

Europium Luminescent Polymeric Microspheres Fabricated by Spray Drying Process

Priscilla Paiva Luz · Ana Maria Pires ·
Oswaldo Antonio Serra

Received: 3 December 2007 / Accepted: 30 January 2008 / Published online: 22 February 2008
© Springer Science + Business Media, LLC 2008

Abstract The spray drying method was used to prepare luminescent microspheres. These microspheres were prepared by spraying an aqueous solution of dextrin and an europium(III) complex with subsequent drying in a hot medium. The spray dried powder was characterized by scanning electron microscopy (SEM) and photoluminescence spectroscopy (PL). Particle size distribution was estimated from SEM images. The ultrasonic spray drying technique was successfully applied to yield a microparticulated and red luminescent powder composed by the $[\text{Eu}(\text{dpa})_3]^{3-}$ (dpa = dipicolinic acid) complex incorporated in dextrin microspheres.

Keywords Europium · Microspheres · Luminescence · Spray drying · Encapsulation

Introduction

Spray drying is by definition the transformation of a pumpable feed from a fluid state (solution, dispersion, or emulsion) into a dried particulate form by spraying the feed

into a hot drying medium [1, 2]. This technique involves evaporation from an atomized feed by mixing the spray and the drying medium. The complete process consists basically of a sequence of four steps: atomization, mixing of spray and air, evaporation, and product separation [3–7].

During the atomization step, the feed is splitted in many microdroplets. As a result, the surface area of the liquid is large and promotes an efficient heat exchange [7]. So, solvent evaporation is rapid and the temperature of the droplets can be kept far below the drying air temperature. For this reason, spray drying can be applied in both heat resistant and heat sensitive materials [8].

Selection of the atomizer is one of the most important choices in spray dryer design and has significant effect upon the size distribution of the final dried particles. The most important atomizer characteristics from the standpoint of product quality are uniformity of drop size, control of drop size distribution, and spray homogeneity. Common forms of atomizers are pressure atomizers, centrifugal (wheel) atomizers, and pneumatic (two-fluid) atomizers [4, 8, 9]. However, a novel spray drying technique consisting of feeding a fluid through an ultrasonic atomizer has been developed, which leads to smaller particle size [6, 9–12].

Although most often considered a dehydration process successfully employed for the drying of solutions, slurries, and pastes, spray drying is an important and widely used technology in many research and industrial fields. Spray drying can also be used as an encapsulation method once it entraps the “active” material within a protective matrix that is essentially inert to the material being encapsulated [3, 13]. Microencapsulation is a technique in which a membrane, usually a polymer, encloses small particles of solid, liquid or volatile compounds with the objective of offering protection to the core material from adverse environmental conditions such as undesirable effects of light, moisture and

P. P. Luz · O. A. Serra
Department of Chemistry, FFCLRP, University of São Paulo,
Ribeirão Preto, SP, Brazil

A. M. Pires
Department of Physics, Chemistry and Biology,
FCT-UNESP,
Presidente Prudente, SP, Brazil

O. A. Serra (✉)
Department of Chemistry, Rare Earth Laboratory,
University of São Paulo,
Av. Bandeirantes, 3900,
14040-901 Ribeirão Preto, SP, Brazil
e-mail: osaserra@usp.br

oxygen, thus contributing to an increase in the shelf life of the product [14, 15].

Common polymers for these encapsulation processes include carbohydrates, gums and cellulose esters and ethers [16]. In particular, polysaccharide-based microparticles have gained much more attention in developing micro-particulated systems because of their flexibility to obtain a desirable drug release profile, cost-effectiveness and broad regulatory acceptance [17].

Red emitters are widely studied, especially those bearing the Eu^{3+} ion as activator. To be applied as a red phosphor, a material must have a high color purity (CIE x coordinate [18] higher than 0.65), besides an acceptable quantum efficiency. For Eu^{3+} -activated compounds, this is possible when the red emissions (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ at ~ 610 nm) are predominant over the orange emissions (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ at ~ 590 nm).

The narrow emission bands of rare earth ions arise from weakly allowed $f-f$ emissive transitions that are parity forbidden and well shielded from the local environment by $5s^2$ and $5p^6$ electrons [19]. In addition, lanthanides in aqueous solution are known to be either non-fluorescent or weakly fluorescent due to their low molar absorptivities and poor quantum yields. It happens also due to the non-radiative relaxation of Ln^{3+} ion through coupling with OH vibrational modes from solvent molecules [20].

The spectral distribution is a consequence of the symmetry around the Eu^{3+} ions, and different host lattices lead to different spectral distributions [21]. The intense interest in the photophysical properties of lanthanide ion complexes has been stimulated strongly by Lehn [22], who proposed that such complexes could be considered as light conversion molecular devices (LCMDs) and suggested the term “antenna effect”. This effect denotes a sequence of absorption, energy transfer, and emission phenomena involving distinct absorbing (the ligand) and emitting (the lanthanide ion) components, thus overcoming the very small absorption coefficients of the lanthanide ions [23–25].

In the majority of the systems studied, the excited singlet state of the ligand undergoes fast intersystem crossing (ISC) to the triplet state enhanced by the increased spin-orbit (LS) coupling induced by the heavy lanthanide ion. It is widely believed that it is from this triplet state that energy transfer occurs to the lanthanide ion through either a Dexter or a Förster mechanism [26].

Among the many types of complexes studied, the family of $[\text{Ln}(\text{dpa})_3]^{3-}$ is of particular interest because it fully satisfies the most frequent eight- and nine-coordination of Ln^{3+} [26]. Dipicolinates form a salt class of isomeric carboxylic acids containing heterocyclic nitrogen atom and two carboxylate groups that can coordinate the lanthanide cations [27]. This is in contrast to the β -diketone ligands that are commonly used to chelate Ln^{3+} and usually require an additional “neutral” ligand to obtain full coordination [26, 28].

Therefore, this work reports an efficient method to produce $[\text{Eu}(\text{dpa})_3]^{3-}$ complex encapsulated in dextrin microspheres by spray drying process, with a very intense red emission.

Experimental

Synthesis of europium dipicolinate complex $[\text{Eu}(\text{dpa})_3]^{3-}$

Eu^{3+} chloride solution was prepared by dissolution of Eu_2O_3 (99.99%—Rhône-Poulenc/Rhodia®) in concentrated chlorhydric acid. $[\text{Eu}(\text{dpa})_3]^{3-}$ was prepared by dissolving EuCl_3 (5.0 μmol) and 2,6-dpa (15.0 μmol) in 40.0 ml of water. The pH was adjusted to approximately 6 with diluted NH_4OH (Fig. 1) [29].

Fabrication of luminescent microspheres

To the complex solution, 200 mg of dextrin (ACROS®) was added and the final volume was completed to 50.0 mL with water. Later, the solution was heated at 70 °C and stirred for 1 h. The final solution was stirred at room temperature for 23 h.

The microencapsulation process was made by using the spray dryer built in our laboratory [30]. In this process, microdroplets from feed solution were produced through an ultrasonic atomizer (Vigo Ar®) and were dried inside a tubular vertical furnace (EDG®). The inlet and outlet temperatures (280 and 275 °C, respectively) for the drying chamber were chosen according to the polymer thermal features. A cellulose membrane (Millipore®) owing a 0.025- μm micropore diameter supported on a sintered plate filter was used in order to collect the particles. A vacuum pump (Heidolph®) was used to separate the dried material from the air, and a filter flask placed inside a vessel containing cold water was used to hold the condensed water vapor.

Microspheres characterization

Morphological

Dextrin- $[\text{Eu}(\text{dpa})_3]^{3-}$ microspheres prepared by spray drying were morphologically characterized by SEM on a Zeiss® EVO 50 microscope (EHT=15 kV). To acquire the

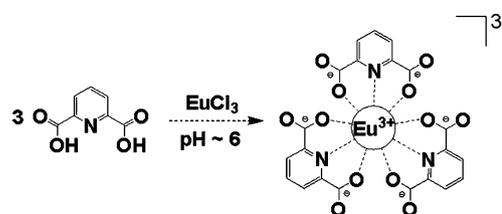


Fig. 1 Synthesis representation of $[\text{Eu}(\text{dpa})_3]^{3-}$

SEM images, the powder was dispersed in chloroform under ultrasound stirring, supported on an aluminum stub, and then coated by a gold thin layer using a sputtering system (Bal-Tec SCD-050) after drying. Diameter size distribution of particles was estimated from SEM images.

Spectroscopical

Emission and excitation spectra of $[\text{Eu}(\text{dpa})_3]^{3-}$ dextrin microspheres were recorded on a SPEX TRIAX 550 FLUOROLOG III spectrofluorometer. Emission spectra were corrected for the wavelength dependence of the detection system sensitivity by using a correction curve supplied by the equipment software. Excitation spectra were correct dividing the obtained spectrum by the lamp one that was generated simultaneously from an internal reference. The luminescence lifetime measurements were acquired using a SPEX 1934D phosphorimeter equipped with a pulsed xenon lamp as an excitation source. A reference solution of $[\text{Eu}(\text{dpa})_3]^{3-}$, prepared as described in the experimental section, was also analyzed by luminescence spectroscopy.

Results and discussion

Fabrication of luminescent microspheres

In the present work, we produced red luminescent microspheres composed by $[\text{Eu}(\text{dpa})_3]^{3-}$ loaded in dextrin. The dried powder was collected over the membrane as shown in Fig. 2.

Microspheres characterization

Morphological

The morphology of the $[\text{Eu}(\text{dpa})_3]^{3-}$ incorporated in dextrin microparticles were examined by SEM (Fig. 3).

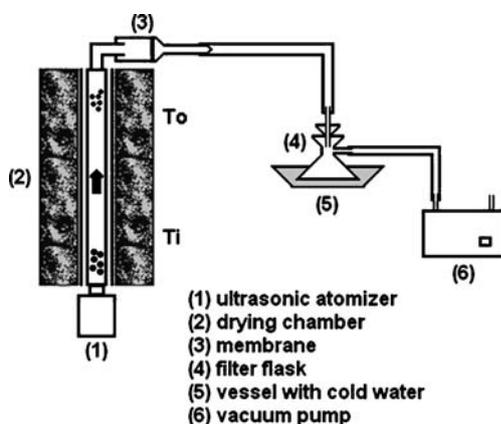


Fig. 2 Illustrative scheme of the co-current ultrasound spray drying system built in our laboratory [30]

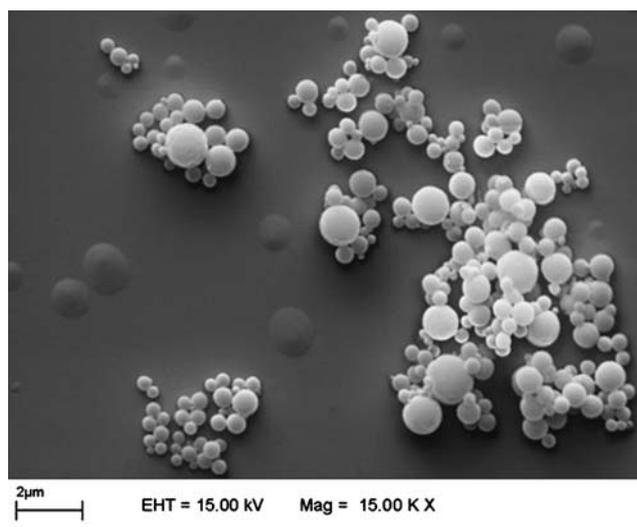


Fig. 3 SEM image of the $[\text{Eu}(\text{dpa})_3]^{3-}$ incorporated in dextrin microspheres using the developed ultrasonic spray drying technique

The SEM image reveals that the prepared particles have spherical shape with a smooth surface. Diameter size distribution of particles was estimated from SEM images [31]. In the total, a thousand particles were analyzed and the average diameter was estimated to be $0.6 \pm 0.3 \mu\text{m}$.

Luminescence

The $[\text{Eu}(\text{dpa})_3]^{3-}$ reference solution and the $[\text{Eu}(\text{dpa})_3]^{3-}$ complex encapsulated in dextrin microspheres, powder form, were analyzed by luminescence spectroscopy (Figs. 4 and 5, respectively).

In agreement with the discussion presented in the introduction, the recorded spectra for the reference solution, Fig. 4, evidence that Eu^{3+} emits via ligand excitation at the $\pi \rightarrow \pi^*$ absorption maximum (280 nm) followed by energy intramolecular transfer to the Eu^{3+} excited levels, thus enhancing the red emission. In addition, the strength of the luminescent signal is orders of magnitude stronger than that observed for direct excitation (395 nm) of the Eu^{3+} ion (Fig. 4). Moreover, the comparison between the $[\text{Eu}(\text{dpa})_3]^{3-}$ luminescence spectra before, Fig. 4, and after microspheres loading, Fig. 5, ensured that the spray drying process does not change the structure of the complex. It is important to emphasize that the $[\text{Eu}(\text{dpa})_3]^{3-}$ complex encapsulated in dextrin microspheres spectra, Fig. 5, were recorded at 77 K in order to minimize vibronic influences and increase spectral resolution, although the luminescent property of this powder at room temperature is so high as at 77 K.

It has been well established that at pH 6–7 the complexation is complete and the Eu^{3+} coordination sphere is made by six oxygen atoms forming a trigonal prism with three nitrogen atoms capping the faces and in a plane normal to the C_3 axis

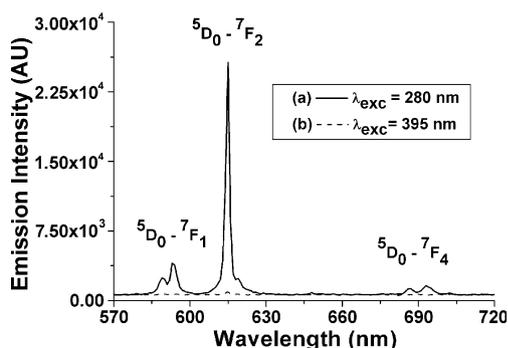


Fig. 4 Eu^{3+} emission spectra at room temperature of $[\text{Eu}(\text{dpa})_3]^{3-}$ ($10 \times 10^{-5} \text{ mol L}^{-1}$) reference solution with excitation at (a) ligand $\pi \rightarrow \pi^*$ absorption (280 nm) and (b) ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ Eu^{3+} transition (395 nm)

[32]. The symmetry of $[\text{Eu}(\text{dpa})_3]^{3-}$ is D_3 , allowing 0, 2, 1 and 3 lines for the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0,1,2,4}$ transitions, respectively [29]. From the evaluation of the set of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0-4}$ transitions of Eu^{3+} , shown in the emission spectra of Figs. 4 and 5, it is possible to confirm that in the synthesized complex the activator ion occupies a D_3 high symmetry site.

We also analyzed the ${}^5\text{D}_0$ emission lifetime of $[\text{Eu}(\text{dpa})_3]^{3-}$ aqueous solution and microencapsulated (Fig. 6). These lifetimes were estimated by first order decay fittings (Origin[®]) and are 1.75 and 1.66 ms, respectively. Our results agree with the literature, that

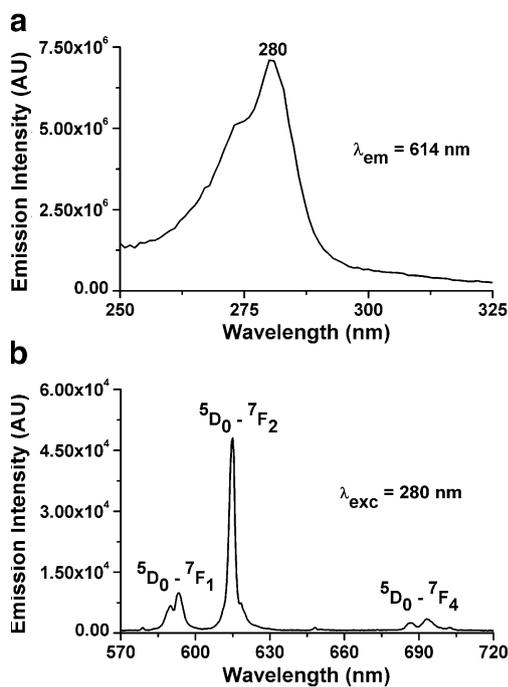


Fig. 5 Luminescent spectra at 77 K of $[\text{Eu}(\text{dpa})_3]^{3-}$ encapsulated in dextrin microspheres: **a** excitation spectrum with emission fixed at the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ Eu^{3+} maximum transition (614 nm). **b** Emission spectrum upon ligand $\pi \rightarrow \pi^*$ excitation (280 nm)

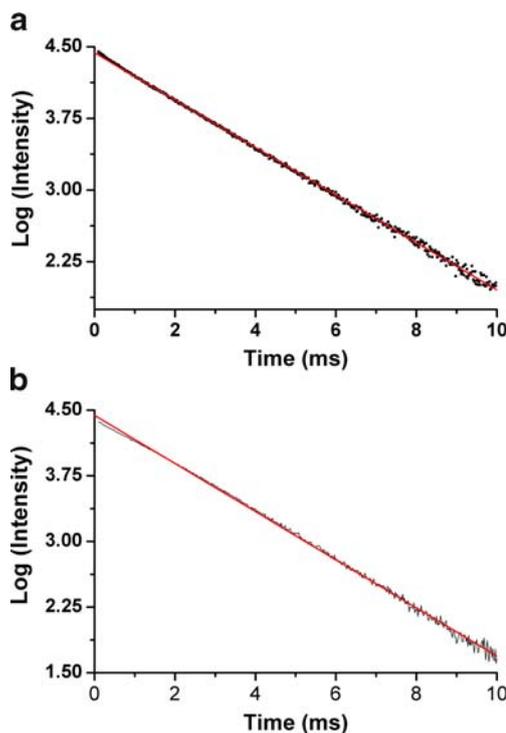


Fig. 6 Emission lifetimes of ${}^5\text{D}_0$ level of $[\text{Eu}(\text{dpa})_3]^{3-}$ **a** aqueous solution and **b** microencapsulated

reports a ${}^5\text{D}_0$ emission lifetime of 1.71 ms for $[\text{Eu}(\text{dpa})_3]^{3-}$ aqueous solution [26]. As the experimental decay curve of the ${}^5\text{D}_0$ level of Eu^{3+} could be fitted by a single exponential decay curve, it is possible to suggest that the activator center occupies a single or very similar symmetry sites even when the Eu-complex is encapsulated [33].

The excited state quantum efficiency was calculated from the emission spectra and from the luminescence lifetimes [34, 35]. We used the following equation to obtain the ${}^5\text{D}_0$ quantum efficiency:

$$\phi = A_r / (A_r + A_{nr}) \quad (1)$$

where ϕ is the excited state quantum efficiency, and A_r and A_{nr} are ${}^5\text{D}_0$ the radiative and non-radiative decay rates, respectively.

If we consider,

$$\tau^{-1} = A_r + A_{nr} \quad (2)$$

where τ is the ${}^5\text{D}_0$ emission lifetime, the Eq. 1 becomes,

$$\phi = A_r \cdot \tau \quad (3)$$

The A_r value was obtained by summing all the A_{0j} radiative rates for each ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ transition ($A_r = \sum A_{0j}$). In

the case of Eu^{3+} , $A_r = A_{01} + A_{02} + A_{03} + A_{04}$, which is related to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions ($0 \leq J \leq 4$).

$$A_r = \frac{A_{01}E_{01}}{S_{01}} \left(\sum_{J=1}^4 \frac{S_{0J}}{E_{0J}} \right) \quad (4)$$

where E_{0J} (cm^{-1}) is the average transition energy and S_{0J} is the integrated intensity of the emission transition. Moreover, it is well known that the nature of magnetic-dipole transitions is independent of the crystal field surrounding the metal ion. So, the radiative rate of A_{01} is estimated to be 50 s^{-1} [34, 35].

From Eq. 3 and the previous calculated emission lifetime, we were able to obtain the ${}^5\text{D}_0$ quantum efficiencies. According to the calculus, the quantum efficiencies are 50% and 37.4% for $[\text{Eu}(\text{dpa})_3]^{3-}$ aqueous solution and microencapsulated, respectively.

The predominance of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition displayed by $[\text{Eu}(\text{dpa})_3]^{3-}$ encapsulated in dextrin microspheres results in the red emission, whose CIE chromaticity coordinates ($x=0.68$ and $y=0.31$) attend perfectly the requirement for the red standard ($x>0.65$) [18].

Conclusion

First of all, we have succeeded in encapsulating a well-known europium coordination complex in a polymeric matrix by ultrasound spray drying, resulting in luminescent microspheres. The recorded spectra evidenced that Eu^{3+} ions emit via ligand excitation at the $\pi \rightarrow \pi^*$ transition (280 nm) followed by an energy intramolecular transfer to the Eu^{3+} excited levels, thus enhancing the red emission (antenna effect). In addition, the intensity of the luminescent signal is orders of magnitude stronger than that observed for direct excitation of the Eu^{3+} ion.

The comparison between $[\text{Eu}(\text{dpa})_3]^{3-}$ luminescence spectra before and after the microspheres loading ensured that the spray drying process does not change the structure of the complex. $[\text{Eu}(\text{dpa})_3]^{3-}$ -loaded dextrin emission lifetime and quantum efficiency were only slightly lower. The microencapsulation process enables the formation of a protective matrix around the encapsulated material. In this sense, we have applied the ultrasonic spray drying encapsulation technique to protect the complex from factors that might cause its deterioration, thereby extending the phosphor shelf time and making it easy to manipulate.

Acknowledgements The authors gratefully thank Dr R. F. Silva for helpful discussions and FAPESP for financial support and scholarships.

References

- Loksuwan J (2007) Characteristics of microencapsulated b-carotene formed by spray drying with modified tapioca starch, native tapioca starch and maltodextrin. *Food Hydrocoll* 21(5–6):928–935
- Braga GK, Oliveira WP (2007) Manufacturing drug loaded chitosan microspheres by spray drying: development, characterization, and potential use in dentistry. *Dry Technol* 25(2):303–310
- Ré MI (1998) Microencapsulation by spray drying. *Dry Technol* 16(6):1195–1236
- Mujumdar AS (1995) Handbook of industrial drying. Marcel Dekker, New York
- www.buchi.com, accessed on May 2007
- Freitas S, Merkle HP, Gander B (2004) Ultrasonic atomisation into reduced pressure atmosphere-envisaging aseptic spray-drying for microencapsulation. *J Control Release* 95(2):185–195
- Asaji K (1979) Microcapsule processing and technology. Marcel Dekker, New York
- Giunchedi P, Conte U (1995) Spray-drying as a preparation method of microparticulate drug delivery systems: an overview. *S. T.P. Pharma Sci* 5(4):276–290
- Okuyama K, Lenggoro IW (2003) Preparation of nanoparticles via spray route. *Chem Eng Sci* 58(3–6):537–547
- Avvaru B, Patil MN, Gogate PR, Pandit AB (2006) Ultrasonic atomization: effect of liquid phase properties. *Ultrasonics* 44(2):146–158
- Suh WH, Suslick KS (2005) Magnetic and porous nanospheres from ultrasonic spray pyrolysis. *J Am Chem Soc* 127(34):12007–12010
- Abdullah M, Iskandar F, Shibamoto S, Ogi T, Okuyama K (2004) Preparation of oxide particles with ordered macropores by colloidal templating and spray pyrolysis. *Acta Mater* 52(17):5151–5156
- Ré MI (2006) Formulating drug delivery systems by spray drying. *Dry Technol* 24(4):433–446
- Xie Y-L, Zhou H-M, Zhang Z-R (2007) Effect of relative humidity on retention and stability of vitamin A microencapsulated by spray drying. *J Food Biochem* 31(1):68–80
- Desai KGH, Park HJ (2005) Encapsulation of vitamin C in tripolyphosphate cross-linked chitosan microspheres by spray drying. *J Microencapsul* 22(2):179–192
- Chiou D, Langrish TAG (2007) Development and characterisation of novel nutraceuticals with spray drying technology. *J Food Eng* 82(1):84–91
- Desai KG (2007) Properties of tableted high-amylose corn starch-pectin blend microparticles intended for controlled delivery of diclofenac sodium. *J Biomater Appl* 21(3):217–233
- Santa-Cruz PA, Teles FS. Spectra Lux Software v.2.0, Ponto Quântico 2003, Nanodispositivos/RENAMI.
- Moynihan S, Lacopino D, O'Carroll D, Doyle H, Tanner DA, Redmond G (2007) Emission colour tuning in semiconducting polymer nanotubes by energy transfer to organo-lanthanide dopants. *Adv Mater* 19(18):2474–2479
- Panigrahi BS (2002) A fluorimetric study of terbium, europium and dysprosium in aqueous solution using pyridine carboxylic acids as ligands. *J Alloys Compd* 334(1–2):228–231
- Porcher P (1999) In: Saez R, Caro PA (eds) Rare earths. Editorial Complutense, Madrid
- Lehn JM (1990) Perspectives in supramolecular chemistry—from molecular recognition towards molecular information processing and self-organization. *Angew Chem Int Ed* 29(11):1304–1319
- Zhao B, Chen X-Y, Cheng P, Liao D-Z, Yan S-P, Jiang Z-H (2004) Coordination polymers containing 1D channels as selective luminescent probes. *J Am Chem Soc* 126(47):15394–15395
- Cicillini SA, Calefi PC, Neri CR, Nassar EJ, Serra OA (1999) Use of polymeric resin in the formation of SiO_2 hybrid gels. *J Non-Cryst Solids* 247(1–3):114–119

25. DeOliveira E, Neri CR, Serra OA, Prado AGS (2007) Antenna effect in highly luminescent Eu^{3+} anchored in hexagonal mesoporous silica. *Chem Mater* 19(22):5437–5442
26. George MR, Golden CA, Gossel MC, Curry RJ (2006) Modified dipicolinic acid ligands for sensitization of europium(III) luminescence. *Inorg Chem* 45(4):1739–1744
27. Puntus LN, Zolin VF, Babushkina TA, Kutuza IB (2004) Luminescence properties of isomeric and tautomeric lanthanide pyridinedicarboxylates. *J Alloy Compd* 380(1–2):310–314
28. Binnemans K (2005) Handbook on the physics and chemistry of rare earths. Elsevier, Amsterdam
29. Fernandes A, Jaud J, Dexpert-Ghys J, Brouca-Cabarrecq C (2001) Study of new lanthanide complexes of 2,6-pyridinedicarboxylate: synthesis, crystal structure of $\text{Ln}(\text{Hdipic})(\text{dipic})$ with $\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$, luminescence properties of $\text{Eu}(\text{Hdipic})(\text{dipic})$. *Polyhedron* 20(18):2385–2391
30. Luz PP, Pires AM, Serra OA (2007) A low-cost ultrasonic spray dryer to produce spherical microparticles from polymeric matrices. *Quim Nova* 30(7):1744–1746
31. ImageJ 1.38 bundled with Java 1.6.0_02.
32. Gmelin L (1980) Gmelin Handbuch der Anorganischen Chemie—Sc, Y, La–Lu rare earth elements (Part D1—coordination compounds). Springer, Berlin
33. Blasse G, Grambmaier BC (1994) Luminescent materials. Springer, Berlin
34. de Mello Donegá C, Alves Júnior S, de Sá GF (1997) Synthesis, luminescence and quantum yields of $\text{Eu}(\text{III})$ mixed complexes with 4,4,4-trifluoro-1-phenyl-1,3-butanedione and 1,10-phenanthroline-N-oxide. *J Alloys Compd* 250(1–2):422–426
35. Kodaira CA, Brito HF, Malta OL, Serra OA (2001) Luminescence and energy transfer of the europium (III) tungstate obtained via the Pechini method. *J Lumin* 101(1–2):11–21