

# White emission phosphors based on Dy<sup>3+</sup>-doped into anhydrous rare-earth benzenetricarboxylate complexes

Ivan G.N. Silva<sup>a</sup>, Jiang Kai<sup>a,b</sup>, Maria C.F.C. Felinto<sup>c</sup>, Hermi F. Brito<sup>a,\*</sup>

<sup>a</sup> Departamento de Química Fundamental, Instituto de Química da Universidade de São Paulo, Cidade Universitária, 05508-000 São Paulo, SP, Brazil

<sup>b</sup> Departamento de Química, Pontifícia Universidade Católica de Rio de Janeiro, Gávea, 22451-900 Rio de Janeiro, RJ, Brazil

<sup>c</sup> Centro de Química de Meio Ambiente, Instituto de Pesquisas Energéticas e Nucleares, CNEN, Cidade Universitária, 05508-000 São Paulo, SP, Brazil

## ARTICLE INFO

### Article history:

Received 14 July 2012

Received in revised form 28 November 2012

Accepted 2 December 2012

Available online 10 January 2013

### Keywords:

Benzenetricarboxylate

Dysprosium doped complexes

White light emission

Photoluminescence

## ABSTRACT

White light emitting rare earth anhydrous complexes RE(TMA):Dy<sup>3+</sup> (RE<sup>3+</sup> = Y<sup>3+</sup> and Lu<sup>3+</sup>) containing the trimesic acid ligands (TMA) were synthesized and characterized by elemental analysis, X-ray diffraction patterns, thermogravimetric analysis and infrared spectroscopy. The crystallinity and thermostability of these luminescent materials were determined. Since the first excited triplet state ( $T_1$ : 24,000 cm<sup>-1</sup>) of TMA ligand is located at higher energy than the main emitting <sup>4</sup>F<sub>9/2</sub> level (21,000 cm<sup>-1</sup>) of the Dy<sup>3+</sup> ion, TMA can act as efficient luminescent sensitizer in the intramolecular energy transfer of RE(TMA):Dy<sup>3+</sup> material. The near-white emission colour originated from the intraconfigurational transitions of Dy<sup>3+</sup> ion <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>1</sub> is discussed.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

The carboxylate complexes have been gaining ground in the area of coordination compounds in the past decades due to the variety of their molecular structures which enables different chemical applications in solid state as gas storage molecular devices [1], nanostructured magnetic materials [2]. These properties allow the construction of a wide range of coordination compounds and their widespread use in many areas of knowledge, such as synthesis precursor materials [3], biomarkers [4], and optical markers [5].

Rare earth ions (RE) have been widely used as emitting centres in luminescent applications, such as organic light emitting devices (OLEDs) [6], emergency signalling [7], luminescent markers [8] and display panels [9]. Some of the RE<sup>3+</sup> ions exhibit visible emission, for example, the Eu<sup>3+</sup>, Tb<sup>3+</sup> and Tm<sup>3+</sup> ions emit in the red, green and blue region, respectively [10]. The RE<sup>3+</sup> luminescence properties depend mainly on the electronic energy level structures that are little affected by their chemical environments owing to the effective shielding of the 4f electrons by the filled 5s and 5p external sub-shells [11]. Furthermore, to overcome the small molar absorptivity coefficients (<1 L mol<sup>-1</sup> cm<sup>-1</sup>) of the RE<sup>3+</sup> ions, the coordination ligands such as carboxylate and β-diketonate groups are widely used, mainly because of their high absorptivity coefficient and luminescence sensitising abilities. This phenomenon is often denoted as the *antenna effect*, largely used in the design and synthesis of luminescent complexes [12].

\* Corresponding author. Tel.: +55 11 30913708; fax: +55 11 38155579.

E-mail address: [hefbrito@iq.usp.br](mailto:hefbrito@iq.usp.br) (H.F. Brito).

From the point of view of RE<sup>3+</sup> optical characteristics, Dy<sup>3+</sup> (4f<sup>9</sup>) ion has relatively large energy gap between their <sup>4</sup>F<sub>9/2</sub> emitting and <sup>6</sup>H<sub>1</sub> ground levels. The first triplet state ( $T_1$ ) position of TMA ligand is around 24,000 cm<sup>-1</sup>, which is above the emitting <sup>4</sup>F<sub>9/2</sub> level (~21,000 cm<sup>-1</sup>) of the Dy<sup>3+</sup> ion [13], permitting the ligand-to-metal energy transfer in the TMA complexes. On the other hand, Y<sup>3+</sup> (4d<sup>0</sup>) and Lu<sup>3+</sup> (4f<sup>14</sup>) ions exhibit no luminescence originated from the 4f intraconfigurational transitions. In addition, the Y(TMA) and Lu(TMA) complexes present no water molecules in the coordination sphere as a result of the smaller ionic radii of Y<sup>3+</sup> and Lu<sup>3+</sup> cations [14]. Therefore, trivalent dysprosium ion and RE(TMA) complexes were selected in the present study as the optical activator and host matrices, respectively.

It is reported the synthesis, characterization and optical properties of the non-doped RE(TMA) and doped RE(TMA):Dy<sup>3+</sup>(x%) materials (RE<sup>3+</sup>: Y and Lu; x: 0.1%, 0.5%, 1.0%, 5.0% and 10% mol) in this work. Photoluminescence data were obtained from the excitation and emission spectra and lifetimes measurements. The non-radiative energy transfer from the excited triplet state ( $T$ ) of TMA ligand to the emitting <sup>4</sup>F<sub>9/2</sub> level of the Dy<sup>3+</sup> ion as function of concentration (x% mol) were also investigated. The RE(TMA):Dy<sup>3+</sup>(x%) phosphors yield white-light emission.

## 2. Experimental section

### 2.1. Synthesis of the doped RE(TMA) system

The RE<sup>3+</sup> chlorides were obtained from their respective oxides RE<sub>2</sub>O<sub>3</sub> (Cstarm, 99.99%) by digestion of its aqueous suspension

with the addition of concentrated hydrochloric acid until pH reaches 6.  $\text{RECl}_3 \cdot (\text{H}_2\text{O})_6$  crystals were obtained and dried by water bath and afterwards stored under reduced pressure.

The trimesic acid (benzene-1,3,5-tricarboxylic acid – Fluka, 97%),  $\text{H}_3(\text{TMA})$  (Fig. 1), was used without further purification. Considering the  $\text{RE}^{3+}$  ions as hard acids, the binding of these ions with carboxylates (hard base) is favoured because of their high negative charge density [15]. Since the pKa's of the  $\text{H}_3(\text{TMA})$  are 3.12, 3.89 and 4.70 [16], its aqueous solution was prepared by the addition of 1 M sodium hydroxide solution until pH reached  $\sim 6.0$ . At this condition, all carboxylate groups are deprotonated.

For the preparation of the doped  $\text{RE}(\text{TMA})\text{:Dy}^{3+}(x\%)$  materials, 50 mL of  $\text{RECl}_3$  ( $\sim 0.050$  M) aqueous solution of  $\text{Y}^{3+}$  or  $\text{Lu}^{3+}$ , with the required molar ratio of  $\text{Dy}^{3+}$  (0.1%, 0.5%, 1.0%, 5.0% and 10%) was dripped slowly ( $\sim 1$  drop per second) over 200 mL of previously prepared  $(\text{TMA})^{3-}$  ligand aqueous solution ( $\sim 0.0125$  M) at boiling point at molar ratio 1:1. The reaction was refluxed for about 4 h and the resulting precipitate was filtered and washed with distilled water four times. The obtained complexes are air-stable and non-hygroscopic white crystalline powders. Besides, the complexes are insoluble in different solvents such as acetone, alcohol, DMSO, acetonitrile, chloroform, water or their mixtures [17].

## 2.2. Characterization techniques

Elemental analysis was performed in Perkin-Elmer CHN 2400. The infrared absorption spectra were performed using KBr pellets, with the equipment Bomem MB100 FTIR in the spectral region from 400 to  $4000\text{ cm}^{-1}$ . The X-ray diffraction patterns were recorded by a Miniflex Rigaku ( $\text{Cu K}\alpha 1$ ) from  $4^\circ$  to  $60^\circ$  ( $2\theta$ ). Thermogravimetry curves were obtained with the 2950 TGA HR V5.4A equipment from 30 to  $900^\circ\text{C}$  in a dynamic atmosphere of synthetic air with constant heating ramp of  $5^\circ\text{C min}^{-1}$ .

The photoluminescence study was conducted based on the excitation and emission spectra recorded at room temperature and 77 K, using the front-face data collection mode ( $22.5^\circ$ ), utilizing a 450 W Xenon lamp as excitation source coupled to the equipment SPEX-Fluorolog 2 with double monochromators. With a 150 W pulsed lamp attached to the phosphorimeter SPEX 1934D accessory, photoluminescence decay curves were recorded.

## 3. Results and discussion

The chemical composition of the  $\text{RE}^{3+}$ -TMA system determined by elemental analysis and calculated values are presented in Table S01. These results confirm the general 1:1 ratio between the TMA ligand and  $\text{RE}^{3+}$  ions and the absence of the coordinated water molecules in the  $\text{RE}(\text{TMA})\text{:Dy}^{3+}(x\%)$  system.

The IR spectras were registered at room temperature and presented in Fig. S01. The symmetric  $\nu_s(\text{C}=\text{O})$  and asymmetric  $\nu_{\text{as}}(\text{C}=\text{O})$  stretching modes of the carboxylate group of the TMA

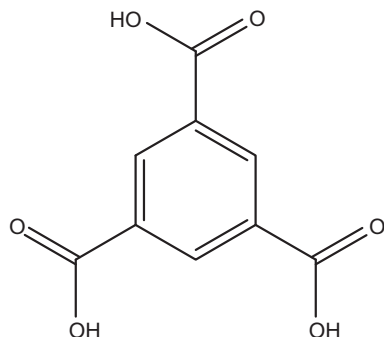


Fig. 1. Structural formula of the 1,3,5-benzenetricarboxylic acid –  $\text{H}_3(\text{TMA})$ .

ligand are observed in the spectral range from 1400 to  $1600\text{ cm}^{-1}$ . The  $\Delta\nu$  for  $\text{Na}_3(\text{TMA})$  is  $195\text{ cm}^{-1}$ ; the  $\Delta\nu$  values of  $\text{RE}(\text{TMA})\text{:Dy}^{3+}(x\%)$  materials are in the range of 150 to  $160\text{ cm}^{-1}$ , indicating bridge-type coordination [18]. The sharp band observed in the infrared spectra of the  $\text{Y}(\text{TMA})\text{:Dy}^{3+}(x\%)$  and  $\text{Lu}(\text{TMA})\text{:Dy}^{3+}(x\%)$  samples around  $3075\text{ cm}^{-1}$  is assigned to C–H bond stretching (Fig. S01). Besides, three sharp absorption bands were identified between 690 and  $780\text{ cm}^{-1}$  which correspond to the out-of-plane C–H bending of the aromatic ring [19]. These IR spectral profiles are characteristics of anhydrous  $\text{RE}(\text{TMA})$  materials.

The powder X-ray diffraction patterns of the doped and non-doped complexes are similar (Fig. 2). In addition, they present resemblances to the X-ray data for the  $\text{Dy}(\text{TMA})$ ,  $\text{Y}(\text{TMA})$  and  $\text{Y}(\text{TMA})\text{:Eu}^{3+}$  anhydrous complexes reported by Serre et al. [20] and for the  $\text{Y}(\text{TMA})\cdot(\text{H}_2\text{O})_6$  hydrated coordination compound reported by Daigebonne et al. [21]. Whereas these X-ray diffraction patterns show small differences in the intensity and peak positions, except for the different intensity ratios between the diffraction peaks possibly due to the platelet-shaped of the samples and the presence of a peak around  $26^\circ$ . Furthermore, when the  $\text{Dy}^{3+}$  doping concentration changes, the diffraction peaks assigned to the  $\text{Y}(\text{TMA})$  and  $\text{Lu}(\text{TMA})$  host matrices show no displacement or formation of new diffraction patterns. These results also indicated the formation of a solid solution between the  $\text{Dy}^{3+}$  ion dopant and the  $\text{RE}^{3+}$ -matrices ( $\text{RE}^{3+}$ : Y and Lu) due to the similarity between the radii of rare earth ions (Fig. 2).

Fig. 3 shows the thermogravimetric curves of  $\text{RE}(\text{TMA})\text{:Dy}^{3+}(x\%)$  system, which present no weight-loss event in the temperature range from 30 to  $450^\circ\text{C}$ , indicating good thermal stability of the samples. This can be explained by the formation of metal-organic framework between the  $\text{RE}^{3+}$  ions and the TMA ligand. The nonappearance of the weight-loss event corresponding to the release of water molecules in this temperature interval also confirms that the  $\text{RE}(\text{TMA})\text{:Dy}^{3+}$  system are anhydrous, corroborating the elemental analysis. On the other hand, in the temperature interval of 450 to  $600^\circ\text{C}$ , the doped system presents only one single-step decomposition of the organic moiety, resulting in the formation of their respective sesquioxides ( $\text{RE}_2\text{O}_3$ ).

## 4. Photoluminescent study

It is noteworthy to mention that the  $\text{Dy}^{3+}$  ion has an odd-electron configuration ( $4f^9$ ). Therefore, it is labelled as a Kramer ion due to its electronic states that are at least doubly degenerate for any crystal-field perturbation. The maximum number of the Stark components for Kramer ions with  $2S+1L_J$  states is  $J + 1/2$  for any symmetry lower than cubic [22].

The excitation spectra of the  $\text{Y}(\text{TMA})\text{:Dy}^{3+}(x\%)$  system with emission monitored at 577 nm corresponding to the  ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$  transition of the  $\text{Dy}^{3+}$  ions are shown in Fig. 4 (left). The broad absorption band centered at 300 nm which is assigned to the TMA ligand is more intense than the narrow absorption peaks arising from 4f intraconfigurational transitions of the  $\text{Dy}^{3+}$  ion [17]. With the increased  $\text{Dy}^{3+}$ -doping, the 4f-4f transitions become more pronounced. From the position of these absorption bands originated from the  ${}^6\text{H}_{15/2}$  ground state of the  $\text{Dy}^{3+}$  ion, the excited energy levels can be attributed as the following (in  $\text{cm}^{-1}$ ):  ${}^4\text{F}_{9/2}$  (21,230);  ${}^4\text{I}_{15/2}$  (22,269);  ${}^4\text{G}_{11/2}$  (23,585);  ${}^4\text{M}_{21/2}$  (25,316);  ${}^4\text{K}_{17/2}$ ,  ${}^4\text{F}_{7/2}$ ,  ${}^4\text{I}_{13/2}$  (25,974);  ${}^4\text{M}_{11/2}$  (26,523);  ${}^6\text{P}_{5/2}$  (27,548);  ${}^4\text{I}_{11/2}$  (28,011),  ${}^4\text{M}_{11/2}$ ,  ${}^6\text{P}_{7/2}$  (28,653);  ${}^4\text{F}_{5/2}$ ,  ${}^4\text{I}_{9/2}$  (29,673) and  ${}^6\text{P}_{3/2}$  (30,864) (Fig. 4 right). As can be observed, the  ${}^6\text{H}_{15/2} \rightarrow {}^6\text{P}_{5/2}$  transition ( $27,548\text{ cm}^{-1}$ ) exhibits the highest intensity among the 4f<sup>9</sup> intraconfigurational transitions, indicating that in this case the direct excitation can be also used these transition from the dysprosium ion.

Download English Version:

<https://daneshyari.com/en/article/1495358>

Download Persian Version:

<https://daneshyari.com/article/1495358>

[Daneshyari.com](https://daneshyari.com)