

## Supporting Information

# Efficient Near-Infrared Emission of A Ytterbium<sup>III</sup> Compound having A Green Light Rhodamine Donor

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### Instruments and experimental procedures

**Materials.** All chemicals purchased were of reagent grade or better and were used without further purification. Lanthanide chloride salts were prepared by dissolving lanthanide oxides with concentrated HCl, and then evaporating at 100 °C until the crystal film formed. Lanthanide nitrate salts were prepared by dissolving lanthanide oxides with concentrated HNO<sub>3</sub>, and then evaporating at 100 °C until the crystal film formed. The elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer. The infrared (IR) spectra were recorded in 400-4000 cm<sup>-1</sup> region on a Nicolet Impact 410 FTIG spectrometer using KBr pellets. <sup>1</sup>H-NMR spectra were recorded on a VARIAN INOVA-400 spectrometer with chemical shifts reported as ppm (in CDCl<sub>3</sub>-d<sub>6</sub>, TMS as internal standard). Mass spectrometric data were obtained on a HP 1100LC/MSD mass spectrometry.

**X-ray Crystallographic Study.** Data collection was performed on a SIEMENS SMART CCD diffractometer with graphite-monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation at room temperature. The structures were solved by direct methods and refined by the full-matrix least-squares on  $F^2$  using the SHELX-97 program.

For compound **1**, except one of the disordered ethyl groups, the non-solvent atoms and were refined anisotropically. Except the solvent molecules, hydrogen atoms were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atom

Two of the ethyl groups and the oxygen atoms on the nitrate ion were disordered into two parts with the site occupancy factors of the atoms being refined by free variable or fixed at 0.5 for each parts, respectively. For compound **2**, several non-solvent atoms and some of the solvent oxygen atoms were refined isotropically. Except the solvent molecules, hydrogen atoms were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms calculated distances and allowed to ride on the parent non-hydrogen atoms.

**Fluorescence Spectroscopies.** Fluorescence spectroscopy data were recorded on an AB-Series 2 luminescence spectrometer. Quantum yields were calculated according to eq. 1,

$$\Phi_{\text{unk}} = \Phi_{\text{std}} \frac{(I_{\text{unk}}/A_{\text{unk}})}{(I_{\text{std}}/A_{\text{std}})} \left( \frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2 \quad (1)$$

where  $\Phi_{\text{unk}}$  and  $\Phi_{\text{std}}$  are the radiative quantum yields of the sample and the standard, respectively,  $I_{\text{unk}}$  and  $I_{\text{std}}$  represent the areas of the corrected emission profiles for the sample and the standard,  $A_{\text{unk}}$  and  $A_{\text{std}}$  are the absorbance values of the sample and the standard at the excitation wavelength, and  $\eta_{\text{unk}}$  and  $\eta_{\text{std}}$  correspond to the indices of refraction of the sample and standard solutions (taken to be equal to the neat solvents). Excitation wavelengths were 420 nm for all samples. Yb(TTA)<sub>3</sub> in toluene (Q = 0.35%; tta = thenoyltrifluoroacetylacetonate)<sup>1</sup> was used as reference for the determination of the absolute quantum yields.<sup>2</sup>

### 1. Synthesis routes and characterization

**Synthesis of HQR1.** Rhodamine-6G hydrozone is prepared according to the literature method.<sup>3</sup> Rhodamine-6G hydrozone (2 mmol, 0.857 g) and 8-hydroxyquinoline-2-carboxaldehyde (2 mmol, 0.346 g) were mixed in 25 ml methanol with 5 drops of glacial acetic acid. The reaction mixture was refluxed for 5 hours. After cooling to the room temperature, the resulting yellow solid was washed by hot methanol for three times to give 0.833 g of **QR1** (yellow solid) in a yield of 69.4%. Anal calc. for **QR1** (C<sub>36</sub>H<sub>33</sub>N<sub>5</sub>O<sub>3</sub>): C, 74.08; H, 5.70; N, 12.00.

Found: C, 74.45; H, 5.64; N, 11.74;  $^1\text{H}$  NMR ( $\text{CDCl}_3-d_6$ )  $\delta$  8.480 (1 H, s), 8.113 (1 H, d,  $J = 8.8$  Hz), 8.060 (1 H, d,  $J = 6.4$  Hz), 8.009 (1 H, d,  $J = 8.4$  Hz), 7.502 (2 H, m,  $J = 12.0$  Hz), 7.363 (1 H, t,  $J = 15.6$  Hz), 7.236 (2 H, t), 7.092 (2H, m,  $J = 11.2$  Hz), 6.462 (2 H, s), 6.366 (2 H, s), 3.221 (4 H, m,  $J = 21.2$  Hz), 1.891 (6 H, s), 1.308 (6 H, t,  $J = 14.0$  Hz).

**Synthesis of  $[\text{Yb}(\text{C}_{36}\text{H}_{33}\text{N}_5\text{O}_3)_2(\text{NO}_3)](\text{CH}_3\text{OH})(\text{H}_2\text{O})$ , **1**.** To a warm suspension of **HQR1** (0.1 mmol, 60.6 mg) in 20 mL methanol was added a solution of  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (0.1 mmol, 44.9 mg) in 5 mL methanol. The color of the solution turned from yellow to dark red. The resulting mixture was stirred for 30 min and left for crystallization in air. Red block crystals suitable for X-ray single-crystal structural determination were obtained in two weeks in a low yield (21.8% based on **HQR1**). Anal. Calcd for **1**  $\text{C}_{75}\text{H}_{80}\text{N}_{11}\text{O}_{13}\text{Yb}$ : C, 59.35; H, 5.32; N, 10.16; Found: C, 59.97; H, 5.12; N, 10.25.

**Synthesis of  $[\text{Gd}(\text{C}_{36}\text{H}_{33}\text{N}_5\text{O}_3)_2\text{Cl}](\text{H}_2\text{O})_{13}$ , **2**.** To a warm suspension of **HQR1** (0.1 mmol, 60.6 mg) and KOH (0.1 mmol, 5.60 mg) in 20 mL methanol and 1 mL  $\text{H}_2\text{O}$  was added a solution of  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  (0.1 mmol, 37.2 mg) in 5 mL methanol. The color of the solution turned from yellow to dark red. The resulting mixture was stirred for 30 min and left for crystallization in air. After four weeks, red crystals were formed in a low yield (24.4% based on **HQR1**). Anal. Calcd for **2**  $\text{C}_{72}\text{H}_{86}\text{ClGdN}_{10}\text{O}_{16}$ : C, 56.15; H, 5.63; N, 9.09. Found: C, 56.64; H, 5.60; N, 9.43.

**Synthesis of  $[\text{Nd}(\text{C}_{36}\text{H}_{33}\text{N}_5\text{O}_3)_2(\text{NO}_3)](\text{CH}_3\text{OH})(\text{H}_2\text{O})$ , **3**.** To a warm suspension of **HQR1** (0.1 mmol, 60.6 mg) in 20 mL methanol was added a solution of  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (0.1 mmol, 44.9 mg) in 5 mL methanol. The color of the solution turned from yellow to dark red. The resulting mixture was stirred for 30 min and left for crystallization in air. Red powder was obtained in one week in a low yield (23.7% based on **HQR1**). Anal. Calcd for **3**  $\text{C}_{75}\text{H}_{80}\text{N}_{11}\text{O}_{13}\text{Nd}$ : C, 60.63; H, 5.43; N, 10.38; Found: C, 60.77; H, 5.23; N, 10.35.

## References:

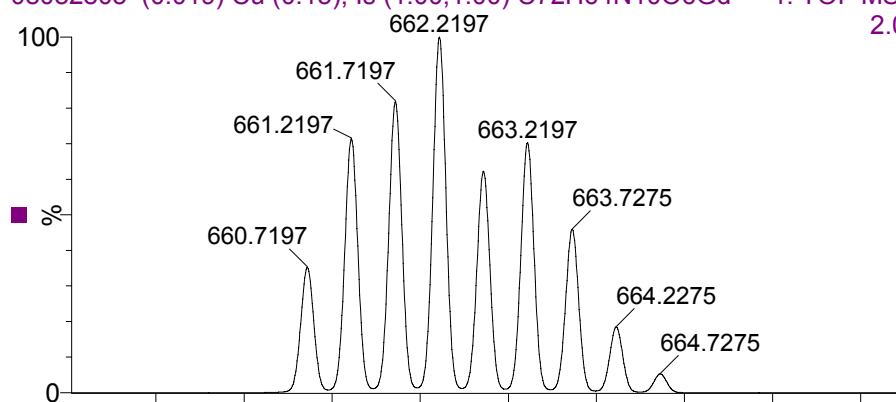
(1) S. B. Meshkova, Z. M. Topilova, D. V. Bolshoy, S. V. Beltyukova, M. P.

Tsvirko and V. Y. Venchikov, *Acta Physica Polonica A*, 1999, **95**, 983-990.

(2) A. Jurisand, V. Balzani, *Coord. Chem. Rev.*, 1988, 84, 85.

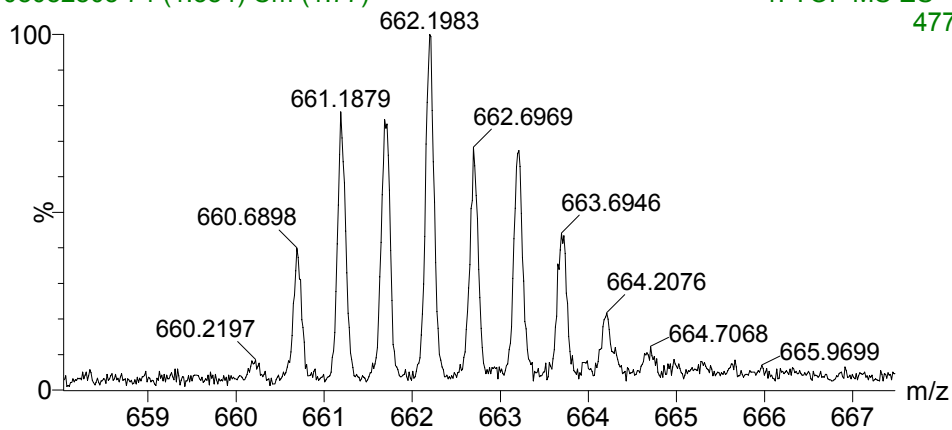
(3) D. Wu, W. Huang, C. Duan, Z. Lin, Q. Meng, *Inorg. Chem.*, 2007, 46,  
1538-1540.

08082805 (0.019) Cu (0.15); Is (1.00,1.00) C72H64N10O6Gd 1: TOF MS ES+  
2.01e12

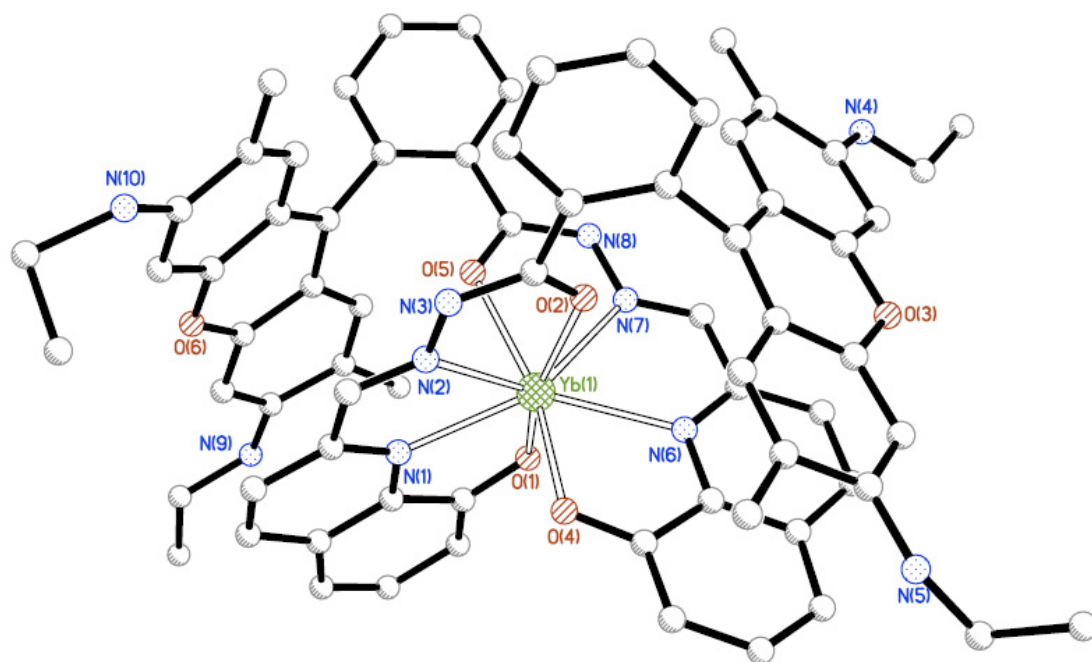


08082805 74 (1.384) Cm (1:77)

1: TOF MS ES+  
477



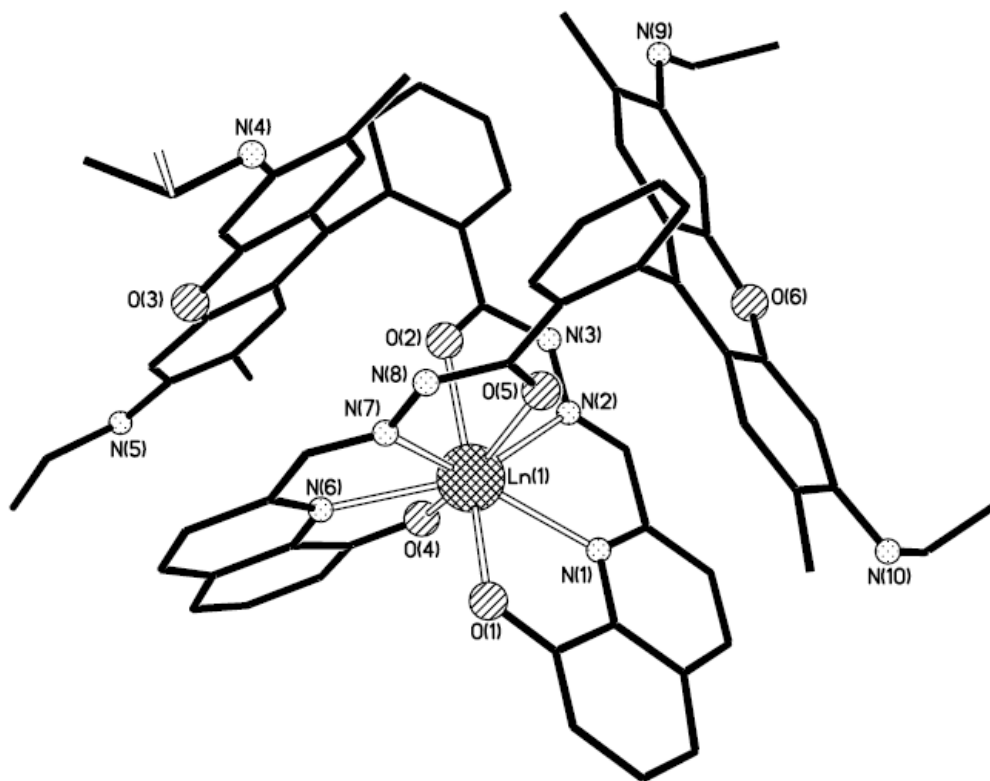
**Figure S1** ESI-MS spectra of the Gd<sup>III</sup> compound 2 at m/z range of 660-670 showing the experimental (Bottom) and theoretical simulation of the peaks (top) corresponding to the Gd(QR1)<sub>2</sub>



**Figure S2** Crystal structure of the Yb<sup>III</sup> compound showing the atomic-numbering scheme, the anions, solvent molecules as well as the hydrogen atoms were omitted for clarity.

**Table S1** Selected Bond distances (Å) and angles (°) of Yb<sup>III</sup> Compound **1**

Yb(1)–O(4)	2.245(3)	Yb(1)–N(1)	2.388(3)
Yb(1)–O(1)	2.255(3)	Yb(1)–N(6)	2.403(3)
Yb(1)–O(2)	2.307(3)	Yb(1)–N(2)	2.449(3)
Yb(1)–O(5)	2.342(3)	Yb(1)–N(7)	2.463(3)
O(4)–Yb(1)–O(1)	97.1(1)	O(4)–Yb(1)–N(7)	132.6(1)
O(4)–Yb(1)–O(2)	91.4(1)	O(1)–Yb(1)–N(7)	81.8(1)
O(1)–Yb(1)–O(2)	161.2(1)	O(2)–Yb(1)–N(7)	80.3(1)
O(4)–Yb(1)–O(5)	162.6(1)	O(5)–Yb(1)–N(7)	63.4(1)
O(1)–Yb(1)–O(5)	91.9(1)	N(1)–Yb(1)–N(7)	134.5(1)
O(2)–Yb(1)–O(5)	84.5(1)	N(6)–Yb(1)–N(7)	63.6(1)
O(4)–Yb(1)–N(1)	86.1(1)	N(2)–Yb(1)–N(7)	130.8(1)
O(1)–Yb(1)–N(1)	68.7(1)	O(4)–Yb(1)–N(2)	83.6(1)
O(2)–Yb(1)–N(1)	128.8(1)	O(1)–Yb(1)–N(2)	132.8(1)
O(5)–Yb(1)–N(1)	83.3(1)	O(2)–Yb(1)–N(2)	64.6(1)
O(4)–Yb(1)–N(6)	69.2(1)	O(5)–Yb(1)–N(2)	79.3(1)
O(1)–Yb(1)–N(6)	84.2(1)	N(1)–Yb(1)–N(2)	64.3(1)
O(2)–Yb(1)–N(6)	83.2(1)	N(6)–Yb(1)–N(2)	137.3(1)
O(5)–Yb(1)–N(6)	126.9(1)	N(1)–Yb(1)–N(6)	140.8(1)



**Figure S3** Crystal structure of the Gd<sup>III</sup> compound showing the atomic-numbering scheme, the anions, solvent molecules as well as the hydrogen atoms were omitted for clarity.



**Table S2** Selected Bond distances (Å) and angles (°) of Gd<sup>III</sup> Compound **2**

Gd(1)–O(1)	2.283(4)	Gd(1)–N(1)	2.477(4)
Gd(1)–O(4)	2.292(4)	Gd(1)–N(6)	2.480(4)
Gd(1)–O(2)	2.412(3)	Gd(1)–N(2)	2.542(5)
Gd(1)–O(5)	2.419(4)	Gd(1)–N(7)	2.562(4)
O(1)–Gd(1)–O(4)	104.0(2)	O(1)–Gd(1)–N(2)	127.6(1)
O(1)–Gd(1)–O(2)	165.7(1)	O(4)–Gd(1)–N(2)	79.4(2)
O(4)–Gd(1)–O(2)	88.0(1)	O(2)–Gd(1)–N(2)	61.7(1)
O(1)–Gd(1)–O(5)	94.0(1)	O(5)–Gd(1)–N(2)	83.9(1)
O(4)–Gd(1)–O(5)	160.6(1)	N(1)–Gd(1)–N(2)	61.3(1)
O(2)–Gd(1)–O(5)	75.3(1)	N(6)–Gd(1)–N(2)	138.5(2)
O(1)–Gd(1)–N(1)	66.6(1)	O(1)–Gd(1)–N(7)	83.1(1)
O(4)–Gd(1)–N(1)	87.6(1)	O(4)–Gd(1)–N(7)	127.4(1)
O(2)–Gd(1)–N(1)	122.6(1)	O(2)–Gd(1)–N(7)	83.4(1)
O(5)–Gd(1)–N(1)	93.0(1)	O(5)–Gd(1)–N(7)	61.4(1)
O(1)–Gd(1)–N(6)	85.9(1)	N(1)–Gd(1)–N(7)	139.1(1)
O(4)–Gd(1)–N(6)	67.7(2)	N(6)–Gd(1)–N(7)	60.9(1)
O(2)–Gd(1)–N(6)	91.7(1)	N(2)–Gd(1)–N(7)	136.5(1)
O(5)–Gd(1)–N(6)	121.8(1)	N(1)–Gd(1)–N(6)	137.6(1)

