*Journal of Alloys and Compounds, 207/208* (1994) 454–456
*JALCOM 3066*

# Organic complexes of $Eu^{3+}$ supported in functionalized silica gel: highly luminescent material

Osvaldo A. Serra, Eduardo J. Nassar, Gilson Zapparolli and Ieda L.V. Rosa
*Chemistry Department, FFCLRP University of São Paulo, Av. Bandeirantes 3900, CEP 14049-901 Ribeirao Preto SP (Brazil)*

## Abstract

Eu III ion and its chelates of 1,10-phenantroline (phen), 2,2-bipyridine (bpy), benzoyltrifluoroacetone (bfa) and acetylacetone (acac) were supported on silica gel (SG) and silica gel functionalyzed with propyl imidazole (IPG). The luminescence studies of Eu III showed an increase in the intensity and lifetime of the Eu IIII $^5D_o \rightarrow {}^7F_2$ transition in the presense of IPG, when compared with SG. The energy transfer from bfa and phen to the Eu III ion was also detected. In these cases, an increase in the intensity and lifetime of Eu III related to the direct excitation at the metallic ion was observed.

## 1. Introduction

Recent progress has been made in the design of lanthanide complexes in which light is absorbed by the ligands and energy is transferred to the emitting metal ion (antenna effect) [1,2]. Many luminescent lanthanide complexes have been synthesized and their chemical and photophysical properties modified by interaction with hosts such as solid interfaces [3]. In these cases, the luminescence efficiency of the $Eu^{3+}$ ion is markedly increased compared to that of the aqueous ion. The organic molecules shield the $Eu^{3+}$ and displace the OH and/or $H_2O$ groups that provide the radiationless decay [4]. Moreover, the ligands have a larger absorption bands than $Eu^{3+}$, amplifying the range of excitation energies. Silica gel glass with trapped $Eu^{3+}$ has already been studied by Reisfeld [5].

In this work, we have studied the luminescent properties of $Eu^{3+}$ and its chelates with 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy), benzoyltrifluoroacetone (bfa) and acetylacetone (acac) supported on silica gel (SG) and silica gel functionalized with propyl imidazole (IPG).

## 2. Experimental section

### 2.1. *Preparation of SG–Eu and IPG–Eu*

All the syntheses were carried out in methanolic medium. A 0.02 M stock solution of $EuCl_3$ was prepared from the oxide. The reaction between 1.5 ml of the $Eu^{3+}$ solution and 500 mg of silica gel (SG) or functionalized silica gel (IPG) occurred under agitation for 30 min. The solid was washed with methanol and dried at 60 °C during 1 h. The IPG was prepared as described in the literature [6].

The ligands phen, bpy, bfa and acac were individually incorporated by the interaction of 1.25, 1.00, 0.70 and 1.25 ml, respectively, of 0.02 M methanolic solutions with 100 mg of SG–Eu or IPG–Eu and processed as above to yield the final solids.

### 2.2. *Luminescent data*

All the luminescent data were obtained with a SPEX FLUOROLOG II spectrofluorometer at room and liquid nitrogen temperatures. The excitation spectra were corrected.

## 3. Results and discussion

Table 1 shows the excitation maxima for all samples at ambient and liquid nitrogen temperatures. The excitation maxima in the SG– and IPG–Eu with the ligands were assigned to the absorption of the ligands. The compounds without the ligands showed the ex-

TABLE 1. Excitation maxima ($\lambda_{max}$) of the supported compounds in IPG and SG for the $Eu^{3+}$ transition $^5D_0 \rightarrow {}^7F_2$ with emission at 612 nm, at 77 K

| IPG–$Eu^{3+}$ $\lambda_{max}$ (nm) | | | | | SG–$Eu^{3+}$ $\lambda_{max}$ (nm) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| phen | bpy | bfa | acac | – | phen | bpy | bfa | acac | – |
| 323 | 304 | 334 | 317 | 391 | 332 | 303 | 328 | 316 | 391 |

*SSDI* 0925-8388(93)03066-R

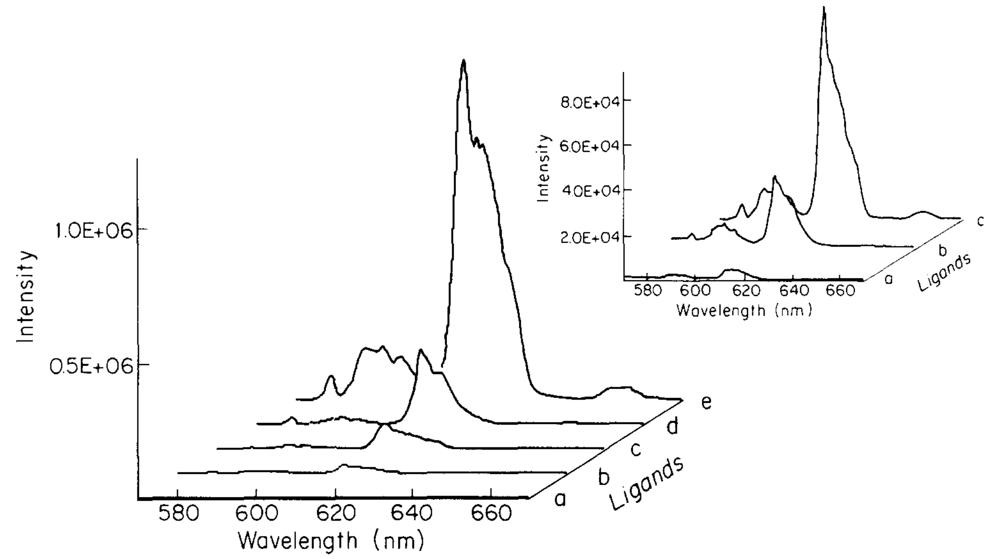

Fig. 1. Emission spectra of the $Eu^{3+}$ IPG compounds at 77 K. (a) IPG–Eu, (b) IPG–Eu–acac, (c) IPG–Eu–bpy, (d) IPG–Eu–bfa, (d) IPG–Eu–phen, for excitation in the maxima indicated in Table 1.

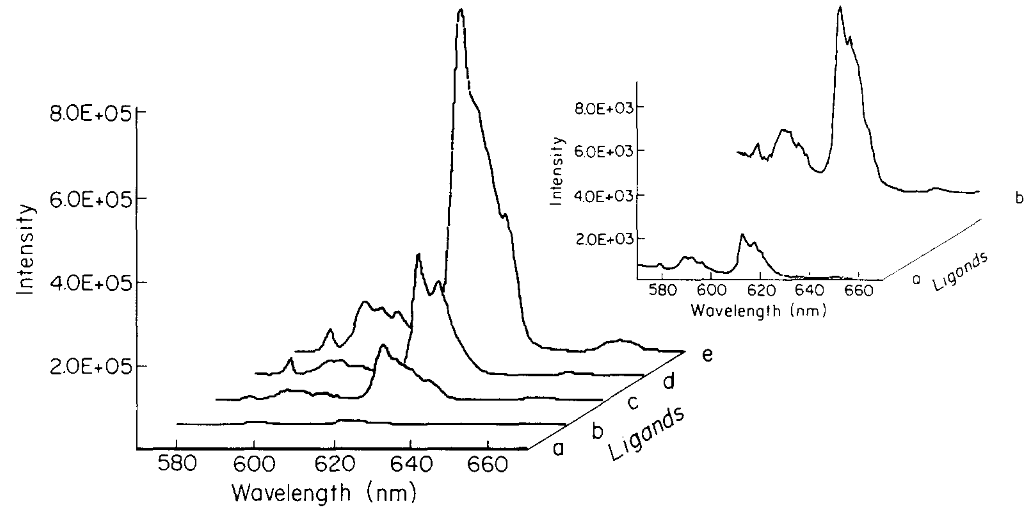

Fig. 2. Emission spectra of $Eu^{3+}$ SG compounds at 77 K. (a) SG–Eu, (b) SG–Eu–acac, (c) SG–Eu–bpy, (d) SG–Eu–bfa, (e) SG–Eu–phen, for excitation in the maxima indicated in Table 1.

TABLE 2. Lifetime, $\tau$ (ms), for the emission of the $Eu^{3+}$ transition $^5D_0 \rightarrow {}^7F_2$ in the samples, for the excitation in the maxima indicated in Table 1

| IPG–$Eu^{3+}$ $\lambda_{max}$ (nm) | | | | | SG–$Eu^{3+}$ $\lambda_{max}$ (nm) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| phen | bpy | bfa | acac | – | phen | bpy | bfa | acac | – |
| 1.07[a] | 0.94 | 0.77 | 0.74 | 0.30 | 0.98 | 0.48 | 0.42 | 0.40 | 0.26 |
| 1.24[b] | 1.18 | 0.98 | 0.86 | 0.39 | 1.10 | 0.47 | 0.44 | 0.57 | 0.33 |

[a] Room temperature ≈298 K. [b] Liquid nitrogen temperature 77 K.

citation maximum at 391 nm due to the $Eu^{3+}$ $^7F_0 \rightarrow {}^5L_6$ transition.

The emission spectra in the region of the $^5D_0 \rightarrow {}^7F_{0,1,2,3}$ transitions are given in Fig. 1 for the IPG–Eu system and in Fig. 2 for the SG–Eu system. For each spectrum, the excitation wavelength corresponded to the maximum in Table 1. The intensity of the $0 \rightarrow 2$ transition was found to increase in the order Gel–Eu < Gel–Eu–acac < Gel–Eu–byp < Gel–Eu–bfa < Gel–Eu–phen. This behavior is directly related to the capacity of the ligands for absorbing and transferring energy to the $Eu^{3+}$. The propyl imidazole removes some of the $H_2O$ molecules and OH groups of the silica around the $Eu^{3+}$, attenuating the vibrational losses. The addition of the ligands increases the emission intensity in both systems. The ligands bind to the $Eu^{3+}$, making the system more rigid, and replace some or all of the $H_2O$ or OH groups bound to the metal ion. The intensity of the emission is thus increased by the more efficient energy transfer through the organic system and the reduction of the OH vibrations which are good quenchers of the luminescence. The breadth of the peaks even at 77 K is much larger than the instrumental resolution (5 Å) and indicates the existence of a number of different states for the $Eu^{3+}$ in all the systems.

The lifetimes the $Eu^{3+}$ $^5D_0 \rightarrow {}^7F_2$ emission in SG and IPG in the absence and in the presence of the ligands are shown in Table 2. At liquid nitrogen temperature, they are larger than at room temperature, which is a reflection of the reduction of loss by vibrational mechanisms. The values decrease from phen to acac but the lifetimes are always greater than for the Gel–Eu systems without additional ligand. The maximum possible number of water molecules or OH groups can be estimated from the correlation due to Horrocks [6] even in the absence of measurements in deuterated systems ($n = q(\tau^{-1}H_2O - \tau^{-1}D_2O)$ and as $q \sim 1$ or 2 for $Eu^{3+}$ and $H_2O$ or OH groups, the value of $\tau^{-1}$ sets an upper limit on $n$). Thus, the maximum number of bound water molecules can be estimated to be one for the IPG–Eu–ligand systems, three for IPG–Eu, one for SG–Eu–phen, two for SG–Eu–bfa, –bpy, –acac and four for SG–Eu. (The maximum number of OH groups could be twice each value.)

## Ackowledgment

This work has been supported by CAPES, CNPq, FAPESP and FINEP.

## References

1 N. Sabbatini, A. Mecati, M. Guardigli, V. Balzani, J.-M. Lehn, R. Zeissel and R. Ungaro, *J. Luminesc., 48&49;* (1991) 463.

2 N. Sabbatini, M. Guardigli and J.-M. Lehn, *Coord. Chem. Rev., 123* (1993) 201.

3 M.P. Hazenkamp, G. Blasse and N. Sabbatini, *J. Phys. Chem., 95* (1991) 783.

4 W. DeW. Horrocks Jr. and D.R. Sudnick, *Acc. Chem. Res., 14* (1981) 384.

5 D. Levy, R. Reisfeld and D. Avnir, *Coord. Chem. Rev., 109* (1984) 593.

6 O. Leal, D.L. Anderson, R.G. Bowman, F. Basolo and R.L. Burwell, *J. Am. Chem. Soc., 97* (1975) 5125.