A Novel Luminescent Chemosensor for Detecting Hg^{2+} Based On the Pendant Benzo Crown Ether Terbium Complex

Dianyi Liu,[a] Kuanzhen Tang,[a] Weisheng Liu,[a] Chengyong Su,[b] Xuhuan Yan,[a] Minyu Tan[a], Yu Tang [a*]

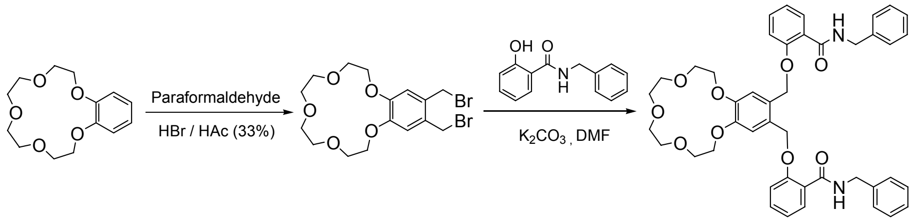
[a] Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University
Lanzhou 730000 (China)
Tel: (+86) 931-891-2552
Fax: (+86) 931-891-2582
E-mail: tangyu@lzu.edu.cn
[b] School of Chemistry and Chemical Engineering, Sun Yat-Sen University
Guangzhou 510275 (China)

Materials and General Methods.

All material and solvents employed in this study were analytical reagents.

Single-crystal data were performed with graphite-monochromated Mo Kα radiation on a Bruker SMART CCD diffractometer and collected by the ω-2θ scan technique. The structure was solved using direct methods and refined with the SHELXTL 97 program package. ^{1}H NMR spectra of the ligand L were recorded on a Varian Mercury 300 spectrometer in $CDCl_3$ solution with TMS as an internal standard. UV-visible spectra were obtained on a Varian cary-100 UV-visible spectrophotometer. Luminescence measurements were made on a Hitachi F-4500 fluorescence spectrophotometer equipped with quartz curettes of 1.0 cm path length. The excitation slit widths was 2.5 nm and emission slit widths was 5.0 nm. The concentration of complex used 1.0×10^{-4} M in methanol with 0.1 M $[(n\text{-Bu})_4N]ClO_4$ as the supporting electrolyte. The luminescence lifetime and quantum yield were recorded on an Edinburgh Instrument FLS-920 time resolved and steady state fluorescence spectrometer.

Synthesis route for the ligand L



Synthesis of 4,5-dibromomethyl-benzo-15-crown-5

4,5-dibromomethyl-benzo-15-crown-5 was prepared by the literature reported method (Tetrahedron, 1990, 46, 2461).

0.845 g benzo-15-crown-5 and 0.6 g paraformaldehyde were dissolved in 7 cm^3 of 33% solution of hydrogen bromide in acetic acid. The reaction mixture was stirred at room temperature for 2 hour, then the reaction mixture was added in 100 cm^3 water, filtered the precipitate to give 1.08 g (75% yield) as the white powder, which was subjected to the next reaction without further purification.

Synthesis of 4,5-bis{[(2'-benzylaminoformyl)-phenoxyl]methyl}-benzo-15-crown-5 (L).

N-benzylsalicylamide (2.724 g, 12 mmol), K_2CO_3 (1.656 g, 12 mmol) and DMF (30 cm^3) were warmed to *ca* 60°C and 4,5-dibromomethyl-benzo-15-crown-5 (2.269 g, 5 mmol) was added. The reaction mixture was stirred at 90°C for 10 h. After cooling down, the mixture was poured into water (200 cm^3). The resulted solid was treated by column chromatography on silica gel using the mixed solution of petroleum ether and ethyl acetate (3:1) as eluent to give L as white powder in 76% yield. m.p. 154-155°C; ^{1}H NMR($CDCl_3$, 300MHz) δ: 3.790(s, 8H), 3.890-3.917(t, 4H), 4.005-4.032(t, 4H), 4.443-4.460(d, 4H), 4.847(s, 4H), 6.729(s, 2H), 6.826-6.854(d, 2H), 7.032-7.112(m, 6H), 7.170-7.206(m, 6H), 7.346-7.403(t, 2H), 7.932-7.950(t, 2H), 8.210-8.241(d, 2H).

Table S1: Crystal date and detail of the structure determination for the complex

Formula	$C_{44}H_{48}N_5O_{19}Tb$
Formula weight	1109.79
Crystal System	orthorhombic
Space group	*Pbca*
a, b, c [Å]	20.528(2), 18.6375(18), 24.389(3)
V [Å^3]	9330.7(18)
Z	8
D(calc) [g/cm^3]	1.580
μ (Mo$K\alpha$) [mm^{-1}]	1.599
F (000)	4512
Crystal Size [mm]	0.25×0.25×0.15
Temperature (K)	293
Radiation [Å]	Mo Kα 0.71073
Theta Min-Max [°]	2.23, 28.25
Tot., Uniq. Data. R(int)	20469, 10066
Observed data [$I > 2.0\ \sigma(I)$]	10066 (0.0476)
R, wR, GOF	0.0610, 0.1238, 1.011
$w=1/[s^2(Fo^2)+(0.0423P)^2+0.0000P]$	where $P=(Fo^2+2Fc^2)/3$
Max. and Av. Shift/Error	0.003, 0.000
Min. and Max. resd. Dens. [e Å^{-3}]	-0.463, 1.204

Figure S1. The H-bond in each pair of neighboring coordination polymeric chain.

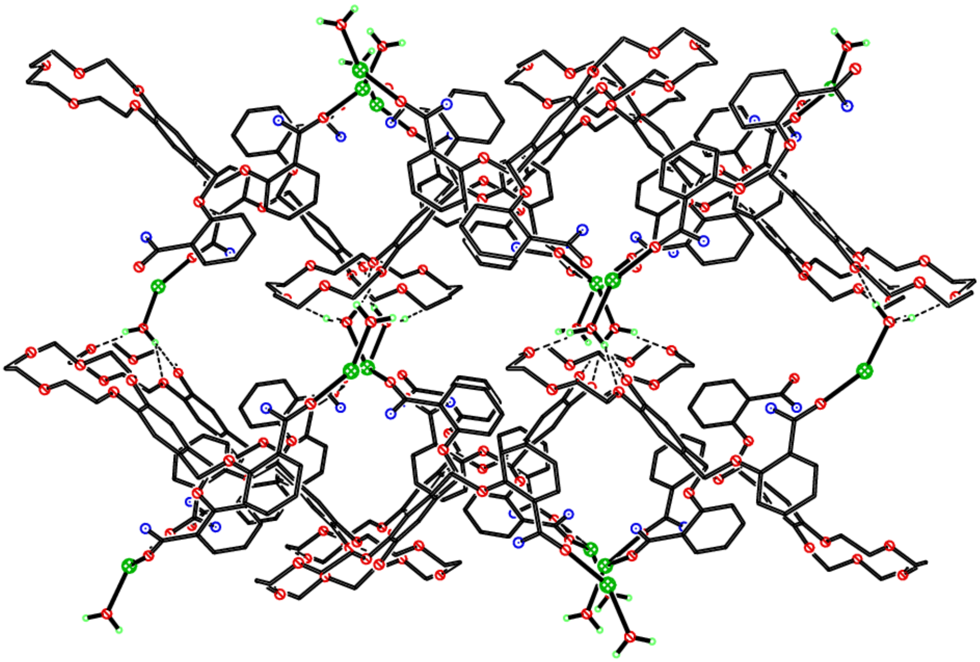


Figure S2. Luminescent spectra of L upon addition different concentrations of Tb^{3+}, the inset shows the changes of the luminescence intensity at λ = 546 nm and it give the complex with 1:1 stoichiometry of L and Tb^{3+}.

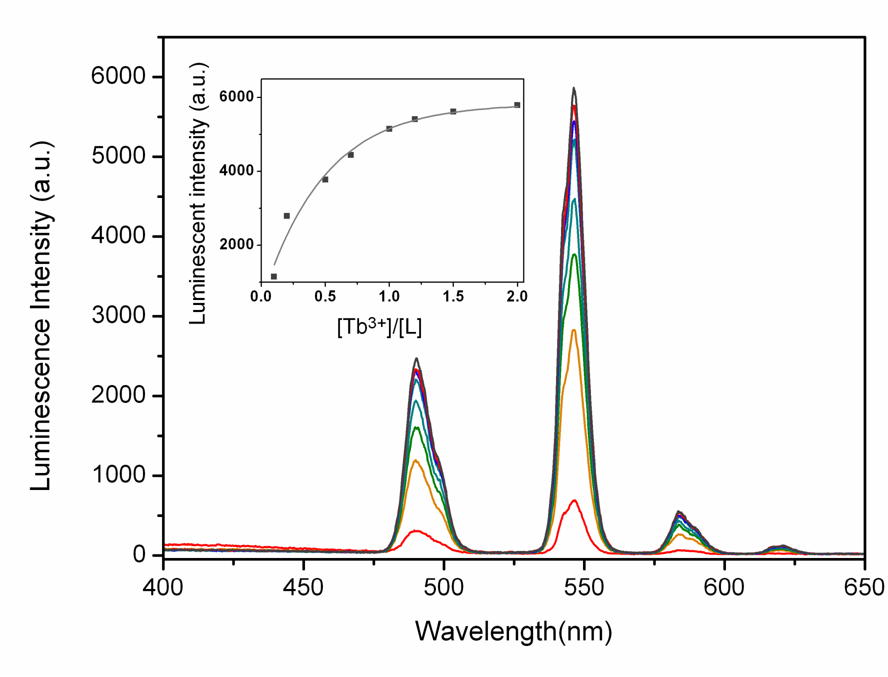


Figure S3. Job's plot of L with Tb^{3+} (luminescence intensity at λ = 546 nm) and it give the complex with 1:1 stoichiometry of L and Tb^{3+}.

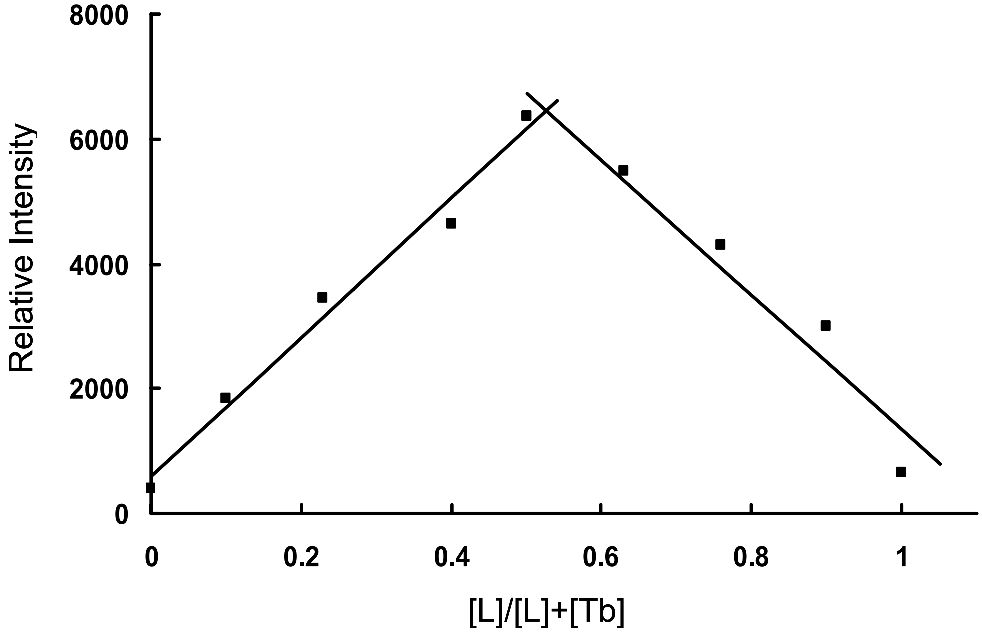
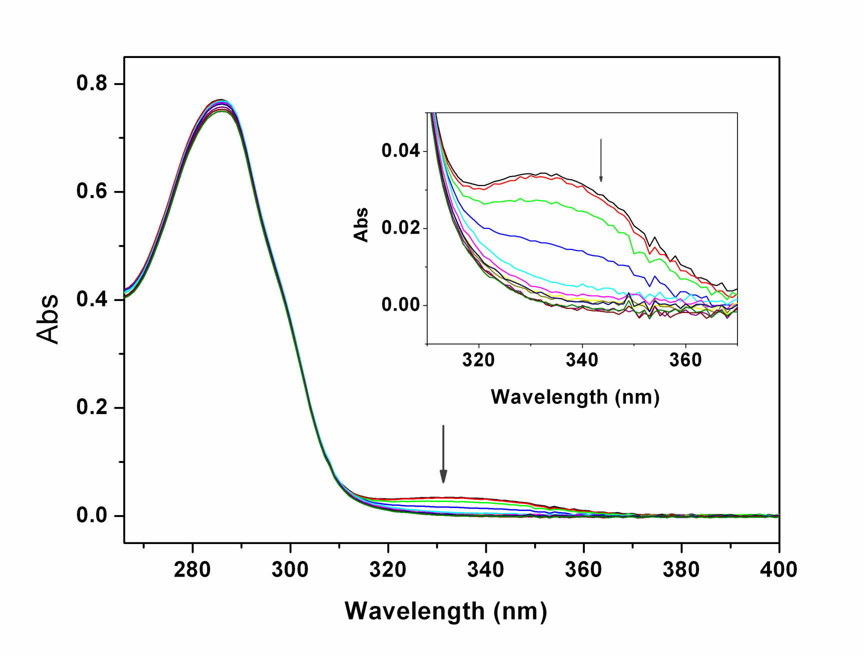


Figure S4. Absorption spectra of [TbL] (1.0×10^{-4} M) in methanol with 0.10 M $[(n\text{-}Bu)_4N]ClO_4$ as the supporting electrolyte in the presence of various concentrations of Hg^{2+} ($0-2.5\times10^{-4}$ M).

a. The changes of the absorption spectrum. The inset shows the spectra magnified between 310-370 nm.



b. The changes of the absorption spectra at $\lambda = 340$ nm.

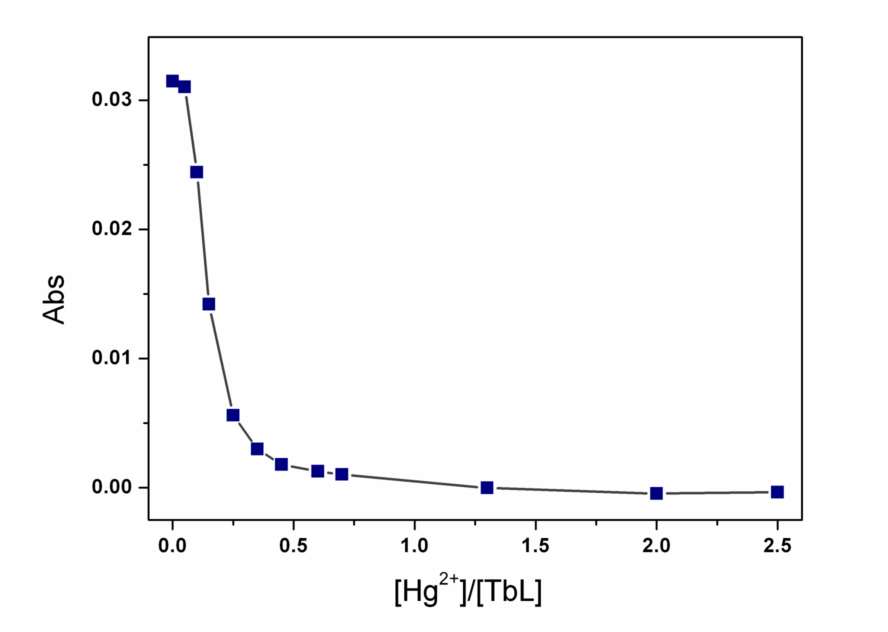


Figure S5. The Luminescence excitation spectra of the Tb(III) complex (1.0×10^{-4} M) in methanol with 0.10 M $[(n\text{-}Bu)_4N]ClO_4$ as the supporting electrolyte.

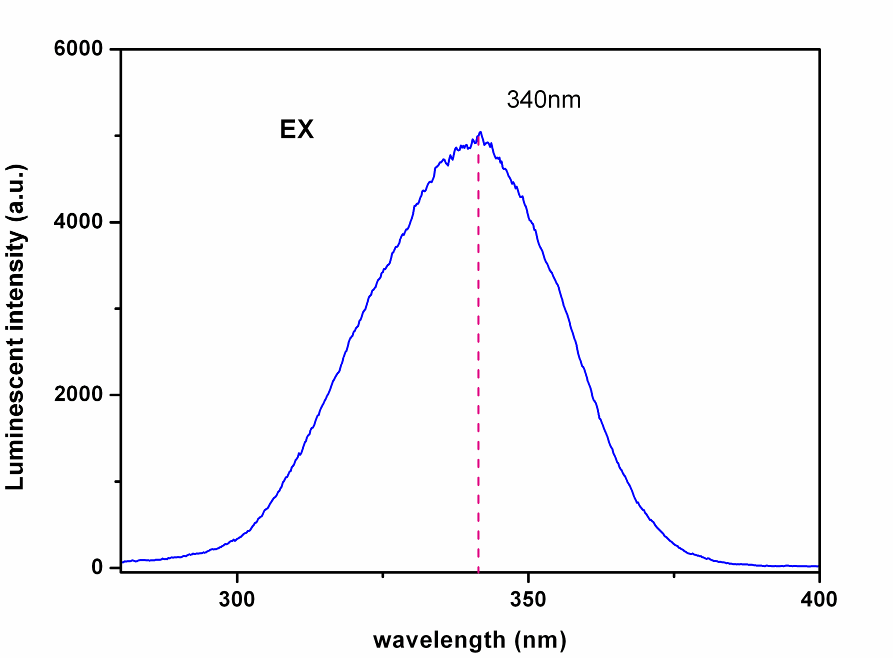


Figure S6. Luminescence emission spectra (excitation at 340 nm) of the Tb(III) complex (1.0×10^{-4} M) in methanol with 0.10 M $[(n\text{-Bu})_4N]ClO_4$ as the supporting electrolyte in the presence of 1.0 equiv of cations.