

Structural and optical properties of metal-organic frameworks of lanthanides

Propiedades estructurales y ópticas de redes metal orgánicas de lantánidos

MEDINA-AMBRIZ, Alan Raúl[†], LOERA-SERNA, Sandra^{*}, ALARCON-FLORES, Gilberto^{**} and AGUILAR-FRUTIS, Miguel Ángel^{**}

[†] Universidad Autónoma Metropolitana, Azcapotzalco, CDMX, México.

^{**} Instituto Politécnico Nacional (IPN), Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada (CICATA), CDMX, México.

ID 1st Author: Alan Raúl, Medina-Ambriz / ORC ID: 0009-0009-0753-8309, CVU CONAHCYT ID: 1232456

ID 1st Co-author: Sandra, Loera-Serna / ORC ID: 0000-0001-9562-3195, CVU CONAHCYT ID: 172467

ID 1st Co-author: Gilberto, Alarcon-Flores / ORC ID: 0000-0002-4094-524X CVU CONAHCYT ID: 170047

ID 1st Co-author: Miguel Ángel, Aguilar-Frutis / ORC ID: 0000-0002-2651-0936, CVU CONAHCYT ID: 18768

DOI: 10.35429/EJB.2023.18.10.1.9

Received January 10, 2023; Accepted June 30, 2023

Abstract

In this work, the synthesis of luminescent metal-organic frameworks (LnMOF) was studied at room temperature using different lanthanides ions as metal centers. LnMOFs are materials that can emit light by absorbing energy from other radiation and have been used mainly as sensors in medicine, optics, electronics, and the chemical industry. The synthesis was carried out by stirring at room temperature and with a stoichiometry of 1:1, using trimesic acid as an organic linker. Structural characterization of these materials was carried out using DRX, FT-IR, and SEM. Synthesis of isorecticular MOFs with Eu, Tb, Dy, Nd, and Er with crystal sizes between 24-64 nm was possible. Regarding the optical properties, these were determined by photoluminescence spectroscopy. The MOFs that presented intense emission and excitation bands were those of Eu, Tb, and Dy, being the most intense of Tb. With the results obtained, it is possible to obtain 3D luminescent MOFs using a simple and easy methodology, which does not involve high-frequency processes such as ultrasound or microwaves, or post-synthesis procedures, which are very frequent and considerably increase the synthesis time or the expense of solvents for material washings but above all a high energy consumption.

Resumen

En este trabajo se estudió la síntesis de marcos metalorgánicos luminiscentes (LnMOF) a temperatura ambiente utilizando diferentes iones lantánidos como centros metálicos. Los LnMOFs son materiales que pueden emitir luz absorbiendo energía de otras radiaciones y se han utilizado principalmente como sensores en medicina, óptica, electrónica e industria química. La síntesis se llevó a cabo por agitación a temperatura ambiente y con una estequiometría de 1:1, utilizando ácido trimésico como enlazador orgánico. La caracterización estructural de estos materiales se llevó a cabo mediante DRX, FT-IR y SEM. Fue posible la síntesis de MOFs isorecticulares con Eu, Tb, Dy, Nd, y Er con tamaños de cristal entre 24-64 nm. En cuanto a las propiedades ópticas, éstas se determinaron mediante espectroscopia de fotoluminiscencia. Los MOFs que presentaron bandas de emisión y excitación intensas fueron los de Eu, Tb, y Dy, siendo la más intensa la de Tb. Con los resultados obtenidos, es posible obtener MOFs luminiscentes 3D mediante una metodología sencilla y fácil, que no implica procesos de alta frecuencia como ultrasonidos o microondas, ni procedimientos post-síntesis, que son muy frecuentes y aumentan considerablemente el tiempo de síntesis o el gasto de disolventes para el lavado del material pero sobre todo un elevado consumo energético.

Frameworks; emission; lanthanides

Estructuras, Emisión, Lantánidos

Citation: MEDINA-AMBRIZ, Alan Raúl, LOERA-SERNA, Sandra, ALARCON-FLORES, Gilberto and AGUILAR-FRUTIS, Miguel Ángel. Structural and optical properties of metal-organic frameworks of lanthanides. ECORFAN Journal-Bolivia. 2023. 10-18:1-9.

* Correspondence to Author (E-mail: sls@azc.uam.mx, galarcon@ipn.mx)

† Researcher contributing first author.

Introduction

Metal-organic frameworks (MOF) or coordination polymers are a solid porous material with a crystalline structure formed by a metallic cluster and an organic ligand [Rocío-Bautista, 2019] to form one-dimensional, two-dimensional or three-dimensional structures [Porcher, *et al.*, 2000]. Among its properties, it stands out that depending on the nature of the components, they present a high chemical and thermal stability, they are materials with large and uniform porosities, up to 90% of the volume is free, these materials have the largest internal surface area in their structure, which gives rise to values that extend beyond 6000 m²/g [Farha, *et al.*, 2012]. All these characteristics make MOFs suitable for use in extraction processes, gas storage, catalysis, and sensors [Rocío-Bautista, 2019].

Speaking of the structure of organic metal frameworks, it can be said that these are crystalline where the lattice points are metallic centers and the links of the structure are the organic ligands, which are also the union bridges between the metallic ions [Pérez Carrasco, *et al.*, 2020]. In this type of structure, the organic binder gives more flexibility and topology diversity to the frameworks. The ligands used in the synthesis of MOF are conjugated organic compounds that, due to their chromophoric characteristics and the interactions of the conjugated bonds with their environment, absorb in the UV-Visible region and acquire structural rigidity in the framework [Rocío-Bautista, 2019].

MOFs can be synthesized using an element that generates MOFs with luminescent properties (LnMOF) as a metal center. In the case of LnMOF, the ions of metal atoms that are commonly used to produce visible light are some transition metals such as chromium (Cr) and manganese (Mn) or ions belonging to the lanthanide family [Garduño-Wilches, *et al.*, 2021]. There are several methods for obtaining LnMOF, the best known being the solvothermal method, the ultrasound method and the microwave-assisted solvothermal method.

LnMOFs are not similar to inorganic complexes, this is due to their symmetrical pores and large surface area. The differences between these two types of materials are due to the absorption of photons by the organic binder, the transfer of energy from the organic binder to the activating center within the organic metal lattice. (antenna effect), the emission of the activator when going from the excited state to the ground state and the rigidity imposed by the ligand constrain the position of the lanthanides in a different way from that observed in inorganic compounds.

In addition, several different mechanisms have been reported by which an LnMOF can present luminescence: emission from the organic ligand, metal-linker transfer, linker-metal transfer, emission promoted by the host molecule [Ríos Carvajal, 2014].

There are many methodologies for the synthesis of MOFs and in some cases different structures can be obtained from the same reaction. Thus, each methodology can have an impact in terms of reaction times, yields, particle size and morphology [Medina-Velázquez, *et al.*, 2016]. Among the different methods there are three main groups: conventional synthesis methods, high-performance methods and alternative synthesis routes [Cárdenas Saavedra, 2019]. In some cases a method can be both high throughput and alternative, so this classification is not entirely suitable for synthetic methods.

The aforementioned methods correspond to unconventional synthesis because they have the following requirements: 1) A lot of energy is needed to carry out LnMOF, which significantly increases the synthesis costs, 2) Solvents such as DMF are used in the processes for obtaining LnMOF or DEF which are highly toxic. Specific conditions are required for the synthesis (vacuum or high pressure) and long times to maintain said conditions. Due to the above, processes are sought that can replace the existing ones or optimize in some way the energy requirements to obtain the LnMOF.

In this project I carry out an alternative synthesis that involves the use of room temperature. In order to be able to obtain LnMOFs in a more environmentally friendly way, that is, avoiding the use of toxic solvents, as well as excessive energy due to the use of sophisticated techniques. The LnMOFs were synthesized from some ions of the lanthanide series such as: europium (Eu^{3+}), dysprosium (Dy^{3+}), neodymium (Nd^{3+}), terbium (Tb^{3+}) and erbium (Er^{3+}). A 1:1 molar ratio of organic ligand and metal precursor, respectively, was used in the synthesis. The physicochemical characteristics of the obtained samples were determined by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and photoluminescence measurements were performed to determine the optical properties.

Methodology

Materials

The reagents were supplied by Sigma-Aldrich and were of analytical grade, used without prior purification processes and are the following: $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%), $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), 1,3,5-benzenetricarboxylic acid (95%), and absolute ethanol (99%).

Synthesis of MOFs

The molar ratios were the same for each solid, 1.0 mmol of the organic binder dissolved in water and 0.5 mmol of the metal precursor dissolved in ethanol were used [Alarcón-Flores, *et al.*, 2015]. Both solutions were mixed dropwise at room temperature and kept stirring for 12 h. The mixture was separated by centrifugation for 30 minutes at 6000 rpm and dried in an oven at 100 °C, finally the solid was stored for further characterization.

Results

MOF structural properties

Figure 1 shows the X-ray diffraction patterns of the samples obtained with Nd, Dy, Eu, Tb and Er. It is observed that the peaks are at the same Bragg angle positions as the theoretical diffractogram.

The latter corresponds to a reported MOF with gadolinium and the organic ligand BTC, with a tetragonal arrangement and a space group $P4_32_1$, the reported framework parameters are $a=b=10.3548 \text{ \AA}$ and $c=14.5872 \text{ \AA}$ [Wang, H. 2017]. The methodology used in the synthesis of Gd-BTC included the addition of hydrochloric acid and DMF, the synthesis was carried out at 80 °C for 12 h. In this work, the synthesis was carried out at room temperature and no acid precursor was required. In the same article, the synthesis was carried out using europium and terbium, obtaining isorecticular structures of gadolinium. Additionally, a change in the relative intensities of the peaks is observed, indicating a crystallinity that depends on the metal center used in the synthesis. To obtain a quantitative analysis, calculations of lattice parameters and crystal sizes, the results are presented in Table 1. It is observed that the calculated lattice parameters are lower in all the MOFs obtained compared to the value reported for Gd-BTC, this result can be attributed to two phenomena: i) the change in the ionic radius of the lanthanides and ii) the contraction of the structure due to the absence of solvent molecules in the pores. To rule out the contraction of the structure due to the ionic radius, the values [Sánchez, R. M.] were investigated and these are presented in Table 1, it is observed that the trend that has the decrease in the value of a_0 and c_0 are not equivalent to the change of the ionic radius, this indicates that the structure is isorecticular, as already mentioned, and that the ionic radius does not directly interfere with the size of the unit cell. In this sense, it is more probable that the change is due to the affinity of the metallic centers with the water molecules, this will be corroborated by the FT-IR analysis.

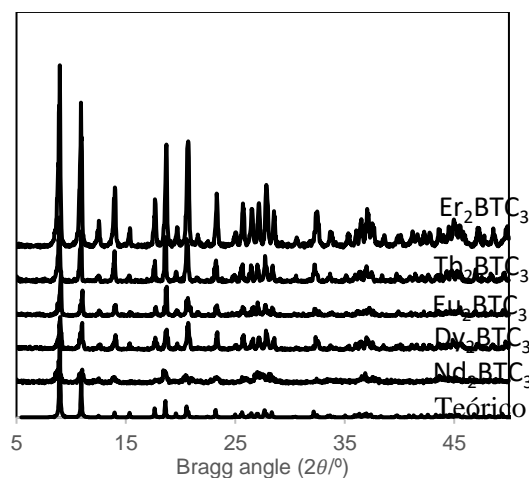


Figure 1 X-ray diffraction of the BTC samples

The crystal size obtained by the Debye-Scherrer equation (Table 1) corresponds to a nanometric material, with a smaller size for the Nd_2BTC_3 sample (24.15 nm), it seems that it obeys the larger ionic radius (1.249 Å) and the larger of 63.25nm for Eu_2BTC_3 . That can be attributed to the large difference in atomic mass (7.72 amu) between Nd and Eu. The MOFs obtained with Dy, Tb and Er have a similar size close to 40 nm, most probably due to their similar ionic radius (1.167, 1.180 and 1.144 Å respectively, see Table 2). The crystal size is related to the amplitude of the peaks, so it is observed that the synthesis methodology is the one that determines the crystallinity of the material.

The most soluble cations and similar to polar solvents are those that they can be easily incorporated into the framework, through the methodology used, since in his way the solubility of the reagents is favored.

LnMOF	a(Å)	c(Å)	D(nm)
Teoric (Gd_2BTC_3)	10.35	14.59	-
Nd_2BTC_3	10.00	13.46	24.15
Dy_2BTC_3	9.82	14.07	49.81
Eu_2BTC_3	9.75	14.02	63.25
Tb_2BTC_3	9.89	14.12	42.84
Er_2BTC_3	9.85	14.36	43.54

Table 1 Lattice parameters and crystal size

	Ionic Ratio (Å)	Atomic mass (amu)
Nd	1.249	144.24
Eu	1.206	151.96
Gd	1.193	157.30
Tb	1.180	158.93
Dy	1.167	162.50
Er	1.144	167.26

Table 2 Ionic ratios of used lanthanides and of Gd

Figure 2 shows the infrared spectra of the samples obtained with Nd, Dy, Eu, Tb and Er, it is observed that there are vibration bands at very similar wave numbers, which indicates the presence of the same functional groups, which is to be expected since the materials were obtained with the same precursors and with the same methodology. Additionally, they present the same crystalline structure, as described in the diffractograms obtained.

According to table 3, it can be said that these structures are made up of an aromatic ring (1600, 1475, 880, 850-800, 780, 770-730, 715-685 cm^{-1}), there is the presence of the carboxylate anion that gives rise to two bands: a strong band of asymmetric stretching near 1650-1550 cm^{-1} and a weaker symmetrical stretching band, the band is near 1400 cm^{-1} , it has structures where there are double bonds (1640-1610, 990, 970, 910, 890, 815, 700 cm^{-1}) and single bonds (1375, 720 cm^{-1}) in the structure. In addition, the broad band between 3200-3500 cm^{-1} corresponding to OH groups, which are attributed to solvent molecules (water or ethanol) present in the pores of the structure, is intensified for Nd and Dy. This result indicates that the coordination of water molecules is not indicative of the increase in the framework parameter observed in XRD, so the change is mostly associated with a 5% error in the measurement, rather than with the amount of solvent in the pores. of the material.

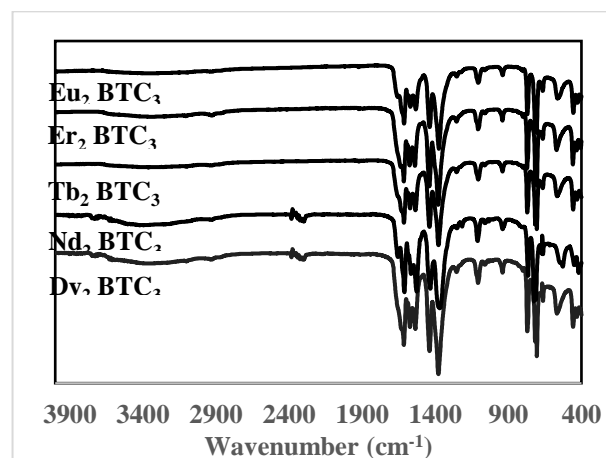


Figure 2 Results obtained by Infrared spectrum by Fourier transform

In addition, it can be said that between 400 and 500 cm^{-1} , there are differences in intensities and this is most probably due to the atomic masses of the elements of the lanthanide series, since, for example, Dy and Er, having greater atomic mass present the most intense peaks see Table 3.

The morphology analysis was achieved only for the Dy_2BTC_3 material at 5,000 and 20,000 magnifications and is presented in Figure 3 (a and b).

Functional group	Band ^a	Wave number (cm ⁻¹)
Aromatics	C=C t	~1600 and ~1475
	C-H d (mono)	770-730 and 715-685
	C-H d (orto)	770-735
	C-H d (meta)	~880 and ~780 and ~690
	C-H d (para)	850-800
Carboxylate anion	C=O t	1650-1550
	C-O t	1400

t= tension vibration d= deformation

Table 3 Vibrational modes and functional group band assignments in the FT-IR spectrum

Source: [Domínguez et. to the. 2019]

Homogeneous cubic-shaped crystals with sizes ranging from 100 to 300 nm are observed, however these crystals are made up of particles with sizes ranging from 24-63 nm according to the DRX results. After carrying out the bibliographic review, no reports of micrographs with these shapes or sizes were found for MOFs synthesized with lanthanides, generally the morphology is in micrometer-sized fibers form or rods [Lian & Yan, 2016; Chen, et al., 2022]. This result indicates that the material can be used in nanotechnology in particular as a drug carrier or cell tracer, due to its nanometric size.

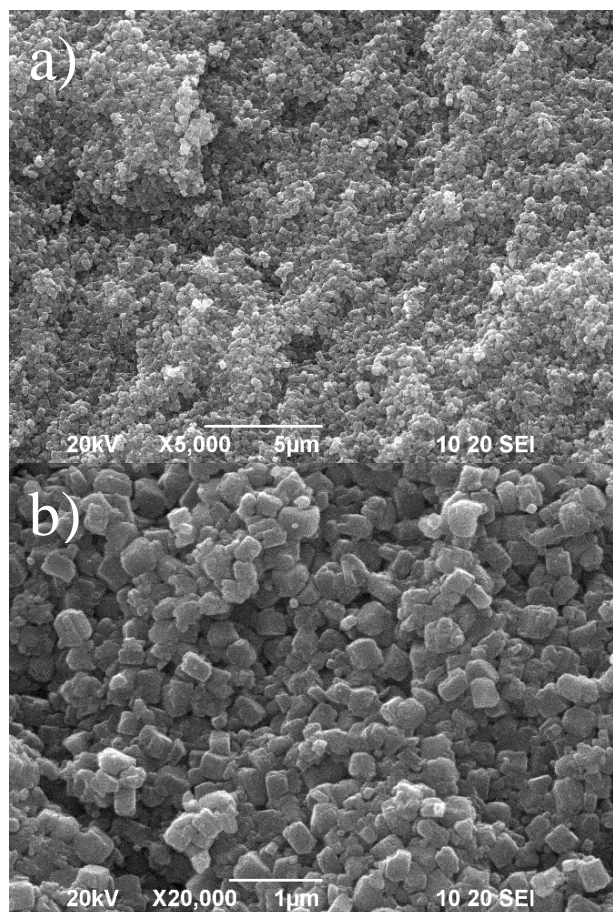


Figure 3 Microscopies of Dy₂BTC₃ at 5,000 magnification (a) and 20,000 magnification (b)

Optical properties of MOFs

The optical properties of the MOFs were obtained only for the luminescent materials (Eu₂BTC₃, Dy₂BTC₃ and Tb₂BTC₃), since Er₂BTC₃ did not present luminescence in the visible region. Figure 4 presents a photo of the materials irradiated with a UV lamp to demonstrate the luminescent property and we observe that the Eu₂BTC₃ MOF has a red color, in the case of Tb₂BTC₃ a green color was present and in the Dy₂BTC₃ MOF it was observed a color between yellow and orange. The emission and excitation spectra of these MOFs were obtained, the results are presented in Figure 5 (excitation spectra), in Eu₂BTC₃ the best excitation energy occurs between 250-260 nm and for Tb₂BTC₃ between 290-300 nm, being the best at 300 nm. approximately and for Dy₂BTC₃ the best excitation energy between 250-260 nm. Once the best excitation wavelength was confirmed, the emission and absorption spectra were obtained. Figure 6 shows the emission spectra, in the case of Eu₂BTC₃ emission bands are observed at 590 nm corresponding to the electronic transition $^5D_0 \Rightarrow ^7F_1$, at 620 nm corresponding to the electronic transition $^5D_0 \Rightarrow ^7F_2$, at 650 nm corresponding to the electronic transition $^5D_0 \Rightarrow ^7F_3$ and 700 nm corresponding to the electronic transition $^5D_0 \Rightarrow ^7F_4$. In the case of the MOF of Tb₂BTC₃ it has emission bands at 480 nm which corresponds to the $^5D_4 \Rightarrow ^7F_6$ transition, at 550 nm due to the $^5D_4 \Rightarrow ^7F_5$ transition, at 580 nm it represents the $^5D_4 \Rightarrow ^7F_4$ electronic transition and at 625 nm due to the transition $^5D_4 \Rightarrow ^7F_3$ [G. Alarcon-Flores et. to the. 2015]. Finally, Dy₂BTC₃ has emission bands at 480 nm corresponding to the $^4F_{9/2} \Rightarrow ^6H_{15/2}$ transition, at 545 nm located at the $^4I_{15/2} \Rightarrow ^6H_{13/2}$ transition, 575 nm corresponding to the $^4F_{9/2} \Rightarrow ^6H_{15/2}$ transition and 620 nm that is observed in the transition $^4I_{15/2} \Rightarrow ^6H_{11/2}$. [Bunzli & Eliseeva (2010)]



Figure 4 Eu₂BTC₃, Dy₂BTC₃, Er₂BTC₃ and Tb₂BTC₃ MOFs.

Figure 7 presents the excitation and absorption spectra of Eu_2BTC_3 , Dy_2BTC_3 and Tb_2BTC_3 . It is observed that the bands for the spectra begin to decay the absorption band between 300 nm and 350 nm. In the Eu_2BTC_3 MOF from 250 nm to 310 nm, excitation and absorption are very similar, so it can be said that where it absorbs more energy, the emission intensity will also be much higher, after 310 nm there is a great difference in intensity and it is said that this MOF will absorb much more energy, but the emission intensity will be much lower.

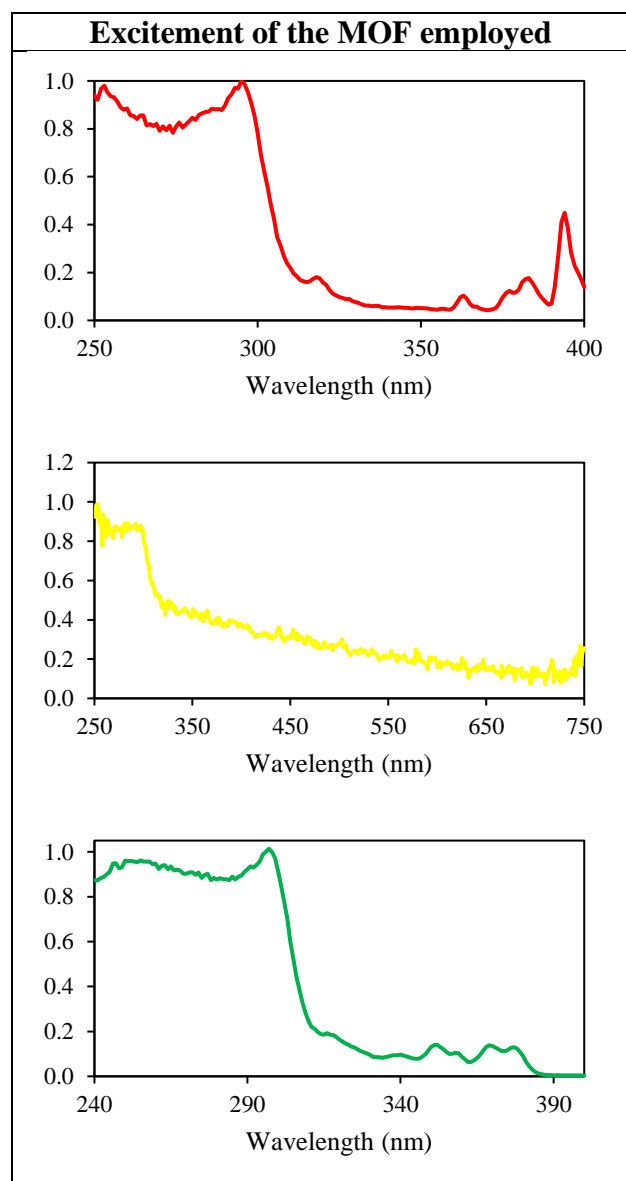


Figure 5 Excitation spectra of Eu_2BTC_3 (red), Dy_2BTC_3 (yellow) and Tb_2BTC_3 (green)

In the case of the MOF of Tb_2BTC_3 it can be seen that it is the same excitation and absorption energy and this excitation energy will produce the maximum intensity. Finally, in the MOF of Dy_2BTC_3 in most of the excitation spectrum it is of lower intensity than the absorption intensity, so it is said that the energy that it absorbs will be greater than the one that is going to be used to emit.

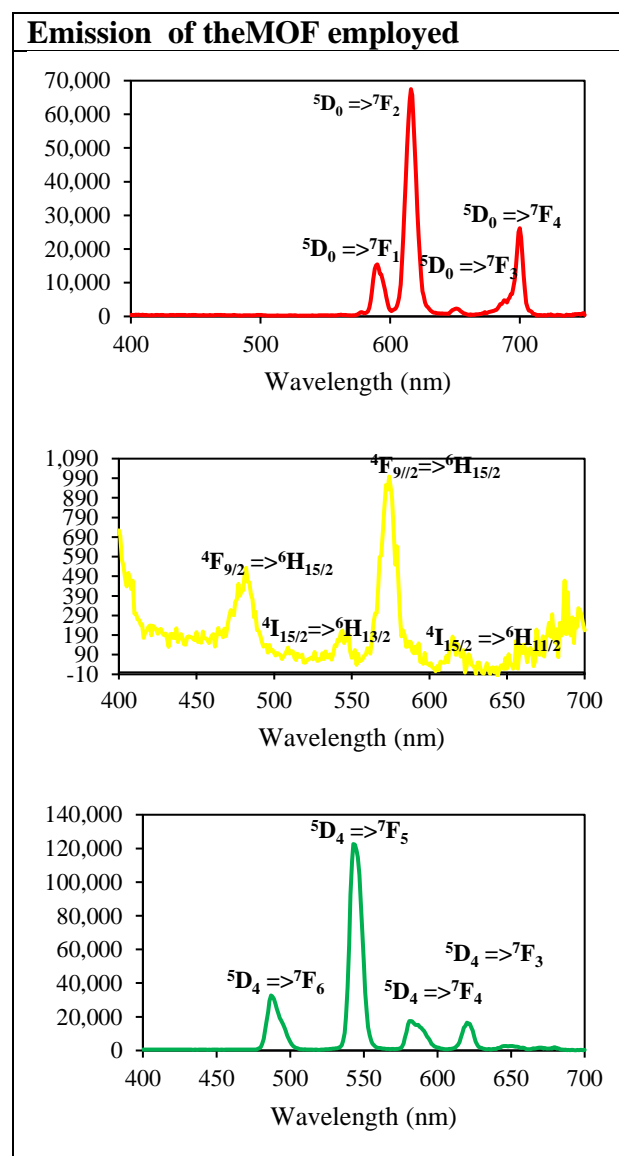


Figure 6 Emission spectra of Eu_2BTC_3 (red), Dy_2BTC_3 (yellow) and Tb_2BTC_3 (green)

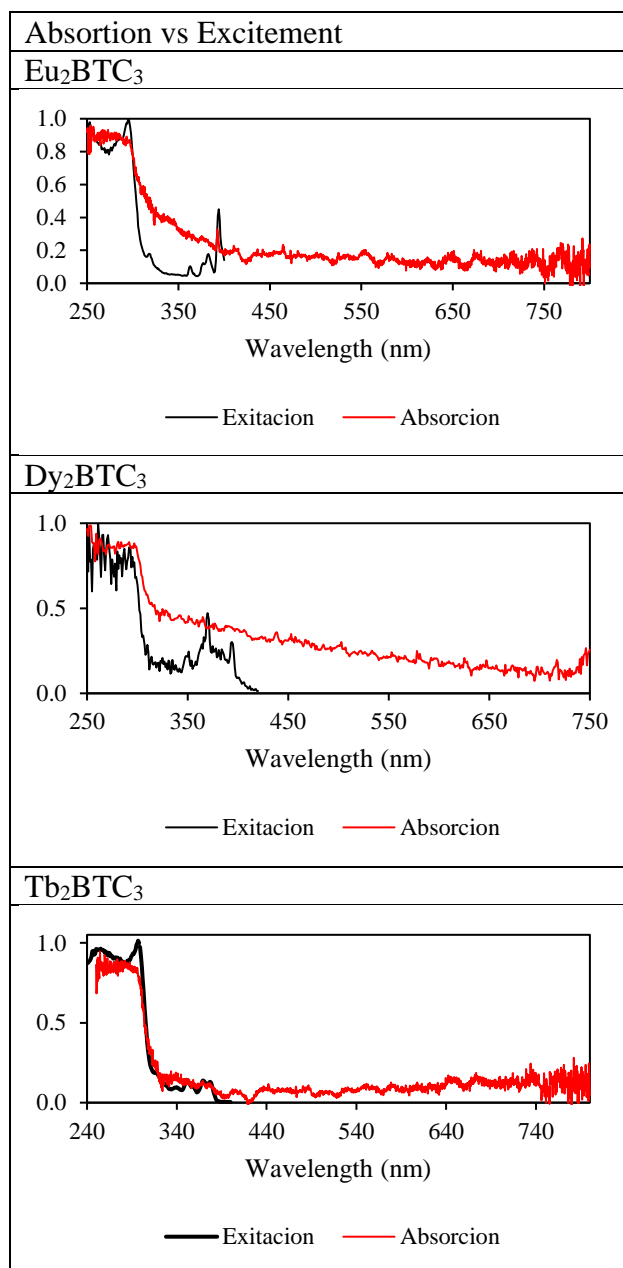


Figure 7. Excitation vs absorption of the synthesized samples

Acknowledgment

To Universidad Autónoma Metropolitana, Azcapotzalco Unit and IPN-CICATA- Legaria Unit for the facilities to carry out this work.

Financing

Funding: This work has been funded by CONAHCYT [grant number 31624, project CB A-S1-31186].

Conclusions

Using the metathesis methodology proposed in this work, which consists of a double displacement chemical reaction, it was possible to obtain five lanthanide metal-organic frameworks at room temperature. The structures obtained are isoreticular with the MOF Gd-BTC, however the synthesis did not require high temperatures, an acid environment or carcinogenic solvents such as DMF. MOFs are nanometric crystals in size and the crystallinity of the structure varies depending on the metallic center used, which changes in ionic radius, electronegativity and solubility, determining parameters in this type of synthesis. In the FT-IR spectra there are vibration bands associated with characteristic functional groups of the 3D framework, with little presence of solvent, it is also highlighted that the band between 400 and 500 cm^{-1} presents a difference in intensity, due to the difference between the atomic weights of the different elements of the lanthanide series, in addition the band between 3200 and 3500 cm^{-1} corresponding to -OH groups, indicates the coordination of water molecules or ethanol molecules present in the pores of the structure, observing that it intensifies for the elements Nd and Dy. The LnMOF presented the antenna effect, which implies that the material takes advantage of the greater amount of energy that is absorbed to produce the emission. This antenna effect occurred when the organic binder absorbed the energy radiated to it, later the absorbed energy was transferred to the lanthanide, which is responsible for carrying out the emission in the visible region of the electromagnetic spectrum. In the absorption and excitation tests, it was found that all the synthesized MOFs present the same absorption spectrum as the BTC structure and by comparing the excitation spectra with the absorption spectra it was determined that there are more wavelengths where energy can be absorbed. to be able to broadcast. The MOFs that presented luminescence were those of Eu, Tb and Dy, being the most intense that of terbium. The results indicate that it is possible to use these materials in nanotechnology applications, so the decrease in the amount of precursors used and the low toxicity is of great importance for the synthesis of MOFs.

References

- Cárdenas Saavedra, J. C. (2019). Tesis de Doctorado. Síntesis, caracterización y evaluación de redes metalo-orgánicas (MOFs) como posibles sensores de metano. Universidad Nacional de Colombia, *Departamento de Química*.
- Chen, Z., Lin, X., Liang, J., Wang, C., Min, J., Wang, Y., & Huang, Y. (2022). Synthesis of Gd (III)-MOF: Dy³⁺ phosphor and kinetics study of its thermal decomposition. *Journal of Thermal Analysis and Calorimetry*, 147(12), 6817-6823. DOI: <https://doi.org/10.1007/s10973-021-11003-x>
- Domínguez-Pérez, L. A., Lagunes-Gálvez, L. M., Barajas-Fernández, J., Olán-Acosta, M. D. L. Á., García-Alamilla, R., & García-Alamilla, P. (2019). Caracterización vibracional de grupos funcionales en granos de cacao durante el tostado usando espectroscopía de infrarrojo por transformada de Fourier. *Acta universitaria*, 29. DOI: <https://doi.org/10.15174/au.2019.2172>.
- Farha, O. K., Eryazici, I., Jeong, N. C., Hauser, B. G., Wilmer, C. E., Sarjeant, A. A., Snurr R. Q., Nguyen S. T., Yazaydin A. Ö., & Hupp, J. T. (2012). Metal-organic framework materials with ultrahigh surface areas: is the sky the limit?. *Journal of the American Chemical Society*, 134(36), 15016-15021. DOI: <https://doi.org/10.1021/ja3055639>
- Alarcón-Flores, G., García-Hipólito, M., Aguilar-Frutis, M., Carmona-Téllez S., Martínez-Martínez, R., Campos-Arias, M.P., Zaleta-Alejandre, R., & Falcony, C. (2015). Synthesis and fabrication of Y₂O₃:Tb³⁺ and Y₂O₃:Eu³⁺ thin films with electroluminescent applications: Optical and structural characteristics. *Materials Chemistry and Physics* vol 149-150, 34-42 (2015). DOI: <https://doi.org/10.1016/j.matchemphys.2014.09.020>
- Garduño-Wilches, I. A., Alarcón-Flores, G., Carro-Gastélum, A., Carmona-Téllez, S., Aguilar-Frutis, M. A., & Loera-Serna, S. (2021). Enhanced photoluminescence quantum yield of terbium nano-MOFs synthesized by microwave assisted solvothermal method. *Nano-Structures & Nano-Objects*, 26, 100736. DOI: <https://doi.org/10.1016/j.nanoso.2021.100736>
- Bunzli, J. C. G., & Eliseeva, S. V. (2010) Basics of Lanthanide Photophysics chapter In book: Springer Series on Fluorescence. Lanthanide Luminescence: Photophysical, Analytical and Biological Aspects Edition: 1 Publisher: Springer Verlag
- Lian, X., & Yan, B. (2016). A lanthanide metal-organic framework (MOF-76) for adsorbing dyes and fluorescence detecting aromatic pollutants. *RSC advances*, 6(14), 11570-11576. DOI: <https://doi.org/10.1039/C5RA23681A>.
- Medina-Velazquez D. Y., Alejandro-Zuniga B. Y., Loera-Serna S., Ortiz E. M., Morales-Ramirez A. D. J., Garfias-Garcia E., Garcia-Murillo A. & Falcony C. (2016). An alkaline one-pot reaction to synthesize luminescent Eu-BTC MOF nanorods, highly pure and water-insoluble, under room conditions. *Journal of Nanoparticle Research*, 18, 1-10. DOI: <https://doi.org/10.1007/s11051-016-3593-9>.
- Pérez Carrasco, C., Medina Velázquez, D. Y., Garfias García, E., Colín Luna, J. A., Barrón Meza, M. Á., & Reyes Miranda, J. (2020). Análisis estructural y luminiscente de redes metal orgánicas de tenoltrifluoroacetona tridopadas con tierras raras. https://revistatediq.azc.uam.mx/Docs/Revista_TeDIQ_2020.pdf.
- Porcher, P., Puche, R. S., Maestro, P., & Cascales, C. (2000). Tierras raras: materiales avanzados. In *Anales de la Real Sociedad española de Química* (No. 4, pp. 11-26). Real Sociedad Española de Química. ISSN-e 2792-5250.
- Ríos Carvajal, T. (2014). Síntesis y caracterización de redes metal-orgánicas (MOF) a partir de ligantes orgánicos tipo fenilenvinileno modificados con grupos electrodonores. Departamento de Química. <https://repositorio.unal.edu.co/handle/unal/52813>
- Rocío-Bautista, P. (2019). Redes metal-orgánicas como alternativa. *BOLETÍN GRASEOA*, 3. <https://analesdequimica.es/index.php/AnalesQuimica/article/view/1515>
- Sánchez, R. M. Determinación de lantánidos mediante espectroscopía de descomposición inducida por láser. <https://core.ac.uk/download/pdf/289986509.pdf>

Wang, H., Zhao, D., Cui, Y., Yang, Y., & Qian, G. (2017). A Eu/Tb-mixed MOF for luminescent high-temperature sensing. *Journal of Solid State Chemistry*, 246, 341-345. DOI:10.1016/j.jssc.2016.12.003.