## Europium(III) mixed complexes with $\beta$ -diketones and *o*-phenanthroline-*N*-oxide as promising light-conversion molecular devices

## Celso de Mello Donegá,\* Severino A. Junior and Gilberto F. de Sá

Departamento de Química Fundamental-CCEN-UFPE, 50670-901, Recife-PE, Brazil

The new complex tris(4,4,4-trifluoro-1-phenyl-1,3-butanedionate)(1,10-phenanthroline-*N*-oxide)europium(III) shows a remarkable luminescence quantum yield at room temperature (66%) upon ligand excitation and a long  ${}^{5}D_{0}$  lifetime (670 µs), which makes it a promising light-conversion molecular device.

The interest in the photophysical properties of lanthanide complexes with organic ligands has been greatly intensified after Lehn's proposition that such complexes could be seen as light-conversion molecular devices (LCMD), coining the term antenna effect to denote the UV-to-visible light conversion process involving distinct absorbing (ligands) and emitting (lanthanide ion) components of the supramolecular species. thus overcoming the very small absorption coefficients of the lanthanide ions. Efficient LCMDs may find many applications, such as luminescent labels in fluoroimmunoassays,<sup>2</sup> lasers,<sup>3</sup> or cheaper phosphors for fluorescent lighting.<sup>4</sup> Thus, the design of complexes of lanthanide ions as efficient LCMDs has become an important theme in supramolecular and coordination chemistry, being pursued by several groups.5,6 The strategy adopted by our group to achieve this goal is based upon both theoretical and experimental approaches.<sup>6–8</sup> In addition, the complexes which we have chosen to investigate have the advantage of being simpler to synthesize than those involving cryptands and macrocyclic ligands.5

Recently, highly luminescent complexes of Eu<sup>III</sup> and Tb<sup>III</sup> with mixed ligands such as picolinic acid *N*-oxide and 2,2':6',2''-terpyridine,<sup>8</sup> or 3-aminopyrazine-2-carboxylic acid and 2,2'-bipyridine *N*,*N'*-dioxide<sup>6</sup> have been synthesised and characterized as efficient LCMDs. Theoretical calculations suggest that the improved efficiencies of complexes containing N-oxide group moieties might be due to the near resonance between the lowest triplet levels and the excited levels of the metal ion.<sup>7</sup>

Considering the points above, we have synthesised the new complex tris(4,4,4-trifluoro-1-phenyl-1,3-butanedionate) (1,10-phenanthroline-N-oxide)europium(III) [Eu(btfa)3-(phenNO).<sup>†</sup> The ligand phenNO was prepared following the method reported by Corey et al.9 The purified phenNO ligand was characterized by C, H, N microanalysis, melting point, IR spectroscopy, and gas chromatography. The starting chemicals were Eu<sub>2</sub>O<sub>3</sub> 99.9% Aldrich, btfa 99% Aldrich and 1,10-phenanthroline monohydrate 99% Aldrich. The ligands were recrystallized in ethanol. Solvents (Aldrich or Merck, reagent grade or better) were used as supplied. The UV-VIS absorption spectra were recorded with a Perkin-Elmer UV-VIS spectrophotometer Lambda 6 Model 2688-002. The IR absorption spectra were measured on a Bruker IF566 FTIR spectrophotometer, using KBr pellet and Nujol mull techniques. The IR spectra provided good evidence that the metal ion is coordinated to the ligands via the C=O and N-O groups, ‡ and that there are no water molecules coordinated to the Eu<sup>III</sup> ion in [Eu(btfa)<sub>3</sub>-(phenNO)]. The coordination is also confirmed by the UV-VIS absorption spectra

The excitation and luminescence spectra and the quantumyield measurements were obtained by using a SPEX Fluorolog DM3000F spectrofluorometer with double-grating 0.22m SPEX 1680 monochromators, and a 450 W Xe lamp as the excitation source. This set-up is equipped with an Oxford LF205 liquid-helium flow cryostat, allowing for measurements down to 4.2 K. The spectra are corrected for the instrumental response. The excitation and luminescence spectra of [Eu-(btfa)<sub>3</sub>(phenNO)] at 4.2 K are shown in Figs. 1 and 2, respectively. Apart from thermal broadening of the lines, the spectra are essentially the same at room temperature. The excitation spectrum evidences a ligand-to-metal energy transfer, since the most intense feature is a broad band corresponding to transitions populating ligand-centred excited states. The emission spectrum consists of Eu<sup>3+</sup> transitions only (<sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>J</sub>,



**Fig. 1** The excitation spectrum of the  ${}^{5}D_{0}$  emission ( $\lambda_{em} = 610.7$  nm) of Eu<sup>3+</sup> in [Eu(btfa)<sub>3</sub>(phenNO)] at 4.2 K. The labels refer to the *J* values of the final level of the excitation transitions  ${}^{7}F_{0} \rightarrow {}^{5}D_{J}$  of Eu<sup>3+</sup>;  $q_{t}$  is the relative quantum output.



Fig. 2 The luminescence spectrum of [Eu(btfa)<sub>3</sub>(phenNO)] at 4.2 K, upon ligand excitation (370 nm).  $\Phi$  gives the radiant power per constant wavelength intervals in arbitrary units. The labels refer to the *J* values of the final level of the emission transition  ${}^{4}D_{0} \rightarrow {}^{7}F_{J}$ .

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J = 0-4), and shows that the Eu<sup>3+</sup> ions occupy a single site, where they experience a low symmetry crystal field with a considerable covalent contribution. The spectra of [Eu-(btfa)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] are similar to those of [Eu(btfa)<sub>3</sub>(phenNO)] but they indicate the co-existence of several complexes with different coordination geometries in the former case.

The quantum yield of the  ${}^{5}D_{0}$  emission of the Eu<sup>3+</sup> complexes, defined as the ratio between the emitted and the absorbed quanta, were determined by comparison with standard phosphors (*viz.* Y<sub>2</sub>O<sub>3</sub>: Eu), whose efficiencies have previously been determined by absolute measurements. This method provides absolute efficiencies while avoiding absolute measurements, and has been described in detail elsewhere.<sup>10</sup> The quantum yield  $q_x$  of a sample is thus given by eqn. (1):

$$q_x = \left(\frac{1 - r_{\rm st}}{1 - r_x}\right) \left(\frac{\Delta \Phi_x}{\Delta \Phi_{\rm st}}\right) q_{\rm st} \tag{1}$$

where  $r_{st}$  and  $r_x$  are the amounts of exciting radiation reflected by the standard and by the sample, respectively, and the terms  $\Delta \Phi_x$  and  $\Delta \Phi_{st}$  give the integrated photon flux (counts s<sup>-1</sup>) for the sample and the standard phosphor, respectively. The values of  $r_{st}$ ,  $r_x$ ,  $\Delta \Phi_x$  and  $\Delta \Phi_{st}$  are obtained for the same excitation wavelength. The method is accurate within 10%. The *q* values were estimated for broad-band (260 nm) and line (only for the  $^{7}F_0 \rightarrow ^{5}D_2$  transition of Eu<sup>3+</sup>) excitations, at room temperature. Absolute *q* values for any other broad-band excitation wavelength  $\lambda_{exc}$  can be established by comparing the relative emission intensities for  $\lambda_{exc}$  and  $\lambda = 260$  nm in the corrected excitation spectra of the sample, taking into account differences in the absorption coefficients. Values of *q* at any temperature *T* can be obtained by comparing the  $\Delta \Phi_x$  values at room temperature and at *T*, under identical instrumental conditions.

The determined quantum yields are given in Table 1, together with lifetime values. Lifetime and rise-time measurements were performed at 298 K, using a set-up described previously.<sup>6</sup> The temporal resolution of the overall system is *ca*. 50 ns.<sup>6</sup> The results clearly show that the substitution of the water molecules by phenNO leads to greatly enhanced quantum yields and longer <sup>5</sup>D<sub>0</sub> lifetimes. This can be ascribed to a more efficient ligand-to-metal energy-transfer and to less efficient nonradiative <sup>5</sup>D<sub>0</sub> relaxation processes. The more pronounced temperature dependence of the *q* values and the larger difference between the values upon ligand and direct Eu<sup>3+</sup> excitation for the hydrated compound show that there are other operative quenching processes, besides the expected multiphonon relaxation *via* the high-frequency H<sub>2</sub>O vibrations. The rise-times clearly indicate that the energy transfer from the

**Table 1** Solid-state photophysical data for the <sup>5</sup>D<sub>0</sub> luminescence of Eu<sup>3+</sup> complexes: lifetimes  $\tau$ , rise-times  $t_r$ , and quantum yields  $q_{\lambda}$  upon ligand ( $\lambda$  = 370 nm) and f-f ( $\lambda$  = 464 nm, <sup>7</sup>F<sub>0</sub>  $\rightarrow$  <sup>5</sup>D<sub>2</sub> transition) excitation

Complex	$q_{370}{}^a$ (%)		q <sub>464</sub> (%)			4 b/
	300K	4K	300K	4K		t <sub>r</sub> 9μs 300K
[Eu(btfa) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ] [Eu(btfa) <sub>3</sub> (phenNO)]	30 66	50 76	40 70	60 80	380 670	4.0 4.0

Experimental errors: a ±10%; b ±5%.

ligand occurs to levels above the  ${}^{5}D_{0}$ , most probably the  ${}^{5}D_{1}$  level, which limits the rate of transfer to the  ${}^{5}D_{0}$  level. A more detailed discussion of these results lies beyond the scope of this communication and will be presented elsewhere.

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## Footnotes

† Synthetic procedure: 20 ml of an ethanolic solution of btfa (1 mmol) was added under stirring to 20 ml of a warm (60–70 °C) aqueous ethanolic solution of Eu(ClO<sub>4</sub>)<sub>3</sub> (1 mmol) at pH 4–5. The pH was then adjusted to 6–7 with dilute NaOH aqueous solution. After refluxing for 4 h a pale yellow precipitate was filtered, recrystallized in ethanol and dried at 80 °C over P<sub>2</sub>O<sub>5</sub> at reduced pressure (>1 mmHg), thus yielding the [Eu(btfa)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] complex. [Eu(btfa)<sub>3</sub>(henNO)] was prepared by adding 40 ml of a warm ethanolic solution of phenNO (1 mmol) to an ethanolic solution containing 1 mmol of [Eu(btfa)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]. The precipitate was filtered, washed with ethanol and dried at 80 °C over P<sub>2</sub>O<sub>5</sub> at reduced pressure. The proposed formulae are consistent with the chemical analysis, thermogravimetric analysis and IR spectra of the complexes.

<sup>‡</sup> The band ascribed to the C=O bending vibration shifts from 1604.5 cm<sup>-1</sup> in the free btfa to 1613.7 cm<sup>-1</sup> in the complex. The N–O stretching shifts from 1273.6 and 1257.0 to 1320.0 and 1291.3 cm<sup>-1</sup>, respectively. The N–O bending shifts from 813.0 and 838.5 to 812.2 and 846.2 cm<sup>-1</sup>, respectively.

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