β-Diketonates of Eu\(^{3+}\), Red Phosphors, Supported on Sol-Gel Functionalised Silica

Eduardo J. Nassar \(^{a,b}\), Osvaldo A. Serra \(^a\), Paulo S. Calefi \(^a\),
Cynthia M.C.P. Manso \(^a\), Cláudio R. Neri \(^a\)

\(^a\)Rare Earth Laboratory, Chemistry Department, FFCLRP, University of São Paulo,
14040-901 Ribeirão Preto - SP, Brazil
\(^b\)Chemistry Institute - UNESP - Araraquara - SP, Brazil

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Silica gel was functionalised with chloropropyl groups through the sol-gel process and then a \(\beta\)-diketone was incorporated into the support. Afterwards, Eu\(^{3+}\) ion and its chelates of 1,10-phenanthroline (phen) and 2,2\(^'\)-bipyridine (bpy), red phosphors, were supported on such silica. Luminescence studies of Eu\(^{3+}\) bound to this new material have shown that there is an increase in the intensity of the emission when the ion is isolated by ligands in the silica matrix. The energy transfer from the ligands phen and bpy to Eu\(^{3+}\) ion was observed in the excitation spectra, which present new bands ascribed to the ligands and/or complex. The Eu\(^{3+}\)-functionalised silica was characterised by TGA and FTIR. TGA analysis showed that there is a large loss of mass around 300 °C, which is ascribed to the organic part of the material. The FTIR spectra presented the vibration modes for Si-C and -CH\(_2\)-. The luminescent properties of the ions surrounding the Eu\(^{3+}\) ion were studied. The decay curve displayed a bi-exponential behaviour, indicating that there is more than one site of Eu\(^{3+}\) on the surface of the silica.

Keywords: rare earth, sol-gel process, functionalised silica, luminescence, red phosphor

1. Introduction

A light-conversion device consists of two discrete components: an “antenna” (light harvesting ligand) and an emitter. For them to function, an intercomponent energy transfer must occur as efficiently as possible \(^1\). Macrocyclic ligands containing heterobiaryl groups bound to Eu\(^{3+}\) and Tb\(^{3+}\) are among the most frequently studied systems. In these complexes, the light is harvested by the heterobiaryl groups, transferred to the rare earth ion and then emitted. The macrocyclic framework protects the rare earth ion and minimises non-radiative deactivations.

In recent years, luminescent lanthanide complexes have been used in photonic devices where light is absorbed by the ligand and energy is transferred to the emitting metal ion (antenna effect) \(^2-6\). This effect involves three factors: i) intensity of ligand absorption; ii) efficiency of ligand-metal energy transfer and iii) efficiency of metal emission. Many luminescent lanthanide complexes have been synthesised and their chemical and photophysical properties have been modified through their interaction with different hosts (e.g. a solid interface).

Oxide surfaces have been used as a host for organic and inorganic molecules and the interaction between the support and the guest molecules \(^7-9\) has been studied. Inorganic supports have been utilised due to their rigidity, stability and inertness. Materials such as ion exchange resins \(^10\), zeolites \(^11,12\), clay \(^13\) and silica \(^2,14,16\) have been used.

In the last decades, the sol-gel technology has called the attention of countless researchers due to its attractive preparation route, which is carried out at low temperature \(^17-20\). The sol-gel process has been employed in important technological processes such as the production of optical fibres and chemical sensors, just to mention some \(^21\). Oxide surfaces modified by organic molecules have also been finding several applications \(^22-24\).

In this work, we have functionalised silica gel with chloropropyl groups either through the sol-gel process or through its treatment with 3-chloropropyltrimethoxsilane (TMOSCl). Then one of the following \(\beta\)-diketones antenna ligands: 2,4-pentanediene (acac), 4,4,4-trifluoro-1-phenyl-
1,3-butanedione (bta), dibenzoylmethylene (dbm) or 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa) was covalently bound to the functionalised silica, so that the latter served as a host for the antenna. Afterwards, Eu$^{3+}$ ion was supported on such silica. Since the energy of the first triplet excited level of the “harvester” determines the energy transfer to Eu$^{3+}$, we also added the heterobiaryal molecules 1,10-phenantrline and 2,2′-bipyridine to the silica materials, so that they functioned as an extra antenna (Fig. 1). When the silica gel was functionalised through the sol-gel technique, it was possible to control the amount of chloropropyl groups on the support and, consequently, the quantity of the covalently bound “antenna” ligands on the matrix. This improved the light emission through the rare earth ion, which is not possible to attain through the conventional silica treatment.

2. Experimental

Silica functionalised with 3-chloropropyl groups was prepared through the sol-gel process, using a TEOS (tetraethylorthosilicate) : TMOSCl 1:1 molar ratio and characterized as described by Nassar et al.\textsuperscript{25}. The reagents were purchased from Aldrich. TEOS and TMOSCl were added to the silica in dry ethanol and then acidic water was added to this solution under stirring. The solvent was evaporated at 30 °C and a white solid was obtained. The solid was dried at 60 °C, overnight.

β-diketone (acac, bta, dbm and hfa) ligation to the functionalised silica carried out with the ligands in their sodium salt form\textsuperscript{26}. This procedure led to the obtention of silica functionalised with propyl acetyl (APG), benzoyl (BPG), dibenzoyl (DPG) and hexafluoro (HPG) ligands. The preparation of APGEu, BPGEu, DPGEu and HPGEu, as well as phen and bpy incorporation, have been previously described\textsuperscript{2}.

The functionalised silica was characterised by TGA using Thermal Analyst 2100-TA Instruments SDT 2960 - Simultaneous DTA-TGA analyser, in air with a heating rate of 10 °C/min from 25 to 900 °C. FTIR spectra were recorded on the Nicolet FT-IR SZDX spectrophotometer in KBr pellets.

The luminescence data were obtained on a Spex Fluorolog II spectrofluorometer at room temperature. The sample was placed in a quartz capillary tube (I.D. = 1.0 mm). The emission was collected at 90 °C from the excitation beam. The slits were placed at 2.0 and 0.5 mm for excitation and emission, respectively, giving a band pass of 7 and 0.9 nm; filters: Oriel 59816 (exc.) and Corning 97612 (em.).

3. Results and Discussion

TGA for the silica prepared through the sol-gel process presented a loss of mass of 10% (w/w) around 98 °C, which is ascribed to water molecules. For the other samples we observed an increase in the loss of mass at temperatures above 280 °C. This shows that the silica was functionalised with propyl β-diketonate groups.

In the DTA curve we observed exothermic transformations with a broad peak between 280-450 °C. Such large exothermic transformation indicates the presence of a non-crystalline solid\textsuperscript{17}.

The FTIR spectra of the samples displayed a characteristic strong absorption band due to the Si-O vibrations (1060 and 1082 cm$^{-1}$). At 1275 cm$^{-1}$, a sharp peak due to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{silica-supported_light_harvesting_devices.png}
\caption{Schematic representation of the silica-supported light harvesting devices.}
\end{figure}
Si-C bond stretching was found. The absorption at 867 cm\(^{-1}\) is due to Si-C bond deformation. At higher frequencies, the asymmetric and symmetric stretching of the methyl C-H bond were detected at 2957 and 2850 cm\(^{-1}\), respectively. This result confirms that the Si-C bond was not broken during the sol-gel process.

The excitation maximum of the Eu\(^{3+}\) ion in the samples without the phen or bpy ligands is at 393 nm, which corresponds to the \(\text{^5}L_6\) level of Eu\(^{3+}\). All emission spectra present the characteristic transitions arising from the \(\text{^5}D_0\) to the \(\text{^7}F_j\) level (\(J = 0, 1, 2, 3 \) and \(4\)) manifolds, excited at their maxima.

The excitation maximum for the samples containing the bpy ligand was ascribed to the ligand itself, since the absorption maximum of free bpy occurs at 309 nm. In the sample containing the phen ligand, the excitation maximum was ascribed to the Eu-phen complex.

The energy transfer from the ligand to Eu\(^{3+}\) occurs via triplet states. It was noticed that in the presence of the ligands phen and bpy, the emission intensity increases due to energy transfer from the ligand to the Eu\(^{3+}\) ion. Moreover, the removal of H\(_2\)O and/or OH around the Eu\(^{3+}\) ion reduces vibrational losses.

The \(\text{^5}D_0\) level of the ion can be depopulated through water, ligands and matrix by vibrational interactions\(^{27}\). The number of water molecules (or OH groups) can be formulated as proposed by Horrocks\(^{28}\) \(q = 1.05 (\tau^{-1}\text{H}_2\text{O} - \tau^{-1}\text{D}_2\text{O})\) even in the absence of measurements in deuterated systems\(^{29}\), considering \(\tau\text{D}_2\text{O} = 50\) ms. In Table 1, we show the experimental lifetimes measurements for hypersensi-

| Samples       | \(\tau\) (ms) | q | Samples       | \(\tau\) (ms) | q |
|---------------|--------------|---|---------------|--------------|---|
| AGPEu         | 0.29         | 3 | DPGEu         | 0.16         | 6 |
| APGEubpy      | 0.52         | 2 | DPGEubpy      | 0.30         | 3 |
| APGEuphen     | 0.78         | 1 | DPGEuphen     | 0.38         | 2 |
| BPGEu         | 0.26         | 4 | HPGEu         | 0.25         | 4 |
| BPGEubpy      | 0.60         | 1 | HPGEubpy      | 0.34         | 3 |
| BPGEuphen     | 0.55         | 2 | HPGEuphen     | 0.42         | 2 |

Figure 2. Emission and excitation spectra of the Eu\(^{3+}\) ion in the sample (a) APGEu, (b) BPGEu, (c) DPGEu and (d) HPGEu.; \(\lambda_{\text{em}} = 612\) nm and \(\lambda_{\text{exc}} = 393\) nm.
tive the $^5D_0 \rightarrow ^7F_2$ transitions of Eu$^{3+}$ and the number of water molecules calculated by Horrocks formula, for all the samples.

All samples presented a decay curve with a bi-exponential behaviour, but we calculated the number of water molecules for the first decay only, since it is responsible for

**Figure 3.** Emission and excitation spectra of the Eu$^{3+}$ ion in the sample (a) APGEu bpy, $\lambda_{em} = 612$ nm and $\lambda_{exc} = 314$ nm; (b) BPGEu bpy, $\lambda_{em} = 612$ nm and $\lambda_{exc} = 316$ nm; (c) DPGEu bpy, $\lambda_{em} = 612$ nm and $\lambda_{exc} = 313$ nm; and (d) HPGEu bpy, $\lambda_{em} = 612$ nm and $\lambda_{exc} = 314$ nm.

**Figure 4.** Emission and excitation spectra of the Eu$^{3+}$ ion in the sample (a) APGEu phen, $\lambda_{em} = 612$ nm and $\lambda_{exc} = 344$ nm; (b) BPGEu phen, $\lambda_{em} = 612$ nm and $\lambda_{exc} = 349$ nm; (c) DPGEu phen, $\lambda_{em} = 612$ nm and $\lambda_{exc} = 345$ nm and (d) HPGEu phen, $\lambda_{em} = 612$ nm and $\lambda_{exc} = 350$ nm.
the major contribution. This behaviour reflects the non-homogeneity of the luminescent species on the silica matrix and is in agreement with the observed asymmetric band corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition.

Figures 2, 3 and 4 present the emission and excitation spectra for all the samples containing Eu$^{3+}$ and phen and bpy ligands, respectively.

The band corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is more intense than that due to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, for all the samples. This is an indication that the symmetry around the Eu$^{3+}$ ion does not contain a centre of inversion$^{30-33}$. The presence of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition indicates that Eu$^{3+}$ is located in one of the Cnv, Cn or Cs symmetry groups$^{29}$.

4. Conclusion

To sum up, in this work we have made use of the sol-gel process to obtain functionalised silica where it was possible to better control the amount of the reactive chloro alkyl groups that bind to the support. Consequently we have been able to build light harvesting materials containing the desired amount of antenna ligands. The new synthetic procedure presented in this paper resulted in the preparation of better silica based red luminescent materials.

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