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# Design, synthesis, crystal structure and photophysical studies of an emissive, terbium based sensor for zinc

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## Abstract

The synthesis, crystal structure and photophysical studies of the probe complex  $\mathbf{Tb} \cdot \mathbf{L}$  are described.  $\mathbf{Tb} \cdot \mathbf{L}$  is a mononuclear complex with a 46-membered macrocyclic rings constructed by intermolecular hydrogen bond. The mononuclear complex  $\mathbf{Tb} \cdot \mathbf{L}$  shows Laporte-forbidden  ${}^{5}\mathbf{D}_{4} \rightarrow {}^{7}\mathbf{F}_{J}$  f–f transitions and exhibits strong green luminescence emission bands in the solid state at ambient temperature which is characteristic of terbium ion. New selective luminescent lanthanide chemosensor for Zn(II) ion based on  $\mathbf{Tb} \cdot \mathbf{L}$  is also described, suggesting host–guest complexation signaling transduction mechanism. © 2007 Elsevier B.V. All rights reserved.

Keywords: Lanthanide complex; Crystal structure; Hydrogen bond, Supramolecular structure; Lanthanide luminescent sensor

The design of chemosensor-molecules that can selectively recognize and signal the presence of a specific analyte through the naked eye, electrochemical and optical response is one of the main achievements of supramolecular chemistry [1]. On account of its simplicity and high sensitivity, luminescence is increasingly important for trace chemical detection [2]. Since the pioneering work on the cation crown ether [3] using luminescence for monitoring low concentrations of metal cations, considerable effort has been devoted to developing luminescent chemosensors for cations, neutral guests and anions [4].

 $Zn^{2+}$  is the second most abundant transition-metal ion after Fe<sup>2+</sup> or Fe<sup>3+</sup> in humans and other mammals [5]. It plays important roles in various biological systems such as neurotransmission, signal transduction, and gene expression [6,7]. The emerging importance of  $Zn^{2+}$  in neurological signalling and some proposed functions [8] in biological systems have generated an urgent demand for the develop-

ment of Zn<sup>2+</sup>-specific molecular probes [9,10], and many Zn<sup>2+</sup> fluorescent sensors have been reported, exhibiting high selectivity and sensitivity over other biologically essential metal ions in specific ranges of concentration [11-14]. However the fluorescence lifetimes of typical organic compounds, including common zinc-selective fluorescent sensor molecules, are in the nanosecond region. On the other hand, luminescent lanthanide complexes, in particular Tb(III) and Eu(III) complexes, have large Stokes shifts, sharp emission profiles and long luminescence lifetimes in the order of milliseconds [15]. These long-lived luminescent compounds have the advantage that short-lived background fluorescence and scattered light decay to negligible levels when a pulse of excitation light is applied and the emitted light is collected after an appropriate delay time. There are only a few reports about luminescence sensors for Zn(II) ions [16]. Moreover, design approach for lanthanide complexes showing a large enhancement upon Zn<sup>2+</sup> addition is limited. From this background, we set out to enlarge the arsenal for detecting  $Zn^{2+}$  by developing a novel luminescent lanthanide complex.

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Here we report the design, synthesis and crystal structure of the novel  $Zn^{2+}$ -sensitive luminescent lanthanide chemosensor  $\mathbf{Tb} \cdot \mathbf{L}$ , upon complexation with  $Zn^{2+}$ , it exhibits enhanced luminescence. Picolylsalicylamide and triethylene glycol di-p-tosylate was prepared according to the literature methods [17,18]. The synthetic route for the ligand 1,9-bis[2-(2'-picolylaminoformyl)-1,4,7,9-tetraoxadecane] (**L**) is shown in Scheme 1 [19].  $\mathbf{Tb} \cdot \mathbf{L}$  was obtained by the reaction of terbium nitrate, **L** in the molar ratio of 1:1 in methanol-ethyl acetate solution [20] and was revealed by X-ray diffraction [21].

Single-crystal X-ray diffraction studies shows  $\mathbf{Tb} \cdot \mathbf{L}$  is a mononuclear complex and the terbium(III) ion is nine coordinated by two agua molecules, six O atoms of bidentate nitrate anions and one carbonyl atoms of L. It is important to note that the molecular geometry of the ligand displays cis-cis conformation as shown in Fig. 1a. The bond angles around the terbium centre range from 51.34(1) to  $154.67(1)^{\circ}$  indicating that the terbium ion is in a somewhat distorted monocapped anti-square prism Fig. 1b. Interestingly, one of the strong coordinated carbonyl oxygen atoms in L are not coordinated in  $\mathbf{Tb} \cdot \mathbf{L}$ which is very important for the construction of supramolecular structures as follows. As shown in Fig. 1c, the coordinated water molecules with nitrogen atoms of the pyridine rings, oxygen atoms of nitrate and carbonyl oxygen atoms of uncoordinated arms, generate strong intermolecular hydrogen bonds. The  $O(O16)-H \cdots N_{pv}(N4)$ distance was found to be 1.854 Å, with an  $O \cdots N$  distance of 2.698 Å and the O–H···N angle of 172.7°, thus the 46membered macrocyclic rings were formed between two adjacent units. The  $O(O16)-H \cdots O_{carbonyl}(O6)$  distance was found to be 1.894 Å, with an O.O distance of 2.729 Å and O-H···O angle of 167.1° which is crucial important to stabilize the mentioned macrocyclic rings. The O(O17)-H···N<sub>py</sub>(N2) distance was found to be 1.950 Å, with an N···O distance of 2.799 Å and the O- $H \cdots N$  angle of 176.9°, the O(O17)- $H \cdots O_{nitrate}(O10)$  distance was found to be 2.054 Å, with an O···O distance of 2.900 Å and O-H···O angle of 173.3°, led to this series of hydrogen bonds being defined as linear, which further assemble macrocyclic rings into a 1D cage-like supramolecular structure (Fig. 1d). These strong hydrogen bonds together with those intramolecular hydrogen bonds play an important role in the stabilization of the structure and what is more, prevent the carbonyl oxygen atoms from coordinating to the terbium ions to form a polymeric structure.

1,9-bis[2-(2'-picolyaminoformyl)-1,4,7,9-tetra-Ligand oxadecane] luminescent in solution and in the solid state. The emission band of the ligand is in the UV region and with the emission in the solid state at 347 and 441 nm which may correspond to the singlet and triplet states. In addition to being fluorescent in the UV and near-UV regions, the ligands can be excited from 270 to 320 nm, making them possible candidates as activators for lanthanide luminescence. Intramolecular energy transfer from the triplet state of the ligand to the resonance level of the lanthanide ion is one of the most important processes influencing the fluorescence quantum yields of lanthanide complexes [22]. In order to acquire the triplet excited state  $T_1$  of the ligand L, the phosphorescence spectra of the Gd(III) nitrate complexes were measured at 77 K in a methanol solution. The triplet state energy levels  $T_1$  of the ligand L in the nitrate complexes, which were calculated from the shortest wavelength phosphorescence bands [22] of the corresponding Gd(III) complexes, is  $22,727 \text{ cm}^{-1}$ . The energy level is above the lowest excited resonance level  ${}^{5}D_{4}$  $(20,400 \text{ cm}^{-1})$  of Tb(III). Looking at the energy of the ligand triplet states in 42 terbium complexes, Latva et al. [23] conclude that the energy back transfer is observed when the energy difference between the  ${}^{5}D_{4}$  level of Tb(III) and the lowest triplet state energy level of the ligand is less than about  $1850 \text{ cm}^{-1}$ . Thus the absorbed energy could be transferred from ligand to the Tb ions without the energy back transfer process. When the compound  $\mathbf{Tb} \cdot \mathbf{L}$  is excited at 323 nm, the luminescence spectrum collected is impressive as the transitions to the ground-state manifold from the emitting  ${}^{5}D_{4}$  level are observed in moderate detail. The dominant peak is the hypersensitive transition,  ${}^{5}D_{4} - {}^{7}F_{5}$ , which is made up of a single intense peak with a shoulder at about one-third the intensity. The  ${}^{5}D_{4} - {}^{7}F_{6}$  is the second largest peak observed and consists of an intense peak with a shoulder at approximately onefifth intensity at lower frequency. The  ${}^{5}D_{4} - {}^{7}F_{4}$  transitions consist of two peaks of equal intensity. The typical emission band at 620 nm corresponding to  ${}^{5}D_{4} - {}^{7}F_{3}$  disappears due to a double-frequency effect [24]. The fluorescence quantum yield  $\Phi$  of the terbium nitrate complex in spectroscopic grade acetonitrile (concentration:



Scheme 1. The synthesis route of the ligand L.



Fig. 1. (a) ORTEP diagram (30% probability ellipsoids) showing the coordination sphere of  $\mathbf{Tb} \cdot \mathbf{L}$ ; (b) the coordination polyhedron of the Tb ion (pale green: Tb ion; red: oxygen atom). The key bond distances and angles (Å and °): Tb(1)–O(5) 2.288(3), Tb(1)–O(16) 2.325(3), Tb(1)–O(17) 2.370(3), Tb(1)–O(10) 2.444(3), Tb(1)–O(13) 2.448(4), Tb(1)–O(14) 2.454(3), Tb(1)–O(7) 2.469(3), Tb(1)–O(8) 2.479(3), Tb(1)–O(11) 2.521(3); O(5)–Tb(1)–O(16) 77.81(12), O(5)–Tb(1)–O(17) 82.31(11), O(16)–Tb(1)–O(17) 149.60(11), O(5)–Tb(1)–O(10) 148.34(13), O(16)–Tb(1)–O(10) 125.88(11), O(17)–Tb(1)–O(10) 81.94(11), O(5)–Tb(1)–O(13) 129.77(13), O(16)–Tb(1)–O(13) 89.95(14), O(17)–Tb(1)–O(13) 85.30(14), O(10)–Tb(1)–O(13) 75.84(13), O(5)–Tb(1)–O(14) 78.21(12), O(16)–Tb(1)–O(14) 77.03(11), O(17)–Tb(1)–O(14) 76.55(11), O(10)–Tb(1)–O(14) 123.98(12), O(13)–Tb(1)–O(14) 51.56(12), O(5)–Tb(1)–O(7) 72.20(12), O(10)–Tb(1)–O(7) 71.12(13), O(13)–Tb(1)–O(7) 142.04(14), O(14)–Tb(1)–O(7) 142.74(12), O(5)–Tb(1)–O(8) 88.64(11), O(16)–Tb(1)–O(8) 79.08(12), O(17)–Tb(1)–O(8) 123.43(12), O(10)–Tb(1)–O(8) 77.53(12), O(13)–Tb(1)–O(8) 136.97(13), O(14)–Tb(1)–O(8) 51.34(11) O(5)–Tb(1)–O(11) 146.67(12), O(16)–Tb(1)–O(11) 74.54(11), O(17)–Tb(1)–O(11) 130.23(11), O(10)–Tb(1)–O(11) 51.51(11), O(13)–Tb(1)–O(11) 68.74(13), O(14)–Tb(1)–O(11) 112.66(12), O(7)–Tb(1)–O(11) 102.96(12), O(8)–Tb(1)–O(11) 68.23(12). (c) The macrocyclic ring formed by hydrogen bond. (d) The cage-like super molecular structure of  $\mathbf{Tb} \cdot \mathbf{L}$ .

 $1.0 \times 10^{-5}$  mol L<sup>-1</sup>) was found to be 0.21 with eosin ( $\Phi = 0.23$ ) as reference. The absence of the ligand-based emission in the spectrum of **Tb** · L also suggests that the energy transfer from the ligand to the Tb(III) center is effective.

The fluorescence spectra were recorded from a solution of  $\mathbf{Tb} \cdot \mathbf{L} (5.0 \times 10^{-6} \text{ M})$  in the absence or presence of various metal ions found at high concentrations in cells, such as K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Zn<sup>2+</sup> as well as transitionmetal ions such as Cr<sup>3+</sup>, Al<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>+</sup>. As shown in Fig. 2, the fluorescence spectra of compound **Tb** · **L** in acetonitrile exhibited a weak emission band at about 545 nm, which was attributed to the intrinsic emission of the Tb(III). Upon addition of  $K^+$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Hg^+$  in a 20-fold excess, no apparent changes in emission spectra were found, however, a strong fluorescence enhancement was obtained in the presence of a small amount of  $Zn^{2+}$  cation. Similar fluorescent enhancement was also observed upon addition of  $Al^{3+}$  cation. However, a smaller emission enhancement was observed even upon addition of  $Al^{3+}$  cation in a 20-fold excess. The shape of the titration curve with the platform upon addition of the  $Zn^{2+}$  cation suggested the formation of a 1:1 stoichiometry host–guest complex. Meanwhile, the complexity of the titration curve with  $Al^{3+}$  cation did not



Fig. 2. Emission spectra (excitation at 308 nm) of **Tb** · **L**( $5\mu$ M) in the presence of various concentrations of Zn<sup>2+</sup>: 0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 3.0, 4.0, 5.0 with respect to **Tb** · **L**. The bands arise from  ${}^{5}\text{D}_{4}{}^{-7}\text{F}_{J}$  and the *J* values of the bands are labelled.

suggest the formation of a simple 1:1 stoichiometry hostguest complex.

The UV-vis absorption spectral change was also monitored during  $Zn^{2+}$  addition. The absorption spectrum of **Tb** · **L** in acetonitrile without  $Zn^{2+}$  had  $\lambda_{max} = 203$  nm and broad band at 291 nm, tailing out to 320 nm (Fig. 3). The absorption spectrum of **Tb** · **L** changed upon addition of  $Zn^{2+}$  (0–1.0 equiv), and then remained at a plateau upon further addition of  $Zn^{2+}$  in accordance with the luminescence spectra. The absorption wavelength changes below 300 nm were supposed to be due to pyridine- $Zn^{2+}$  coordination [15(a)]. Thus, 1:1 complex stoichiometry was observed in both the absorption and the luminescence emission spectra of **Tb** · **L**. Upon addition of a stoichiometric ratio cations such as K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup>,



Fig. 3. Absorbance spectra of 5  $\mu$ M acetonitrile solution of **Tb** · **L** upon addition of Zn<sup>2+</sup>, which was added as Zn(NO<sub>3</sub>)<sub>2</sub>: 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6. 0.7, 0.8, 0.9, 1.0 equiv of Zn<sup>2+</sup> with respect to **Tb** · **L**.

 $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Hg^+$  do not cause any detectable changes in the UV–vis spectra, even when more than 20 stoichiometric ratios of cation are added.

A possible reason for the enhanced luminescence may be as follows. Before coordination with  $Zn^{2+}$ , nitrogen atoms of  $\mathbf{Tb} \cdot \mathbf{L}$  could form an intramolecular hydrogen bond with hydrogen atoms, which resulted in a photoinduced electron-transfer, and the de-excitation occured mainly via a nonradiative pathway. These processes consequently led to the weak fluorescence of  $\mathbf{Tb} \cdot \mathbf{L}$  in acetonitrile solution. Once  $\mathbf{Tb} \cdot \mathbf{L}$  was coordinated with  $\mathbf{Zn}^{2+}$ , the electron-transfer process was forbidden [25], and an extended  $\pi$ -electron conjugation system was formed synchronously. This conjugation system was involved in an intramolecular charge transfer (ICT) process from the ligand donor to the  $Zn^{2+}$  acceptor. Owing to the formation of the extended  $\pi$ electron conjugation system, the  $\mathbf{Tb} \cdot \mathbf{L}/\mathbf{Zn}^{2+}$  system exhibited an enhanced Tb-centred luminescence. Therefore, the participation of nitrogen atoms in binding with Zn(II) complexation helps in the release of fluorescence through efficient intramolecular energy transfer from the pyridyl group to the Tb(III) ion. Thus  $\mathbf{Tb} \cdot \mathbf{L}$  represents a new case of luminescence enhancement with Zn(II) ion. This finding may not only enlarge the arsenal for detecting Zn(II) ion, but also add new merits to the chemistry of salicylamide derivatives, which are usually used as the chromophore for the lanthanide fluorescence and constituents for tunable supramolecular chemistry.

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### Appendix A. Supplementary material

CCDC 644770 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche. 2007.05.021.

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- [19] Picolylsalicylamide (5.0 mmol), potassium carbonate (9.0 mmol) and DMF (100 cm<sup>3</sup>) were warmed to ca. 90 °C and triethylene glycol di-ptosylate (2.0 mmol) was added. The reaction mixture was stirred at 90-95 °C for 48 h. After cooling down, the mixture was poured into water (100 cm<sup>3</sup>) and extracted with CHCl<sub>3</sub>. The CHCl<sub>3</sub> layer was evaporated to dryness to give the crude product, which was recrystallized in ethyl acetate to afford pure ligand L as a white solid, yield 72%. Anal. Found: C, 67.61; H, 5.84; N, 9.53. Calc. for C<sub>32</sub>H<sub>34</sub>N<sub>4</sub>O<sub>6</sub>(%): C, 67.35; H, 6.01; N, 9.82. Major IR bands (KBr; v, cm<sup>-1</sup>): 3382(m), 2920(m), 2880(m), 1649(s, C=O), 1601(m), 1537(s), 1489(m), 1452(m), 1304(s), 1251(s, Ar-O), 1133(s, C-O-C), 1035(s), 755(s), 617(m). <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>): δ 3.44 (4H, s), 3.82 (4H, t, J = 4.5), 4.19 (4H, t, J = 4.6), 4.77 (4H, d, J = 6.0), 6.90-8.52 (16H, m, Ar–H), 8.95 (s, 2H, NH); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ: 45.25, 68.04, 69.11, 70.52, 99.29, 112.60, 121.49, 121.65, 122.07, 132.23, 132.73, 136.67, 148.80, 156.80, 157.71, 165.35. UV-vis (CH<sub>3</sub>CN): 238 nm (38,100  $M^{-1} cm^{-1}$ ), 287 nm(18,000  $M^{-1} cm^{-1}$ ). MS m/z: 571 [M+H<sup>+</sup>].
- [20] The detailed synthesis for Tb · L is as follows: The ligand (0.1 mmol) was dissolved in the minimum amount of ethyl acetate at 60 °C. Tb(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O (0.1 mmol) was also dissolved in the minimum amount of ethyl acetate and added to the ligand solution and left to stir at room temperature for 4 h. 1 cm<sup>3</sup> of methanol was added and filtered. Upon standing the filtrate at room temperature for several weeks, [TbL(NO<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] (Tb · L) was obtained as colorless needles. Yield 52%. Anal. Found (%): C, 39.98; H, 4.24; N, 10.40; Tb, 16.48. Calcd for C<sub>32</sub>H<sub>38</sub>N<sub>7</sub>O<sub>17</sub>O<sub>16</sub>Tb (%): C, 40.39; H, 4.02; N, 10.30; Tb, 16.70. Major IR bands (KBr;  $\nu$ , cm<sup>-1</sup>): 1589 (w), 1569 (w), 1446 (s), 1394 (w), 1276 (w), 1230 (s), 1215 (s), 1146 (s), 1108 (s), 1088 (s), 996 (w) 855 (s), 842 (s) 822 (w), 772 (s), 750 (w) 726 (w), 637 (s) 626 (s), 577 (s), 557 (w), 527(w). UV–vis (CH<sub>3</sub>CN): 203 nm (20,400 M<sup>-1</sup> cm<sup>-1</sup>).
- [21] Crystal diffraction intensities for Tb · L were collected at 298 K on a CCD area detector with graphite-monochromated Mo Ka radiation  $(\lambda = 0.71073 \text{ Å})$ . The structures were solved with direct methods and refined with the full-matrix least-squares technique based on F<sup>2</sup> using the SHELXTL program package. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically, the water hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Crystal data for Tb  $\cdot$  L: crystal dimensions 0.34  $\times$  0.23  $\times$  0.19 mm, Triclinic, space  $P\bar{1}$ , a = 12.457(2) Å, b = 12.900(2) Å, c =14.545(3) Å,  $\alpha = 65.437(3)^{\circ}$ ,  $\beta = 77.343(3)^{\circ}$ ,  $\gamma = 64.425(3)^{\circ}$ ,  $V = 1915.3(6) \text{ Å}^3$ , Z = 2,  $\rho_{calcd} = 1.650 \text{ g cm}^{-3}$ , M = 951.61. Of the 10016 symmetry independent reflections (2.54°<  $\theta$  < 25.01°), 6640 reflections are observed  $[I > 2\sigma(I)]$ . On the basis of all these data and 514 refined parameters, R1 = 0.0339, wR2 = 0.0750 and GOF on  $F^2$ of 1.005 were obtained.
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