

Europium metal organic frameworks: Chemical and Optical properties

Redes metal orgánicas de Europio: Propiedades Químicas y Ópticas

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Abstract

This paper presents the results of synthesizing five metal-organic frameworks (MOFs) of europium with luminescent properties using a stirring methodology at room temperature. The materials were obtained using the organic linkers benzene dicarboxylic acid (BDC), benzene tricarboxylic acid (BTC), naphthalene dicarboxylic acid (NDC), amino benzene dicarboxylic acid (BDC-NH₂) and hydroxybenzene dicarboxylic acid (BDC-OH). XRD and FTIR determined structural and optical properties, and, for three of the materials, SEM. The MOFs obtained have a crystal size of the order of nanometers and presented characteristic functional groups of organic linkers. Optical properties were determined by luminescence spectroscopy, and emission and excitation spectra were obtained. The photoluminescence data of the MOFs showed that the organic linkers were useful for the energy transfer to the lanthanide ion (antenna effect). The material with the highest emission was Eu₂BDC₃, and the one with the lowest was Eu₂(BDC-NH₂)₃. The latter did not present a defined crystalline structure. The Eu₂(BDC-NH₂)₃ and Eu₂(BDC-OH)₃ structures suffered the loss of emission over time. The materials with the highest emission can be used as chemical sensors, cell tracers, and electronic components, including some of their applications.

Resumen

En este proyecto se presentan los resultados de la síntesis de cinco redes metal-orgánicas (MOFs), de europio con propiedades luminiscentes, utilizando una metodología de agitación a temperatura ambiente. Los materiales fueron obtenidos usando los ligandos orgánicos ácido benceno-dicarboxílico (BDC), ácido benceno-tricarboxílico (BTC), ácido naftaleno-dicarboxílico (NDC), ácido amino benceno-dicarboxílico (BDC-NH₂) y ácido hidroxibenceno-dicarboxílico (BDC-OH). Las propiedades estructurales y ópticas se determinaron mediante DRX, FTIR y, para tres de los materiales, SEM. Las MOFs obtenidas tienen tamaño de cristal del orden de nanómetros y presentaron grupos funcionales característicos de los ligandos orgánicos. Las propiedades ópticas se determinaron mediante espectroscopia de luminiscencia y se obtuvieron los espectros de emisión y excitación. Los datos de fotoluminiscencia de las MOFs mostraron que los ligandos orgánicos resultaron ser útiles para la transferencia de energía al ion lantánido (efecto antena). El material con mayor emisión fue Eu₂BDC₃ y el de menor fue Eu₂(BDC-NH₂)₃, este último no presentó una estructura cristalina definida. Las estructuras Eu₂(BDC-NH₂)₃ y Eu₂(BDC-OH)₃ sufrieron la pérdida de emisión con el paso del tiempo. Los materiales con mayor emisión pueden utilizarse como sensores químicos, trazadores celulares, en componentes electrónicos, por mencionar algunas de sus aplicaciones.

Metal-organic frameworks, Europium, Luminescence

Redes metal orgánicas, Europio, Luminiscencia

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Introduction

The incorporation of ions to a transition metal or a rare earth of the lanthanide family in MOFs is encouraging due to the possible benefits for the production of luminescent emission: the ligands maintain minimum distances between adjacent emitting ions, diminishing the effect of reabsorption of the emitted radiation, also known as “*quenching*.” In addition, the ligands can function as energy absorption centers that later transfer it to the ions, exciting them and causing light emission. [Eliseeva & Bunzl, 2010]. In particular, aromatic molecules such as carboxylic acids can significantly help since their delocalized electrons and energy state density facilitate the energy absorption process [Jiang *et al.*, 2001] through the antenna effect.

In this effect, the electron interacts and resonates with the incident electromagnetic radiation, facilitating its excitation to higher energy levels; the relaxation of these electrons can transfer energy to the metal ion, producing light emission. There is a wide variety of binder molecules of this type, for example benzene dicarboxylic acid (BDC), benzene dicarboxylic acid (BTC), naphthalene dicarboxylic acid (NDC), amino benzene dicarboxylic acid (BDC-NH₂) and hydroxybenzene-dicarboxylic acid (BDC-OH), which are aromatic molecules that are suitable for forming luminescent MOFs.

Er²⁺ or Eu³⁺ cations, as such, exhibit weak luminescence, although some peculiarities have been observed in nanoparticles [Yu *et al.*, 2004]. One way to activate them is by inserting them into inorganic compounds or by forming compounds with organic binders that allow an energy transfer to the metal and a symmetry breaking, thus favoring an increase in emission power [Aubouy *et al.*, 2006]. The most common coordination number of europium compounds is 8 [Chen *et al.*, 1999].

There are few reports of work with MOFs with luminescent properties based on the Eu³⁺ lanthanide ion [Habimana *et al.*, 2016; Medina- Velazquez *et al.*, 2016; Mirhosseini *et al.*, 2021]. In this sense, the synthesis commonly used to obtain these materials is solvothermal, and synthesis times range from days to months, except for microwave-assisted synthesis, which lasts 20 minutes.

Conventional synthesis methods for obtaining MOFs represent a problem due to energy requirements, which increase production costs, and the use of toxic and carcinogenic solvents such as dimethylformamide (DMF). Our research group has implemented a synthesis technique by stirring at room temperature, where MOFs with nanometric sizes are obtained. This work presents the results of the structural and optical properties of different europium MOFs using this methodology.

Experimental development

Materials

The reagents used in the synthesis of the MOFs were: hexahydrated europium chloride (EuCl₃ · 6H₂O, 99%) 1,4- chloride benzene dicarboxylic acid (BDC, 98 %), 1,3,5-benzene acid tricarboxylic acid (BTC, 95%) and dimethyl,2-aminobenzene-1,4-dicarboxylate (BDC-NH₂, 90%), dimethyl-2,5-hydroxybenzene-1,4-dicarboxylate (BDC-OH, 99%) and naphthalene-2,6-dicarboxylic acid (NDC, 99%), all from Sigma-Aldrich brand. Solvents were absolute ethanol (99%) and deionized water.

Synthesis of the MOFs

A solution containing 1 mmol of the organic binder in water and another 0.5 mmol of the europium salt in ethanol was prepared. Once dissolved, the Eu solution was added dropwise to the organic binder solution. The mixture was kept under magnetic stirring for 12 h at room temperature. The solid obtained was separated from the liquid by centrifugation and dried in an oven for 4 h at 100°C. The solid was ground in an agate mortar and stored for further characterization.

Characterization of the MOFs

The MOFs were subjected to characterization tests; for the structural analysis, powder X-ray diffraction (XRD) was used, and the determination of the diffractograms was carried out using a Bruker Advance 8 brand diffractometer, at a step of 0.02 °(2θ) every 0.4 seconds. For analysis of functional groups, the characterization of the samples by infrared spectroscopy with Fourier transform (FT-IR), a Perkin-Elmer brand "Spectrum one" spectrophotometer was used, at a resolution of 1 cm⁻¹ and with an attenuated total reflectance (ATR) configuration.

SÁNCHEZ-FABILA, Barbara Michelle, LOERA-SERNA, Sandra and GARDUÑO-WILCHES, Ismael A. Europium metal organic frameworks: Chemical and Optical properties. Journal of Innovative Engineering. 2023

The morphological characteristics of the MOFs were studied using scanning electron microscopy (SEM) on a Jeol model JSM-6390LV microscope, and the atomic composition using a Voyager microanalysis system from Noran Instruments coupled to the microscope. The photoluminescent spectra obtained using the Edinburgh Instruments FS5 spectrofluorimeter equipment determined the luminescent properties. To get the excitation and emission spectra of photoluminescence, tablets were prepared with 100 mg of each sample.

Results

Structural analysis

The diffractogram Figure 1 compares the pattern reported for the structure of DyBTC (H₂O) DMF [Guo *et al.*, 2006] with the pattern obtained for the EuBTC sample. The reported structure is a dysprosium-synthesized MOF and corresponds to a three-dimensional lattice with a P4₃22 space group, with a basic building unit with 7 Dy³⁺ ions coordinated to a BTC ligand. The network has 6 × 6 Å channels along the (0 0 1) plane, as observed in the structure of the diagram in Figure 1, and is obtained by synthesis in the presence of DMF (10 mL) and HNO₃ (6 M) at 60 °C for 7 days. The structure of DyBTC(H₂O)DMF is isorecticular to that obtained in this project for EuBTC; the reported patterns have peaks at the same Bragg angles and with practically the same relative intensities.

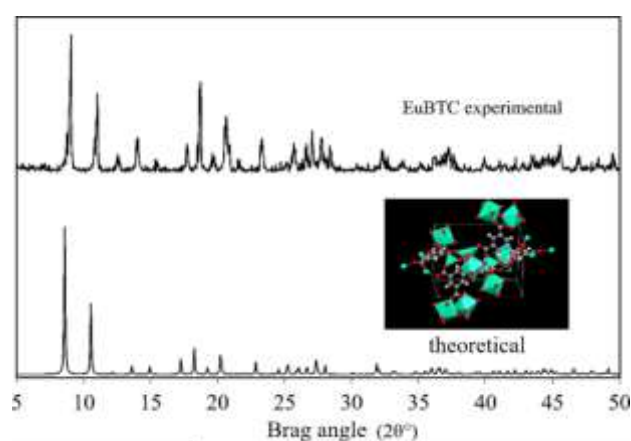


Figure 1 Diffraction pattern of theoretical and experimental EuBTC

Figure 2 compares the XRD patterns of the materials synthesized with bidentate ligands and different functional groups, including all materials prepared with 1,4-benzene dicarboxylic precursors.

The theoretical Eu₂BDC₃ sample corresponds to a pattern reported by [Santos *et al.*, 2017], with a solvothermal method at 120 °C for 3 days. The lattice of this MOF has a space group P1 and is formed by the coordination of 8 Eu³⁺ ions with 6 oxygens coming from the BDC ligands and 2 water molecules. Some missing peaks are observed in the XRD of the synthesized MOFs, indicating that the structure was not completely formed or had lower crystallinity than the reported lattice.

In the case of the sample with -NH₂, there is no defined pattern because the structure is not favored; it is probable that the -OH group generates interactions that tend to the structure, which does not occur for the amino group. The splitting energy can explain the difference between these two functional groups since the -OH is a low-field ligand in the chemical spectrum series, and the -NH₂ is a high field. This is attributed, among others, to the difference in electronegativity of the donor atoms. Since the formation of a coordination compound is sought, chemical factors that can change the donor nature of the carboxylic acids must be considered.

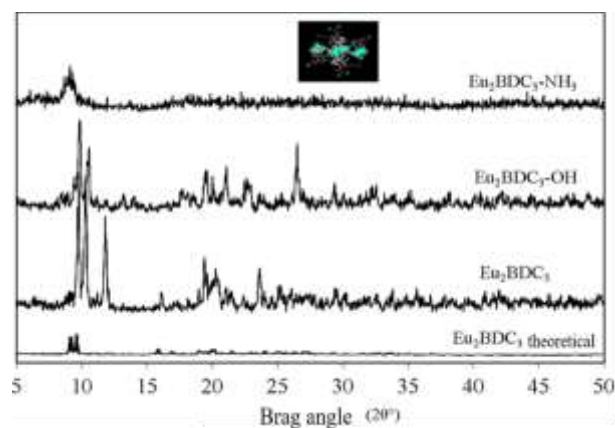


Figure 2 Diffraction pattern of the MOFs: Eu₂BDC₃, Eu₂(BDC-OH)₃, Eu₂(BDC-NH₂)₃

Figure 3 compares the diffractograms of the experimental Eu₂NDC₃ MOFs with one reported for Nd and NDC [Wang *et al.*, 201]. It is observed that the samples present peaks at the same Bragg angles. However, the diffractogram of the experimental MOF has less defined peaks, which is attributed to the low crystallinity of the material. In the work reported by Wang *et al.*, a synthesis at room temperature was used, but this lasted several weeks. The metallic center they studied was neodymium, indicating an isorecticular structure was obtained.

The Nd network comprises bi-dentate ligand chains and has a formula: $\text{Nd}(\text{NDC})_{1.5}(\text{H}_2\text{O})_2 \cdot 2\text{DMA}$. (DMA: dimethylacetamide).

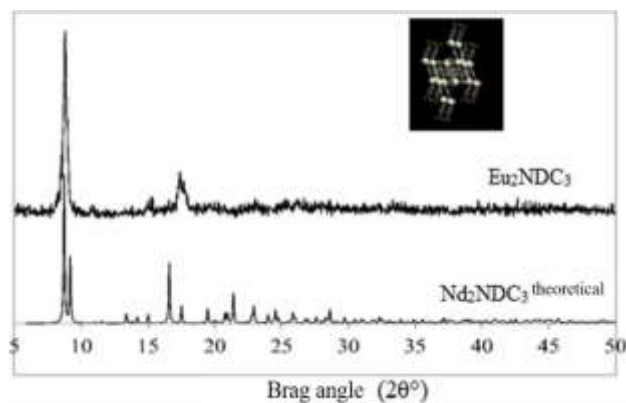


Figure 3 Theoretical and experimental Eu_2NDC_3 diffraction pattern

Crystal size

According to Debye's equation Scherrer (equation 1), the crystal size was determined for the samples EuBTC , Eu_2BDC_3 , $\text{Eu}_2(\text{BDC-OH})_3$, $\text{Eu}_2(\text{BDC-NH}_2)_3$ and Eu_2NDC_3 taking the value of 2θ in the maximum peaks: 9.06, 9.75, 9.82, 9.09 and 7.7°, respectively. The results are described in Table 1.

$$D = \frac{k \cdot \lambda}{B \cos \theta_B} \quad (1)$$

Where D is the crystal size, k is the Scherrer constant (value of 0.9), λ is the wavelength belonging to the line $\text{Cu } \alpha(1.5406 \text{ \AA})$, B is the width of the peak at half height (radians), and θ_B corresponds to the angle of the maximum peak in radians.

The crystal size for all the samples is in the range of 10-100 nm except the sample $\text{Eu}_2(\text{BDC-NH}_2)_3$, which presented a tiny crystal size, previously mentioned that it corresponds to the material that did not give a definite diffraction pattern. The sample with the largest crystal size is the MOF EuBTC with 49 nm. The change in size can be associated with the presence of donor groups in the organic binders. However, the presence of these groups can favor chemical interactions; for the formation of the structure, it is preferable not to have functional groups that interfere with the coordination of the metal and the oxygens of the ligand.

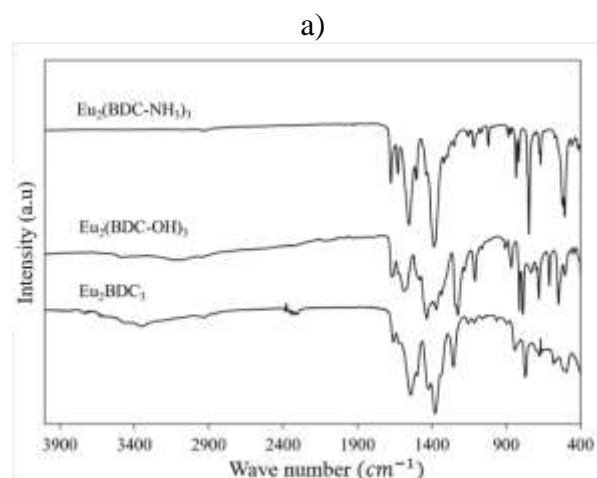
Sample	D (nm)
EuBTC	49
Eu_2BDC_3	22
$\text{Eu}_2(\text{BDC-OH})_3$	16
$\text{Eu}_2(\text{BDC-NH}_2)_3$	5
Eu_2NDC_3	25

Table 1 The crystal size of the MOFs.

Analysis of functional groups

EuBTC , Eu_2BDC_3 , $\text{Eu}_2(\text{BDC-OH})_3$, $\text{Eu}_2(\text{BDC-NH}_2)_3$, and Eu_2NDC_3 are presented. As can be seen, in the spectra of the five samples, there are characteristic bands of the vibration of elongation of the metal-oxygen bond that would be Eu-O , located in the range of $400\text{--}560 \text{ cm}^{-1}$ [Lui *et al.*, 2009], said band reveals that Eu atoms have successfully coordinated with carboxylate groups. In addition, the intense absorption at 3407 cm^{-1} must be the -OH stretching vibration of water, indicating that water molecules act not only as the solvent but also as a reagent for forming the MOFs [Lui *et al.* 2009].

The bands located in the range of $1104\text{--}1110 \text{ cm}^{-1}$ are attributed to the doubling of the C-H bond in the plane of the ring [Silverstein *et al.*, 1967]. All samples exhibit symmetric stretching vibrations of carboxylic groups in the range of $1590\text{--}1480 \text{ cm}^{-1}$ and symmetric vibrations centered at 1381 cm^{-1} [Xu *et al.*, 2011]. Particularly for the MOF Eu_2NDC_3 , the band located at 1908 cm^{-1} characteristic of the CN stretching vibration is presented [Hansen *et al.*, 2022].



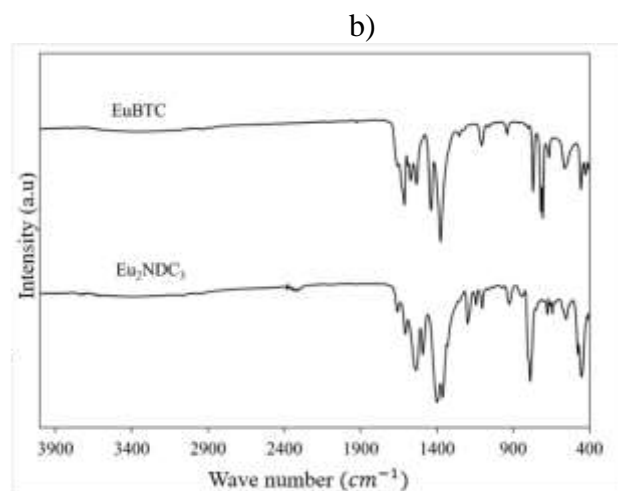


Figure 4 IR spectra of a) Eu_2BDC_3 , $\text{Eu}_2(\text{BDC}-\text{OH})_3$, $\text{Eu}_2(\text{BDC}-\text{NH}_2)_3$ and b) EuBTC and Eu_2NDC_3

Morphology

Figure 5 shows the micrographs with 20,000 magnifications that could be obtained and correspond to the $\text{Eu}_2(\text{BDC}-\text{OH})_3$, $\text{Eu}_2(\text{BDC}-\text{NH}_2)_3$, and Eu_2NDC_3 samples. In the $\text{Eu}_2(\text{BDC}-\text{OH})_3$ material, aggregates of particles reaching $4.5 \mu\text{m}$ and small grains of lighter tonality and asymmetric morphology with a diameter of $0.5-0.8 \mu\text{m}$ are observed. In the $\text{Eu}_2(\text{BDC}-\text{NH}_2)_3$ sample, flower-shaped grains with a size of $7 \mu\text{m}$ are observed, whose petals are $2 \mu\text{m}$ long and $0.95 \mu\text{m}$ wide. Again, the aggregates are covered by tiny grains of $5-10 \text{ nm}$. In the sample Eu_2NDC_3 , the same aggregates are seen (beginning to have a concentric formation), but with greater dispersion, the size is $3-4 \mu\text{m}$, and the petal-shaped crystals are $1.5 \mu\text{m}$ long and $0.6 \mu\text{m}$ wide. These formations have been previously observed in microwave-obtained europium MOFs [Garduño-Wilches *et al.*, 2021].

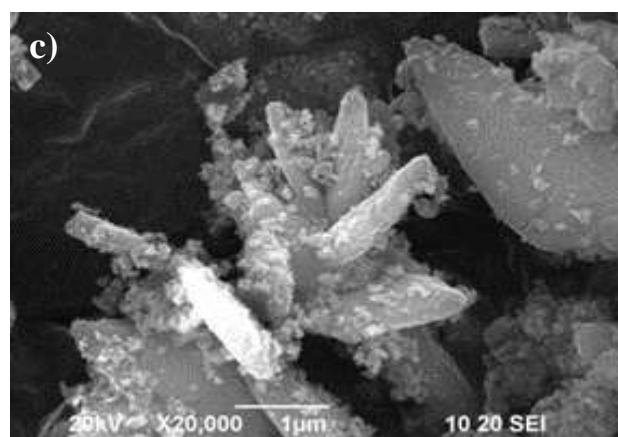
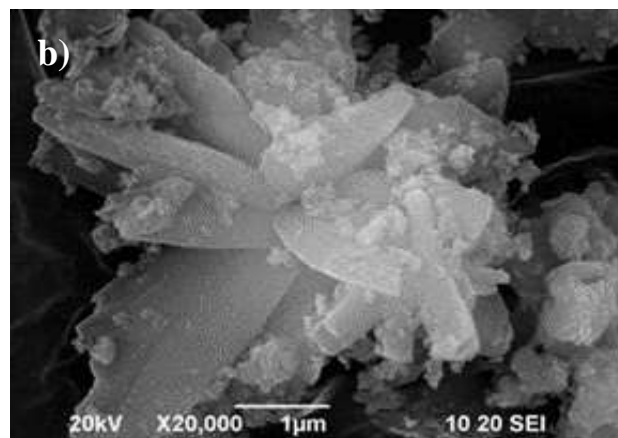
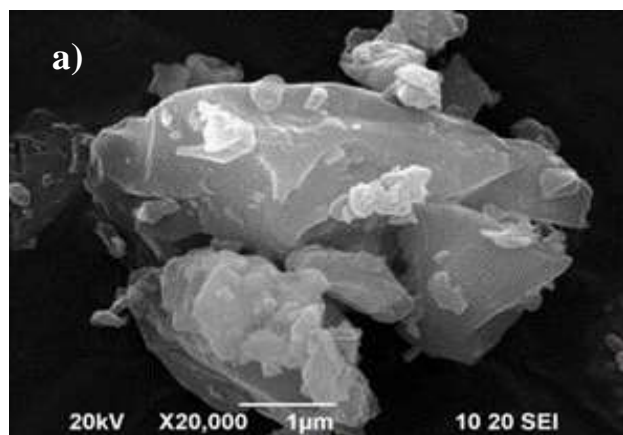


Figure 5 Micrographs of a) $\text{Eu}_2(\text{BDC}-\text{OH})_3$, b) $\text{Eu}_2(\text{BDC}-\text{NH}_2)_3$ and c) Eu_2NDC_3 .

Luminescent properties

The luminescent properties of the materials are described with the excitation and emission spectra to know the influence of the organic ligand (LO) on the lanthanide ion (Ln^{3+}), which are the components of the MOFs synthesized in this work.

Emission spectra

Figure 6 shows the emission spectra of Eu_2BDC_3 , $\text{Eu}_2(\text{BDC}-\text{OH})_3$, $\text{Eu}_2(\text{BDC}-\text{NH}_2)_3$ powders. The excitation wavelengths were set at 305 and 348 nm to obtain these spectra, respectively. In the spectrum of the MOF- Eu_2BDC_3 , the 4 characteristic emission peaks of the transitions between the electronic energy states of the europium ion are shown. They are $5D_0 \rightarrow 7F_J$, where $J=1, 2, 3$ and 4 [Han *et al.*, 2017] are located at 591, 617, 652, and 700 nm, respectively. It should be noted that the two remaining MOFs do not present a very strong intensity in the 4 transition states.

It is observed that the highest intensity peak for the three samples is located between 600 and 630 nm, so the samples present an intense red emission. Differences in the bands of the MOFs were identified: $\text{Eu}_2(\text{BDC-OH})_3$, $\text{Eu}_2(\text{BDC-NH}_2)_3$. The light emission of the sample Eu_2BDC_3 is the one with the highest intensity; the remaining two are of lower intensity, and its band in the $5D_0 \rightarrow 7F_2$ transition state presents two peaks, which is attributed to the splitting of this transition state, in addition, the change in intensity of this can be attributed to the NH_2 and OH groups, which modify the network. Considering that these samples in the DXR spectra present shorter interplanar distances, their crystal size is also smaller; this effect on the crystal is affected by the luminescence intensity they emit.

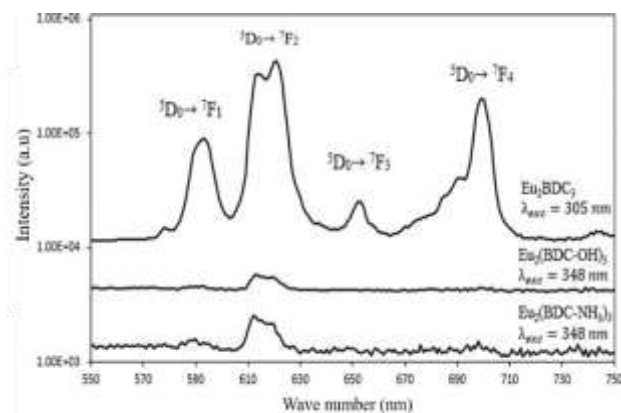


Figure 6 Emission spectra of Eu_2BDC_3 , $\text{Eu}_2(\text{BDC-OH})_3$, $\text{Eu}_2(\text{BDC-NH}_2)_3$

Figure 7 presents the emission spectrum of Eu_2BDC_3 , EuBTC , and Eu_2NDC_3 , monitored with a 305 and 348 nm wavelength, respectively. It is observed that the three MOFs show the four typical transition states of Eu^{3+} and an emission wavelength of 600-630 nm, where the MOF Eu_2BDC_3 presents the highest intensity, 105, followed by EuBTC and Eu_2NDC_3 with an intensity of 104, where the MOF Eu_2NDC_3 is the one with the lowest intensity.

The emission intensity bands of Eu_2BD_3 and Eu_2NDC_3 show two different intensities in the $5D_0 \rightarrow 7F_2$ transition state, similar to the previous MOFs. These differ in emission intensity due to the depopulation of this state because they have a difference in the number of aromatic rings.

In the case of the EuBTC , the number of rings is the same as in the MOF Eu_2BDC_3 . However, the number and positioning of the carboxylate groups will influence the antenna effect between them to impact the emission capacity.

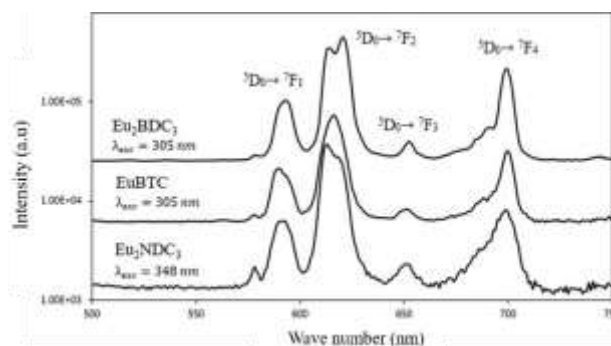


Figure 7 Emission spectra of Eu_2BDC_3 , EuBTC , and Eu_2NDC_3 .

Excitation spectra

The excitation spectra obtained from the samples $\text{Eu}_2(\text{BDC})_3$, $\text{Eu}_2(\text{BDC-OH})_3$, and $\text{Eu}_2(\text{BDC-NH}_2)_3$, with emission wavelengths at 619 and 613 nm, respectively, are presented in Figure 8. A broad absorption band of the excitation energy is observed in the interval of wavelengths of 307 and 350 nm, respectively.

The excitation spectrum of $\text{Eu}_2(\text{BDC})_3$, Figure 8, shows a broad band from 307 to 333 nm and an absorption band at 330 nm, strongly related to the energy transfer between the aromatic rings in the organic phase. Of the MOF and the Eu^{3+} ions (antenna effect), however, for the MOFs $\text{Eu}_2(\text{BDC-OH})_3$ and $\text{Eu}_2(\text{BDC-NH}_2)_3$, this band is shifted to a range of 357 to 370 nm, which is attributed to the functional groups NH_2 and OH .

The shift of the absorption bands of the MOFs to the UV spectrum greatly potentiates its implementation in biomedical applications. However, mediations were carried out after 1 month of the synthesis and previous studies, and the emission capacity in these networks was lost.

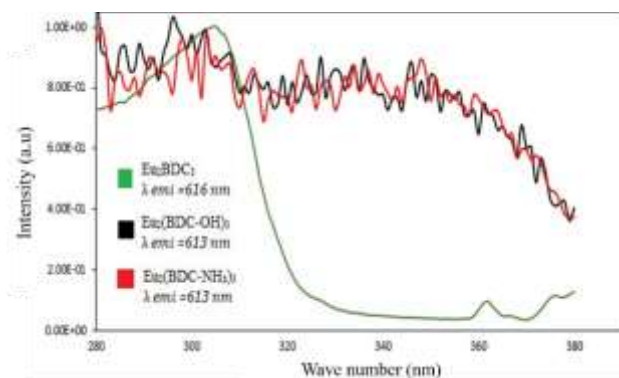


Figure 8 Excitation spectra of $\text{Eu}_2(\text{BDC})_3$, $\text{Eu}_2(\text{BDC-OH})_3$ and $\text{Eu}_2(\text{BDC-NH}_2)_3$

The excitation spectrum of $\text{Eu}_2(\text{BDC})_3$ and EuBTC is represented in Figure 8; the similarity in their patterns is observed. However, their absorption band differs; EuBTC is 300 nm, and $\text{Eu}_2(\text{BDC})_3$ is 310 nm. Unlike the Eu_2NDC_3 (Figure 9) in which this band appears at 350 nm, which is strongly related to the energy transfer between the aromatic rings present in the organic phase of the MOF, in this case, it is naphthalene—and Eu^{3+} ions (antenna effect).

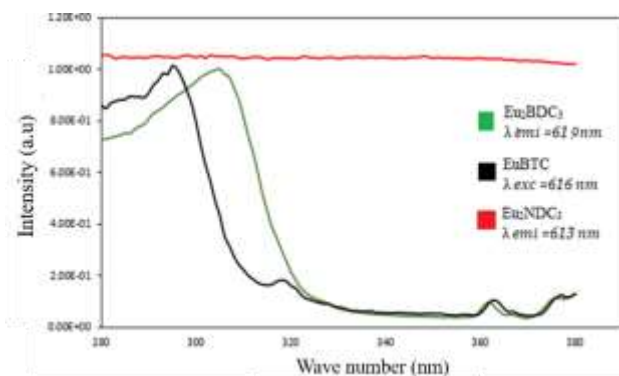


Figure 9 Excitation photoluminescence spectra of Eu_2BDC_3 , EuBTC and Eu_2NDC_3

The results from the photoluminescence spectra demonstrate an energy transfer between the organic ligand and the lanthanide ion. It is reasonable to conclude that a process of absorption and transmission of energy from the aromatic rings of the benzoate groups produces the emission of the Eu^{3+} ions. In this luminescence process, the excitation energy is selective for the aromatic rings of the benzoate since the emitting levels of the Eu^{3+} will be populated through the mechanism of sensitization of the excited state of the benzoate groups where these are working as an antenna since it is the molecule that absorbs the excitation energy and transfers it to the activating ions of the lanthanide series.

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Conclusions

In this work, five different metal-organic networks based on the europium lanthanide ion were synthesized, with the organic ligands (BDC, BDC-OH, BDC-NH₂, BTC, and NDC) obtained by a synthesis method at room temperature, which turned out to be favorable compared to the most reported technique (solvothermal), mainly due to the reduction of reaction times, in addition to not using carcinogenic or harmful solvents for health and the environment. However, it was impossible to obtain a crystalline structure for the material synthesized with BDC-NH₂, which is attributed to the nucleophilicity of the functional group.

The photoluminescence data of the Eu^{3+} complex showed that the organic ligands turned out to be helpful for the energy transfer of the lanthanide ion, because the organic ligands present the ability to transfer the appropriate and sufficient energy to the Eu^{3+} ions, thanks to the mechanism of excitation that takes place in these elements, which is known as the antenna effect.

This study proposes a strategy to increase the luminescence intensity of MOFs by up to two orders of magnitude when treating them with different organic ligands, due to the presence of different numbers of functional groups, such as carboxylates, alcohols, aminos, and aromatic rings. that impact the properties of the MOFs; crystalline structure, grain size, morphology and emission intensity.

The samples $\text{Eu}_2(\text{BDC-OH})_3$ and $\text{Eu}_2(\text{BDC-NH}_2)_3$ showed the ones with the lowest luminescence emission and a decay in this property over time. However, the energy they require to be excited is very favorable, since the wavelength is in the visible spectrum, and they are promising for their use in biomedical applications.

Similar case for the MOF of Eu₂NDC₃, which presents an intense emission and because the ligand has two aromatic rings and allowed the excitation wavelength to be covered in the visible spectrum.

The MOFs with the highest luminescent intensity of exponential order 10⁵ are the MOFs E₂BDC₃ and EuBTC, being the sample Eu₂BD₃ the MOF with the best luminescent properties, which were attributed to the presence of different organic compounds in each of them.

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