

Supporting Information

A Highly Selective and Sensitive Polymer-based OFF-ON Fluorescent Sensor for Hg²⁺ Detection Incorporating Salen and Perylenyl Moieties

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Synthetic procedures and characterization

General methods

NMR spectra were obtained using a Bruker spectrometer 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR and reported as parts per million (ppm) from the internal standard TMS. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. UV-vis spectra were obtained from a Perkin-Elmer Lambda 25 spectrometer. Fluorescence spectra were obtained from a RF-5301PC spectrometer. Thermogravimetric analyses (TGA) was performed on a Perkin-Elmer Pyris-1 instrument under N_2 atmosphere. MS was determined on a Micromass GCT. C, H and N of elemental analyses were performed on an Elementar Vario MICRO analyzer. Molecular weight was determined by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards. Toluene was dried and distilled over CaH_2 and THF was used after distillation over Na/benzophenone. Other chemicals were analytical grade and used without further purification.

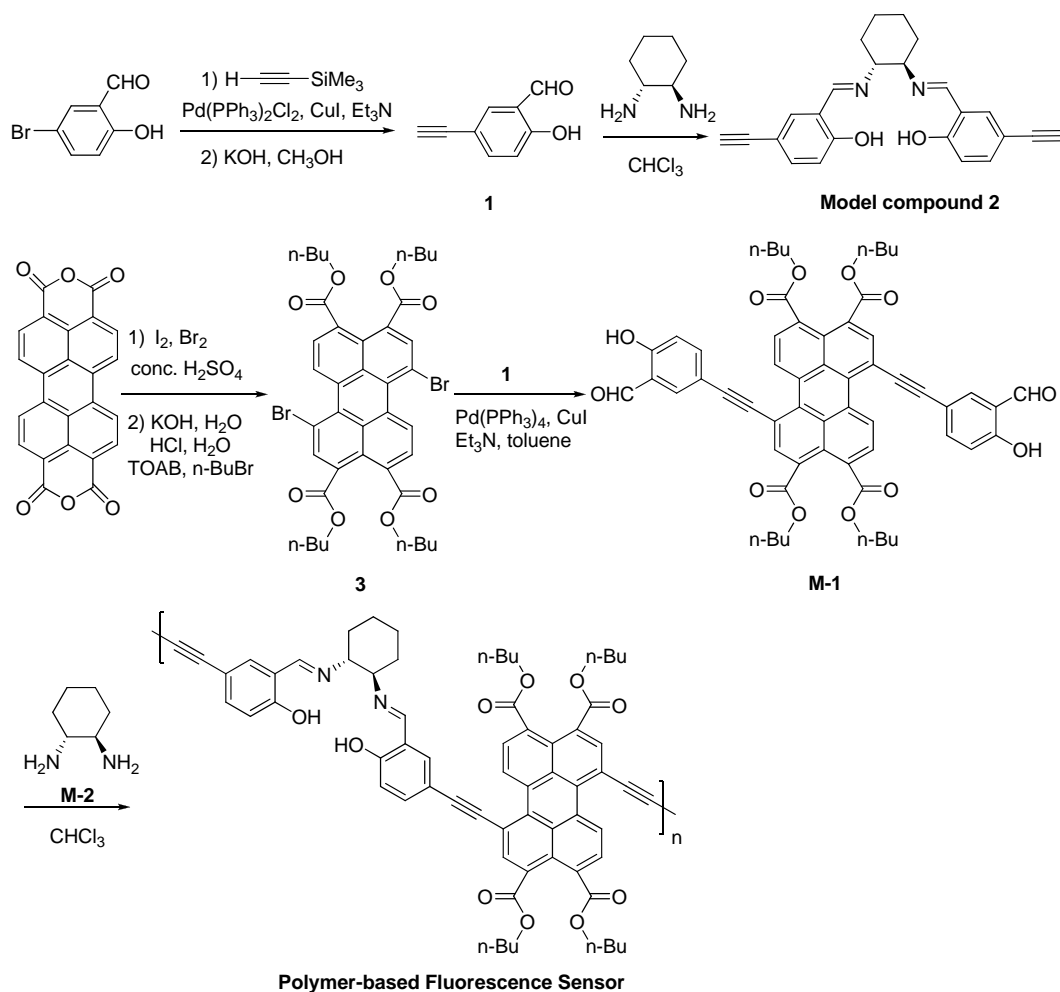


Fig S1. Scheme of synthesis procedures of the model compound 2 and chiral polymer

General procedure of preparation of the polymer

Preparation of 5-trimethylethynylsilylsalicylaldehyde: A mixture of 5-bromo-salicylaldehyde (5.00 g, 24.85 mmol) and Et₃N (40 mL) was bubbled with nitrogen for 30 min, and then CuI (165.7 mg, 0.87 mmol), PdCl₂(PPh₃)₂ (523.3 mg, 0.75 mmol), TMSA (3.66 g, 37.28 mmol) were added to the above solution. The reaction mixture was stirred at 70 °C overnight. The reaction mixture was slowly cooled to room temperature, and the solvent was removed under reduced pressure. The residue was extracted with CH₂Cl₂ (3×50 mL), and the combined organic layers were dried over anhydrous Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel with petroleum ether as eluent to afford 4.3 g of a white solid 5-trimethylethynylsilylsalicylaldehyde (80% yield). ¹H NMR (300 MHz, CDCl₃): δ11.12 (s, 1H), 9.87 (s, 1H), 7.72 (d, J = 2.1 Hz), 7.61 (dd, J = 8.7, 2.1 Hz), 6.97 (d, J = 8.7 Hz), 0.27 (s, 9H).

Preparation of 5-ethynylsalicylaldehyde (1): 5-Trimethylethynylsilylsalicylaldehyde (3.0 g, 13.74 mmol) and KOH (1.15g, 20.61 mmol) were dissolved in the mixed solvents of CH₂Cl₂ and methanol (1:1 v/v) and stirred at room temperature until the complete disappearance of the starting material 5-trimethylethynylsilylsalicylaldehyde by TLC monitoring. The reaction mixture was poured into 1 M HCl solution, and stirred for 1 h. The aqueous phase was extracted with CH₂Cl₂ (3×30 mL), and the organic layer was dried over anhydrous Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (60/1) as eluent to afford 1.81 g of a white solid 5-ethynylsalicylaldehyde (1) (90% yield). ¹H-NMR (300 MHz, CDCl₃): δ 11.15 (s, 1H), 9.89 (s, 1H), 7.75 (d, J = 2.1Hz, 1H), 7.66 (dd, J = 8.7, 2.1 Hz, 1H), 6.99 (d, J = 8.7Hz, 1H), 3.06 (s, 1H).

Preparation of the model compound (2): A mixture of 5-ethynylsalicylaldehyde (584.6 mg, 4.0 mmol) and (*R,R*)-1,2-diaminocyclohexane (228.4 mg, 2.0 mmol) were dissolved in 20 mL methanol. The reaction mixture was stirred at 40 °C for 12 h. After being cooled to room temperature, the solvent was removed by a rotary evaporator. The crude product was recrystallized from ethyl acetate and petroleum ether to afford 592 mg of a yellow solid the model compound (2) (80% yield). $[\alpha]_D^{25} = -0.059$ (*c* = 0.49, THF). ¹H NMR (300 MHz, CDCl₃): δ 13.57 (s, 2H), 8.23 (s, 2H), 7.37 (dd, J = 8.4 Hz, 1.8 Hz, 2H), 7.34 (d, J = 1.8 Hz, 2H), 6.88 (d, J = 1.8 Hz, 2H), 3.33-3.37 (m, 2H), 2.97 (s, 2H), 1.46-1.99 (m, 8H).

Preparation of 1,7-dibromoperylene-3,4:9,10-tetracarboxylic tetrabutylate (3): 1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid dianhydride (5.00 g, 9.09 mmol) and KOH (1.27 g, 22.72 mmol) were dissolved in 50 ml H₂O at 70 °C. After filtration, the filtrate was acidified with aqueous hydrochloric acid solution (ca. 1 mol·L) until the pH value is 8-9. A mixture of tetraoctyl ammonium bromide (1.49 g, 2.72 mmol) (TOAB) and 1-bromobutane (5.48g, 39.99 mmol) was added to the above solution. The solution was refluxed under vigorous stirring for 4 h, and then the mixture was cooled to the room temperature. The mixture was extracted with CHCl₃ (3×50 mL). The combined organic layers were washed with saturated brine water (50 mL), dried over anhydrous Na₂SO₄, concentrated and then precipitated by ethanol. The collected yellow solid was washed with 200 ml of ethanol for three times. The product was dried in vacuum at 80 °C to give 6.26 g (85% yield) of the yellow solid product 1,7-dibromoperylene-3,4,9,10-tetracarboxylic tetrabutylate. ¹H NMR (300 MHz, CDCl₃): δ 8.82 (d, J=8.1, 2H), 8.27 (s, 2H), 8.30 (d, J=7.8 Hz, 2H), 4.37 (m, 8H), 1.82 (m, 8H), 1.52 (m, 8H), 1.02 (m, 12H). ¹³C NMR (300 MHz, CDCl₃): δ 167.8, 167.0, 136.4, 131.5, 130.8, 130.3, 130.2, 128.8, 127.4, 126.3, 118.5, 65.7, 30.4, 19.1, 13.7 ppm.

Preparation of 1,7-bis((3-formyl-4-hydroxyphenyl)ethynyl)perylene-3,4:9,10-tetracarboxylic tetra-

butylate (M-1): The compound (**2**) (1.00 g, 1.23 mmol), CuI (12.92 mg, 0.068 mmol), Pd(PPh₃)₄ (71.28 mg, 0.062 mmol), and the compound **1** (396.65 mg, 2.71 mmol) were added to a mixture of 10 mL Et₃N and 40 mL toluene in Schlenk tube. The reaction mixture was stirred at 70 °C under a N₂ atmosphere overnight. After cooling to room temperature, the organic phase was washed with 60 mL of water three times. The organic phase was washed with saturated brine water (20 mL), dried over Na₂SO₄. After the solvent was evaporated, the crude products were purified by silica gel column chromatography with petroleum ether as eluent to afford 110 mg of a red solid 1,7-bis((3-formyl-4-hydroxyphenyl)-ethynyl)perylene-3,4:9,10-tetracarboxylic tetrabutylate (**M-1**). (9.48 % yield). ¹H NMR (300 MHz, CDCl₃): δ 11.27 (s, 2H), 9.98 (s, 2H), 9.45 (d, 2H), 8.29 (t, 4H), 7.84 (m, 4H), 7.11 (d, 2H), 1.80 (m, 8H), 1.51 (m, 8H), 1.02 (m, 12H). ¹³C NMR (300 MHz, CDCl₃): δ 195.9, 168.1, 167.7, 165.6, 161.9, 139.7, 137.1, 135.6, 133.3, 132.2, 130.4, 130.2, 129.6, 129.5, 127.1, 126.5, 120.5, 118.5, 117.7, 114.4, 93.4, 90.2, 30.5, 19.1, 3.7 ppm. MS (ESI) Calcd for C₅₈H₅₂O₁₂, 940.35; Found, 939.33 [M-H]⁻. FT-IR (KBr, cm⁻¹): 3400, 2958, 2871, 2194, 1721, 1661, 1591, 1549, 1485, 1399, 1284, 1173, 1125, 839, 758. Anal. Calcd for C₅₈H₅₂O₁₂: C, 74.03; H, 5.57. Found: C, 74.06; H, 5.54.

Preparation of the polymer-based fluorescence sensor: A mixture of **M-1** (90.0 mg, 0.095 mmol) and (*R,R*)-1,2-diaminocyclohexane (10.9 mg, 0.095 mmol) was dissolved in CHCl₃ (20 mL). The reaction mixture was stirred at room temperature overnight. The solution was concentrated, and was then precipitated by methanol. The product was filtrated and washed with methanol several times and dried under vacuum to afford 60 mg of the dark-red polymer (59% yield). GPC: M_w = 12480; M_n = 7710; PDI = 1.6. [α]_D²⁵ = -270.00 (c = 0.001, THF). ¹H NMR (300 MHz, CDCl₃): δ 9.04-9.52 (m, 1H), 8.03-8.40 (m, 5H), 7.45-7.53 (m, 2H), 7.00 (s, 1H), 4.36 (s, 8H), 3.45-3.51 (m, 1H), 1.93-2.13 (m, 5H), 1.78 (s, 11H), 1.48 (s, 11H), 1.02 (s, 14H). FT-IR (KBr, cm⁻¹): 3440, 2952, 2189, 1719, 1634, 1629, 1487, 1389, 1276, 1164, 1078, 830. Anal. Calcd for C₆₄H₆₄N₂O₁₀: C, 75.27; H, 6.32; N, 2.74. Found: C, 75.21; H, 6.29; N, 2.70.

Solution NMR Spectra

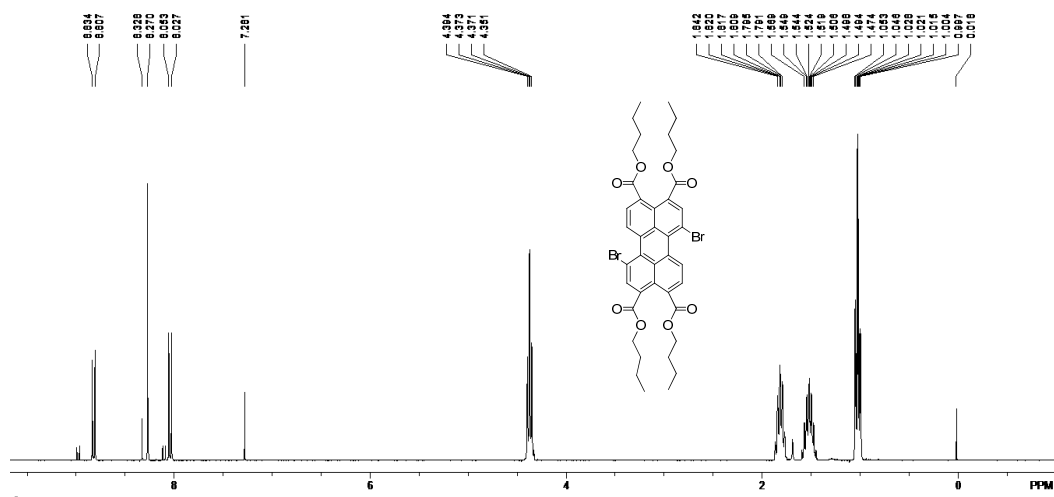


Fig S2: ^1H NMR spectrum of the compound 3 in CDCl_3 .

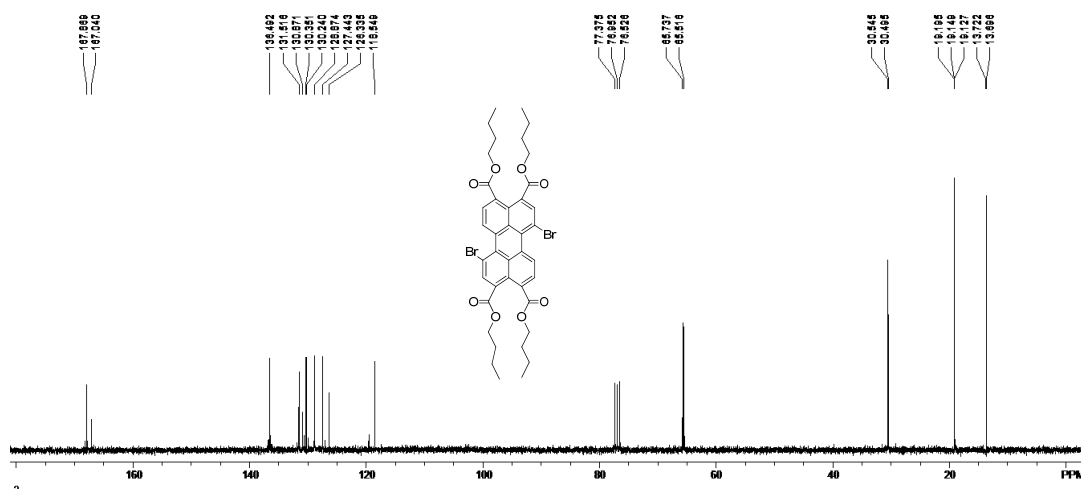


Fig S3. ^{13}C NMR spectrum of the compound 3 in CDCl_3 .

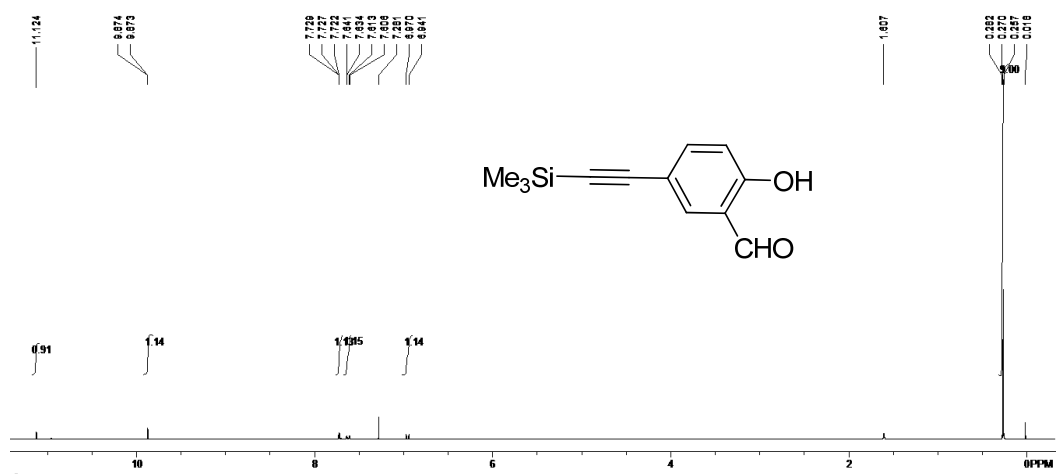


Fig S4. ^1H NMR spectrum of 5-trimethylethynylsalicylaldehyde in CDCl_3 .

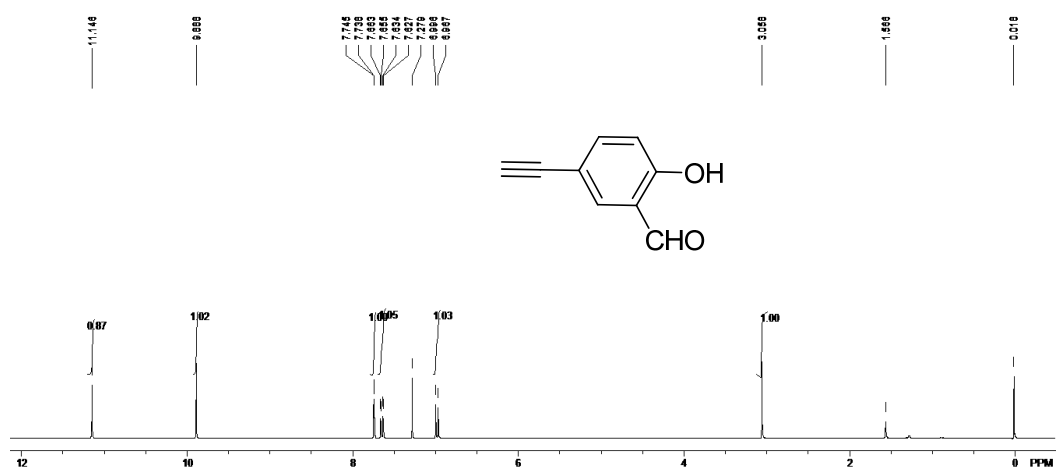


Fig S5. ^1H NMR spectrum of the compound 1 in CDCl_3 .

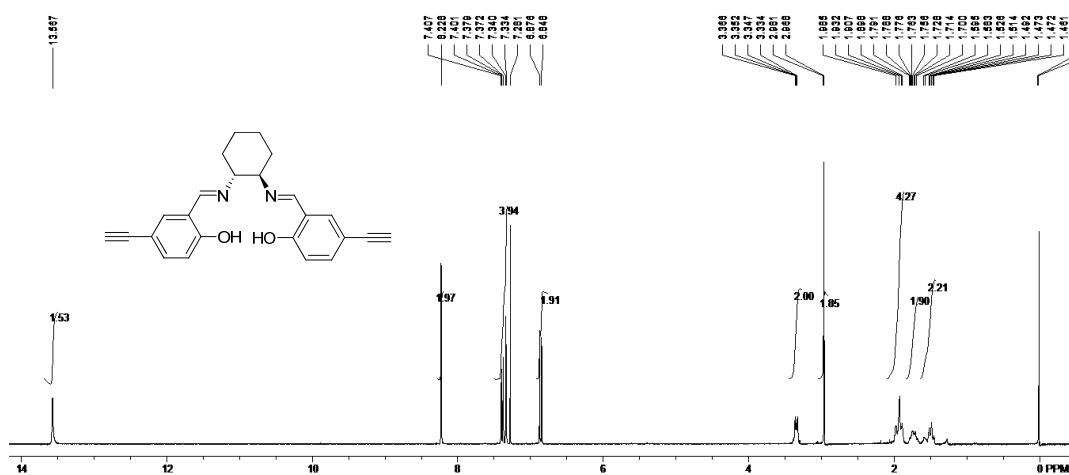


Fig S6. ^1H NMR spectrum of model compound 2 in CDCl_3 .

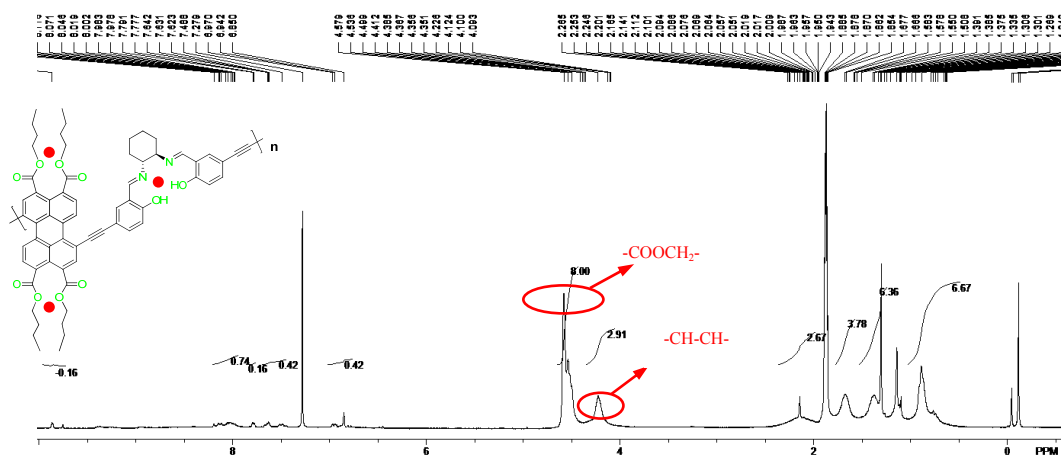


Fig S10. ¹H NMR spectrum of the chiral polymer in CDCl₃ addition of Hg²⁺ in ration of 1:3 (in CD₃CN).

Thermogravimetric analysis of the conjugated polymer

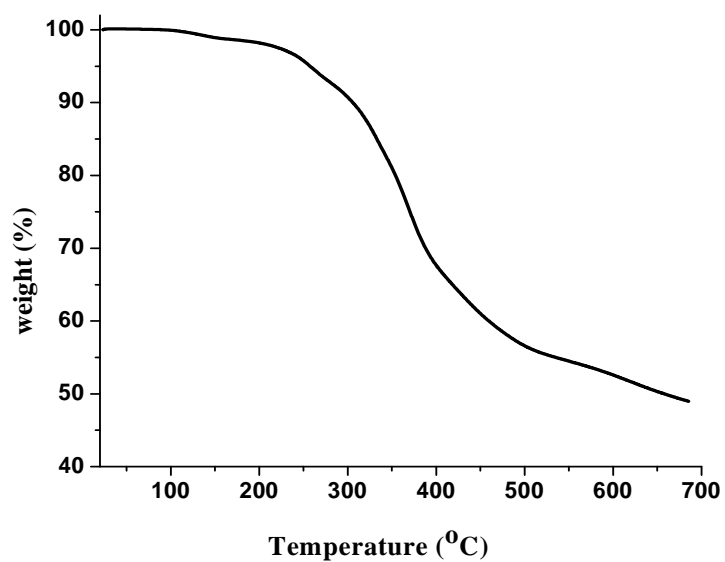


Fig S11. TGA curve of the polymer.

Calculation of the detection limit

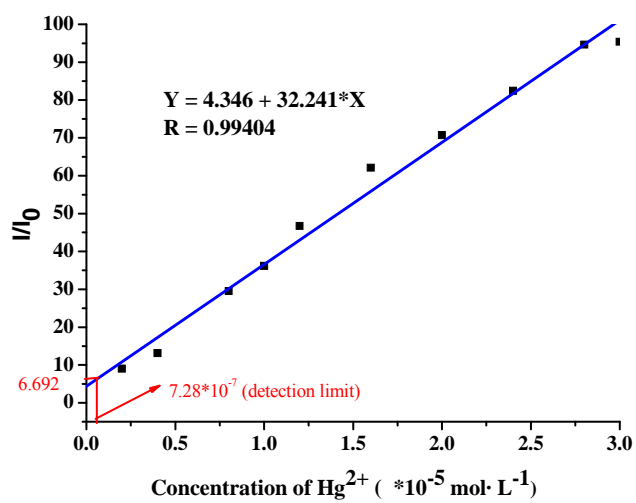


Fig S12. Calculation process of the detection limit of this polymer sensor on Hg²⁺.

Responsive behavior of the chiral polymer on various metal ions

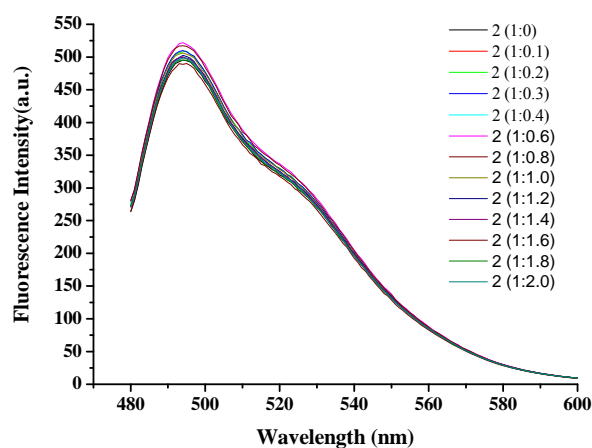


Fig S13. Fluorescence spectra of compound **3** ($1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ in THF) with increasing amounts of Hg^{2+} in CH_3CN ($\lambda_{\text{ex}} = 430 \text{ nm}$).

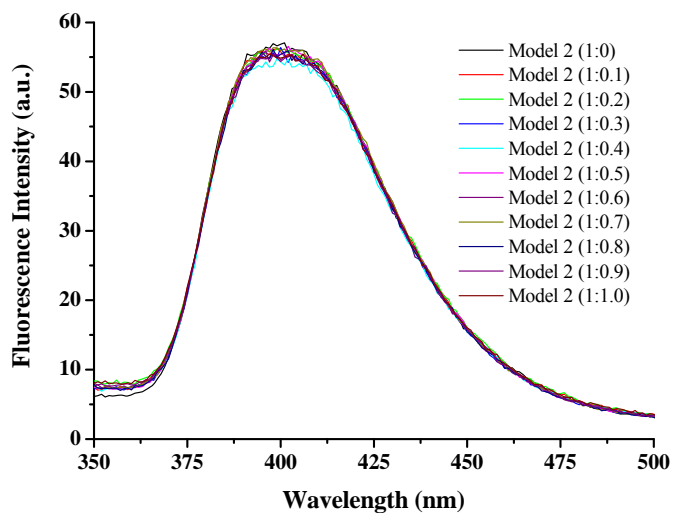


Fig S14. Fluorescence spectra model **2** ($1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ in THF) with increasing amounts of Hg^{2+} in CH_3CN ($\lambda_{\text{ex}} = 310 \text{ nm}$).

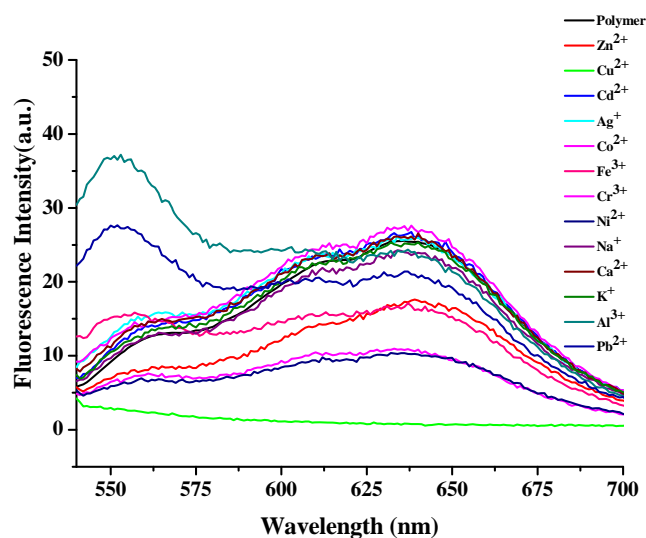


Fig S15. Fluorescence spectra of the polymer ($1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) in the presence of various transition metal ions, such as Zn^{2+} , Cu^{2+} , Cd^{2+} , Ag^+ , Co^{2+} , Fe^{3+} , Cr^{3+} , Ni^{2+} , Na^+ , Ca^{2+} , K^+ , Pb^{2+} in CH_3CN (each $3.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) ($\lambda_{\text{ex}} = 440 \text{ nm}$).

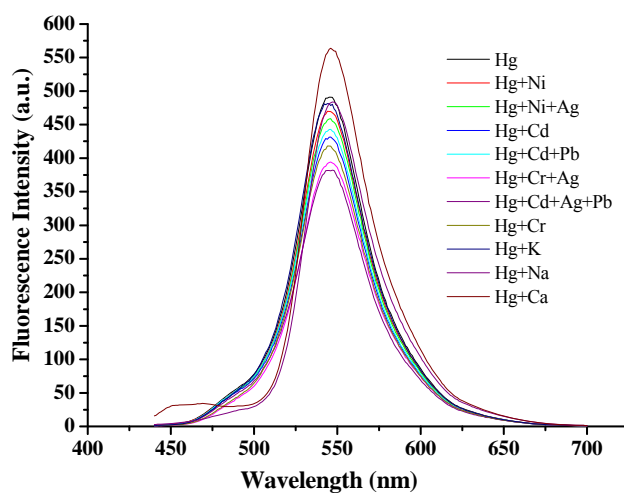


Fig S16. Fluorescence enhancement response of the polymer sensor ($1.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) in the presence of mixed ions (each $3.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) ($\lambda_{\text{ex}} = 440 \text{ nm}$).