



The 17th International Conference on Luminescence and Optical Spectroscopy of Condensed Matter (ICL2014)

## Red luminescence in calix[4]arene-europium hybrid material

A. M. Soares<sup>a</sup>, B. S. Barros<sup>b\*</sup>, J. Kulesza<sup>a</sup>, S. Alves-Júnior<sup>a</sup>, V. O. Campos<sup>b</sup>, M. Bochenka<sup>c</sup>

<sup>a</sup>Department of Fundamental Chemistry, Federal University of Pernambuco (UFPE), Recife 50670-901, PE, Brazil

<sup>b</sup>School of Science and Technology, Federal University of Rio Grande do Norte (UFRN), Natal 59078-970, RN, Brazil

<sup>c</sup>Department of Chemistry and Technology of Functional Materials, Chemical Faculty, Gdansk University of Technology (GUT), G. Narutowicza 11/12, 80-233 Gdansk, Poland

### Abstract

Inorganic-organic hybrid material based on  $\text{Eu}^{3+}$  and calix[4]arene bearing four carboxylic acid groups has been synthesized via hydro(solvo)thermal method assisted by microwave irradiation. The obtained sample was characterized by FT-IR, PXRD, SEM and photoluminescence. The results showed the formation of coordination polymer with low symmetry around  $\text{Eu}^{3+}$  ion. The monoexponential luminescence decay lifetime reveals that all  $\text{Eu}^{3+}$  ions occupy the same coordination environment.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of The Organizing Committee of the 17th International Conference on Luminescence and Optical Spectroscopy of Condensed Matter

**Keywords:** coordination polymers; europium; calix[4]arene; microwave-assisted hydro(solvo)thermal synthesis; luminescence

### 1. Introduction

During last decades calix[4]arenes have received much attention due to their interesting complexing properties. Their unique cavity-like structure is able to encapsulate cations, anions or even neutral molecules, Gutsche (1989), Kulesza et al. (2012). Calixarene derivatives appended with groups having hard donor atoms have been widely studied as excellent candidates for hosting hard lanthanide cations and the luminescent properties of such complexes have been already reported by Hazenkamp et al. (1990) and D'Alessio et al. (2012). The formation

\* Corresponding author. Tel.: +55 84 33422347; fax: +55 8433422303.

E-mail address: [brauliobarros@ect.ufrn.br](mailto:brauliobarros@ect.ufrn.br)

of inorganic-organic hybrids based on calixarenes is of particular interest once such materials may combine properties of both the ligand and the structural framework. Recently, the use of calixarenes as building blocks in a self-assembly of new extended structures, coordination polymers, has been investigated by Liu et al. (2011) e Bew et al. (2012). In particular, lanthanide - hybrid materials are very promising functional materials due to their potential applications in luminescent sensing, light-emitting etc.

In this work, a new inorganic-organic hybrid material based on calix[4]arene-tetracarboxylic acid and  $\text{Eu}^{3+}$  was prepared *via* rapid microwave-assisted hydro(solvo)thermal method for the first time. Microwave assisted synthesis is advantageous in comparison to the conventional heating due to the reduced time of reaction, generally higher yield and better control of morphology. The luminescent properties of the obtained material are also reported here.

## 2. Experimental section

### 2.1. Materials and methods

The parent *p*-*tert*-butylcalix[4]arene was purchased from Alfa Aesar and the starting material was modified with four carboxylic acid groups to act as a ligand in a synthesis of coordination polymer. 25,26,27,28-tetrakis(hydroxycarbonylmethoxy)-*p*-*tert*-butylcalix[4]arene (abbreviated here as calix-TA) shown in Figure 1 was prepared in two-step synthesis according to the known literature procedure described by Arnaud-Neu et al. (1989), Arnaud-Neu et al. (1992).

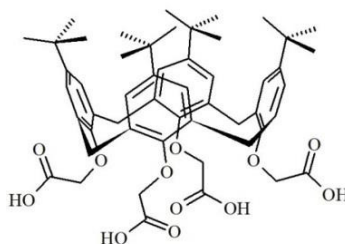


Fig. 1. Chemical structure of calix-TA used in this work for a synthesis of coordination polymer.

Solvents dimethylformamide (DMF) and ethanol (EtOH) were acquired from Vetec and were used as received without further purification. Europium (III) oxide  $\text{Eu}_2\text{O}_3$  was purchased from Aldrich. To obtain europium (III) chloride  $\text{EuCl}_3$ , the corresponding oxide was treated with concentrated hydrochloric acid HCl. Synthesis was performed in a microwave model CEM Focused Microwave™ Synthesis System Discover S-Class. Powder X-ray diffraction (PXRD) data were recorded at room temperature on a Siemens diffractometer model D5000 with  $\text{Cu K}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation. Fourier Transform Infrared spectra (FT-IR) were measured on a Bruker spectrometer (model IFS66) at the range of  $4000\text{-}400 \text{ cm}^{-1}$  using KBr pellets. The morphology of the sample was verified using a scanning electron microscope Model: Shimadzu SS-550 and 15kV electron beam. Photoluminescence (PL) excitation and emission spectra were collected in the solid state at room temperature using a FLUOROLOG3 ISA/Jobin-Yvon spectrofluorometer equipped with Hamamatsu R928P photomultiplier, SPEX 1934 D phosphorimeter and a pulsed 150W Xe-Hg lamp.

### 2.2. Synthesis of organic-inorganic hybrid material calix-TA-Eu

In a beaker, 44 mg (0.05 mmol) of calix-TA were dissolved in 12 mL of DMF and stirred for 10 minutes to assure the complete dissolution of the ligand. Subsequently, an EtOH/ $\text{H}_2\text{O}$  (v/v 3:1 mL) solution of  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.05 mmol, 18.31 mg) was added. The reaction mixture was placed in a glass-tube reactor and the synthesis was performed in a microwave at  $85^\circ\text{C}$  for 40 minutes. The resulting white powder was filtered off, washed with DMF and ethanol and dried in oven at  $60^\circ\text{C}$  for 2h.

### 3. Results and discussion

#### 3.1. Powder X-ray diffraction

The PXRD patterns of the obtained sample calix-TA-Eu and for comparison of the pure ligand calix-TA are shown in Figure 2. The absence of the diffraction peaks of the pure ligand in the PXRD pattern of calix-TA-Eu indicates the possible formation of ligand-metal interactions, most probably, a coordination polymer. It was impossible to identify the obtained phase suggesting that a new structure, never reported before, was prepared. The diffraction peaks of the obtained samples are well defined indicating a formation of crystalline structure.

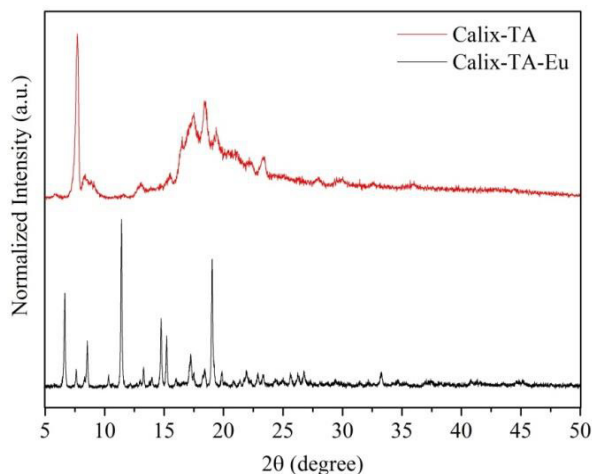


Fig. 2. PXRD patterns of the obtained sample calix-TA-Eu and of the pure ligand calix-TA.

#### 3.2. FT-IR Spectra

Figure 3 presents the IR spectra of the obtained sample calix-TA-Eu and for comparison of the pure ligand calix-TA. The residual peak at  $1746\text{ cm}^{-1}$  (also observed in the IR spectra of the pure ligand, corresponding to the stretching vibration of COOH group) suggests that not all carboxylic acid groups in the resulting sample are deprotonated. This can be also confirmed by the presence of the broad band at  $2969\text{ cm}^{-1}$  attributed to the stretching vibration of O-H band in COOH group. On the other hand, new bands in the region of  $1636\text{--}1572\text{ cm}^{-1}$  and  $1451\text{--}1428\text{ cm}^{-1}$ , corresponding to the stretching asymmetric and symmetric vibrations of  $\text{COO}^-$  groups, respectively, can be observed. The presence of these bands indicates unequivocally that the carboxylate groups are coordinated to the metal center. According to Deacon and Phillips (1980), the difference between wavelengths of  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  stretching vibrations may provide useful information on the coordination modes of carboxylates. A significant number of peaks in this region indicates the presence of various coordination modes. The highest value observed  $\Delta\nu = 208\text{ cm}^{-1}$  signifies that some carboxylates in calix-TA-Eu are bonded to europium cation in a monodentate fashion. Moreover, other values, generally all with  $\Delta\nu < 200\text{ cm}^{-1}$  suggest bidentate and/or chelate coordination modes.

Most probably, the solvent molecules  $\text{H}_2\text{O}$  and DMF are present in the structure. The peak at  $1662\text{ cm}^{-1}$  can be attributed to the stretching vibration of C=O bond of coordinated DMF. The second peak indicating the presence of DMF in the structure may be observed at  $1327\text{ cm}^{-1}$  and corresponds to the stretching vibration of C-N bond of DMF. A broad band at  $3400\text{ cm}^{-1}$  and a band at  $837\text{ cm}^{-1}$  can be attributed, respectively, to the  $\nu$  N-H and  $\delta$  N-H of dimethylamine originated from the hydrolysis of DMF. A broad band at around  $3200\text{ cm}^{-1}$  is attributed to  $\nu$  (O-H) stretching vibrations of water molecules present in the structure of calix-TA-Eu.

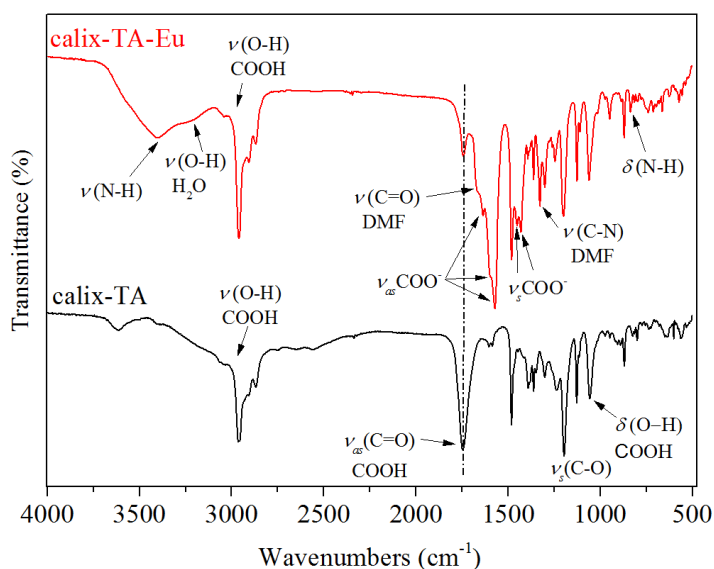


Fig. 3. FT-IR spectra of the prepared sample calix-TA-Eu and of the pure ligand calix-TA.

### 3.3. Scanning electron microscope

Figure 4 presents the micrographs of the calix-TA-Eu and of the pure ligand calix-TA. The SEM images of the obtained sample show elongated plate-like morphology with particle of variable length between 10-20  $\mu\text{m}$ . On the other hand the pure ligand has no specific morphology showing irregular agglomerates larger than 100  $\mu\text{m}$ .

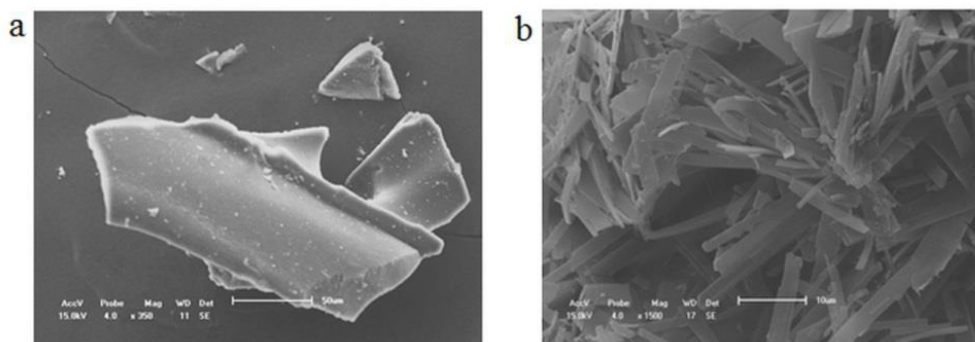


Fig. 4. SEM images of: (a) pure ligand calix-TA and (b) coordination polymer calix-TA-Eu.

### 3.4. Luminescent properties of calix-TA-Eu

The luminescence of the solid calix-TA-Eu has been investigated at room temperature. The excitation spectrum of the sample, recorded in the region of 250-550 nm by monitoring emission at 619 nm related to the  $\text{Eu}^{3+}$   $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition, is presented in Figure 5. Only sharp bands corresponding to the  $f-f$  transitions of the  $\text{Eu}^{3+}$  cation can be observed. The emission spectrum of the calix-TA-Eu powder obtained under excitation at 394 nm shows sharp peaks characteristic of transitions  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  ( $J = 0, 1, 2, 3 \text{ e } 4$ ) of  $\text{Eu}^{3+}$  ions (Figure 6a). This sample exhibited strong red luminescence due to high intensity of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  electric dipole transition observed at 619

nm, much higher than that observed for the  $^5D_0 \rightarrow ^7F_1$  magnetic dipole transition. While magnetic dipole transitions are always allowed, electric dipole transitions will be observed only if the europium ions occupy sites without inversion symmetry. Therefore, the ratio of the emission intensities of transitions  $^5D_0 \rightarrow ^7F_2$  and  $^5D_0 \rightarrow ^7F_1$ , so called asymmetry factor, gives more information about the degree of environment asymmetry around  $\text{Eu}^{3+}$  ion, Judd (1962).

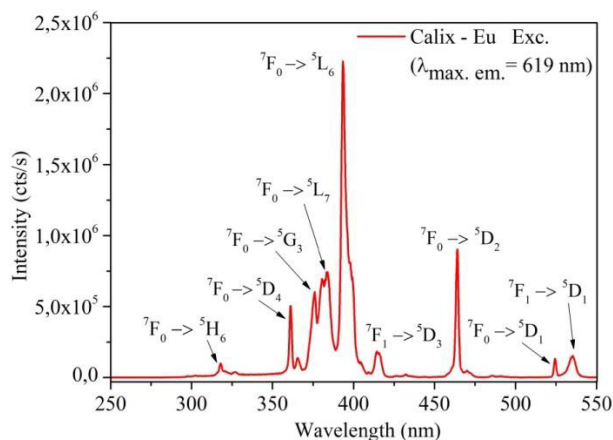


Fig. 5. The excitation spectrum of calix-TA-Eu with  $\lambda_{\text{emis}} = 619$  nm recorded in the solid state at room temperature.

The high asymmetry factor obtained for sample calix-TA-Eu equal to  $A = 4.81$  is indicative of emission originating from  $\text{Eu}^{3+}$  centers in a low symmetry coordination site. This value is much higher than for a typical calixarene- $\text{Eu}^{3+}$  inclusion complex reported in the literature ( $A = 2.73$ ) by Sengupta et al. (2014), what also may suggest the formation of a coordination polymer. Moreover, the presence of a peak at 578 nm corresponding to the transition  $^5D_0 \rightarrow ^7F_0$  confirms a low-symmetry environment of  $\text{Eu}^{3+}$  ions in the sample. Since both the ground ( $^7F_0$ ) and emissive ( $^5D_0$ ) states are nondegenerated, the single peak observed in this region indicates that all  $\text{Eu}^{3+}$  ions have the same coordination environment.

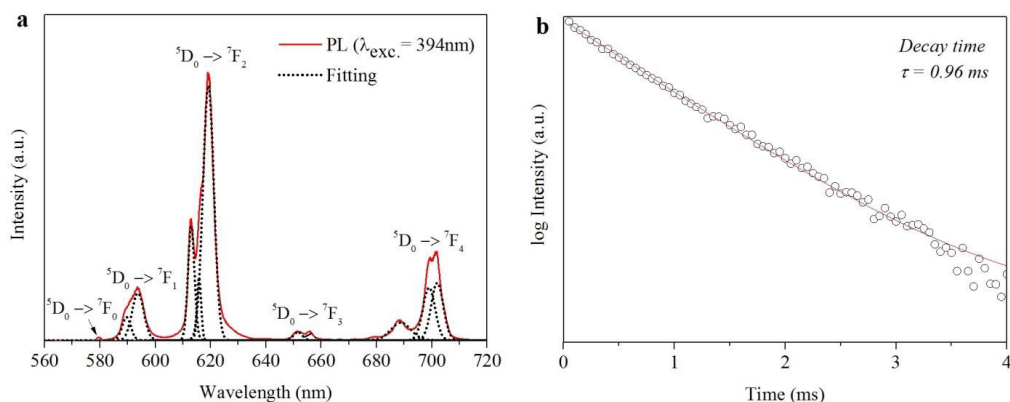


Fig. 6. PL emission spectrum (a) and decay time (b) of calix-TA-Eu recorded in the solid state at room temperature.

The lifetime of the excited  $^5D_0$  level was measured at room temperature upon direct ion excitation (Figure 6b). The luminescence decay of the sample is monoexponential which according to the literature, Klink et al.

(2000), indicates that all europium ions occupy the same coordination environment.

#### 4. Conclusion

A new inorganic-organic hybrid material based on calix[4]arene-tetracarboxylic acid and  $\text{Eu}^{3+}$  was prepared via rapid hydro(solvo)thermal microwave-assisted method. The results of PXRD and IR indicated the formation of a coordination polymer with different coordination modes of carboxylates groups including monodentate, bidentate and/or chelate. The obtained coordination polymer calix-TA-Eu exhibits red intense luminescence upon direct excitation of the  $\text{Eu}^{3+}$  ion at 394 nm. The analysis of emission peaks indicates the low symmetry around the  $\text{Eu}^{3+}$  ion. The monoexponential luminescence decay lifetime reveals that all  $\text{Eu}^{3+}$  ions occupy the same coordination environment.

#### Acknowledgements

The authors thank School of Science and Technology/UFRN, Federal University of Pernambuco, Gdansk University of Technology and FACEPE.

#### References

- Arnaud-Neu, F., Barret, G., Cremin, D., Deasy, M., Ferguson, G., Harris, S. J., Lough, A. J., Guerra, L., McKerverey, M. A., Schwinghyphen-Weill, M. J., Schwinte, P., 1992. Selective alkali-metal cation complexation by chemically modified calixarenes. Part 4. Effect of substituent variation on the  $\text{Na}^+/\text{K}^+$  selectivity in the ester series and X-ray crystal structure of the trifluoroethyl ester. *Journal of the Chemical Society, Perkin Transactions, 2*, 1119-1125.
- Arnaud-Neu, F., Collins, E. M., Deasy, M., Ferguson, G., Harris, S. J., Kaitner, B., Lough, A. J., McKerverey, M. A., Marques, E., 1989. Synthesis, X-ray crystal structures, and cation-binding properties of alkyl calixaryl esters and ketones, a new family of macrocyclic molecular receptors. *Journal of the American Chemical Society*, 111, 8681-8691.
- Bew, S. P., Burrows A. D., Duren, T., Mahon, M. F., Moghadam, P. Z., Sebestyeny, V. M., Thurston, S., 2012. Calix[4] arene-based metal-organic frameworks: towards hierarchically porous materials. *Chemical Communications*, 48, 4824-4826.
- D'Alessio, D., Muzzioli, S., Skelton, B. W., Stagni, S., Massi, M., Ogden, M. I., 2012. Luminescent lanthanoid complexes of a tetrazole-functionalised calix[4]arene. *Dalton Transactions*, 41, 4736-4739.
- Deacon, G. B., Phillips, R. J., 1980. Relationships between the carbon-oxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination. *Coordination Chemistry Reviews*, 33, 227-250.
- Gutsche, C. D., Calixarenes: Monographs in Supramolecular Chemistry. 1989, In: Stoddart J. F. (Ed.), RSC, Cambridge.
- Hazenkamp, M. F., Blasse, G., Sabbatini, N., Ungaro, R., 1990. The Solid State Luminescence of the Encapsulation Complex of  $\text{Eu}^{3+}$  in *p*-t-Butyl-calix[4]arene Tetraamide. *Inorganica Chimica Acta*, 172, 93-95.
- Judd, B. R., 1962. Optical Absorption Intensities of Rare-Earth Ions. *Physical Review*, 127, 750-761.
- Klink, S. I., Grave, L., Reinhoudt, D. N., M. van Veggel, F. C. J., 2000. A Systematic Study of the Photophysical Processes in Polydentate Triphenylene-Functionalized  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Yb}^{3+}$ , and  $\text{Er}^{3+}$  Complexes. *The Journal of Physical Chemistry A*, 104, 5457-5468.
- Kulesza, J., Bochenska, M., Hubscher-Bruder, V., 2012, Lower Rim Functionalised calix[4]arenes. Synthesis and studies of their binding properties. LAP Lambert Academic Publishing, Saarbrücken.
- Liu, L.-L., Ren, Z.-G., Zhu, L.-W., Wang, H.-F., Yan, W.-Y., Lang, J.-P., 2011. Temperature-Driven Assembly of Ln(III) (Ln = Nd, Eu, Yb) Coordination Polymers of a Flexible Azo Calix[4]arene Polycarboxylate Ligand. *Crystal Growth and Design*, 11, 3479-3488.
- Sengupta, A., Godbole, S. V., Mohapatra, P. K., Iqbal, M., Huskens, J., Verboom, W., 2014. Judd-Ofelt parameters of diglycolamide-functionalized calix[4]arene  $\text{Eu}^{3+}$  complexes in room temperature ionic liquid for structural analysis: Effects of solvents and ligand stereochemistry. *Journal of Luminescence*, 148, 174-180.