

Preparation and photoluminescence properties of functionalized silica materials incorporating europium complexes

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ABSTRACT

In the present work, the surface of the Eu–BTC = [Eu(EMA)(H₂O)₂], [Eu(TLA)(H₂O)₄] and [Eu(TMA)(H₂O)₆] complexes (EMA = 1,2,3-benzenetricarboxylate, TLA = 1,2,4-benzenetricarboxylate and TMA = 1,3,5-benzenetricarboxylate) was modified using 3-aminopropyltriethoxysilane (APTES) by a new microwave assisted method that proved to be simple and efficient. According to our observations, the most efficient luminescence is the material based on APTES incorporating [Eu(TMA)(H₂O)₆] complexes, denoted as Eu–TMA–Si, shows the highest emission efficiency. Therefore, it is proposed as a promising material for molecular conjugation in clinical diagnosis.

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1. Introduction

The development of functionalized silica particles containing luminescent materials has received special attention because of their biological applications such as optical markers *in vitro* and *in vivo*, clinical diagnosis and drug delivery [1–6]. The incorporation of Eu³⁺-complexes into modified silica particles combine optical characteristics of Eu³⁺-complexes and properties of inorganic oxides, resulting in organic–inorganic hybrid materials [7,8].

The essence of photoluminescence spectroscopy of the trivalent rare earth ions (RE³⁺) is associated with their characteristic narrow emission bands arising from the intraconfigurational 4f–4f transitions [9,10], exhibiting monochromatic emission colours. Eu³⁺-complexes have been routinely applied in the development of efficient light conversion molecular devices (LCMDs) [11,12]. The use of Eu³⁺ ion as an efficient luminescent probe is due to: (a) the pure red emission colour; (b) the excited ⁵D₀ state, which is well separated (~12,000 cm^{−1}) from ground ⁷F_{0–6} manifolds; (c) the emitting ⁵D₀ state and the ground ⁷F₀ state are non-degenerate; (d) long luminescence decay time for the emitting ⁵D₀ level (milliseconds) and (e) exceptionally large Stokes' shift when the emission spectra are obtained through direct excitation of the ⁵L₆ level (~395 nm). These characteristics make them outstanding luminescent materials as potential fluoroimmunoassay probes

[13]. However, coordination compounds are often excluded from the photonic markers use due to their poor thermal stability and mechanical properties. In order to overcome this disadvantage, some works have incorporated these complexes into sol–gel glass, polymers, liquid crystal, silica matrix, porous glass and mesoporous materials [14,15].

New optical markers are still developing, and rare earth materials are proposed as very attractive candidates. RE³⁺-complexes containing carboxylate ligands are one the most largely investigated kind of coordination compounds due to excellent properties, such as high luminescence intensity and high thermal stability when compared to classical solid coordination compounds [16–18].

Tetraethoxysilane compounds have been used in the Stöber [19,20] or microemulsion methods [21,22], traditional routes for preparing functionalized silica particles. However, microwave assisted methods using 3-aminopropyltriethoxysilane (APTES) proved to be a simple and efficient method for silica surface modification involving incorporation of complexes. APTES is used to provide an amine terminal to allow the conjugation to biomolecules [23,24]. In addition, this method discards the use of toxic organic solvents and surfactants.

This work presents the development of a new process to obtain silica particles incorporating Eu³⁺-complexes using APTES as a source of amino-functionalized silica. The synthesis was adapted from the literature [25], where the Y₂O₃:Eu³⁺ sample was used as label. The preparation technique is based on the utilization of microwave irradiation to prepare aminated silica materials incorporating Eu³⁺-complexes.

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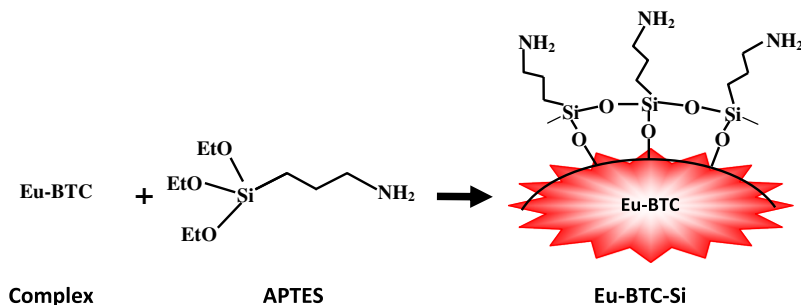


Fig. 1. Schematic representation of surface modification of the Eu-BTC complexes with APTES, symbolized as Eu-BTC-Si particles.

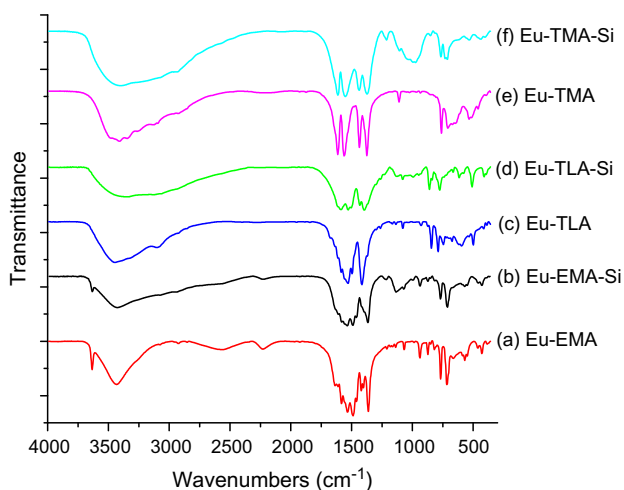


Fig. 2. Infrared spectra of (a) Eu-EMA complex, (b) Eu-EMA-Si material, (c) Eu-TLA complex, (d) Eu-TLA-Si material, (e) Eu-TMA complex and (f) Eu-TMA-Si material.

2. Experimental

The Eu-BTC complexes – $[\text{Eu}(\text{EMA})(\text{H}_2\text{O})_2]$, $[\text{Eu}(\text{TLA})(\text{H}_2\text{O})_4]$ and $[\text{Eu}(\text{TMA})(\text{H}_2\text{O})_6]$ where EMA = 1,2,3-benzenetricarboxylate,

TLA = 1,2,4-benzenetricarboxylate and TMA = 1,3,5-benzenetricarboxylate – were synthesized as reported by Rezende et al. [18]. The synthesized complexes (5 mg) were mixed in a beaker with 5 mL of undiluted APTES. The mixture was agitated in the ultrasonic bath for 5 min, then heated for 1 min at maximum power on the rotating stage in the microwave oven [25], followed by another 5 min of sonication. The heating and stirring procedures were repeated until the suspension became a viscous mixture followed by heat treatment at 150 °C for 30 min, and then was kept at room temperature overnight. Thus, the amino-functionalized silica incorporating the Eu-BTC complexes (Fig. 1), named as Eu-BTC-Si, were suspended in distilled water and centrifuged. The Eu-BTC-Si solid materials were washed with distilled water and dried in air.

Infrared absorption spectra (IR) were recorded using Nicolet-Magna 850 spectrometer with KBr pellets, in the spectral range from 4000 to 400 cm^{-1} . The SEM micrographs were obtained in a Field Emission Scanning Electron Microscope model JEOL JSM 7401F. The solid samples were deposited on a double-sided copper tape, attached to the sample holder. The Particle Induced X-ray Emission measurements (PIXE) were irradiated with a proton beam of 2.4 MeV for 10 min. A filament of tungsten was used as an emitter of electrons to neutralize the charge accumulated in the samples. X-ray diffraction patterns (XRD) of the samples were conducted with a Rigaku Miniflex II (30 kV and 15 mA) using $\text{Cu K}\alpha$.

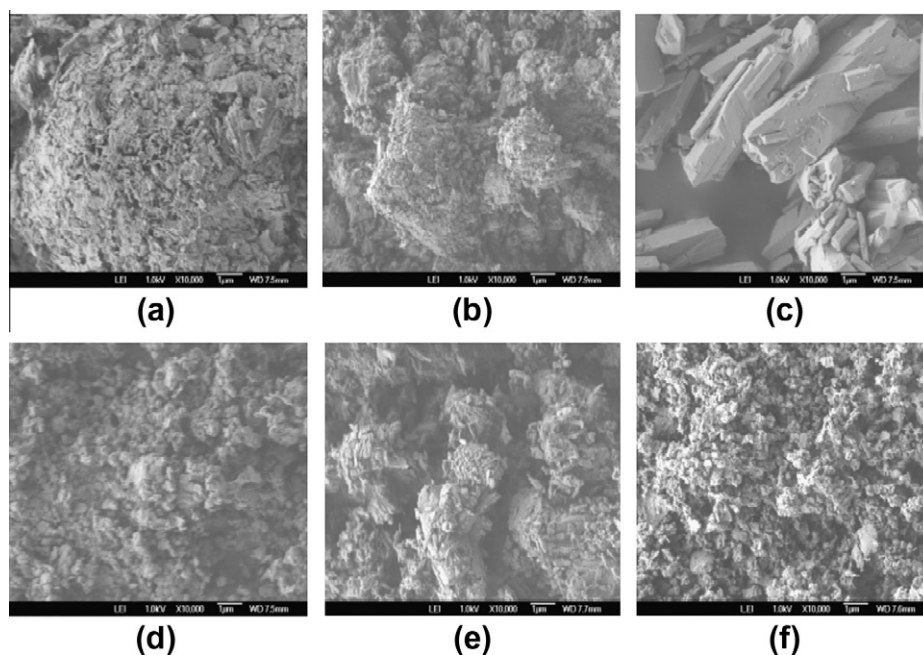


Fig. 3. SEM images of (a) Eu-EMA, (b) Eu-TLA, (c) Eu-TMA, (d) Eu-EMA-Si, (e) Eu-TLA-Si, (f) Eu-TMA-Si.

radiation (1.5406 Å) in interval of 3–80° (2θ), using the powder XRD method.

Luminescent spectra were recorded at nitrogen temperature collected at an angle of 22.5° (front face) in a spectrofluorimeter (SPEX-Fluorolog 2) with double grating 0.22 m monochromator (SPEX 1680) using a 450 W xenon lamp as excitation source. Luminescence decay curves were recorded at room temperature using the phosphorimeter (SPEX 1934D) accessory coupled with the spectrofluorimeter.

The microwave oven used in this work was a 1-kW basic domestic unit.

3. Results and discussion

The new preparation process involves the hydrolysis and condensation of the APTES promoted by microwave irradiation incorporating the Eu-BTC complexes, without the addition of water and solvents.

It is observed in Fig. 2 that the IR spectra of the Eu-BTC complexes and Eu-BTC-Si materials exhibit a broad band in the spectral range from 3700 to 3000 cm⁻¹ due the O-H stretching vibration. Besides, It is noted the characteristic absorption bands assigned to the ν_{as}(COO) and ν_s(COO) stretching vibrational modes of the carboxylate group at 1539 and 1437 cm⁻¹ for EMA, 1531 and 1430 cm⁻¹ for TLA and 1560 and 1438 cm⁻¹ for TMA ligands, respectively. Therefore, the Eu-BTC-Si materials exhibit absorption bands assigned to the typical vibrational modes found in the Eu-BTC complexes [18], indicating that the complexes have been incorporated in the silica modified with amine groups matrix without decomposition. In addition, the bands assigned to the asymmetrical stretching vibrational mode ν_{as}(Si-O-Si), are located at 1100 cm⁻¹ for the IR spectra of the Eu-BTC-Si materials, indicating the formation of siloxane bonds (Fig. 2b,d and f) [26].

Table 1

Concentration of primary amine groups in nmol mg⁻¹ determined by colorimetric method using ninhydrin and molar ratio between Si and Eu obtained by PIXE.

Samples	[NH ₂]/nmol mg ⁻¹	Si/Eu
Eu-EMA-Si	1652	0.02
Eu-TLA-Si	3630	0.08
Eu-TMA-Si	43,597	0.65

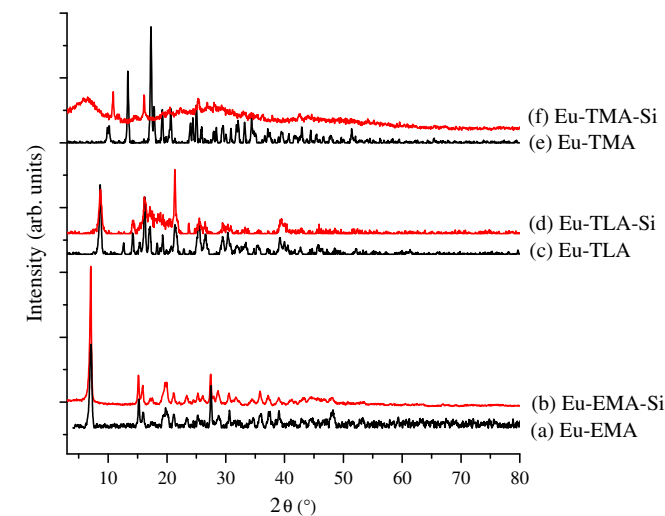


Fig. 4. The XRD patterns of (a) Eu-EMA complex, (b) Eu-EMA-Si material, (c) Eu-TLA complex, (d) Eu-TLA-Si material, (e) Eu-TMA complex and (f) Eu-TMA-Si material.

The morphologies of the Eu-BTC complexes and Eu-BTC-Si particles (Fig. 3) were examined using Scanning Electronic Microscopy technique. The difference in morphology between Eu-BTC complexes and Eu-BTC-Si materials can be attributed to the network of aminated silica on the material surface. The amino-functionalized

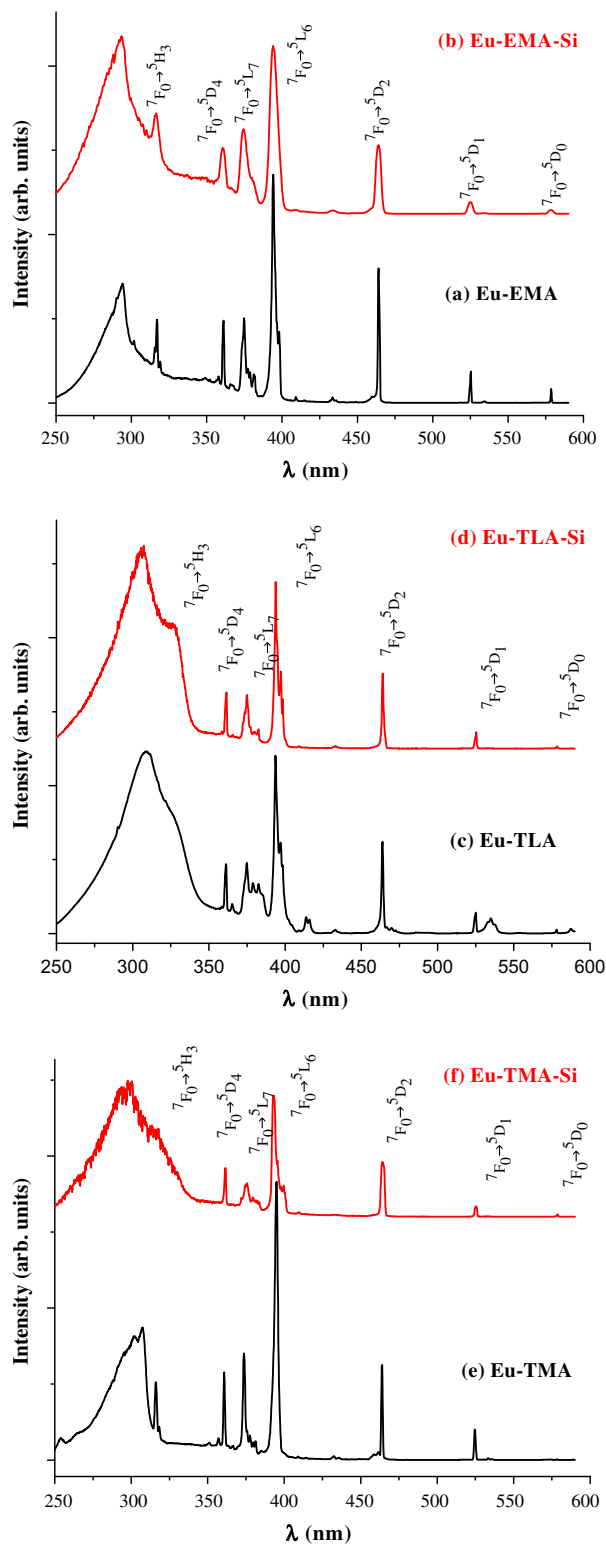


Fig. 5. Excitation spectra obtained at 77 K of (a) Eu-EMA complex, (b) Eu-EMA-Si material, (c) Eu-TLA complex, (d) Eu-TLA-Si material, (e) Eu-TMA complex and (f) Eu-TMA-Si material.

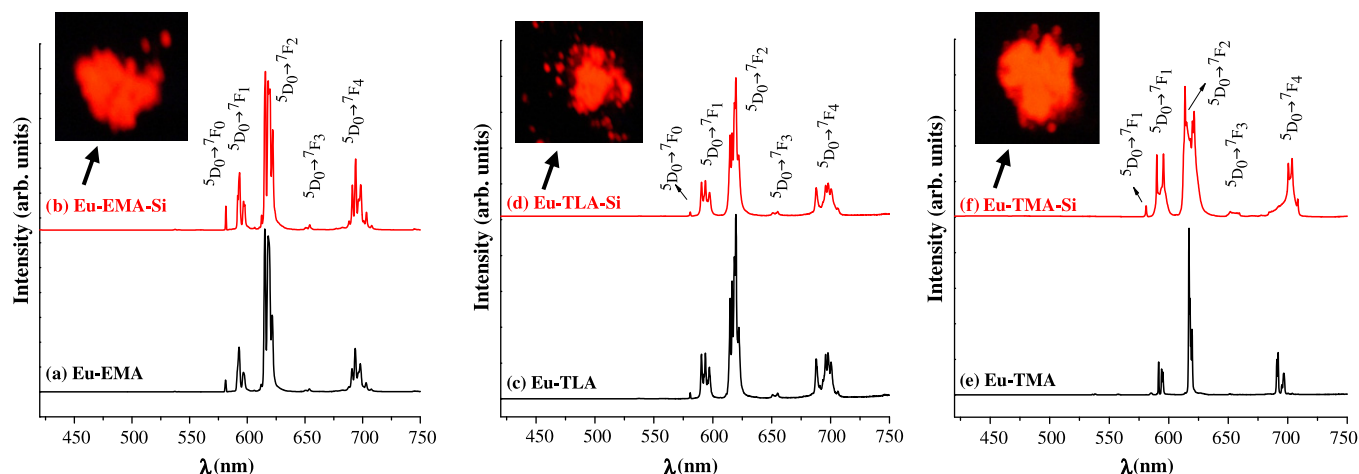


Fig. 6. Emission spectra of Eu-BTC complexes and Eu-BTC-Si functionalized materials obtained at 77 K under excitation at 394 nm of Eu^{3+} ion. The inset figures show the red emission colour of functionalized materials when irradiated with an ultraviolet lamp at 365 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

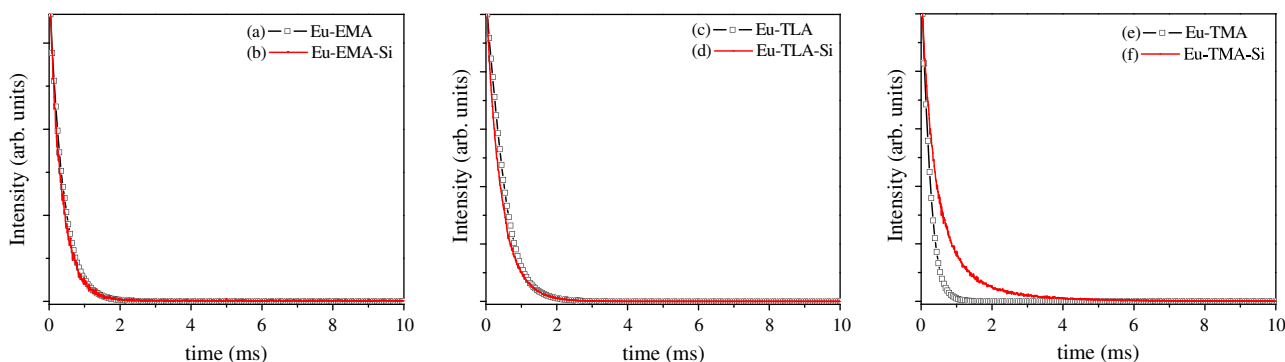


Fig. 7. Luminescence decay curves at room temperature of the emitting $^5\text{D}_0$ level of the (a) Eu-EMA complex, (b) Eu-EMA-Si material, (c) Eu-TLA complex, (d) Eu-TLA-Si material, (e) Eu-TMA complex and (f) Eu-TMA-Si material.

materials exhibit heterogeneous conglomerates of aggregates of irregular shapes. It is noted that the modification of the Eu-TMA surface is more effective.

Functionalized silica particles containing complexes have a bridge connection with biomolecules owing to the NH_2 groups. Therefore, it is necessary to verify the presence and quantify this group in these materials. Table 1 presents the results of the quantification of the primary amines based on ninhydrin test [27]. The behaviour presented in the quantification of the NH_2 groups indicates an increasing of concentration of NH_2 groups in the matrix immobilizing the Eu-BTC complexes in the following ligand order: $\text{EMA} < \text{TLA} < \text{TMA}$.

The Si to Eu molar ratio (Table 1) was obtained by PIXE analysis of the materials using the characteristic atomic emission of electromagnetic radiation (X-rays). The same behaviour presented in the quantification of the primary amine groups was observed.

The Fig. 4 shows XRD patterns of the Eu-BTC complexes and Eu-BTC-Si materials. Based on the XRD data it is observed the absence of the characteristic band of amorphous silica for the Eu-EMA-Si material (Fig. 4b), suggesting a low concentration of silica in this sample. On the other hand, the XRD patterns of the Eu-TLA-Si and Eu-TMA-Si materials reveal a broad band centred at $2\theta = 20^\circ$ and 25° , respectively, that can be assigned to the characteristic diffraction band of amorphous SiO_2 , indicating the presence of amino-functionalized silica in the surface of the material. The characteristic diffraction peaks of the precursor complexes (Fig. 4d and f) can be also observed.

The excitation spectra (Fig. 5) of the complexes and Eu-BTC-Si materials were recorded at liquid nitrogen temperature (77 K) monitoring in the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at 614 nm. Narrow absorption bands around 317, 361, 375, 394, 415, 464, 534 and 579 nm were attributed to characteristic $4f-4f$ intraconfigurational transitions of the Eu^{3+} ion corresponding to the $^7\text{F}_0 \rightarrow ^5\text{H}_3$, $^7\text{F}_0 \rightarrow ^5\text{D}_4$, $^7\text{F}_0 \rightarrow ^5\text{L}_7$, $^7\text{F}_0 \rightarrow ^5\text{L}_6$, $^7\text{F}_0 \rightarrow ^5\text{D}_3$, $^7\text{F}_0 \rightarrow ^5\text{D}_2$, $^7\text{F}_0 \rightarrow ^5\text{D}_1$ and $^7\text{F}_0 \rightarrow ^5\text{D}_0$ transitions, respectively. On the other hand, a broad band in the spectral range 250–350 nm is attributed to singlet states of the BTC ligands.

Fig. 6 exhibits the emission spectra recorded at 77 K in the spectral range of 420–720 nm with excitation at 394 nm upon europium ion. The emission spectra show characteristic $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0-4$) transitions of Eu^{3+} , with the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition as the most prominent one, which can give information about the chemical environment of the Eu(III) ion.

From the luminescence decay curves (Fig. 7) of the emitting $^5\text{D}_0$ level for the complexes and aminated silica materials were determined the lifetime values (τ) (Table 2). The photoluminescence decay curves fit, with a bi-exponential behaviour, suggest that there is more than one type of chemical environment around the Eu^{3+} ion.

The experimental intensity parameters Ω_λ ($\lambda = 2$ and 4), radiative rates (A_{0J}) for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions and emission quantum efficiency (η) were determined (Table 2) in order to get further information on the chemical environment of the Eu^{3+} ions in these samples.

Table 2

Photoluminescent data of the Eu–BTC and Eu–BTC–Si samples. The experimental intensity parameters Ω_λ (10^{-20} cm²), lifetimes τ (ms), radiative emission coefficient A_{rad} (s^{−1}), non-radiative emission coefficient A_{nrad} (s^{−1}), and quantum efficiency η (%) were obtained at room temperature.

Samples	Ω_2	Ω_4	A_{rad}	A_{nrad}	A_{tot}	τ	η
Eu–EMA	14	10	622	2015	2637	0.38	24
Eu–EMA–Si	11	8	510	2326	2836	0.35	18
Eu–TLA	10	9	463	1653	2116	0.47	22
Eu–TLA–Si	7	8	400	1958	2358	0.42	17
Eu–TMA	11	10	525	3820	4345	0.23	12
Eu–TMA–Si	8	7	373	992	1365	0.73	27

The emission quantum efficiency (η) of the ⁵D₀ emitting level of compounds were obtained based on the luminescence data (emission spectrum and emission decay curve), according to the equation [11]:

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nrad}}} \quad (1)$$

where A_{rad} is the radiative emission rate which is given by $A_{\text{rad}} = \sum_j A_{0j}$ and A_{nrad} is the non-radiative decay rate. The total decay rate is experimentally determined from the lifetime of the emitting level ($\tau^{-1} = A_{\text{tot}} = A_{\text{rad}} + A_{\text{nrad}}$).

The experimental intensity parameters (Ω_2 and Ω_4) were determined using Eq. (2), following the method reported in Ref. [11]

$$A_{J'} = \frac{4e^2\omega^3}{3hc^3} \frac{1}{2J+1} \chi \sum_{\lambda=2,4} \Omega_\lambda \langle {}^5D_0 \| U^{(\lambda)} \| {}^7F_J \rangle^2 \quad (2)$$

where $A_{0\lambda}$ are the coefficients of spontaneous emission for the ⁵D₀ → ⁷F _{λ} transitions ($\lambda = 2$ and 4), χ is the Lorentz local field correction term that is given by $\chi = n(n^2 + 2)^2/9$ (n = refractive index = 1.5), and $\langle {}^7F_\lambda \| U^{(\lambda)} \| {}^5D_0 \rangle^2$ are the squared reduced matrix elements whose values are 0.0032 and 0.0023 to $\lambda = 2$ and 4 , respectively.

Interestingly enough, an abnormally high intensity of the ⁵D₀ → ⁷F₄ transition was observed, which is also reflected by the high values of the Ω_4 intensity parameters when comparing with the values of the Ω_2 ones (Table 2) [28]. This suggests that the incorporation of the Eu³⁺-complexes in the aminated silica material modifies the local structure towards a point symmetry occupied by the Eu³⁺ ion closer to a centre of inversion [29], even though a portion of the complexes may be situated on the particle surfaces. However, at the moment we have insufficient data to quantify this ratio.

The results demonstrated that the surface modification of the Eu–BTC complexes with aminated silica occurs effectively for the TMA ligand. This behaviour supports the idea that the processes of hydrolysis and condensation of APTES depend of the precursor complexes. This may be associated with the number of coordinated water in the complex as well as the spatial arrangement. The characterization and photoluminescent properties showed that the Eu–EMA–Si and Eu–TLA–Si materials were slightly changed compared to the precursor complexes, indicating that the processes of condensation and hydrolysis were not so effective. Thus, these luminescent systems have preserved the characteristics of the complexes. On the other hand, the Eu–TMA–Si material presents different characteristics from the complex precursor as verified in the results of the IR, XRD, PIXE, SEM and photoluminescent properties.

4. Conclusions

In summary, a kind of material incorporating Eu–BTC complexes has been prepared by a new method and has been characterized. The materials showed characteristic emission of Eu³⁺ ions. According to our results the most efficient luminescent system is the Eu–TMA–Si material, presenting the highest quantum efficiency $\eta = 27\%$. The outstanding aspect is clearly the transparency of the material based on modified silica, allowing the full detection of the Eu³⁺-complex luminescence. Therefore, it is a promising candidate for molecular conjugation in clinical diagnosis.

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References

- [1] L. Bergman, J. Rosenholm, A. Öst, A. Duchanoy, P. Kankaanpää, J. Heino, M. Lindén, J. Nanomater. (2008) (Article ID: 712514).
- [2] J. Shen, L.D. Sun, C.H. Yan, Dalton Trans. 42 (2008) 5687–5697.
- [3] N. Sanvicens, M.P. Marco, Trends Biotechnol. 26 (2008) 425–433.
- [4] I.P. Roof, M.D. Smith, S. Park, H.-C. zur Loye, J. Am. Chem. Soc. 131 (2009) 4202–4203.
- [5] J. Wu, G. Wang, D. Jin, J. Yuan, Y. Guan, J. Piper, Chem. Commun. 3 (2008) 365–367.
- [6] J.-C.G. Bünzli, Chem. Rev. 110 (2010) 2729–2755.
- [7] K. Binnemans, Chem. Rev. 109 (2009) 4283–4374.
- [8] R.F. Martins, R.F. Silva, R.R. Gonçalves, O.A. Serra, J. Fluoresc. 20 (2010) 739–743.
- [9] J.-C.G. Bünzli, Chem. Lett. 38 (2009) 104–109.
- [10] D. Ananias, M. Kostova, F.A.A. Paz, A.N.C. Neto, R.T. De Moura Jr., O.L. Malta, L.D. Carlos, J. Rocha, J. Am. Chem. Soc. 131 (2009) 8620–8626.
- [11] G.F. de Sá, O.L. Malta, C.D. Donega, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. Silva Jr., Coord. Chem. Rev. 196 (2000) 165–195.
- [12] J. Kai, D.F. Parra, H.F. Brito, J. Mater. Chem. 18 (2008) 4549–4554.
- [13] H.F. Brito, O.L. Malta, M.C.F.C. Felinto, E.E.S. Teotonio, In: J. Zabicky (Ed.), The Chemistry of Metal Enolate, John Wiley & Sons Ltd., England, 2009, pp. 131–184.
- [14] Y. Chen, Q. Chen, L. Song, H.-P. Li, F.-Z. Hou, Micropor. Mesopor. Mater. 122 (2009) 7–12.
- [15] Y. Wang, W. Qin, J. Zhang, C. Cao, J. Zhang, Y. Jin, X. Ren, Z. Zheng, S. Lü, Solid State Commun. 142 (2007) 689–693.
- [16] P. Gawrysiewicz, J. Sokolnicki, J. Legendziewicz, Coord. Chem. Rev. 249 (2005) 2489–2509.
- [17] E.E.S. Teotonio, G.M. Fett, H.F. Brito, A.C. Trindade, M.C.F.C. Felinto, Inorg. Chem. Commun. 10 (2007) 867–872.
- [18] E.R. Souza, I.G.N. Silva, E.E.S. Teotonio, M.C.F.C. Felinto, H.F. Brito, J. Lumin. 130 (2010) 283–291.
- [19] S. Masse, G. Laurent, F. Chuburu, C. Cadiou, I. Déchamps, T. Coradin, Langmuir 24 (2008) 4026–4031.
- [20] L. Petit, J. Griffin, N. Carlie, V. Jubera, M. García, F.E. Hernández, K. Richardson, Mater. Lett. 61 (2007) 2879–2882.
- [21] C.L. Wu, J.Q. Hong, X.Q. Guo, C.B. Huang, J.P. Lai, J.S. Zheng, J.B. Chen, X. Mu, Y.B. Zhao, Chem. Commun. 6 (2008) 750–752.
- [22] X. Gao, J. He, L. Deng, H. Cao, Opt. Mater. 31 (2009) 1715–1719.
- [23] S.R. Corrie, R. Vogel, I. Keen, K. Jack, D. Kozak, G.A. Lawrie, B.J. Battersby, P. Fredericks, M. Trau, J. Mater. Chem. 18 (2008) 523–529.
- [24] S.-W. Ha, C.E. Camalier, G.R. Beck Jr., J.-K. Lee, Chem. Commun. 20 (2009) 2881–2883.
- [25] J. Feng, G. Shan, A. Maquieira, M.E. Koivunen, B. Guo, B.D. Hammock, I.M. Kennedy, Anal. Chem. 75 (2003) 5282–5286.
- [26] M. Muroya, Bull. Chem. Soc. Jpn. 64 (1991) 1019–1021.
- [27] O.D. Shapilov, V.G. Kayumov, A.I. Krashenyuk, J. Anal. Chem. USSR 38 (1983) 436–438.
- [28] L.D. Carlos, Y. Messaddeq, H.F. Brito, R.A.S. Ferreira, V. de Zea Bermudez, S.J.L. Ribeiro, Adv. Mater. 12 (2000) 594–598.
- [29] R.A. Sá Ferreira, S.S. Nobre, C.M. Granadeiro, H.I.S. Nogueira, L.D. Carlos, O.L. Malta, J. Lumin. 121 (2006) 561–567.