Supporting information for

**Fluorescent Recognition of Hg\(^{2+}\) 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.** \(^1\)H 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 (1R, 2R)-(-)-1,2-cyclohexanediamine (154 mg, 1.34 mmol) were dissolved in dry CH$_2$Cl$_2$ under N$_2$, and the mixture was stirred at room temperature for 2 d. After evaporation of the solvent, the crude product was purified by recrystallization with CH$_2$Cl$_2$/methanol to afford compound (S)-2 as a yellow solid. This compound (336.4 mg, 0.4 mmol) was combined with NaBH$_4$ (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 CH$_2$Cl$_2$/methanol (20/1) to afford compound (S)-3 as a white solid (190 mg, 56%). $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 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 C$_{56}$H$_{57}$N$_4$O$_4$ [MH]$^+$: 849.4374; found: 849.4379.
**Part III. Supplementary Figures.**

**Fig. S1.** The $^1$H 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 \((S)-3+\text{Hg(OAc)}_2\) (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+} (λ_{exc} =365 nm).
Fig. S9. The steady-state fluorescence emission spectra of the (S)-3 ligand versus Hg^{2+} (λ_{exc} = 365 nm).

Fig. S10. (a) Fluorescence decay profiles of (S)-3 in methanol; (b) Fluorescence decay profiles of (S)-3+ Hg^{2+} (1 equiv.) in methanol.