

Luminescent Ln³⁺ nitrobenzoato complexes: first examples of sensitization of green and red emission†

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Received (in West Lafayette, IN, USA) 11th February 2004, Accepted 10th March 2004

First published as an Advance Article on the web 23rd March 2004

The first examples of luminescent lanthanide complexes with an *o*-nitrobenzoic acid-based ligand, 2-nitro-4-thiophen-3-yl benzoic acid, have been isolated. The structural and preliminary photophysical characterization is presented.

The emission of light from lanthanide ions arises from f–f transitions, which result in emission bands with extremely narrow bandwidth and no theoretical cap on the quantum efficiency. This makes lanthanide ions very attractive for a variety of applications, such as chromophores for LEDs and as probes and labels in a variety of biological and chemical applications.¹ Since these transitions are spin- and parity-forbidden, the excited state of the lanthanide ion is populated through intramolecular energy transfer from the ligand or ligands, which therefore serve as sensitizers. Sensitizers such as aromatic carboxylic acids have been widely studied as they are of ecological importance.² These compounds have the ability to complex cations in general and have proved to efficiently sensitize lanthanide ion luminescence. In contrast to other aromatic carboxylic acids, nitrobenzoic acid derivatives have failed to demonstrate lanthanide sensitization.³ In fact, Panigrahi demonstrated that addition of *o*- and *m*-nitrobenzoic acid to a Tb³⁺ solution resulted in quenching of the characteristic emission, even when in the presence of triethylphosphine oxide, which reduces the coordination of solvent molecules to the lanthanide ion.⁴ Other studies involving nitrobenzoic acid derivatives dealt only with the thermal stability of lanthanide complexes of 4- and 5-chloro derivatives of 2-, 3- and 5-nitrobenzoic acid,⁵ and the thermodynamics of complexation of lanthanide complexes of 3-nitrobenzoic acid.⁶ To date, the modus of coordination of the ligand to the lanthanide has been the subject of speculation.

In our search for systems capable of complexing rare earth ions into a polymer film for application in multi-color polymer light-emitting diodes (PLEDs), we have synthesized 2-nitro-4-thiophen-3-yl benzoic acid as our ligand and sensitizer.⁷

Despite the demonstrated inability of *m*- and *o*-nitrobenzoic acid to sensitize emission from Eu(III) and Tb(III),^{3,4} we have successfully isolated red- and green-luminescent Eu(III) and Tb(III) complexes of our ligand that show characteristic emission as solids and in solution. Slow diffusion of an ethanolic solution of EuCl₃·6H₂O into an aqueous solution of the potassium salt of 2-nitro-4-thiophen-3-yl benzoic acid yielded colorless plate-shaped X-ray quality crystals of the Eu(III) complex (**1**) within two weeks. Similar crystals of the Tb(III) complex (**2**) were isolated by using an ethanolic solution of TbCl₃·6H₂O. The solid-state structure of **1** is shown in Fig. 1. **1** and **2** are isostructural and crystallize in a triclinic centrosymmetric unit cell.† Four and a half water molecules crystallize in the asymmetric unit. Each complex molecule is dimeric, containing two Ln(III) ions surrounded by six ligands. The Ln–Ln distances are 4.006 (**1**) and 3.965 Å (**2**). The ligands show three different coordination modes to the Ln ions: bidentate, bridging bidentate and bidentate with an oxygen atom bridging two metal ions and another oxygen atom coordinating to one of the ions (triply coordinated). This is shown in Fig. 2 for complex **1**. O(3), O(4) and O(15), O(16) are part of two bidentate

bridging carboxylate groups. O(11) and O(12) belong to the carboxylate ligand which binds in a bidentate fashion to the Eu(1) ion. Two other carboxylate groups bridge the two Eu ions in a triply coordinated manner. The other carboxylate group binds similarly and O(8) bridges the two Eu metal centers. The coordination sphere of the metal ion is completed by two additional water molecules bonding *via* O(25) and O(26), producing a coordination number of nine at the Eu center. In **1**, the Eu–O bonds range from 2.363(3) to 2.568(3) Å, which falls within the expected range for this type of complex.⁸ The longest Eu–O bonds involve the oxygen atoms of one of the triply coordinated ligands [Eu(1)–O(23) 2.568(3), Eu(1)–O(24) 2.560(3) Å] and the shortest that of a water molecule [Eu(1)–O(25) 2.363(3) Å] and another bridging oxygen atom of a triply coordinated ligand [Eu(1)–O(8) 2.383(3) Å]. In **2**, the Tb–O distances fall in the range 2.339(3) to 2.540(4) Å, which is consistent with values reported in the literature.⁹ Analogous to the europium complex, the longest Tb–O bonds are to the oxygen atoms of one of the triply coordinated carboxylate ligands [2.536(4) and 2.540(3) Å] and the shortest to a water molecule and to the bridging oxygen atom of the other triply coordinated ligand. The coordination polyhedron around the Ln³⁺ ions can be described both as a distorted tricapped trigonal prism and as a monocapped square antiprism; it is difficult to distinguish these two geometries in this case. As correctly assumed by Ferenc⁵ on the basis of IR spectroscopy, there is no evidence of direct coordination between

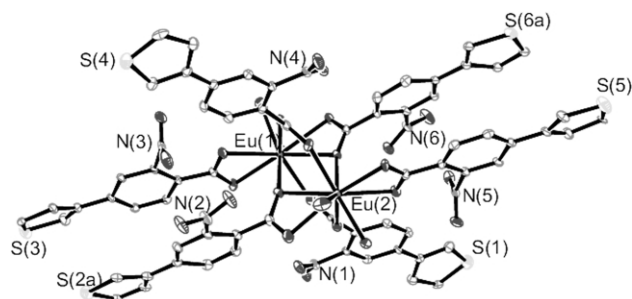


Fig. 1 ORTEP plot of **1** (50% probability thermal ellipsoids).

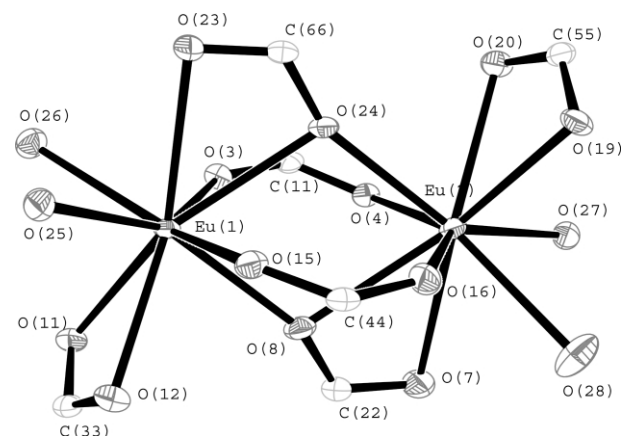


Fig. 2 ORTEP plot of the coordination sphere of the Eu(III) ions in **1** (50% probability thermal ellipsoids).

† Electronic supplementary information (ESI) available: absorption and excitation spectra of **1** and **2** in ethanol. See <http://www.rsc.org/suppdata/cc/b4/b402038c/>

the lanthanide ions and the nitro groups on the benzene rings. Bürgstein and Roesky described nitrophenolate complexes of Y and Lu in which coordination of the nitro group was achieved, although this was only possible under rigorous exclusion of water to avoid coordination of water molecules to the metal ions.¹⁰ In common with many structures involving thiophene,¹¹ the degree of disorder in both structures presented here is high. Modeling the disorder gives two different positions for selected thiophene rings, where the rings are rotated approximately 180° around the C–C bond to the benzoate, with occupancy factors of 80% for the major and 20% for the minor component.

The crystalline complexes display emission colors characteristic of Eu³⁺ or Tb³⁺ when irradiated with a hand-held UV lamp (254 nm). These complexes have low solubility in water and aqueous solutions of these complexes do not luminesce at their maximum concentration of 10^{−4} M. However, both complexes dissolve in ethanol and are luminescent in this solvent. The emission spectra of **1** and **2** are shown in Fig. 3. The spectrum of **1** displays characteristic emission bands at 594 (⁵D₀ → ⁷F₁), 619 (⁵D₀ → ⁷F₂), 653 (⁵D₀ → ⁷F₃) and 700 nm (⁵D₀ → ⁷F₄). The emission bands for **2** are seen at 548 (⁵D₄ → ⁷F₅), 589 (⁵D₄ → ⁷F₄) and 623 nm (⁵D₄ → ⁷F₃). These spectra show that the energy transfer from the ligand to the Ln³⁺ ion is moderately efficient, under the experimental conditions used. The ligand-centered emission is only partially quenched as evidenced by the low values of the relative quantum yield for metal-centered emission (Table 1).¹² The inefficient quenching of the ligand-centered emission can be further seen from the broad bands with low intensity around 530 nm that partially overlap with the metal-centered emission, as shown in Fig. 3. We are currently investigating the luminescence behavior in more detail.

To the best of our knowledge, these are the first reported examples of luminescent nitrobenzoate-containing europium and

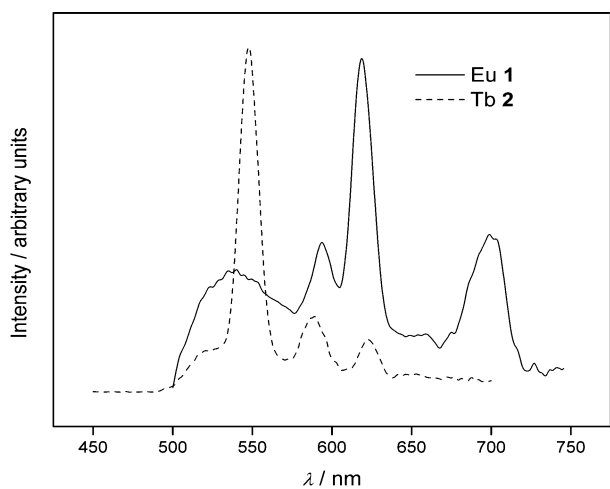


Fig. 3 Emission spectra of **1** (—) and **2** (---) in ethanol: [**1**] = 2.16 × 10^{−6} M, [**2**] = 2.16 × 10^{−4} M.¹²

Table 1 Luminescence lifetimes and quantum yields for **1** and **2**

Complex	$\tau/\mu\text{s}$	Φ_{rel}
1	327 ± 5	0.005
2	578 ± 63	0.033

terbium complexes. We have demonstrated that a coordinative interaction between the nitro group and the lanthanide ions is not present in the complexes. The thiophene ring in the ligand should allow for its polymerization; however, the nitrobenzoic acid moiety hinders the 2-position sterically and prevents polymerization. We are therefore in the process of derivatizing the ligand to allow for efficient polymerization.¹³

We gratefully acknowledge Dr Brendan Twamley and Dr Gilles Muller for helpful discussions, and Syracuse University and PRF for financial support.

Notes and references

‡ Crystal data for **1**: C₆₆H₅₃Eu₂N₆O_{32.5}S₆, $M = 1947.43$, $a = 11.372(2)$, $b = 17.016(3)$, $c = 20.126(4)$ Å, $\alpha = 112.99(3)$, $\beta = 96.74(3)$, $\gamma = 90.22(3)^\circ$, $V = 3555.3(12)$ Å³, triclinic, space group $P\bar{1}$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 2.023$ mm^{−1}, $T = 89(2)$ K, final $R_1 (I > 2\sigma) = 0.0462$, $wR_2 (I > 2\sigma) = 0.1121$, GOF (on F^2) = 1.088. For **2**: C₆₆H₅₃Tb₂N₆O_{32.5}S₆, $M = 1961.35$, $a = 11.416(2)$, $b = 16.896(3)$, $c = 20.075(4)$ Å, $\alpha = 113.09(3)$, $\beta = 96.85(3)$, $\gamma = 90.46(3)^\circ$, $V = 3530.1(12)$ Å³, triclinic, space group $P\bar{1}$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 2.264$ mm^{−1}, $T = 89(2)$ K, $R_1 (I > 2\sigma) = 0.0485$, $wR_2 (I > 2\sigma) = 0.1173$, GOF (on F^2) = 1.063. The majority of hydrogen atoms were added geometrically and their parameters constrained to the parent site. For both complexes, the water hydrogen atoms could not be located on the difference map and could not be added geometrically. These have been omitted, although the formulae are correct. CCDC 224937 and 224938. See <http://www.rsc.org/suppdata/cc/b4/b402038c/> for crystallographic data in CIF or other electronic format.

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- Solutions ($\mu = 0.01$ M NEt₄Cl) were prepared under nitrogen atmosphere with ethanol dried by standard methods. Slit widths were 5 nm and a scan rate of 125 nm s^{−1} was used. The relative quantum yields of **1** and **2** were determined against Eu(terpy)₃(ClO₄)₃¹⁴ ($\Phi = 1.3\%$)¹⁵ and Tb(terpy)₃(ClO₄)₃¹⁴ ($\Phi = 4.7\%$)¹⁶ respectively, as 1 × 10^{−3} M degassed and dry acetonitrile solutions¹⁵.
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