

Supporting information for

Fluorescent Recognition of Hg²⁺ by a 1,1'-Binaphthyl-Based Macrocycle: A Highly Selective Off-On-Off Response

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Part I. Materials and methods.

Materials. (S)-(-)-1,1'-Bi-2-naphthol was purchased from LianYunGang Chiral Chemical (China) Co., LTD and purified by recrystallization. Chloromethyl methyl ether was obtained from Xiya Reagent and used as received. n-Butyllithium solution (2.5 M in hexane) was obtained from Aladdin Reagent (Shanghai) while the (1R, 2R)-(-)-1,2-Cyclohexanediamine was brought from TCI and they were used as received. All other solvents were obtained from Aladdin Reagent and were used as received.

Methods. ¹H NMR (400 MHz) spectra were recorded on a Bruker AV 400 NMR spectrometer operated in the Fourier transform mode. UV-Vis absorption spectra were recorded on a Beijing Persee TU-1901 UV-Vis spectrometer. Melting points of crystals were recorded on a SGW-X4 (Shanghai Precision and Scientific Instrument Co., Ltd.) illuminated microscope melting point apparatus. HRMS spectra were recorded on a BrukerDaltonics Bio TOF mass spectrometer. Steady-state fluorescence emission spectra was recorded on a FluoroMax-4 spectrofluorometer (Horiba Scientific) and analyzed with an Origin integrated software FluoroEssence (v2.2). Fluorescence lifetime data were acquired with a 1MHz LED laser with the excitation peak at 370 nm (NanoLED-370). Lifetime data were analyzed with DataStation v6.6 (Horiba Scientific).

Part II. Synthesis.

(*S*)-**3**. Compound (*S*)-**1** (458 mg, 1.34 mmol) and (1*R*, 2*R*)-(-)-1,2-cyclohexanediamine (154 mg, 1.34 mmol) were dissolved in dry CH₂Cl₂ under N₂, and the mixture was stirred at room temperature for 2 d. After evaporation of the solvent, the crude product was purified by recrystallization with CH₂Cl₂/methanol to afford compound (*S*)-**2** as a yellow solid. This compound (336.4 mg, 0.4 mmol) was combined with NaBH₄ (30.3 mg, 0.8 mmol) and ethanol (50 mL), which was degassed with nitrogen and heated at reflux for 6 h. After removal of the solvent, the crude product was purified by column chromatography on silica gel eluted with CH₂Cl₂/methanol (20/1) to afford compound (*S*)-**3** as a white solid (190 mg, 56%). ¹H NMR (400 MHz, acetone-*d*₆) δ 0.92–1.12 (m, 8H), 1.52 (s, 4H), 2.03–2.15 (m, 4H), 2.27 (s, 4H), 4.22 (d, *J* = 14.0 Hz, 4H), 4.38 (d, *J* = 14.6 Hz, 4H), 7.04 (d, *J* = 8.4 Hz, 4H), 7.09–7.15 (m, 4H), 7.16–7.23 (m, 4H), 7.65 (s, 4H), 7.76 (d, *J* = 8.0 Hz, 4H). HR-MS: *m/z* calcd for C₅₆H₅₇N₄O₄ [MH]⁺: 849.4374; found: 849.4379.

Part III. Supplementary Figures.

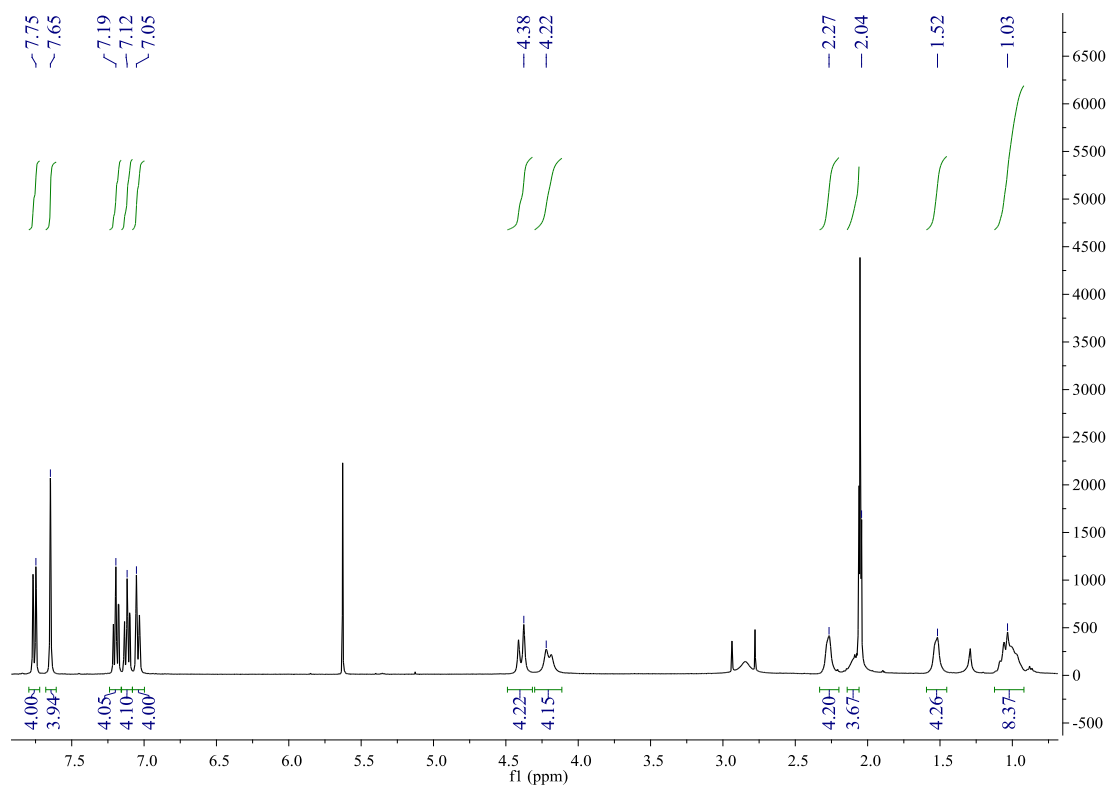


Fig. S1. The ¹H NMR of (S)-3.

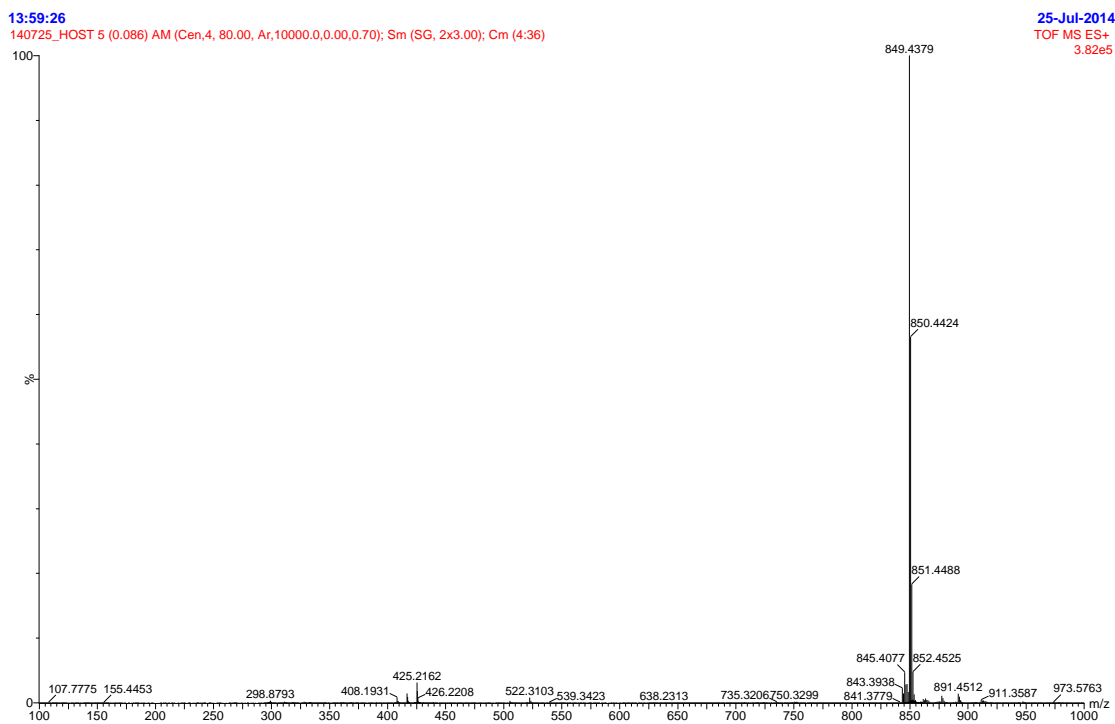


Fig. S2. TOF mass spectra of (S)-3.

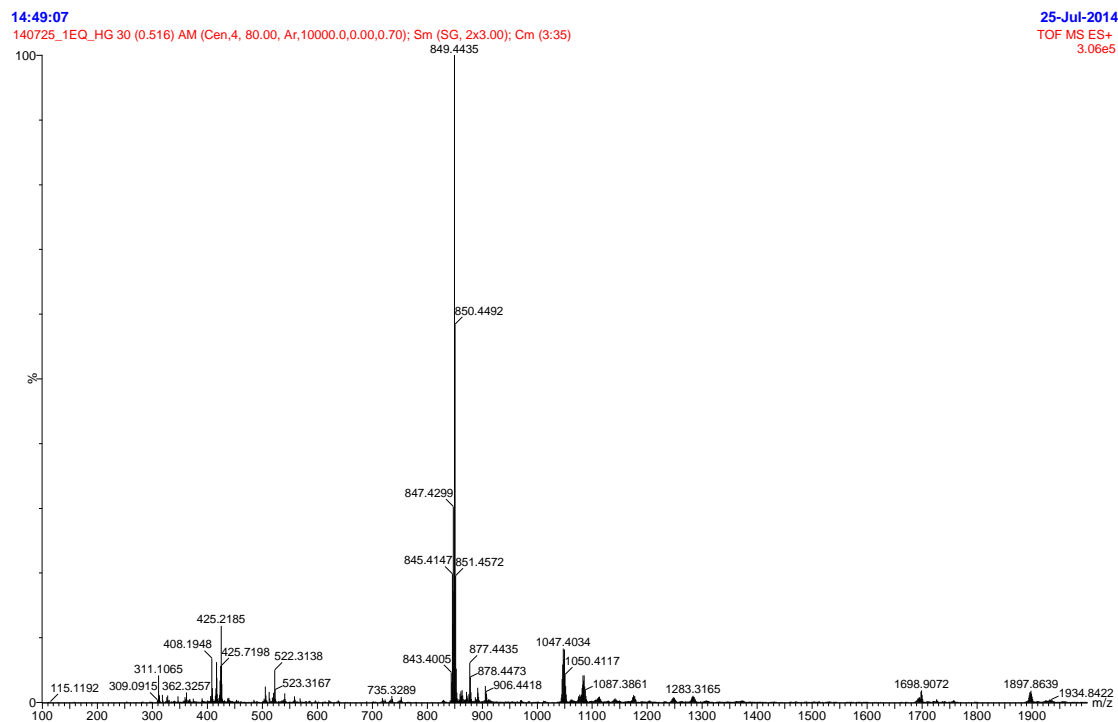


Fig. S3. TOF mass spectra of (*S*)-**3**+ Hg(OAc)₂ (1 equiv.).

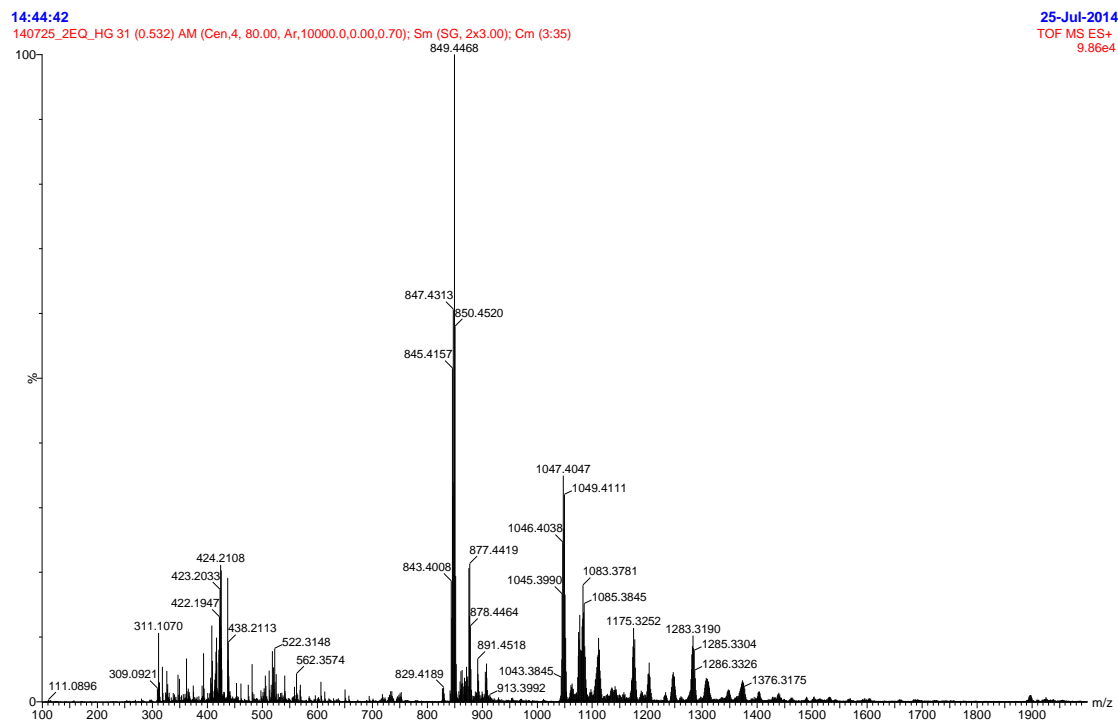


Fig. S4. TOF mass spectra of (*S*)-**3**+ Hg(OAc)₂ (2 equiv.).

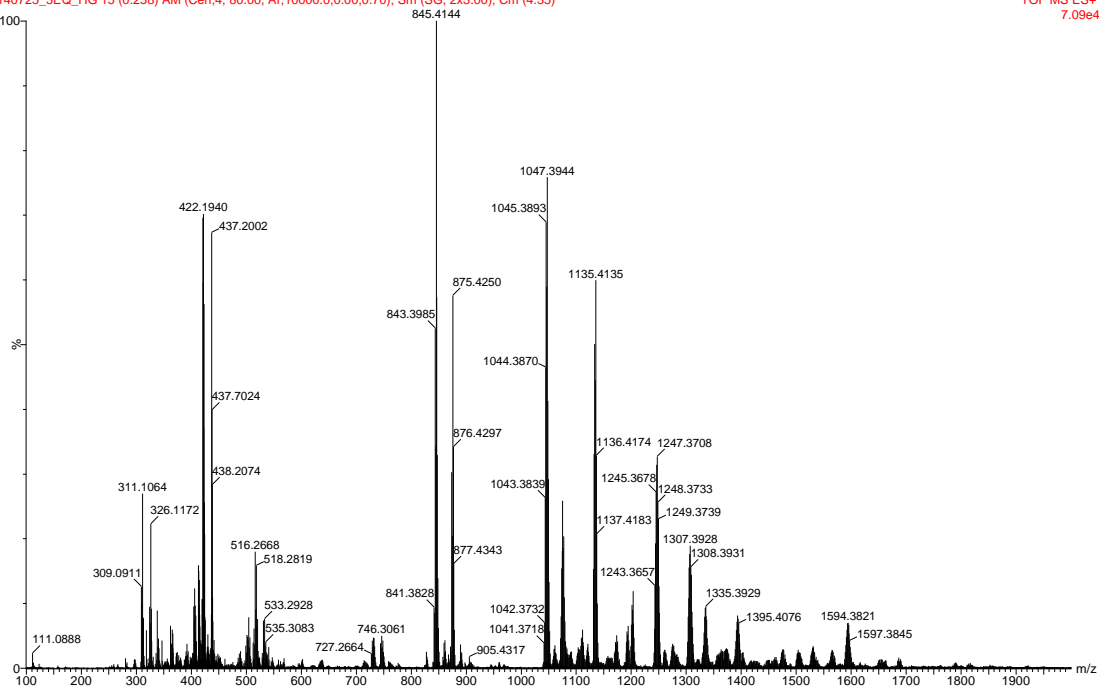


Fig. S5. TOF mass spectra of (*S*)-**3**+ Hg(OAc)₂ (3 equiv.).

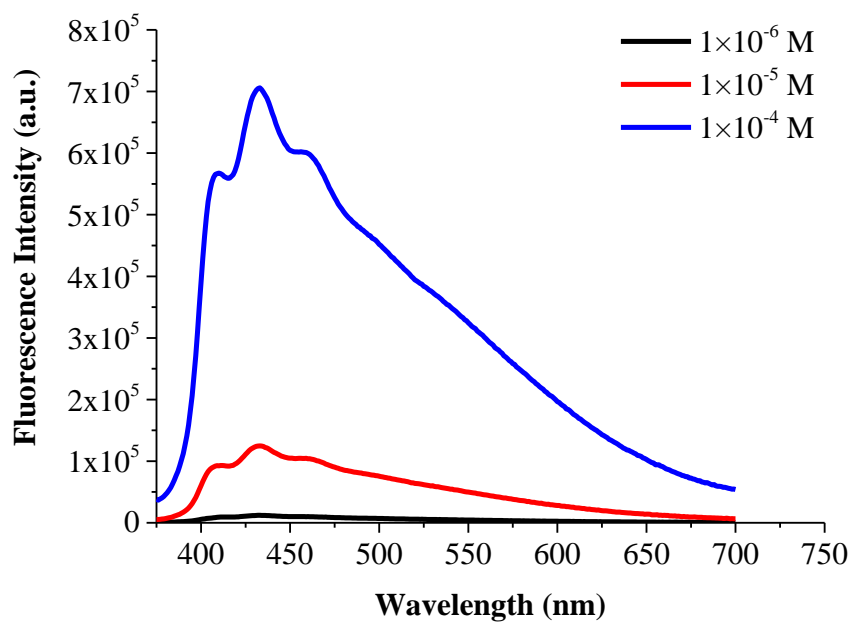


Fig. S6. Steady-state fluorescence emission spectra of (*S*)-**3** with various concentration ($\lambda_{\text{exc}} = 365 \text{ nm}$).

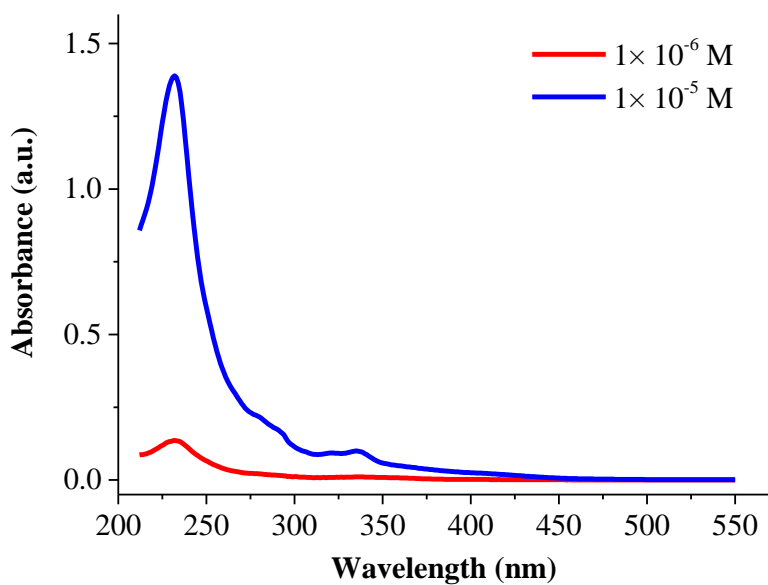


Fig. S7. UV-vis absorption spectra of (*S*)-**3** with various concentration.

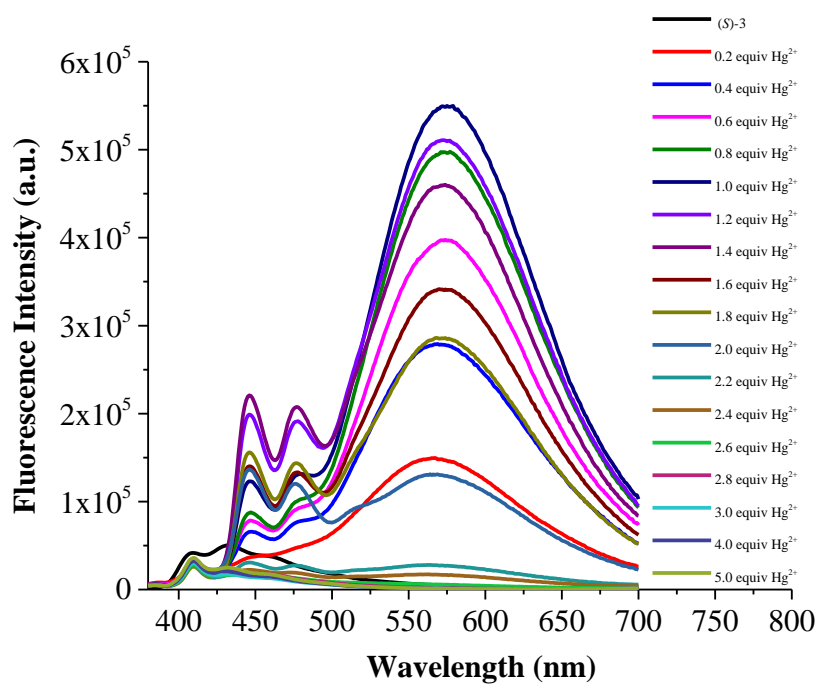


Fig. S8. Steady-state fluorescence emission spectra of the (*S*)-**3** ligand (1.0×10^{-5} M in methanol) versus the concentration of Hg^{2+} ($\lambda_{\text{exc}} = 365$ nm).

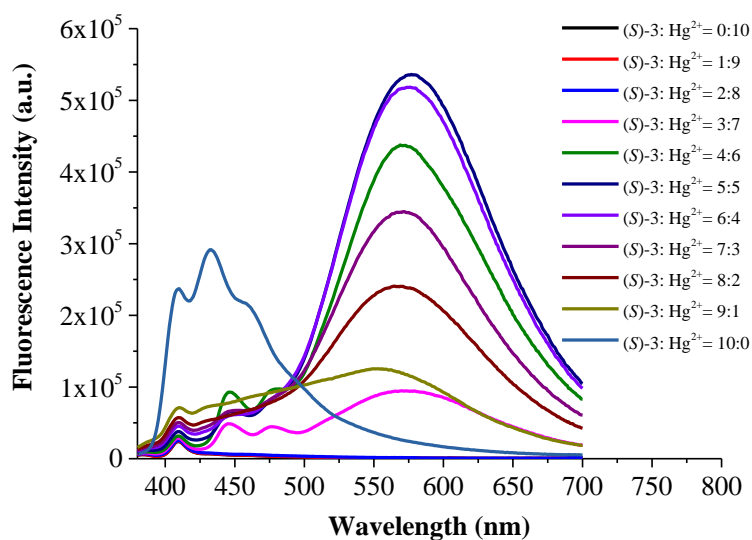


Fig. S9. The steady-state fluorescence emission spectra of the (S)-3 ligand versus Hg²⁺ ($\lambda_{\text{exc}} = 365 \text{ nm}$).

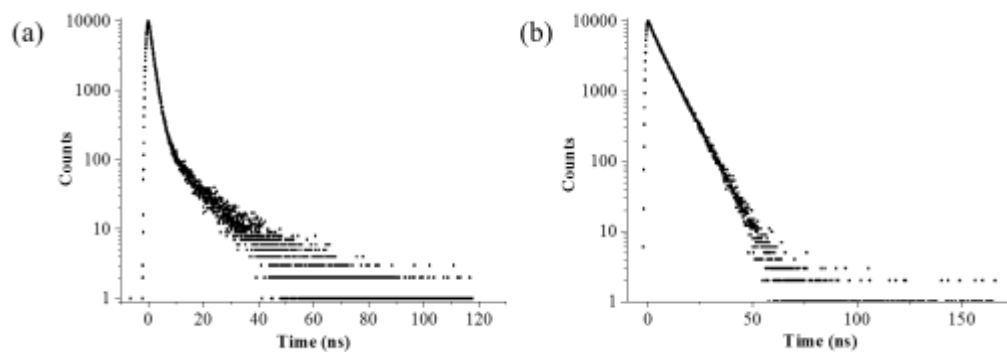


Fig. S10. (a) Fluorescence decay profiles of (S)-3 in methanol; (b) Fluorescence decay profiles of (S)-3 + Hg²⁺ (1 equiv.) in methanol.