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A Step Forward Unraveling the Lanthanides Discrimination Puzzle: Structure-Selectivity Relationship Based on Phenanthroline Diimides Ligands Towards Europium and Terbium Detection in Water

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* Corresponding authors: <u>xiaoyan.tang@pku.edu.cn</u> (Xiaoyan Tang) and <u>liwang862011@gmail.com</u> (Li Wang) Materials and Characterizations. All chemicals and ultradry solvents were purchased from Energy Chemical Inc. and used as received unless otherwise stated. Other analytical pure solvents were purchased from Bei Jing Tong Guang Fine Chemicals Company. Metal complexes in their nitrate forms were purchased from Aladdin with purity of 99.99%. Nuclear Magnetic Resonance spectroscopy (NMR) was collected on a VARIAN-600 MHz NMR spectrometer in deuterated dimethyl sulfoxide (DMSO-d₆). High resolution mass spectrometric (HRMS) analyses were performed on a 12 T Solarix MALDI-FT-ICR MS (Bruker Daltonics). UV-vis spectra were collected on a Hitachi 3900H spectrometer with 1-cm cuvettes at 25 °C. Absorbance in the range of 250 to 600 nm were recorded with scan speed of 1200 nm/min and sampling interval of 1 nm. Photoluminescence spectra (PL) and photoluminescence excitation spectra (PLE) were recorded on a Hitachi F-4600 spectrometer (S/N: 2633-003) with excitation of 300 nm. The excitation and emission slits were 5/5 nm. Fourier transform infrared (FT-IR) spectroscopy was performed on a Brucker Tensor 27 spectrometer; data were recorded in the range of 500 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Electrochemical data were collected on a CHI660D electrochemical analyser with a three-electrode cell architecture in dry DMF. A Pt disk (diameter = 3 mm, Part No. BZ-PT, GaoSS Union), Pt wire (Part No. Pt0537, GaoSS Union) and Ag/AgCl (Part No. R1038, GaoSS Union) were used as working, counter and reference electrode, respectively. The ligands concentrations were set to 1×10^{-3} M with 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as supporting electrolyte. The scan rate was set to 100 mV/s. Both Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were recorded with redox potential calibrated by the ferrocene/ferrocenium (Fc/Fc+) in the same solution.

Ligand photoluminescence quantum yields. The quantum yield of both Phen-2DIBA and Phen-2DIBA-re were measured relative to quinine bisulfate in 0.05 M H₂SO₄ ($\Phi = 0.54$).¹ The same stock solutions of Phen-2DIBA and Phen-2DIBA-re were used and diluted into DI water such that all absorbances at 310 nm were almost the same (A = 0.1). The absorption and emission spectra were then recorded for quinine bisulfate, Phen-2DIBA and Phen-2DIBA-re. The fluorescence spectra were integrated and the quantum yields were calculated according the following equation:²

$$\phi_{S} = \phi_{R} \left(\frac{I_{S}}{I_{R}}\right) \left(\frac{1 - e^{-A_{R}}}{1 - e^{-A_{S}}}\right) \left(\frac{n_{S}}{n_{R}}\right)^{2}$$

Where the subscripts S and R denoted the sample and reference. ϕ_S is the quantum yield of the standard under known conditions; I is the emission spectra integration; A is the absorbance at the excitation wavelength; n is the refractive index of the solution.

Lns(III) sensing experiments. 2.2 mg of both Phen-2DIBA and Phen-2DIBA-re were dissolved in 0.5 mL dry DMSO to give the ligand stock solutions of 10 mM. Then 160 μ L of as-prepared stock solutions were diluted by 80 mL DI water to give the 2×10⁻⁵ M of ligand solutions. Lanthanides salts of La(NO)₃·6H₂O, Ce(NO)₃·6H₂O, Pr(NO)₃·6H₂O, Nd(NO)₃·6H₂O, Sm(NO)₃·6H₂O, Eu(NO)₃·6H₂O, Gd(NO)₃·6H₂O, Tb(NO)₃·5H₂O, Dy(NO)₃·5H₂O, Ho(NO)₃·5H₂O, Er(NO)₃·6H₂O, Tm(NO)₃·6H₂O, Yb(NO)₃·6H₂O and Lu(NO)₃·6H₂O were prepared in their corresponding stock solutions in water with concentrations of 100 mM. 10 μ L of each lanthanide cation solution was added to the 5 mL ligand solutions. The final solutions were mixed thoroughly by vertexing for 5 minutes. The metal to ligand ratios were 10. The absorption and emission spectra were then recorded.

Ratiometric sensing and determine the limits of detection. Ratiometric sensing of **Phen-2DIBA** and **Phen-2DIBA-re** towards Eu(III) and Tb(III) were done in aqueous media. Briefly, 10 mM stock solution of **Phen-2DIBA** and **Phen-2DIBA-re** in DSMO were prepared as described in the previous section, which were then diluted to 2×10^{-5} M by adding 80 mL DI water to the 160 µL 10 mM ligand stock solutions. 0, 1, 2, 4, 5, 6, 8, 10, 20, 40, 50, 60, 80, 100 µL of Eu(NO)₃·6H₂O in water with concentration of 1 mM were separately added into 5 mL 2×10^{-5} M of **Phen-2DIBA** to give the Eu(III)/**Phen-2DIBA** solutions with M/L ratios of 0, 0.1, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0, 2.0, 4.0, 5.0, 6.0, 8.0, 10, respectively. The final solutions were mixed thoroughly by vertexing for 5 minutes before absorption and emission spectra were taken. Similar procedures were followed for **Phen-2DIBA-re** with Tb(III). Limits of detections are calculated from emission titration experiments, emission peaks at 590 nm for **Phen-2DIBA/Eu(III)** and 544 nm for **Phen-2DIBA-re**/Tb(III) were used. Data in the low Ln³⁺ range were normalized between the minimum and maximum values as below:

$$\frac{I_x - I_0}{I_{max} - I_0}$$

Linear regression curves were then fitted to the normalized data and the point at which the line crosses the abscissa axes was considered as the detection limit.³⁻⁵

Anti-interfering experiments. To show the selective sensing of **Phen-2DIBA** and **Phen-2DIBA-re** towards Eu(III) and Tb(III) in the presence of other Lns(III). Stock solution of **Phen-2DIBA**/Eu(III) (ratio of 1/10) was prepared and divided into 13 equivalents, to which 10 times (with respect to the ligand) of other Lns(III) was added. The mixtures were mixed thoroughly and then absorption and emissions were recorded. Similar procedures were applied for **Phen-2DIBA-re**/Tb(III).

IR sample preparations. Fourier transform infrared (FT-IR) spectroscopy was performed on a Brucker Tensor 27 spectrometer; data were recorded in the range of 500 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. The ligand/metal ratios were set to 1 by dissolving equal molar of **Phen-2DIBA** and **Phen-2DIBA-re** with Eu(NO)₃·6H₂O and Tb(NO)₃·5H₂O in methanol. The mixtures were left stirring at room temperature for at least 12 hours before evaporated to dry. The as-prepared powers were mixed with KBr at the mass percentages of ca. 2%.

ESI-MS characterizations. High resolution mass spectrometric (HRMS) analyses were performed on a 12 T Solarix MALDI-FT-ICR MS (Bruker Daltonics). The premixed ligand/metal mixtures (ligand/metal = 1:1, in methanol and stirred at room temperature for at least 12 hours) were introduced through a 15 μ L syringe with a stainless-steel needle. The nebulizer gas pressure was set to 8 psi and the operating nitrogen was employed at 5 L/min. The source temperature was set to 200 °C with the capillary voltage of 3500 V. The ESI source in positive mode with broadband detection was utilized. Typically, mass range over 50 to 1200 were recorded. The m/z values and the absolute magnitudes of all peaks were obtained with Bruker Data Analysis software and exported to text files and reproduced with Origin 2021.

DFT calculations. Theoretical investigations were performed with the B3LYP hybrid density functional and 6-31G(d,p) basis set in the Gaussian03 program.⁶ The fluorescence spectra were calculated based on the time-dependent density functional theory. The electron transition with the largest oscillator strength nearby was analysed for each structure.

Ligand synthesis and characterizations



Scheme S1. Synthesis of two phenanthroline ligands discussed in this paper.

Phen-2DIBA was synthesized according to our recent publication through a two-step procedure.^{7, 8} The starting material of 1,10-phenanthroline-2,9-diamine for the synthesis of **Phen-2DIBA-re** was converted from dichloride phenanthroline.⁹

Synthesis of Phen-2DIBA-re

1,10-phenanthroline-2,9-diamine (210 mg, 1 mmol) was dissolved in 20 mL dry DMF, then glutaric anhydride (5 equivalent, 570 mg, 5 mmol) was added into the solution. The mixture was left stirring for 12 hours at room temperature before water was added to quench the reaction. The pale-yellow precipitate was collected by filtration and washed successively with water, methanol and ether. Pale yellow solid of 300 mg was afforded with a yield of 68%.

¹H NMR (600 MHz, DMSO-*d*₆) δ 12.09 (s, br, 1H), 10.68 (s, 1H), 8.66 – 8.28 (m, 2H), 7.82 (s, 1H), 2.55 (t, *J* = 7.4 Hz, 2H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.87 (p, *J* = 7.4 Hz, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 174.56, 172.66, 151.52, 143.96, 138.75, 126.54, 124.86, 116.15, 40.38, 40.24, 40.10, 39.96, 39.82, 39.68, 39.55, 35.68, 33.44, 20.82. ESI-MS calculated for [M-H]⁻: 437.1466, measured at 437.1468; [M-2H+Na⁺]⁻: 459.1286, measured 459.1287.



Fig. S1. ¹H NMR spectrum of **Phen-2DIBA-re** in DMSO-*d*₆.



Fig. S2. ¹³C NMR spectrum of Phen-2DIBA-re in DMSO-d₆.



Fig. S3. 2D H-H COSY NMR spectrum of Phen-2DIBA-re in DMSO-d₆.



Fig. S4. ESI-MS spectrum of Phen-2DIBA-re in negative mode.

Speculated species	Calculated m/z	Measured m/z
H_2N NH^-	209.0832	209.0832
HN = 0	323.1149	323.1150
HN NH ⁻ HN NA ⁺ O	345.0969	345.0970
	437.1466	437.1468
$\begin{array}{c c} & & & \\ & & & \\ & & & \\ & &$	459.1286	459.1287

Table S1. Species assignment of Phen-2DIBA-re.



Fig. S5. Solubility tests for **Phen-2DIBA** and **Phen-2DIBA-re**. a) Images of both ligands right after heated at 80 °C for 10 minutes; b) Images of both ligands after cooling down to room temperature (25 °C). Conditions: 5 mM ligands in 1.5 M HNO₃.



Fig. S6. Excitation spectra for **Phen-2DIBA** and **Phen-2DIBA-re** monitored at the emission peaks marked on Fig. 1b and 1e in the main text. The conditions were the same as that described for Fig. 1.



Fig. S7. Absorption and emission spectra for quinine bisulfate (in 0.05 M H₂SO₄), **Phen-2DIBA** (in DI water) and **Phen-2DIBA-re** (in DI water). Excitation wavelengths for PL were all 310 nm.

Table S2. Calculation of relative photoluminescence quantum yield for Phen-2DIBA and Phen-2DIBA-re from Fig. S7.

	Ι	A	${\Phi}$
Quinine biSulfate	853280	0.099	0.54
Phen-2DIBA	53213	0.093	0.036
Phen-2DIBA-re	74817	0.109	0.043



Fig. S8. Absorption and emission changes for **Phen-2DIBA-re** as a function of heating time at 80 °C showing the ligand change from its aggerate state to single molecular state. The arrows showed the spectra changing direction with the initial and final curves were marked in black and blue, respectively. Excitation wavelengths for PL were 300 nm.



Fig. S9. Emission spectra of **Phen-2DIBA** with the addition of 10 equivalent Ln(III) cations. The data was the same as that shown in Fig. 2b and the origins of the characteristic emission peaks from Sm(III), Eu(III) and Tb(III) were marked on the figures. Excitation wavelengths for PL were 300 nm.



Fig. S10. Excitation spectra monitored at 591 and 614 nm for **Phen-2DIBA** titrated with 10 equivalent Eu(III). Both emissions resembled the absorption of **Phen-2DIBA** indicating the sensitization of **Phen-2DIBA** towards Eu(III).



Fig. S11. Emission spectra of **Phen-2DIBA-re** with the addition of 10 equivalent Ln(III) cations. The data was the same as that shown in Fig. 2e and the origins of the characteristic emission peaks from Eu(III) and Tb(III) were marked on the figures. Excitation wavelengths for PL were 300 nm.



Fig. S12. Excitation spectra monitored at 491 and 545 nm for **Phen-2DIBA-re** titrated with 10 equivalent Tb(III). Both emissions resembled the absorption of **Phen-2DIBA-re** indicating the sensitization of **Phen-2DIBA-re** towards Tb(III).



Fig. S13. The response time for **Phen-2DIBA** and **Phen-2DIBA-re** towards Eu(III) and Tb(III) by monitoring the most intense emission peaks at 614 nm and 544 nm for Eu(III) and Tb(III) as functions of time. Gray area indicates the minimum mixing time requested in our case. The error bars represented the averaged data from 5 parallel experiments.



Fig. S14. Anti-interfering performances of **Phen-2DIBA** to Eu(III) with other Lns(III). Left panel showed Lns added into **Phen-2DIBA**/Eu(III) (1/10) in aqueous media. Middle panel showed the ligand was added into the metal mixtures with ratios of 1. Red bars represented **Phen-2DIBA**/Eu(III) (1/10) emissions at 614 nm with interfering cations and black bars were 614 nm emission intensities for **Phen-2DIBA**/Lns(III) (1/10). Excitation wavelengths for PL were 300 nm.



Fig. S15. Anti-interfering performances of **Phen-2DIBA-re** to Tb(III) with other Lns(III). Left panel showed Lns added into **Phen-2DIBA-re**/Tb(III) (1/10) in aqueous media. Middle panel showed the ligand was added into the metal mixtures with ratios of 1. Red bars represented **Phen-2DIBA-re**/Tb(III) (1/10) emissions at 544 nm with interfering cations and black bars were 544 nm emission intensities for **Phen-2DIBA-re**/Lns(III) (1/10). Excitation wavelengths for PL were 300 nm.



Fig. S16. Intra-lanthanides sensing performances for **Phen-2DIBA** and **Phen-2DIBA-re** towards all Lns(III) in HNO₃ (pH = 3). Excitation wavelengths for PL were 300 nm.



Fig. S17. Sensing stabilities of **Phen-2DIBA** (top) and **Phen-2DIBA-re** (bottom) towards Eu(III) and Tb(III) in pH ranges of 1-7 within 10 hours. Excitation wavelengths for PL were 300 nm.



Fig. S18. Sensing of **Phen-2DIBA** (top) and **Phen-2DIBA-re** (bottom) towards Eu(III) and Tb(III) with different interfering ions. The experiments were conducted by comparing the PL intensities at the most intensive emission peaks of Eu(III) and Tb(III) with/without adding interfering ions. 10 equivalents of each ion were used. Excitation wavelengths for PL were 300 nm.

Model	ExpGro1
Equation	y = A1 * exp(x/t1) + y0
Plot	Phen-2DIBA with Eu(III) @ 590 nm
y0	999.13397 ± 5.63199
A1	-1013.21233 ± 12.55886
t1	-0.37906 ± 0.0099
Reduced Chi-Sqr	200.34704
R-Square (COD)	0.99844
Adj. R-Square	0.99816

Table S3. Curve-fitting results for **Phen-2DIBA** with dataset of emission changes at 590 nm.

Table S4. Curve-fitting results for **Phen-2DIBA-re** with dataset of emission changes at 544 nm.

Model	ExpGro3	
Equation	y = A1*exp(x/t1) + A2*exp(x/t2) + A3*exp(x/t3) + y0	
Plot	Phen-2DIBA-re with Tb(III) @ 590 nm	
у0	$1.40202E7 \pm 4.9884E8$	
A1	$-1638.14098 \pm 574.62618$	
t1	-0.7545 ± 0.16276	
A2	$-3741.21669 \pm 1020.86957$	
t2	-3.90919 ± 2.15292	
А3	$-1.40146\text{E7} \pm 4.9884\text{E8}$	
t3	$-118018.63708 \pm 4202644.01763$	
Reduced Chi-Sqr	603.83459	
R-Square (COD)	0.99993	
Adj. R-Square	0.99987	



Fig. S19. Determine LOD for **Phen-2DIBA** towards Eu(III) in water. Data derived from Fig. 3c in the main text and LOD was calculated to 15 nM.



Fig. S20. Determine LOD for **Phen-2DIBA-re** towards Tb(III) in water. Data derived from Fig. 3f in the main text and LOD was calculated to $2.95 \mu M$.



Fig. S21. Sensing behaviours of **Phen-2DIBA-re** towards all Lns(III) in water when **Phen-2DIBA-re** was in single molecular state by preheating of **Phen-2DIBA-re** aqueous solution at 80 °C for 12 hours. Much stronger ligand emissions were detected as previous discussed and weaker sensing toward Tb(III). Excitation wavelengths for PL were 300 nm.

Supporting Information References

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