

# Luminescent properties of europium-1,4-benzenedicarboxylate synthesized at room temperature

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## ABSTRACT

The properties of metal-organic materials as flexibility, low density, high porosity, low economical methods of synthesis; increases the advantage to use them like luminescent materials for optoelectronic devices. In this paper we carried out the synthesis of the solid hybrid europium-1,4-benzenedicarboxylate different molar ratios, constructed from a metal ion and an organic ligand. Therein the luminescent properties of each of the powders (different molar ratios) the emission band of greater efficiency was determined studied, also characterizations as infrared spectrometry (IR), X-ray diffraction (XRD) and thermal analyzes were performed gravimetric (TGA).

**Keywords:** metal organic-frameworks, luminescence, europium-1,4-benzenedicarboxylate.

## 1 INTRODUCTION

For many years the lanthanides have been considered as a series of complex, difficult to understand elements, however, research on them has not been adequate. In view of the many properties that have, in the last decade, there have been numerous studies and publications on this research field, resulting in high demand with the aim of designing and creating materials that meet the requirements of various areas such as chemistry, biochemistry, medicine, industrial, technological and environmental, to solve various problems [1].

One of the properties for which the lanthanides have generated substantial interest, is photoluminescent characteristics manifest. It is for this reason; it has also intensified development in the design of ligands capable of forming complexes with these metals, to enhance their luminescent properties.

Luminescence is a property, due to electro phenomena, of great importance in the development of new technologies. In addition, a decade ago it was discovered that some polymers exhibit this property with characteristics of intensity and efficiency enough to be used in technological edge applications (cathode luminescence materials, electroluminescent materials, lamps, matches x-ray, laser, scintillator crystals, among others more) [2]. The luminescent phenomenon means the de-excitation of an

atom or molecule, photon emission. This phenomenon plays a fundamental role in life. Processes such as vision and achievements as the sequencing of the human genome and information technology, would be impossible to conceive without luminescence. Likewise, it has become an alternative to new energy-saving technologies. The luminescence is associated with solid inorganic impurities and structural defects which act as activators, such as transition metal, lanthanide and actinide, ionic crystals, semiconductors [3].

The MOF's (metal organic framework) or complex organic metal are a new class of (organic bridge) hybrid materials constructed from metal ions, with geometry defined coordination, and organic ligands are usually carboxylates. These hybrid materials have been studied for applications in gas storage, catalysis processes, in sensors, in nonlinear optics, in molecular recognition, among others [4-7].

The complexes formed with lanthanide ions and polydentate organic ligands, have photoluminescent properties have shown very important, which makes them good candidates for use in the manufacture of materials exhibiting these characteristics [8].

Organic ligands have the ability to absorb radiation; this leads to the reception of energy, which can be transfer as a receiving antenna. This phenomenon can be borne by the called antenna effect, which is observed in lanthanide complexes with organic ligands where high emission intensity centered metal to excite the absorption bands of the ligands shown [9].

In 2009 was carried out large-scale synthesis of organo-metallic  $\text{Eu}(1,3,5\text{-BTC}) \cdot 6\text{H}_2\text{O}$ , nanocrystals with specific morphologies as cables, butterfly and flower shape, structure through a synthesis at room temperature. In this study the synthesis parameters, such as concentration, the molar ratio of the reactants, reaction temperature, and surfactant; play an important role in controlling the morphology of the final products [8]. The aim of this work is to study the morphology and physicochemical properties of Eu-BTC hybrid material by varying the molar ratios of 1,3,5-BTC organic binder and metal nitrate  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ .

## 2 EXPERIMENTAL SECTION

### 2.1 Materials

Benzene-1,3,5-tricarboxylic acid (BTC, 95% purity) and europium (III) chloride hexahydrate (99.9% purity) were purchased from Sigma-Aldrich. Anhydrous ethanol (99% of purity, Aldrich) and deionized water were used as solvents.

## 2.2 Synthesis process

Eu-BTC was prepared using the procedure reported by Loera-Serna et al. [4] BTC, was dissolved in 150 ml of deionized water. Then, a solution of europium chloride hexahydrate and 40 ml of ethanol was added drop by drop. The molar ratio was vitiated as Table 1. The synthetic mixture was stirred at room temperature for 12 h. The resulting Eu-BTC product was isolated by centrifugation and dried at 323K for 2 h.

Sample (Eu:BTC)	BTC (g)	EuCl <sub>3</sub> ·6H <sub>2</sub> O (g)
0.5:0.5	0.083	0.183
1.0:1.0	0.166	0.367
2.0:2.0	0.332	0.734
0.5:1.5	0.249	0.183
0.25:0.5	0.083	0.092
0.5:1.0	0.166	0.183

Table 1: Molar ratio of BTC and EuCl<sub>3</sub>·6H<sub>2</sub>O.

## 2.3 Characterization

Materials were characterized by X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FT-IR), thermogravimetric analyses (TGA) and luminescence spectroscopy. XRD patterns were collected on a powder diffractometer (Philips X'PERT PRO) coupled to a copper anode X-ray tube was used to identify the crystalline structure of each sample by XRD. The Cu K $\alpha$  radiation (45 kV, 40 mA,  $\lambda = 1.5406 \text{ \AA}$ ) was selected with a diffracted beam monochromator and with a step size of  $0.01^\circ$  and a time per step of 0.9 s. The FT-IR spectra ( $4000\text{--}650 \text{ cm}^{-1}$ ) were obtained with a resolution of  $2 \text{ cm}^{-1}$  at room temperature on a Bruker Tensor-27 spectrometer, fitted with a DTGS detector. The FT-IR spectra were recorded through the ATR technique. The TGA experiments were preformed under N<sub>2</sub> atmosphere at a rate of  $5^\circ\text{C}/\text{min}$  with a TA TGA Q500 (TA Instruments, USA). The samples were heated from room temperature to  $500^\circ\text{C}$ . The photoluminescent properties were recorded employing a Horiba Model Fluoromax spectrophotometer at room temperature.

## 3 RESULTS AND DISCUSSION

Figure 1 present diffractograms of synthesized samples. It can be seen that the solid preparations with molar ratios 0.5: 0.5, 1: 1, 2: 2, 1.5: 0.5 and 1: 0.5 corresponding to the Eu(BDC) structure reported by Serre et al [10], the its Miller indices were indexed using the database CSD (Cambridge Structural database). The solid in the molar

ratio 0.5: 0.25, has a low intensity diffraction peaks and the presence only of the main peak and some additional peaks is observed, corresponding to a crystalline unidentified compound. This result suggests that a low concentration of europium does not favor the formation of the structure, while the same molar ratios and binder europium, Eu generate hybrid solid (BDC) with higher crystallinity. The basis of all diffractograms obtained online, is not completely linear, suggesting the presence of amorphous material in all solid synthesized.

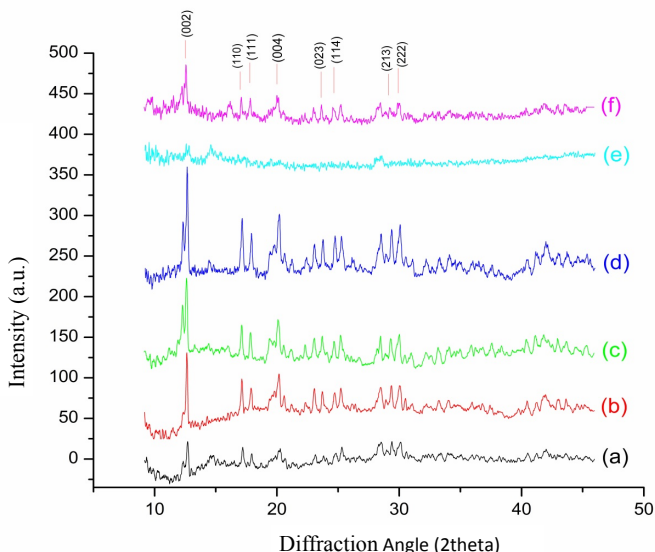


Figure 1: Diffractograms of (a) 0.5:0.5, (b) 1.0:1.0, (c) 2.0:2.0 (d) 0.5:1.5, (e) 0.25:0.5 and (f) 0.5:1.0 samples.

Figure 2 shows the IR spectra of the synthesized samples. The bands around  $505.87$ ,  $505.91$ , and  $508.27 \text{ cm}^{-1}$  in spectra (a), (b) and (c) respectively, accuse the stretching vibration Eu, suggesting that europium atoms have been coordinated with  $-\text{COO}$  functional groups. Moreover, absorption  $3459.53$ ,  $3459.50$  and  $3425.20 \text{ cm}^{-1}$  are due to stretching vibration of the water molecules and OH groups. The bands appearing in the wavenumber of  $1585.63\text{--}1536.39$  and  $1396.27\text{--}1311.16 \text{ cm}^{-1}$  Figure 2 (a),  $1585.47\text{--}1503.83$   $1397.14\text{--}1310.72 \text{ cm}^{-1}$  and Figure 2 (b), and  $1398.28\text{--}1310.71$   $1584.85\text{--}1503.03 \text{ cm}^{-1}$  Figure 2 (c) are attributed to the stretching vibration of the  $-\text{COO}$  groups ionized ligand.

Figure 3 shows the IR spectra of (a) Eu 0.5:1.5 BDC, (b) Eu 0.25:0.5 BDC y (c) Eu 0.5:1.0 BDC. The bands around  $507.85$ ,  $508.13$  and  $507.78 \text{ cm}^{-1}$  for (a), (b) and (c) spectra, are due to the stretching vibration Eu, which like Figure 2 are attributed to the coordination of europium atoms with functional group  $-\text{COO}$ . Moreover, absorption  $3461.63$ ,  $3454.87$  and  $3461.84 \text{ cm}^{-1}$  are due to stretching vibration of water molecules. The bands appearing in  $1585.73\text{--}1504.52$  and  $1398.52\text{--}1311.43 \text{ cm}^{-1}$  spectrum (a),  $1585.21\text{--}1504.02$  and  $1396.45\text{--}1310.95 \text{ cm}^{-1}$  spectrum (b), and  $1398.04\text{--}1311.44$  and  $1585.67\text{--}1504.40 \text{ cm}^{-1}$  spectrum

(c) are assigned to stretching vibration of the  $-\text{COO}$  groups ionized ligand.

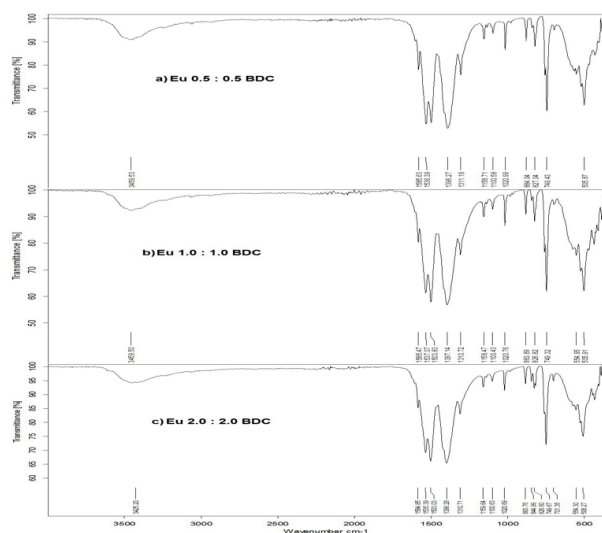


Figure 2: FT-IR spectra of (a) 0.5:0.5, (b) 1.0:1.0 and (c) 2.0:2.0 samples.

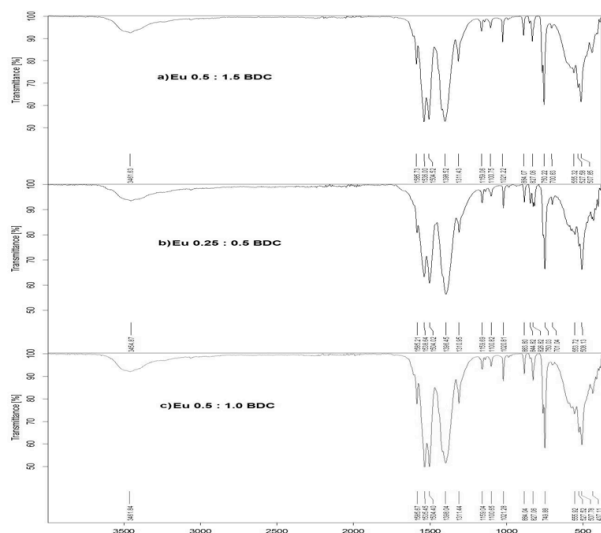


Figure 3: FT-IR spectra of (a) 0.5:1.5, (b) 0.25:0.5 and (c) 0.5:1.0 samples.

Figure 4 present TGA of synthesized samples. The first weight loss and ambient temperature up to  $100^\circ\text{C}$  corresponding to the loss of  $\text{H}_2\text{O}$  and  $\text{EtOH}$  occluded in the structure. The collapse or degradation of the MOF is given to a temperature of about  $468.23^\circ\text{C}$ . There is a remnant of material in all samples may be due to  $\text{Eu}_2\text{O}_3$ , europium carbonate and  $\text{C}$  [11]. The solid preparations contain between 5.2 and 8.4% by weight of solvent that begins to release upon heating, some of the water molecules are physisorbed in the structure and others are coordinated to the metal centers, therefore for some samples loss highest recorded until  $142.8^\circ\text{C}$  [5]. The solid with higher

degradation temperature of molar ratio was 0.25: 0.5 ( $489.07^\circ\text{C}$ ), while the temperature was lower than 0.5: 1.5 ( $461.78^\circ\text{C}$ ). Although the sample with molar ratio of 0.25: 0.5 not presents the same crystallography solids other, this material is located within the thermal parameters (solvent loss, decomposition temperature and percentage of remaining material) than the other samples synthesized. That is, the way in which the solid structure does not determine the thermal stability of the structure, or the amount of solvent occluded therein.

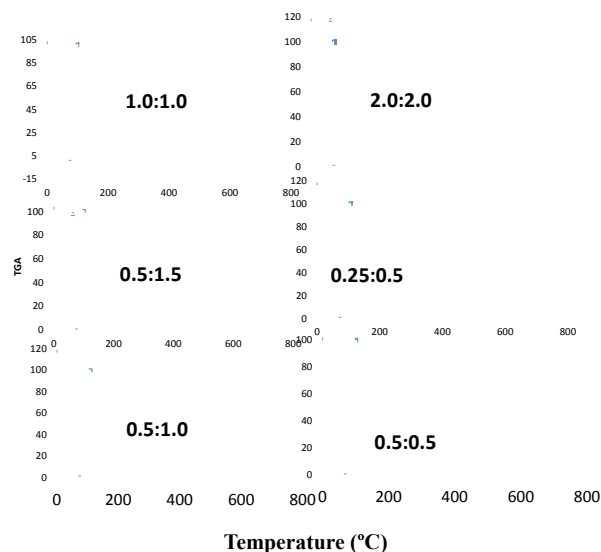


Figure 4: TGA of synthesized samples.

The  $\text{Eu}^{3+}$  emits in the red spectral line, so the lines in the area is due to transitions  $^5\text{D}_0$  to  $^7\text{F}_J$  ( $J = 1, 2, 3$  and 4 transitions). The emission spectrum was obtained from 200-550 nm excitation and emission shows particular peaks of  $\text{Eu}^{3+}$  ions; These band are: (593.78 nm)  $^5\text{D}_0$  to  $^7\text{F}_1$ , (616.66 nm)  $^5\text{D}_0$  to  $^7\text{F}_2$ , (653.48 nm)  $^5\text{D}_0$  to  $^7\text{F}_3$ , and (698.25 nm)  $^5\text{D}_0$  to  $^7\text{F}_4$ , Figure 5 [11]. All these transitions appear in each molar ratio, but with less intensity.

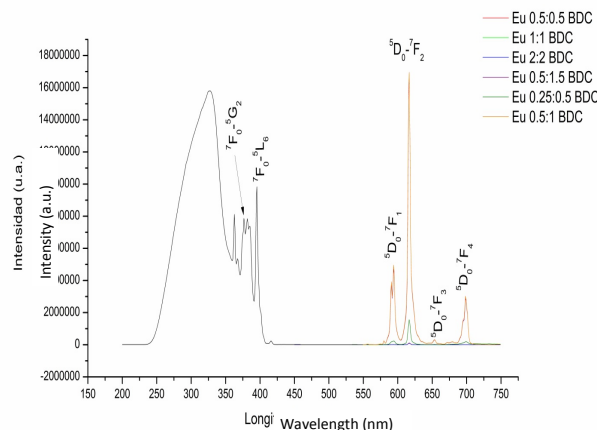


Figure 5: Excitation and emission spectrum of synthesized samples.

The most striking was the molar ratio of 0.5:1.0 with respect to the other 5 samples. Still it can be seen that the second best molar ratio was 0.5:1.5, while the others only represent less intensity but follow the same spectral behavior regarding the luminescent intensity higher.

## 4 CONCLUSIONS

We synthesize the solid Eu(BDC) with molar ratios of 0.5:0.5, 1.0:1.0, 2.0:2.0, 1.5:0.5 and 1.0:0.5. It was determined that the low concentration europium does not favor the formation of the structure, while the same molar ratios and binder europium, generate hybrid solid Eu(BDC) with higher crystallinity. In the IR stretching vibration europium observed, suggesting that the metal atoms are coordinated with the functional groups of -COO. The solids are synthesized degradation temperature ranging from to 461.78 °C (for 0.5:1.5) to 489.07 °C (for 0.25: 0.5).

All materials synthesized have a particular excitation and emission peaks of  $\text{Eu}^{3+}$  ions of presented;  $\text{Eu}^{3+}$ ; (593.78 nm)  $^5\text{D}_0$  to  $^7\text{F}_1$ , (616.66 nm)  $^5\text{D}_0$  to  $^7\text{F}_2$ , (653.48 nm)  $^5\text{D}_0$  to  $^7\text{F}_3$ , and (698.25 nm)  $^5\text{D}_0$  to  $^7\text{F}_4$  with different intensities ratio being 0.5:1.0 the highest.

## REFERENCES

- [1] C. Bouzigues, T. Gacoin, A. Alexandrou. *ASC Nano*, 5, 8488-8505, 2001.
- [2] S. V. Eliseevaab, J.-C. G. Büünzli. *New J. Chem.*, 35, 1165–1176, 2011.
- [3] D. L. Dexter. *J. Chem. Phys.*, 21, 836-850, 1953.
- [4] S. Loera-Serna, L. López- Núñez, J. Flores, R. López- Simeon, H. I. Beltrán, *RSC Advances*, 3, 10962-10972, 2013.
- [5] S. Loera-Serna, M. A. Oliver-Tolentino, M. L. López-Núñez, A. Santana-Cruz, A. Guzmán-Vargas, R. Cabrera-Sierra, Hiram I. Beltrán, J. Flores. *J. Alloys and Compounds*, 540, 113-120, 2012.
- [6] S. Bourrelly, B. Moulin, A. Rivera, G. Maurin, S. Devautour-Vinot, C. Serre, T. Devic, P. Horcajada, A. Vimont, G. Clet, M. Daturi, J.-C. Lavalley, R. Denoyel, P. Llewellyn, Ge. Férey, S. Loera-Serna. *J. Am. Chem. Soc.*, 132, 9488-9498, 2010.
- [7] P. L. Llewellyn, P. Horcajada, G. Maurin, T. Devic, N. Rosenbach, S. Bourrelly, C. Serre, S. Loera-Serna, D. Vincent, Y. Filinchuk, G. Férey. *J. Am. Chem. Soc.*, 131, 13002-13008, 2009.
- [8] K. Liu, H. You, Y. Zheng, G. Jia, L. Zhang, Y. Huang, M. Yang. *Crst. Eng. Comm.* 11, 2622-2628, 2009.
- [9] D. Y. Medina-Velazquez, B. Y. Alejandro-Zuniga, S. Loera-Serna, E. M. Ortiz, A. J. Morales-Ramirez, S. Carmona-Tellez, A. Garcia-Murillo, C. Falcony. *J. Nanoparticle Research*, 2016, send article.

- [10] C. Serre, F. Millange, J. Marrot, G. Férey. *Chem. Mater.*, 14, 2409-2415, 2002.
- [11] L. B. Mariscal, S. Carmona-Téllez, G. Alarcón-Flores, A. N. Meza-Rocha, H. S. Murrieta, C. Falcony. *ECS J. Solid State Science Tec.*, 4, R97-R104, 2015.