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

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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 $^5D_0$ 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,[1] thus overcoming the very small absorption coefficients of the lanthanide ions. Efficient LCMDs may find many applications, such as luminescent labels in fluoroimmunoassays,[2] lasers,[3] or cheaper phosphors for fluorescent lighting.[4] 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.[6–8] 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^{III} and Tb^{III} with mixed ligands such as picolinic acid *N*-oxide and 2,2′:6′,2″-terpyridine,[8] or 3-aminopyrazine-2-carboxylic acid and 2,2′-bipyridine *N,N*′-dioxide[6] 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.[7]

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).† 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_2O_3 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^{III} ion in [Eu(btfa)$_3$-(phenNO)]. The coordination is also confirmed by the UV–VIS absorption spectra.

The excitation and luminescence spectra and the quantum-yield 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)$_3$(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^{3+} transitions only ($^5D_0 \rightarrow {}^7F_J$,

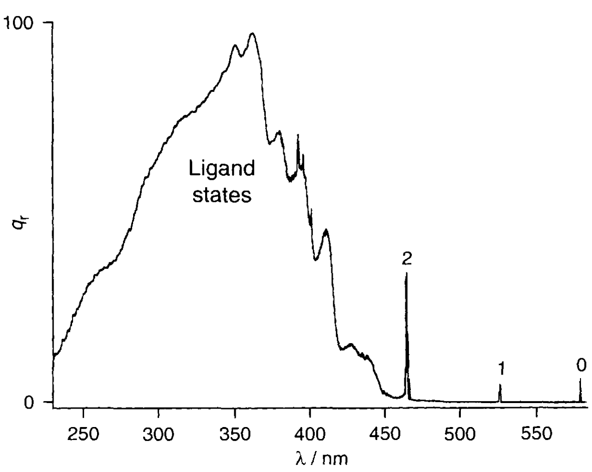

Fig. 1 The excitation spectrum of the $^5D_0$ emission (λ_{em} = 610.7 nm) of Eu^{3+} in [Eu(btfa)$_3$(phenNO)] at 4.2 K. The labels refer to the *J* values of the final level of the excitation transitions $^7F_0 \rightarrow {}^5D_J$ of Eu^{3+}; q_r is the relative quantum output.

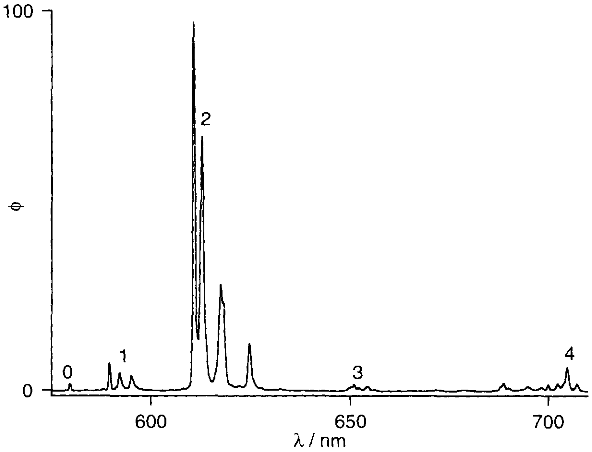

Fig. 2 The luminescence spectrum of [Eu(btfa)$_3$(phenNO)] at 4.2 K, upon ligand excitation (370 nm). Φ gives the radiant power per constant wavelength intervals in arbitrary units. The labels refer to the *J* values of the final level of the emission transition $^4D_0 \rightarrow {}^7F_J$.

J = 0–4), and shows that the Eu^{3+} ions occupy a single site, where they experience a low symmetry crystal field with a considerable covalent contribution. The spectra of $[Eu(btfa)_3(H_2O)_2]$ are similar to those of [Eu(btfa)$_3$(phenNO)] but they indicate the co-existence of several complexes with different coordination geometries in the former case.

The quantum yield of the $^5D_0$ emission of the Eu^{3+} complexes, defined as the ratio between the emitted and the absorbed quanta, were determined by comparison with standard phosphors (*viz.* Y_2O_3: 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.[10] The quantum yield q_x of a sample is thus given by eqn. (1):

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

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^{-1}) 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 $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+}) excitations, at room temperature. Absolute q values for any other broad-band excitation wavelength λ_{exc} can be established by comparing the relative emission intensities for λ_{exc} and λ = 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.[6] The temporal resolution of the overall system is *ca.* 50 ns.[6] The results clearly show that the substitution of the water molecules by phenNO leads to greatly enhanced quantum yields and longer $^5D_0$ lifetimes. This can be ascribed to a more efficient ligand-to-metal energy-transfer and to less efficient non-radiative $^5D_0$ relaxation processes. The more pronounced temperature dependence of the q values and the larger difference between the values upon ligand and direct Eu^{3+} excitation for the hydrated compound show that there are other operative quenching processes, besides the expected multiphonon relaxation *via* the high-frequency H_2O vibrations. The rise-times clearly indicate that the energy transfer from the ligand occurs to levels above the $^5D_0$, most probably the $^5D_1$ level, which limits the rate of transfer to the $^5D_0$ level. A more detailed discussion of these results lies beyond the scope of this communication and will be presented elsewhere.

Table 1 Solid-state photophysical data for the $^5D_0$ luminescence of Eu^{3+} complexes: lifetimes τ, rise-times t_r, and quantum yields q_λ upon ligand (λ = 370 nm) and f–f (λ = 464 nm, $^7F_0 \rightarrow {}^5D_2$ transition) excitation

	$q_{370}{}^a$ (%)		q_{464} (%)		τ^b/µs	$t_r{}^b$/µs
Complex	300K	4K	300K	4K	300K	300K
$[Eu(btfa)_3(H_2O)_2]$	30	50	40	60	380	4.0
[Eu(btfa)$_3$(phenNO)]	66	76	70	80	670	4.0

Experimental errors: ^{a} ±10%; ^{b} ±5%.

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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 $Eu(ClO_4)_3$ (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_2O_5 at reduced pressure (> 1 mmHg), thus yielding the $[Eu(btfa)_3(H_2O)_2]$ complex. [Eu(btfa)$_3$(phenNO)] was prepared by adding 40 ml of a warm ethanolic solution of phenNO (1 mmol) to an ethanolic solution containing 1 mmol of $[Eu(btfa)_3(H_2O)_2]$. The precipitate was filtered, washed with ethanol and dried at 80 °C over P_2O_5 at reduced pressure. The proposed formulae are consistent with the chemical analysis, thermogravimetric analysis and IR spectra of the complexes.

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

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