

Efficient near-UV photosensitization of the Tb(III) green luminescence by use of 2-hydroxyisophthalate ligands†

Laurent Benisvy,^a Patrick Gamez,^a Wen Tian Fu,^a Huub Kooijman,^b Anthony L. Spek,^b Andries Meijerink^c and Jan Reedijk^{*a}

Received 1st April 2008, Accepted 3rd April 2008

First published as an Advance Article on the web 16th April 2008

DOI: 10.1039/b805507f

The first examples of lanthanide complexes with a 2-hydroxyisophthalate ligand are reported; the blue-emitting ligand acts as a very efficient sensitizer of the Tb(III) green emissions and does so in the near-UV region.

The search for new line-emitter lanthanide-based luminescent materials for light emitting diodes¹ (LEDs) and lighting applications² is an important and active research area both in academia and industry. With the recent invention of the blue- and near-UV light emitting diode (LED)³ based on direct excitation of GaN-based semiconductors by electrical current, the lighting market has taken what is likely to be a slow revolutionary turn. Indeed, the use of LEDs to produce white light emitting devices (white LEDs) would mean the substitution of the environmentally unfriendly, traditional lamps by more energy efficient, miniaturised and easy-processed white LEDs. By analogy to the tricolour fluorescent lamps in the market, white LED could be produced by covering near-UV LED (emitting at 370 nm) with blue, green and red phosphors. For that, the phosphor should be capable of efficiently converting near-UV radiation into narrow-band emissions. However, the commonly used Eu³⁺ and Tb³⁺-doped oxide materials—known for their sharp red and green emissions, respectively, upon excitation at 254 nm—do not absorb efficiently at 370 nm (*e.g.* (Ce,Tb,Gd)MgB₅O₁₀, mainly used in tubular fluorescent lamps, absorbs only to about 10% at 370 nm). Therefore, the search for stable inorganic rare-earth phosphors with high absorptions in the near-UV/blue spectral region is an attractive research task.

In this respect, lanthanide coordination compounds are regarded to be potential phosphor candidates.⁴ Indeed, the sensitization of the green and red emission from Tb(III) and Eu(III) ions, by various types of ligand, including diketonate, aromatic carboxylic acids and others, has been reported.^{5–7} In these compounds direct transitions to the excited 4f levels of the Ln(III) ion are spin and parity forbidden, but efficient population of the emitting 4f excited states is achieved through the so-called ‘antenna effect’,⁸ *i.e.* *via* intramolecular energy transfer from the ligand excited state to a

Ln f-excited state. In some cases, relatively high quantum yields ($\Phi > 0.5$) have been obtained.^{5–7} However, most of these compounds are excited in the UV-region; and to-date, only very few compounds are reported to be capable of sensitizing Ln(III) in the near-UV region (*e.g.* 360–400 nm).^{9–12} Herein, we report the first lanthanide coordination compounds, [Ln₂(H₂L⁻)₆(H₂O)₄].4H₂O (Ln = La **1**, Tb **2**) bearing the 2-hydroxyisophthalate ligand H₂L⁻. ‡ The newly reported blue-emitting ligand acts as an efficient sensitizer of the Tb(III) green emissions and does so in the near-UV region.

The 5-*tert*-butyl-2-hydroxybenzene-1,3-dioic acid ligand was synthesised in four steps, as reported in the literature.¹³ The reaction of H₃L and Ln(CF₃SO₃)₃·6(H₂O)_{*n*} in a 3 : 1 ratio in water under hydrothermal conditions (110 °C, sealed/pressure tube) affords single crystals of [Ln₂(H₂L⁻)₆(H₂O)₄].4H₂O (Ln = La **1**, Tb **2**) in *ca.* 80% yield. X-Ray crystallographic characterisations have shown that both compounds are isomorphous and isostructural. The molecular structure of **2** (see Fig. 1) has been fully determined by X-ray crystallography.§ ¶ The asymmetric unit of a crystal of **2** consists of one Tb(III) ion, three singly deprotonated unique ligands H₂L⁻ (designated as ligands A, B, and C; Scheme 1), two coordinated water molecules and two free water molecules. The dinuclear of composition [Tb₂(H₂L⁻)₆(H₂O)₄] (**2**) is formed over a crystallographic inversion centre (Fig. 1).

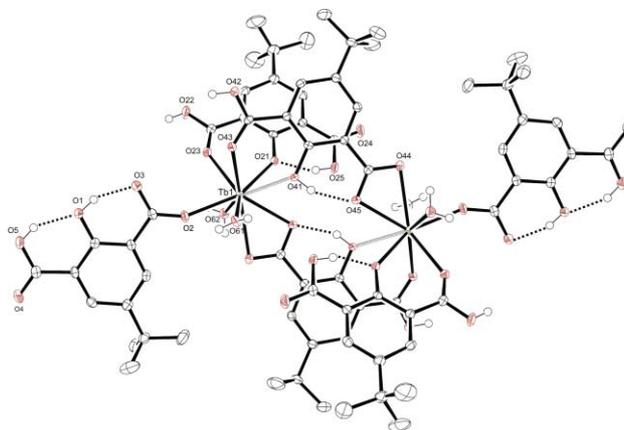
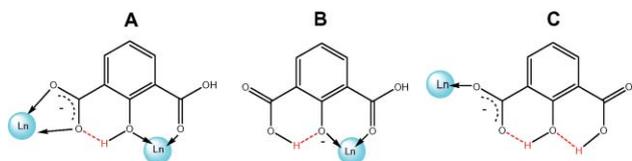


Fig. 1 ORTEP representation (30% displacement ellipsoids) of compound **2**. The non-coordinated water (O71, O72) molecules have been omitted for clarity. Selected bond distances (Å): Ln1–O2 2.3296(16), Ln1–O21 2.2832(15), Ln1–O23 2.3736(14), Ln1–O41 2.6694(14), Ln1–O43 2.4555(14), Ln1–O61 2.4388(15), Ln1–O62 2.3833(16), Ln1–O44# 2.5865(13), Ln1–O45# 2.4637(16). symmetry code # = 1 – x, 1 – y, –z.

^aLeiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands. E-mail: reedijk@chem.leidenuniv.nl; Fax: +31-71-5274345; Tel: +31-71-5274451

^bBijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands
^cCondensed Matter and Interfaces, Debye Institute, Ornsteyn Laboratory, Princetonplein 5, 3584 CC Utrecht, The Netherlands

† Electronic supplementary information (ESI) available: Synthesis details and luminescence decay curve. CCDC reference number 676961. For ESI or crystallographic data in CIF or other electronic format see DOI: 10.1039/b805507f



Scheme 1 Schematic representation of the binding modes and the resonance forms of H_2L^- in $[\text{Ln}_2(\text{H}_2\text{L}^-)_6(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$.

Each Tb(III) ion possesses an O_9 -coordination sphere; the geometry of which is best described as a highly distorted tricapped trigonal prism.¹⁴ Seven Tb–O bond distances ranging from 2.2832(15) Å to 2.4637(16) Å are as expected, and two, Tb–O44 and Tb–O41, are relatively long with lengths of 2.5866(13) and 2.6694(14) Å, respectively.¹⁵ Each, A, B and C ligand displays a specific coordination mode associated with a specific protonation site (Scheme 1). The bridging ligand A binds one Tb ion through an O,O-bidentate salicylate mode, and the other Tb ions with an O,O-bidentate carboxylate. The ligands B and C bind only one Tb ion, either through one monodentate or bidentate O,O-carboxylate, respectively. Each ligand exhibits strong/intermediate O–H...O salicylate-type intramolecular hydrogen bonding; with O...O distances ranging from 2.465(4) Å to 2.549(3) Å and O–H...O angles from 149(6) to 164(4)° (Fig. 1, Scheme 1).¹⁶ Such features are believed to play a key role for the blue-emitting luminescence properties of these ligands, *vide infra*.

The dinuclear complexes interact with each other to form a 2-dimensional H-bonding network in the (0 0 1) plane (Fig. 2 and 3). Along the *a*-axis the dinuclear units are connected through a complicated multiple H-bonding network containing 16 hydrogen-bonds involving O-carboxylates, and coordinated and non-coordinated water molecules; Fig. 3. The O...O distances involved range from 2.668(2) to 2.998(2) Å. These hydrogen bonds appear to hold the dinuclear units together strongly, as indicated by the intermolecular Tb...Tb distance of 5.9328(7) Å, strikingly shorter than the Tb...Tb distance (intramolecular) of 6.7680(8) Å within the dinuclear complex. Along the *b*-axis, the ligands of type C (see Scheme 1) appear to connect the chains together by means of: (a) hydrogen-bonding between the non-coordinated carboxylic carbonyl O-atom O4 and one of the coordinated water molecules (O61) of an adjacent complex ((O4...O61 = 2.804(2), Å), Fig. 2; (b) non-covalent interactions between the phenol rings of two inversion related ligands C. The geometrical parameters for this interaction; *i.e.* the centroid-centroid distance (3.9891(12) Å), the

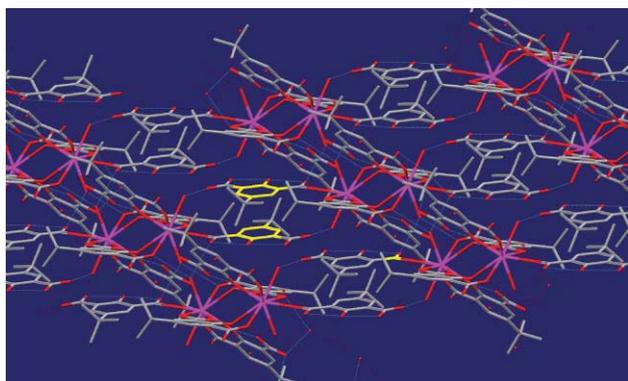


Fig. 2 Representation of the structure of the 2-D network of **2**.

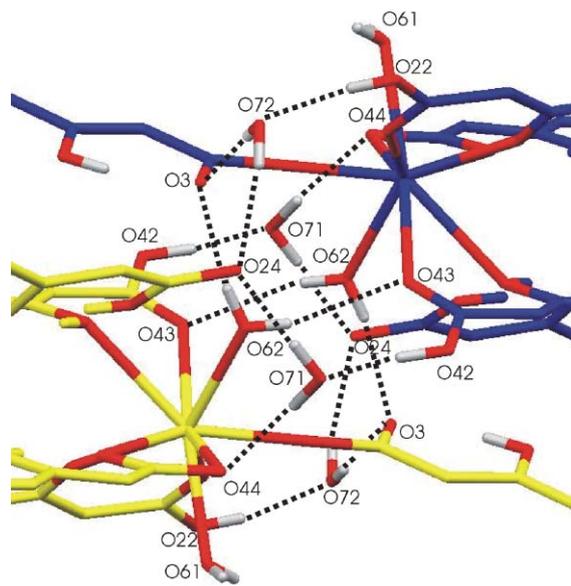


Fig. 3 Representation of the intermolecular H-bonding interactions in the (0 0 1) plane between two molecules of **2** along the *a*-axis.

centroid-to-plane distance (3.386 Å) and the angle between the two planes (0°) strongly indicate a π - π stacking interaction between the two phenol rings.¹⁷ Interestingly, the latter rings are off-set by 2.1 Å, which places the two phenolic O-atoms at a relatively short distance of 3.4134(14) Å above/below the two centroids (see Fig. 2).

The photoluminescence properties of compounds **1** and **2**, in the solid state, have been investigated. The excitation spectra for **1** (Fig. 4) and **2** are identical exhibiting a continuous maximum absorption from 200 nm to nearly 400 nm. This correlates well with the ligand-based electronic absorptions at 265 nm and 348 nm exhibited by both compounds. The emission spectrum of **1**, using a 370 nm excitation wavelength, displays a broad blue emission centred at 450 nm (Fig. 2); the life-time of which has been determined to be < 50 ns. Such a short life-time is typically obtained for the spin-allowed emission from the singlet excited state of organic emitters.⁵ Such blue-emissions have also been reported for ester salicylate derivative organic compounds. In these molecules a tautomeric structure, where the *ortho*-hydroxy hydrogen is transferred to the carbonyl oxygen, has been invoked for the triplet excited state.¹⁸ This process is facilitated by the intramolecular O–H...O salicylate-type hydrogen bonding, similar to those exhibited by compound **2**. Thus, we assigned the blue emission of **1** as ligand-based. To the best of our knowledge, this is the first time that a blue-luminescence, based on the 2-hydroxyisophthalate motif, has been revealed.

Compound **2**, upon excitation at 370 nm, displays characteristic Tb(III) emission bands corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($J = 3-6$) transitions at 489, 547, 583, 622 nm, respectively (Fig. 4). The emission spectrum is dominated by the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition peaking at 547 nm giving the compound an intense green luminescence. It is noteworthy that there is no apparent residual ligand-based emission in the 400–480 nm region, indicating an efficient energy transfer from the ligand π -excited states to the terbium f-excited states. This possibility is further confirmed by the remarkably high quantum yield (Φ) of 0.52, comparable to

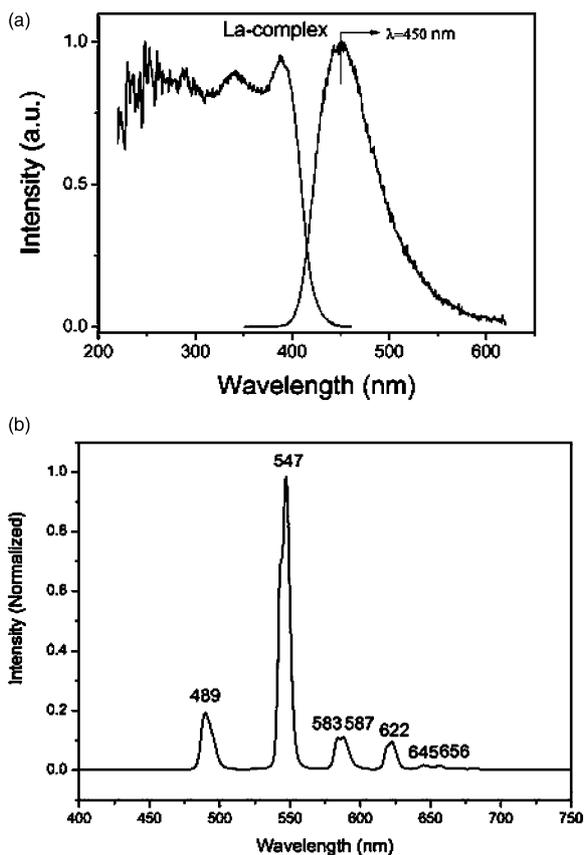


Fig. 4 Excitation and emission spectra of **1** (top) and emission spectrum of **2** (bottom), recorded at room temperature on solid samples. The excitation spectrum is measured for the maximum emission at 450 nm; emission spectra are recorded with excitation at 370 nm.

those recently reported by Petoud *et al.* for 2-hydroxyphthalamide Tb(III) complexes.¹⁹ The decay time of the emission has been fitted to a single exponential with a life-time close to a millisecond ($\tau = 0.856$ ms, see Fig. S11†). The radiative life-time for the 5D_4 state of Tb³⁺ is typically 1.5–2.5 ms. The measured life-time of 0.86 ms is about half of the radiative decay time which shows that the radiative and non-radiative decay rates from the 5D_4 state are similar. This is consistent with the measured quantum yield (0.52). Probably, the mechanism for non-radiative decay is multi-phonon relaxation due to coupling with the high energy OH-vibrations of OH-groups coordinated to the Tb³⁺ ion.

In conclusion, herein we have reported the first Ln(III) coordination compounds bearing the 2-hydroxyisophthalate binding motif. These preliminary studies have indicated that 2-hydroxyisophthalate ligands are capable of converting efficiently near-UV light to strong Tb(III) green emission in compound **2**, thereby acting as an efficient sensitizer of the Tb(III) luminescence.

These findings make 2-hydroxyisophthalate ligands good candidates for the construction of new phosphors for UV-LED technology. Derivatization of the ligand phenol ring will not only allow careful tuning of the excitation wavelength, but will

also permit its attachment onto a solid support, thus finding possible application in polymer light-emitting diodes (PLED). Efforts toward these goals are in progress.

This work has been supported financially by the Graduate Research School Combination “Catalysis”, a joint activity of the graduate research schools NIOK, HRSMC and PTN. Financial support from COST Action D21/003/01 and the Netherlands Technology Research Foundation (STW) applied science division of the Netherlands Organisation for Scientific Research (NWO) are thankfully acknowledged (grant number 5751).

Notes and references

† Although the 2-hydroxyisophthalate ligand is known, reports on its coordination behaviour are scarce. To our knowledge, only a few transition metal compounds bearing 2-hydroxyisophthalate have been reported to date, *i.e.* with V(IV) and Cu(II).²⁰

‡ Crystal data for **2**: C₇₂H₉₄O₃₈Tb₃, colourless block, $M = 1885.33$, triclinic, space group $P\bar{1}$ (no 2), $a = 10.5080(10)$, $b = 12.5528(10)$, $c = 16.649(2)$ Å, $\alpha = 88.623(12)$, $\beta = 73.953(12)$, $\gamma = 69.668(12)^\circ$, $V = 1972.7(4)$ Å³, $Z = 1$, $D_c = 1.587$ g cm⁻³, $T = 150(2)$ K, $F(000) = 960$, $\mu(\text{MoK}\alpha) = 1.872$ mm⁻¹, 57160 reflections collected, 8599 unique ($R_{\text{int}} = 0.043$). The final agreement factors are $R_1 = 0.0201$ for 7989 data with $F > 4\sigma(F)$ and, $R_1 = 0.0241$, $wR_2 = 0.046$ for 8599 data.

¶ Thanks to the excellent quality of the crystals, all OH hydrogen atoms have been localized in a difference density map.

- (a) J. Kido and Y. Okamoto, *Chem. Rev.*, 2002, **102**, 2357; (b) J. C. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048.
- T. Jüstel, H. Nikol and C. Ronda, *Angew. Chem., Int. Ed.*, 1998, **37**, 3084.
- (a) S. Nakamura and G. Fasol, *The Blue Laser Diode*, Springer, Berlin, 1997; (b) S. Nakamura, *MRS Bull.*, 1997, 29.
- H. Boerner, T. Jüstel, H. Nikol and C. Ronda, Philips N.V., Ger. Pat., DE-B 19 708 407.9, 1997.
- R. C. Evans, P. Douglas and C. J. Winscom, *Coord. Chem. Rev.*, 2006, **250**, 2093.
- M. Latva, H. Takalo, V.-M. Kulkala, C. Matesescu, J. C. Rodriguez-Ubis and J. Kankare, *J. Lumin.*, 1997, **75**, 149.
- G. F. de Sá, O. L. Malta, C. de Mello Donegá, A. M. Simas, R. L. Longo, P. A. Santa-Cruz and J. E. F. da Silva, *Coord. Chem. Rev.*, 2000, **196**, 165.
- N. Sabbatini, M. Guardigli and J.-M. Lehn, *Coord. Chem. Rev.*, 1993, **123**, 201.
- A. Dadabhoy, S. Faulkner and P.-G. Sammes, *J. Chem. Soc., Perkin Trans. 2*, 2000, 2359.
- B. Yang, L.-M. Fu, Y. Wang, J.-P. Zhang, W.-T. Wong, X.-C. Ai, Y.-F. Qiao, B.-S. Zou and L.-L. Gui, *Angew. Chem., Int. Ed.*, 2004, **43**, 5010.
- K. Manseki and Shozo Yanagida, *Chem. Commun.*, 2007, 1242.
- C. P. Montgomery, D. Parker and L. Lamarque, *Chem. Commun.*, 2007, 3841.
- C. J. Fahrni and A. Pfaltz, *Helv. Chim. Acta*, 1998, 491.
- M. G. B. Drew, *Coord. Chem. Rev.*, 1977, **24**, 179.
- A. de Bettencourt-Dias and S. Wishvanathan, *Dalton Trans.*, 2006, 4093.
- G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, 1997.
- (a) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525; (b) C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
- H.-C. Lüdemann, F. Hillenkamp and R. W. Redmond, *J. Phys. Chem. A*, 2000, **104**, 3884.
- S. M. Petoud, S. M. Cohen, J.-C. G. Bünzli and K. N. Raymond, *J. Am. Chem. Soc.*, 2003, **125**, 13324.
- (a) E. Solaria, A. Klose, C. Florani, N. Re, A. Chiesi-Villa and C. Rizzoli, *Polyhedron*, 1996, **15**, 4103; (b) J. D. Crane and A. Mclaughlin, *Inorg. Chem. Commun.*, 2004, 7, 499.