprocal space in a combination of phi and omega scans to reach a resolution of 0.8 Å (58.91° in θ), using a Bruker APEX2 software suite (each exposure of 10 s covered 0.5° in ω).

Single crystals of Eu-psa and Eu,Gd-psa compounds were mounted on an Agilent Gemini A four circle kappa-diffractometer equipped with an enhance Mo X-ray source operated at 2 kW power (50 kV, 40 mA) to generate Mo Kα radiation (λ = 0.71073 Å), and an Agilent EOS area detector. Diffraction data were collected employing omega scans to reach a resolution of 0.8 Å (29.1° in θ), using a CrysAlisPro software suite (each exposure of 100 s covered 1° in ω).

Eu-psa was measured at low temperature (170K) with an Oxford Cryosystem Desktop Cooler.

Unit cell dimensions were determined by a least-squares fit of reflections with I >2σ(I). A semiempirical absorption and scale correction based on equivalent reflection was carried out using SADABS. Space group determinations were carried out using XPREP. The structures were solved by direct methods and refined by anisotropic full-matrix least-squares using SHELXL-2014. A summary of the conditions for data collection and structure refinement is given in Table 1. The coordinated water hydrogen atoms were refined using constraints. All calculations were performed using the following: SMART software for data collection; SAINT plus program for integration and scale correction of data; SHELXTL to resolve and refine the structure and to prepare material for publication; and ATOMS and MERCURY for molecular graphics.

2.3. Powder X-Ray Diffraction (PXRD). X-ray powder diaphragm were obtained with a Rigaku D-MAX-IIIC diffractometer using Cu Kα radiation (λ=1.5418 Å) and NaCl and quartz as external calibration standards. The best counting statistics were achieved using a scanning step of 0.02° between 5° and 60° Bragg angles with an exposure time of 5 s per step.

2.4. Thermodiffraometry. Thermodiffraometry measurements were performed in a Panalytical X’pert PRO 0/20 geometry diffractometer with a Johannson monochromator, using Cu Kα radiation.

2.5. Thermal Analysis. Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) were performed with Shimadzu TGA-51, DTA-50 and DSC-60 apparatus under flowing air at 50 mL min⁻¹, and a heating rate of 10 °C min⁻¹. X-ray powder diffraction was applied for further characterization of the pyrolysis products.

2.6. Scanning Electron Microscopy (SEM). The images were obtained on Zeiss LE01450VP equipment and Energy Dispersive Analysis of X-ray Spectroscopy (EDS) study was performed on an EDAX Genesis 2000 (see Figure S2). Samples were placed on an adhesive carbon tape coated with gold.

2.7. Atomic Force Microscope (AFM). The measurements were acquired using a Digital Instruments Multimode AFM with Nanoscope III controller. AFM images were acquired in tapping mode with all parameters including set-point, scan rate and feedback gains adjusted to optimize image quality and minimize the force between the probe and sample. The Eu-psa-10 particles present in the ultrasonicated ethanolic suspensions were collected and dispersed by drop casting the colloidal suspensions onto a glass flat substrate for characterization under AFM.

2.8. Solid State Luminescence Measurements. The steady state and time resolved luminescence measurements were done on a double Edinburgh Instruments FLS920/FSP920 spectrometer setup, using a 450W xenon lamp as the steady state excitation source and a 60W pulsed xenon lamp as the time resolved excitation source (operating at a pulse frequency of 100 Hz for the europium samples). The emission was detected by a Hamamatsu R928P photo multiplier tube, sensitive between 200 and 900 nm. Excitation spectra were corrected for the xenon lamp emission profile, whereas emission spectra were corrected for the detector response curve. All measurements were carried out at a step size of 0.1 nm.

2.9. Fourier Transform Infared Spectroscopy (FTIR) and Variable Temperature Fourier Transform Infared Spectroscopy (VT-FTIR). FTIR spectra were recorded with a Nicolet Protegé 460 spectrometer in the 4000–225 cm⁻¹ range with 64 scans and a spectral resolution of 4 cm⁻¹ by the KBr pellet technique. For the Eu-psa compound, a variable-temperature cell was required.

3. Results and discussion

3.1. Crystal structures of Ln(III)-psa compounds

The structural description is based on the single-crystal data of the Eu-psa compound and specific information about the Sm-psa one will be given when necessary.

There are two crystallographically nonequivalent Ln(III) ions and three psa ligands in the asymmetric unit of the compound. The Ln1 ions are surrounded by eight oxygen atoms, all coming from carboxylate groups, while the Ln2 ones are...
nonacoordinated through eight oxygen atoms from carboxylate groups and the remaining one from the coordinated water molecule (see Figure 1-left). The coordination polyhedra geometry of Ln1 ions can be described as triangulated dodecahedra while the corresponding geometry for the Ln2 ones is consistent with a monocapped square antiprism. The bond lengths fall in the range 2.296(6)-2.638(6) Å for [Eu1O] and between 2.310(7) and 2.656(7) Å for the [Sm1O] polyhedra; the bond distances for the [Eu2O] and [Sm2O] ones are 2.372(6)-2.605(6) Å and 2.382(7)-2.630(6), respectively.

Table 1: Crystallographic data for Sm-psa, Eu-psa and Eu,Gd-psa compounds.

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All psa ligands coordinate four metal ions and two of them (Types A and B) exhibit the same coordination modes, i.e. by a chelate-bridge mode by one carboxylate group and as bidentate-bridge by the other one. These ligands adopt a gauche conformation with dihedral angles C1A-C2A-C3A-C4A = -62.87° (Type A) and C1B-C2B-C3B-C4B = -51.87° (Type B) for Sm-psa compound, Type A = 64.58°, Type B = -53.01°). A third ligand (Type C) presents a more complex coordination mode, connecting four adjacent Ln(III) through a chelate-bridge mode by one carboxylate extreme and a tridentate-bridge mode by the other one (see Figure 2-a). This ligand presents a torsion angle C1C-C2C-C3C-C4C = 65.18° for the Eu-psa compound and C3-C14-C13-C6 = 62.45° for the Sm-psa one.

The chelate-bridge carboxylate groups belonging to the three psa conformers are responsible for the metal-condensation leading to 1D secondary building units (SBUs) composed by infinite chains of edge-sharing polyhedra that run in zig-zag along the [001] direction. In these structures, the type A ligands are the real linkers since they connect the SBUs allowing the formation of the organic-inorganic bidimensional framework. The distance between adjacent Ln(III) ions inside the chain is 3.985 Å for those bonds involving Type B and C psa, whereas it is 4.006 Å for those formed by Type A and C ones (Figure 1-right).

As can be seen in Figure 3, the resultant framework is 2D covalently bonded with layers stacked in [100] direction through weak π-π interactions of type C-H···C=C with an edge-orientation, the distances H···C=C are in the range 3.3-3.9 Å.

These MOFs can be classified as I'O¹ according to the classification proposed by Cheetham et al. The coordinated water molecules are oriented towards the spaces delimited by the SBUs and although their hydrogen atoms could not be localized, a strong H-bond interaction...
involving a carboxylate group should exist, since the distance O1w···O10 is 2.685 Å.

The analysis of the crystal structure reveals that these MOFs are almost isomorphous with those of Er(III)\(^{13a}\) and Lu(III)\(^{13b}\) and the related 2,2-dimethylsuccinate (2,2-dms) ligand, corresponding to the P2\(_1\)/c space group (S.G.) with cell parameters \(a = 11.1794(5), b = 18.2208(8), c = 12.7944(6), \beta = 112.4270(10)\)\(^{1a}\) for the Er-compound, and \(a = 11.1375(4), b = 18.0442(5), c = 12.7462(4), \beta = 112.4964(4)\)\(^{1c}\) for the Lu-compound. The exact isomorphic character is not verified since there are subtle differences in the coordination modes of the 2,2-dms ligands in comparison with those of the psa ones (see Figure 2-b). Such differences lead to SBUs composed by 1D chains of alternating edge-sharing and vertex-sharing polyhedral in the related dms frameworks instead of all edge-sharing polyhedra as in the psa-based compounds. The incidence of two methyl substituents in the same carbon atom is comparable to the presence of one bulky phenyl group as substituent, since the resultant frameworks are almost identical. Moreover, in both types of nets a complex coordination mode can be identified (corresponding to the psa Type C ligand) called “malonate mode”\(^{13a}\) since this is frequent in malonate but unusual in longer aliphatic dicarboxylates.

Finally, the Eu,Gd-psa compound is isostructural to those containing all-Eu or all-Sm ions as can be verified by the single-crystal data displayed in Table 1.

Due to the fact that in this structure there are two different crystallographic sites for the Ln(III) ions, the structure was solved and refined twice exchanging the metal ion in each position in order to determine if each one occupies an unique crystallographic site or if they are disordered over the two sites. The anisotropic thermal displacement parameters of each lanthanide atom and the corresponding final R and wR refinement values did not show significant differences when the position of the Gd(III) ion was exchanged with the Eu(III) one. Thus, regarding the limitation of the XRD technique to distinguish atoms with similar scattering factors and considering the results obtained for the described solution/refinement procedure, the presence of both Ln(III) ions in both crystallographic sites seems to be the most appropriate structural model.

3.2. Topological analysis

The crystal structure of the Ln-psa compounds was analyzed with the TOPOS program\(^{24}\) in order to determine the underlying topology\(^{35}\) of the associated simplified net. To this end, the simplification procedure takes into account the fact that the SBU consists of infinite zig-zag chains. As can be seen in the sequence I-IV of Figure 4, the deconstruction process of each layer to obtain the corresponding simplified net can be understood as the extraction of the SBU (drawn in green) and the psa Type A (drawn in yellow). The topological roles of psa Type B and C (marked in gray) are not considered since they are only decorating the SBU. As a result, the simplified net can be described as a 3-connected unival node, Shubnikov plane net, Schlafli symbol (4,8\(^2\))\(^{36}\).

By the same method, the same topology can be obtained for the almost isomorphic compounds based on Er(III)\(^{13a}\) (or Lu(III)\(^{13b}\)) ions and the related 2,2-dms ligand. However, if a ghost atom is located on the centroid position between adjacent Ln(III) ions, another 3-connected net belonging to the hcb type (Shubnikov hexagonal plane net, Schlafli symbol (6\(^2\))) is obtained, as it was recently reported in a highlight of REE MOFs\(^{37}\). As can be seen from the comparison of fes and hcb topological types for all the Ln(III)-psa frameworks (Figure 5), the fes net describes better the 2D connectivity; besides, it can be obtained without any extra node (as requires the obtainment of the hcb type), which is preferred for simpler topological analysis procedures.
3.3. Vibrational and Thermal analysis

The interpretation of the IR spectrum of the Eu-psa compound was performed by considering the most important internal vibrations of water molecules, carboxylate, methylene and phenyl groups and their comparison with those observed in H₂psa and related compounds. The assignment of these modes, particularly the librational ones, was performed by comparing the spectra of partially and completely dehydrated Eu-psa samples obtained with a VT-FTIR cell. The IR spectra for all the compounds are available in ESI (Figures S3 and S4). The band in the OH stretching zone is located at frequency values consistent with the presence of water molecules that are involved not only in coordination to a metal ion but also in hydrogen bonds in the lattice. In both spectra the bands located at 910, 725 and 645 cm⁻¹ correspond to water librational modes since they are strongly affected with increasing temperature and totally disappear when dehydration takes place (Figure S3). The variety of coordination types exhibited by the carboxylate groups is evidenced in the splitting of their corresponding stretching modes. Two bands at 1595 and 1560 cm⁻¹ are assigned to the ν as (OCO) whereas a pair of bands at 1415 and 1400 cm⁻¹ are associated with the corresponding symmetric mode. Additionally, a component at higher frequency (1625 cm⁻¹) can be tentatively ascribed to the “malonate mode” derived from the psa Type C conformation. Several works dealing with metal malonate complexes that contain the six-membered ring originating in the mentioned mode, report this band as the spectroscopic evidence.

The ν(CH) modes of the corresponding aromatic and aliphatic groups appear above and below 3000 cm⁻¹, respectively. The bands located at 1455 and 1435 cm⁻¹ are assigned to δ(CH3). Similar features regarding frequency values and intensities are found in the Sm-psa and Eu,Gd-psa spectra.

The thermal data for Sm-psa, Eu-psa and Eu,Gd-psa compounds are presented in ESI; the Δm % values calculated on the basis of the determined stoichiometries show a good agreement with the experimental ones. The corresponding TGA and DTA curves for Eu-psa are displayed in Figure 6a while Figures S5 and S6 show the curves for the remaining compounds.

The dehydration process is associated with a weak endothermic signal that is hardly detectable in the DTA curves but perfectly visible in the corresponding DSC experiments (Figure 6b and Figure S7). Thermal evolution proceeds with the decomposition of the organic linkers through three steps leading to the formation of the respective Ln₂O₃. The corresponding mass decays are accompanied by strong exothermic DTA peaks. According to the thermodiffractometry experiments showed in Figure 6c, a slight expansion of the crystalline cell of Eu-psa is observed when heating up to the dehydration temperature. The recovering of the original structure once room temperature is reached again, demonstrates that the reversibility of the process is not fully complete. This fact is also supported by the DSC curves registered on a heating-cooling-heating cycle.
3.4. Miniaturization-exfoliation experiments

Regarding the optical and magnetic properties of Ln-MOFs, their applications in thin film devices have received special attention during the last decade.\(^{41}\) The specific applications such as gas sorption\(^{42}\) and photoluminescence\(^{43}\), depend greatly on the ability to control size and shape of individual crystallites as well as their assembly on various supporting surfaces.\(^{23}\) The miniaturization of MOFs has already become one of the most prosperous disciplines in current chemistry of these compounds as it bridges the gap between fundamental MOF science and prospective applications.\(^{44}\) Thus, it is very important to synthesize individual nanoscale Ln-MOF crystallites that are useful for film preparation.\(^{45}\) Diverse techniques have been developed with the aim to produce nanometer-sized MOFs such as reverse microemulsion\(^{46}\), microwave-assisted synthesis\(^{47}\) and the use of capping agents.\(^{48}\) Here, we used NaOAc as capping agent to reduce the crystal size of Eu-psa crystallites and represents, as far as we know, the first example of attempting miniaturization in Ln-succinate compounds.

In the absence of NaOAc, Eu-psa crystals exhibit an average length of \(\sim 182 \mu m\) (Figure 7a). Increasing amounts of the salt lead to changes both in crystal shape and size. The formation of aggregates composed by capped crystals, whose sizes are almost half of the original ones, becomes clear in the presence of 3 mmol NaOAc (Figure 7b-c). Finally, when 10 mmol NaOAc are added to the conventional synthesis, the formation of quasi rounded particles of 43 \(\mu m\) diameter composed by stick-shaped crystals with thickness ranging 700 - 800 nm and lengths about 6 \(\mu m\) is observed (Figure 7d). The nature of these samples was investigated by PXRD and FTIR techniques (Figures S8 and S9) confirming the presence of a unique phase consistent with the bulk one (Eu-psa). Extra unknown phases occur with the addition of more than 10 mmol NaOAc (i.e. 15 and 20 mmol).

As it was described in section 2.1.3., the surface topography of the exfoliated nanosheets was characterized by means of AFM, while PXRD and FTIR measurements determined that no modifications occur in relation to the bulk phase (Figure S10 and S11). The PXRD pattern of the exfoliated Eu-psa-10 sample shows a strong preferred orientation of the (100) and (200) crystallographic planes that result statistically more exposed by deposition of the obtained nanolayers. This is an expected fact since exfoliation can only takes place through that direction in which non-covalent interactions ensure the packing of the layers (see Figure S12). We found that the Eu-psa-10 framework present in the 0.28 mg mL\(^{-1}\) ethanolic suspension was partly exfoliated to a thickness of around 20 \(\mu m\), corresponding to \(\sim 20\) elementary host layers, while retaining lateral dimensions of up to 0.5 \(\mu m\) (see Figure 8). Delamination of the crystals in the suspension containing a higher concentration (5.46 mg mL\(^{-1}\)) occurs in a less extent, leading to wider nanolayers of \(\sim 50\) \(\mu m\) thickness, showing the concentration of the sonicated suspension is an important factor to consider in order to achieve a controlled exfoliation degree.

Figure 7: SEM micrographs of Eu-psa-1 (label scale 20 \(\mu m\)) (a), Eu-psa-2 (label scale 20 \(\mu m\)) (b), Eu-psa-3 (label scale 30 \(\mu m\)) (c) and Eu-psa-10 (label scale 3 \(\mu m\)) (d).

Figure 8. Demonstration of the Tyndall effect in colloidal suspensions containing exfoliated nanolayers of Eu-psa-10. The path of the green laser beam is invisible in pure ethanol (ignoring reflections by the glass surfaces) (a). The laser beam is clearly visible through a colloidal solution comprising 0.28 mg of Eu-psa-10 particles suspended in 1 mL ethanol (b). AFM 2D height image of the nanolayers, obtained by sonication of an ethanolic suspension containing 8.2 mg mL\(^{-1}\) of Eu-psa-10 (c).
3.5. Luminescence properties

According to a significant number of specialized articles, the PL properties of materials can be characterized by the following measurements: 1) luminescence spectra, defined as intensity as a function of wavelength \( I = f(\lambda) \), 2) quantum yield (Q), which gives the efficiency of the luminescence process and is defined as the ratio of the number of emitted photons released in the process of luminescence to the number of absorbed photons, and 3) observed lifetime \( (\tau_{\text{obs}}) \) which refers to the average time the molecule stays in its excited state before emitting a photon and is determined as being inversely proportional to the sum of the rate constants of the radiative \( (k_r) \) and the nonradiative \( (k_{nr}) \) processes:

\[
\tau_{\text{obs}} = 1/(k_r + k_{nr})
\]

In the present section, the PL properties of Sm-psa and Eu-psa compounds are presented and discussed in terms of their emission spectra and lifetimes. Moreover, a deeper analysis of such properties for the Eu(III) ions in different crystallographic environments was also performed by comparison with the corresponding features of the related Eu-2,3-dms, \([\text{Eu}_2(\text{C}_6\text{H}_{12}\text{O}_6)_2\text{H}_2\text{O})_3]\) 3D framework. Finally, the PL performance of Eu-psa samples with reduced particle size with and without exfoliation treatment was evaluated.

Upon excitation at 402.5 nm, in the \( ^4L_{13/2} \rightarrow ^6H_{5/2} \) transitions (Table S1), the Sm-psa shows the typical Sm(III) emission peaks (Figure 9) at 561.7, 597.8, 644.7 and 705 nm, which have been assigned to the corresponding electronic transitions in Table S2. No peaks were visible in the NIR range for this sample. Similar features were found for the Sm-2,3-dms compound previously reported. The CIE (Commission Internationale de l’Eclairage) chromaticity diagram showing the luminescence color is displayed as an inset in Figure 9. The corresponding luminescence decay profile is given in Figure S13 from which it can be seen that the experimental curve fits satisfactorily with a mono-exponential decay. The calculated lifetime \( (\tau) \) is 3.50 \( \mu s \).

All the Eu-MOFs under the present study show the typical europium-based luminescence. The emission spectra for Eu-psa and Eu-2,3-dms are given in Figure 10 and the assignment of the observed electronic transitions can be found in Table S3. Figure S14 shows the excitation spectra of the Eu-2,3-dms, Eu-psa, Eu,Gd-psa and Sm-psa compounds. A weak underlying broad band at short wavelengths is visible in the excitation spectra of Eu-psa and Eu,Gd-psa, most likely originating from the \( \pi^* \rightarrow \pi \) or \( \pi^* \rightarrow \sigma \) transitions from the psa linkers. The most intense peaks in the spectrum, however, correspond to transitions within the Eu(III) ion’s 4f shell. In the case of Eu-2,3-dms, all peaks correspond to transitions within the Eu(III) ion’s 4f shell. This fact suggests that hardly any “antenna effect” is observed in these compounds. As a result, the luminescence shown by the Eu-MOFs can be obtained by exciting the lanthanide ion directly in its \( ^{2S+1}L_J \) electronic energy levels, provided that these are at high enough energy to allow the lanthanide-centered luminescence. The corresponding assignment of the 4f/4f excitation transitions for the Eu-MOFs is presented in Table S4.

Upon excitation at 393.5 nm for Eu-psa and 393.3 nm for Eu-2,3-dms, the typical Eu(III) emission is obtained, and the emission peaks of the compounds correspond to the transitions from \( ^5D_{0} \rightarrow ^7F_{J} \) \( (J = 0–6) \) in the 550 - 850 nm range. Among these emission lines, the most striking red emission derives from the \( ^5D_{0} \rightarrow ^7F_{2} \) transition in both Eu-MOFs emission spectra. When the peaks labeled “a” in the emission spectra are magnified only one peak can be seen. As this peak corresponds to a transition between two non-degenerate energy levels, there can only be one peak present in the spectra when only one crystallographic site is present, as this peak cannot be split by the crystal field. This would therefore suggest only one independent crystallographic Eu(III) site. This is in agreement with the crystallographic data that determines two nearly
identical sites in Eu-2,3-dms structure (triclinic, P1 S.G.) where the Eu(III) ions are nine-coordinated by eight oxygen atoms coming from carboxylate groups and the remaining one from a coordinated water molecule; however, the emission spectrum does not reflect the presence of two different crystallographic environments in Eu-psa (Figure 10). It should be mentioned that inequivalent but similar coordination environments can give rise to very comparable \( ^5D_0 \rightarrow ^7F_0 \) peaks, which can overlap and be seen as one peak.

Table 2 lists the luminescence decay times that have been recorded for both Eu-compounds. The decay traces can be found in Figures S13. When two crystallographic environments are different enough, it is assumed that each Eu(III) ion would have its own decay profile, leading to the necessity of two exponential terms to fit the decay curve. For Eu-2,3-dms, the decay curve can be satisfactorily fitted with a single exponential function with \( \tau_{obs} = 0.520 \) ms, in agreement with the near identical nature of the Eu coordination environments in this material. The luminescence decay profile of Eu-psa however shows a biexponential behavior yielding lifetimes values of \( \tau_1 = 0.533 \) ms (91.5\%) and \( \tau_2 = 1.171 \) ms (8.5\%) with an average luminescence decay time calculated from the biexponential fit \( \tau_{ave} = 0.587 \) ms. This reflects the presence of two sufficiently different Eu coordination environments in this material.

The ratio between the intensity of the \( ^5D_0 \rightarrow ^7F_2 \) and the \( ^5D_0 \rightarrow ^7F_1 \) transitions \( [R=I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)]^{\%} \) is another interesting parameter that allows to relate the PL properties with the structural features. As it was mentioned above, the strongest emission in these compounds is assigned to the \( ^5D_0 \rightarrow ^7F_2 \) hypersensitive transition, which is an electric dipole transition. The hypersensitive nature of this specific transition translates into a greater sensitivity to the crystal field symmetry of the coordination sphere of the Eu(III) ion. In contrast, the \( ^5D_0 \rightarrow ^7F_1 \) transition is a magnetic dipole one and its intensity is virtually independent of the environment of the Eu(III) ion. The higher this ratio R, the more intense the red emission of the \( ^5D_0 \rightarrow ^7F_2 \) transition and the lower the symmetry of the Eu(III) environment. As can be observed in Table 2, the R value for Eu-psa is higher than that of Eu-2,3-dms, thus indicating a more asymmetric environment around the Eu(III) ions in the former compound. Thus, it is noteworthy that the luminescence decay profile features as well as the R values are in good agreement with the crystallographic data in both cases.

![Image](https://example.com/image.png)

**Figure 10:** Emission spectra of Eu-compounds in the 570 to 680 nm (top) and 670 to 830 nm (bottom). The inset shows the corresponding CIE diagram with the chromaticity coordinates \( x,y \) for Eu-psa (0.66, 0.34).

For a correct evaluation of the PL efficiency of both Eu-MOFs, the intrinsic quantum yields (\( Q_{Ln} \)) were calculated (see Table 2). This parameter, along with the efficiency of sensitization, determines the overall luminescence quantum yield (Q). Assuming that non radiative and radiative processes are essentially involved in the depopulation of the \( ^5D_0 \) state, the \( Q_{Ln} \) can be expressed as:

\[
Q_{Ln} = k_r/(k_r+k_{nr})
\]  

Thus, \( Q_{Ln} \) of the luminescence expresses how well the radiative processes compete with the non-radiative processes described by eqn. (2). In general, contributions of the \( k_{nr} \) include back-energy transfer to the sensitizer, electron transfer quenching and quenching by matrix vibrations. Moreover, vibrations commonly found in organic molecules (C-H, O-H, N-H) can have important contributions to \( k_{nr} \).

The radiative contribution \( k_r \) can be calculated from the equation:

\[
k_r = 1/\tau_{rad}
\]
The so-called radiative lifetime $\tau_{\text{rad}}$ can be approximated for Eu(III) by the equation\(^\text{10}\):

$$k_r = \left(1/\tau_{\text{rad}}\right) = A_{\text{MD,0}} \cdot n^3 \cdot (I_{\text{tot}}/I_{\text{MD}})$$

(4)

Here, $A_{\text{MD,0}}$ is the spontaneous emission probability of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ magnetic dipole transition equal to 14.65 s\(^{-1}\), $n$ is the refractive index (1.5), $I_{\text{tot}}$ is the total integrated emission of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions and $I_{\text{MD}}$ is the integrated emission of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition.

If the radiative lifetime, $\tau_{\text{rad}}$, is known, $Q_{\text{Ln}}$ can be calculated using the observed luminescence lifetime. Basing on eqn. (1) and (4), the intrinsic quantum yield can be calculated as:

$$Q_{\text{Ln}} = \frac{\tau_{\text{obs}}}{\tau_{\text{rad}}}$$

(5)

At the same time, knowledge of both $\tau_{\text{obs}}$ and $\tau_{\text{rad}}$ enables determination of the overall rate of non-radiative deactivation. Hence, the radiative lifetime is an important parameter in the photophysical description of lanthanide luminescence. Considering that not much is known about the PL parameters of europium ions in MOFs, $k_r$, $k_{\text{nr}}$, and $Q_{\text{Ln}}%$ for the Eu-compounds reported here are summarized in Table 2.

The fact that the $Q_{\text{Ln}}%$ for Eu-2,3-dms is lower than the respective value for Eu-psa could be explained in terms of the water content, since high frequency vibrations of water molecules contribute efficiently to the quenching of the $^5\text{D}_0$ luminescence. The former compound exhibits two water molecules per asymmetric unit instead of only one in the latter one. In addition, high concentration of metallic centers is also detrimental for the luminescence efficiency through cross-relaxation and energy transfer processes. Then, the so-called concentration quenching of the luminescence, should be more marked in the 3D Eu-2,3-dms where the inorganic chains are separated by 5.9 Å along the $b$ direction (via the gauche-dms ligands) and 9.5 Å along the $c$ direction (via the trans-2,3-dms anions). The Eu-psa framework exhibits layers containing chains of polyhedra spaced by 7.368 Å; in turn, a higher distance of 15.42 Å separates successive layers, as previously described in the crystallographic section.

Table 2: Photophysical parameters of the Eu-MOFs [*]

<table>
<thead>
<tr>
<th>R</th>
<th>$\tau_{\text{obs}}$ (ms) ± SE**</th>
<th>$\tau_{\text{rad}}$ (ms)</th>
<th>$k_r$ (s(^{-1}))</th>
<th>$k_{\text{nr}}$ (s(^{-1}))</th>
<th>$Q_{\text{Ln}}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu-2,3-dms</td>
<td>4.4 ± 0.0446</td>
<td>2.64</td>
<td>379</td>
<td>1562</td>
<td>19.5</td>
</tr>
<tr>
<td>Eu-psa</td>
<td>4.7 ± 0.0202</td>
<td>2.59</td>
<td>386</td>
<td>1318</td>
<td>22.6</td>
</tr>
<tr>
<td>Eu-psa-10 (suspension)</td>
<td>3.5 ± 0.0109</td>
<td>4.76</td>
<td>210</td>
<td>989</td>
<td>17.5</td>
</tr>
<tr>
<td>Eu-psa-10 (powder)</td>
<td>3.4 ± 0.0014</td>
<td>3.73</td>
<td>268</td>
<td>911</td>
<td>22.7</td>
</tr>
<tr>
<td>Eu,Gd-psa</td>
<td>4.0 ± 0.0009</td>
<td>2.68</td>
<td>373</td>
<td>774</td>
<td>32.5</td>
</tr>
</tbody>
</table>

* The intrinsic quantum yields $Q_{\text{Ln}}$ have been calculated using equations (2) to (5). Each $\tau_{\text{obs}}$ measurement was performed by triplicate. **SE: standard error.

The PL performance of an ethanolic suspension containing the miniaturized and further exfoliated Eu-psa-10 sample (Eu-psa-10 suspension) was investigated and compared with the corresponding one of the miniaturized - non exfoliated powder sample. The emission spectra of these samples are displayed in Figure 10, a detailed comparison is shown in Figure S15 and the corresponding excitation spectra are depicted in Figure S16. The assignment of the electronic transitions corresponding to the excitation and emission spectra are found in Tables S5 and S6, respectively, while their photophysical parameters are displayed in Table 2.

The relative intensities and splitting of the transition peaks are very similar in the emission spectra of Eu-psa-10 (suspension) and Eu-psa-10 (powder). The spectra feature the well-known Eu(III)-centered luminescence except for the $^5\text{D}_0 \rightarrow ^7\text{F}_5$ transition which is occasionally visible at around 750 nm but cannot be detected in these spectra. In addition, the $^5\text{D}_0 \rightarrow ^7\text{F}_6$ transition peak which appears at 807.4 nm is not visible in the emission spectrum of the suspension. The $^5\text{D}_0 \rightarrow ^7\text{F}_6$ peak shows two components in the spectra of these samples, this fact being an interesting difference to remark with respect to the Eu-psa in the bulk form.

The $Q_{\text{Ln}}%$ for Eu-psa and Eu-psa-10 (powder) are similar, thus indicating that this parameter is not affected at least with this degree of particle size reduction. However, if the rate constants of deactivation processes or non-radiative de-excitation ($k_{\text{nr}}$) of Eu-psa-10, both in suspension and powdered phases, are compared, a significant decrease is observed with respect to that of the Eu-psa sample. This fact may be a consequence of the diminution in the particle size and consequent increase of the ratio of Eu ions at the surface with respect to Eu ions lying inside the particule, which in turn reduces the proportion of ions possessing in their immediacy other ones that can quench the luminescence. In other words, by decreasing the particle size, a certain reduction of the concentration quenching is achieved. Furthermore, if the Eu-psa-10 (suspension) and Eu-psa-10 (powder) i.e. exfoliated and not exfoliated, respectively, are compared, it is observed that the first one has a slightly higher $k_{\text{nr}}$ value, this being probably due to the fact that in the interface layer-solvent, there are ethanol molecules that can interact with the ions at the surface and partially deactivate their emission through vibronic mechanisms involving the OH groups of the solvent\(^51\). The value of the $Q_{\text{Ln}}%$, being dependent on the refractive index, seems not to reflect the improvement reached with miniaturization-exfoliation experiments. Even though it is out of the scope of this article, on the basis of these results, we think that obtaining Eu-psa nanolayers exhibiting promising luminescent parameters, suggests that a thin film obtained from their deposition could exhibit a luminescence performance at least comparable to that of the bulk material, but having the advantage of being suitable to be incorporated into optical devices. Studies of thin film...
preparation by deposition of these Ln-psa nanolayers will be the focus of future research, since the preliminary results are quite auspicious.

Another approach to evaluate the impact of the concentration quenching, consisted in replacing 44.5% of the Eu(III) amount by Gd(III) ion to avoid the transfer of energy between Eu(III) centers, resulting in the mixed compound Eu,Gd-psa. Moreover, the Gd(III) also acts as a sensitizing ion for the Eu(III) ones. As it can be noted in Table 2, the Q_{Ln}% and the lifetime, notably increase for Eu,Gd-psa whereas its k_{nr} value is less than that observed for all the Eu-psa samples, suggesting that an efficient avoidance in the electron transfer quenching between Eu(III) centers was achieved. The corresponding emission spectrum is presented in Figure 10. It has been shown before that Gd(III) codoping in luminescent lanthanide materials can lead to a significant increase in the (intrinsic) quantum yield of the codoped materials. As it was already mentioned, despite only a few works dealing with a complete report of PL parameters for Eu-MOFs are found in the literature, a suitable comparison can be performed on the basis of the PL reported by Gai et al. for Eu-MOFs containing aromatic tetra- or hexacarboxylic acids as ligands. In this paper, the obtained Q_{Ln}% decreases from 20 to 10 as the ratio coordinated water/metal ion increases from 0.5 to 4, due to the deactivation process caused by the OH oscillators, as could be expected. In comparison, our results are especially promising for the Eu,Gd-psa compound, as not only the concentration quenching but also the presence of coordinated water in the inner sphere could be avoided.

Moreover, if both strategies are combined, i.e. miniaturization-exfoliation and direct replacement experiments, a highly promising layered material for thin films development can be easily obtained. We demonstrate here that by reducing the efficiency of the non-radiative pathways, an increase in the luminescence lifetime and quantum yields should be expected.

Conclusions

The reaction between Ln(III) ions (Sm, Eu and Eu-Gd) and 2-phenylsuccinic acid under solvothermal conditions led to new isostructural MOFs featuring 2D bonded layers composed by infinite zig-zag chains of octa- and ninecoordinated Ln polyhedra. The layered nature of these frameworks makes them suitable for their exfoliation in nanolayers. Miniaturization assays using sodium acetate as capping agent, and further exfoliation via ultrasonication were successfully carried out for the Eu(III) phase. Scanning electron microscopy confirms a diminution of the particle size of ~96% after miniaturization experiments with 10 mmol of the capping agent, leading to an average crystal length of ~6 μm. This procedure also modifies the morphology of the bulk crystals resulting in quasi rounded aggregates composed by stick-shaped smaller crystals. The ethanolic suspension containing the mentioned miniaturized sample shows after ultrasonication, the characteristic Tyndall effect associated with colloidal systems. According to the atomic force microscopy measurements, the rod-shaped crystals were readily separated into nanolayers ranging from about 20 to 50 nm. The PL measurements demonstrate a lanthanide-centered luminescence by direct excitation in their \(^{2}S_{1/2} \rightarrow ^{4}I_{_{7/2}}\) electronic energy levels without evidence of “antenna effect”. The PL properties of the bulk materials are consistent with the structural findings. Non-radiative processes in the Eu-psa were efficiently reduced either by partial replacement of the emitting centers by the sensitizing Gd(III) ion or through the miniaturization-exfoliation procedure. This fact is reflected in a higher intrinsic quantum yield in the former case and in a longer luminescence lifetime for the second one. The combination of both strategies seems to be a promising method for synthesizing and exploration of highly photoluminescent lanthanide–organic frameworks and can be considered as an interesting possibility for preparing thin films for optical devices.

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Notes and references

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\(^{e}\) Electronic Supplementary Information (ESI) available: Crystallographic data in CIF format, synthesis details, powder XRD patterns, TG-DTA-DSC curves, FTIR spectra, excitation spectra, lifetimes curves and assignations tables of absorption and emission transitions. CCDC reference numbers 1002152, 1002153 and 1002154 contain crystallographic data for this paper. These data can be obtained free from the Cambridge Crystallographic Data via www.ccdc.cam.ac.uk/data_request/cif. See DOI: 10.1039/b000000x/
34 V. A. Blatov, D. M. Proserpio, CrystEngComm., 2014, 14, 3576.
36 V. A. Blatov, M. O’Keeffe, D. M. Proserpio, CrystEngComm., 2009, 12, 44.
Highlight

Three new layered 2D Ln-MOFs based on 2-phenylsuccinate, Sm, Eu and Eu/Gd showed a suitable platform for obtaining exfoliatable frameworks with promising photoluminescent properties for potential applications as thin films.