

Supporting Information
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Fluorescence-based polybinaphthyls incorporating triazole moiety for Hg²⁺ recognition via click chemistry

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General experimental

NMR spectra were obtained using a 300-Bruker spectrometer 300 MHz for ¹H NMR and 75 MHz for ¹³C 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. TGA was performed on a Perkin-Elmer Pyris-1 instrument under N₂ atmosphere. Specific rotation was determined with a Ruololph Research Analytical Autopol III. 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. All solvents and reagents were commercially available A.R. grade.

Metal Ion Titration

Each metal ion titration experiment was started with a 3.0 mL polymer solution with a known concentration (1.0×10^{-5} mol·L⁻¹ in toluene). Mercury perchlorate salt, PdCl₂ and other various metal salts (nitrate, 3.0×10^{-3} or 1.0×10^{-2} mol·L⁻¹ in CH₃CN) were used for the titration. Polymer-metal complexes were produced by adding aliquots of a solution of the selected metal salt to a toluene solution of the chiral polymer. All kinds of measurements were monitored 2 h after addition of the metal salt to the polymer solution.

(*R*)-6,6'-Dibutyl-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (1)^[1]

(*R*)-6,6'-Dibromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (5.9 g, 11.1 mmol) was dissolved in anhydrous THF (50 mL), *n*-BuLi (15.0 mL, 2.5 mol·L⁻¹ in hexanes, 37.5 mmol) was added by

syringe injection at -78°C under a N_2 atmosphere. After the reaction mixture was stirred for 10 min, $n\text{-C}_4\text{H}_9\text{Br}$ (5.3 g, 38.7 mmol) was added to the above solution at -78°C under a N_2 atmosphere. The reaction mixture was gradually warmed to room temperature and stirred overnight. The mixture was extracted with ethyl acetate ($2\times 100\text{ mL}$). The combined organic layers were washed with water and brine, and then dried over anhydrous Na_2SO_4 . After removal of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/ethyl acetate) (30:1, v/v) to afford a colorless viscous product **2** in 70.4% yield (3.8 g). $[\alpha]_{\text{D}}^{25} = +38.0$ (c 0.5, CH_2Cl_2). ^1H NMR (300 MHz, CDCl_3): δ 7.93 (d, 2H, $J = 9.0$ Hz), 7.71 (s, 2H), 7.60 (d, 2H, $J = 9.0$ Hz), 7.19 (s, 4H), 5.12 (d, 2H, $J = 6.6$ Hz), 5.01 (d, 2H, $J = 6.6$ Hz), 3.21 (s, 6H), 2.79 (t, 4H, $J = 7.2$ Hz), 1.75-1.67 (m, 4H), 1.48-1.41 (m, 4H), 0.98 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 152.6, 138.5, 132.9, 130.4, 129.0, 128.1, 126.6, 125.9, 121.7, 117.5, 95.3, 55.7, 35.9, 33.8, 22.8, 14.3. FT-IR (KBr, cm^{-1}): 2956, 2929, 2857, 1596, 1500, 1480, 1241, 1151, 1028. MS (EI, m/z): 486 (M^+ , 7%), 410 (100%), 382 (48%), 339 (34%).

(*R*)-6,6'-dibutyl-3,3'-diiodo-2,2'-bisoctoxy-1,1'-binaphthyl (2**)^[1]**

Compound **1** (3.69 g, 7.58 mmol) was dissolved in 30 mL of anhydrous THF, 10.6 mL of $n\text{-BuLi}$ ($2.5\text{ mol}\cdot\text{L}^{-1}$ in hexane, 26.53 mmol) was added by syringe injection at room temperature under a N_2 atmosphere. The solution was stirred for 6 h at room temperature, and then the solution of iodine (7.7 g, 30.32 mmol in 30 mL of THF) was slowly injected to the mixed solution at -78°C under a N_2 atmosphere. The mixture was then stirred overnight while the temperature was gradually warmed to room temperature. The reaction was quenched with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (30 mL). After removal of solvent under reduced pressure, the residue was extracted with ethyl acetate ($2\times 50\text{ mL}$), the combined organic layers were washed with water and brine twice. The solution was concentrated to give a crude product of (*R*)-6,6'-dibutyl-3,3'-diiodo-2,2'-bismethoxymethoxy-1,1'-binaphthyl which was directly used without purification. The crude product was dissolved in the mixed solvents of 30 mL of ether and 30 mL of methanol. 35 mL of HCl ($12\text{ mol}\cdot\text{L}^{-1}$) solution was added to the above the solution. The solution was stirred at room temperature for 8 h. After the removal of solvent under reduced pressure, the residue was extracted with ethyl acetate ($2\times 50\text{ mL}$). The combined organic layers were washed with 10% aqueous Na_2CO_3 and brine twice and dried over anhydrous Na_2SO_4 . After removal of solvent, the cruder product was purified by chromatography on silica gel with petroleum ether/acetone (50:1,

v/v) as an eluent to afford a yellow viscous product (*R*)-6,6'-dibutyl-3,3'-diiodo-2,2'-binaphthol in the yield of 38.8 % (1.91 g). $[\alpha]_D^{25} = +65.0$ (*c* 0.3, CH₂Cl₂). mp: 58-60 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.47 (s, 2H), 7.58 (s, 2H), 7.19 (dd, 2H, *J* = 8.7 Hz, 1.5 Hz), 7.03 (d, 2H, *J* = 8.7 Hz), 5.36 (s, 2H), 2.74 (t, 4H, *J* = 7.5 Hz), 1.69-1.61 (m, 4H), 1.43-1.36 (m, 4H), 0.99-0.90 (m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 149.5, 139.7, 139.3, 131.5, 130.8, 129.5, 125.6, 124.3, 112.5, 86.3, 35.4, 33.3, 22.3, 13.9. FT-IR (KBr, cm⁻¹): 3476, 2925, 2854, 1572, 1500, 1441, 1362, 1143. MS (EI, *m/z*): 650 (*M*⁺, 100%), 607 (100%).

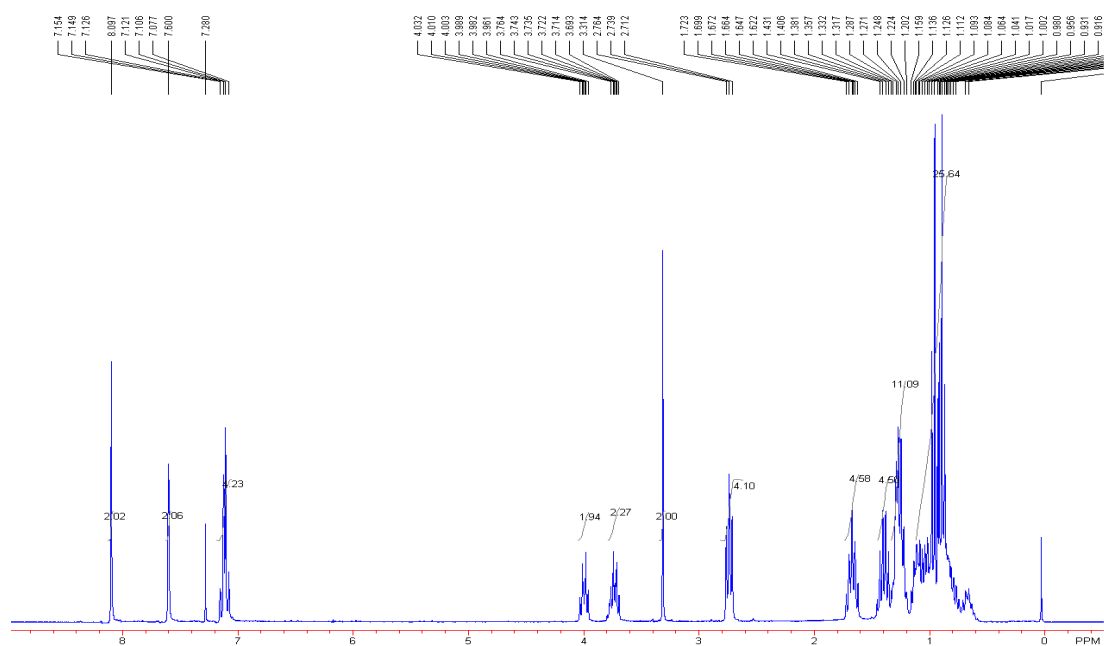
A mixture of (*R*)-6,6'-dibutyl-3,3'-diiodo-2,2'-binaphthol (1.7 g, 2.62 mmol), K₂CO₃ (2.53 g, 18.34 mmol), and *n*-C₈H₁₇Br (2.0 g, 10.46 mmol) was dissolved in 80 mL of anhydrous CH₃CN. The solution was refluxed overnight. After being evaporated to dryness, the residue was extracted with ethyl acetate (2×50 mL). The solution was washed with water and brine twice and then dried over anhydrous Na₂SO₄. After removal of solvent, the cruder product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (40:1, v/v) as an eluent to afford a yellow liquid (*R*)-6,6'-dibutyl-3,3'-diiodo-2,2'-bis(octoxy)-1,1'-binaphthyl in 77.8% yield (1.78 g). $[\alpha]_D^{25} = -17.9$ (*c* 0.73, THF). ¹H NMR (300 MHz, CDCl₃): δ 8.43 (s, 2H), 7.54 (s, 2H), 7.13 (dd, 2H, *J* = 8.7 Hz, 1.8 Hz), 7.06 (d, 2H, *J* = 8.7 Hz), 3.86-3.79 (m, 2H), 3.38-3.31 (m, 2H), 2.74 (t, 4H, *J* = 7.8 Hz), 1.72-1.62 (m, 4H), 1.43-1.33 (m, 4H), 1.30-1.21 (m, 9H), 1.17-1.03 (m, 7H), 0.98-0.88 (m, 16H), 0.85-0.82 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 153.3, 139.7, 138.8, 132.3, 132.2, 128.3, 125.8, 125.6, 125.0, 92.9, 73.3, 35.4, 33.1, 31.7, 29.6, 29.1, 28.9, 25.3, 22.6, 22.3, 14.1, 13.9. FT-IR (KBr, cm⁻¹): 2954, 2927, 2856, 1568, 1465, 1228, 1149, 1026. MS (EI, *m/z*): 874 (*M*⁺, 2%), 762 (5%), 650 (100%), 607 (4%). Anal. calcd for C₄₄H₆₀I₂O₂: C, 60.41; H, 6.91. Found: C, 60.47; H, 6.86.

(*R*)-6,6'-dibutyl-3,3'-diethynyl-2,2'-bis(octoxy)-1,1'-binaphthyl (*R*-M-1)

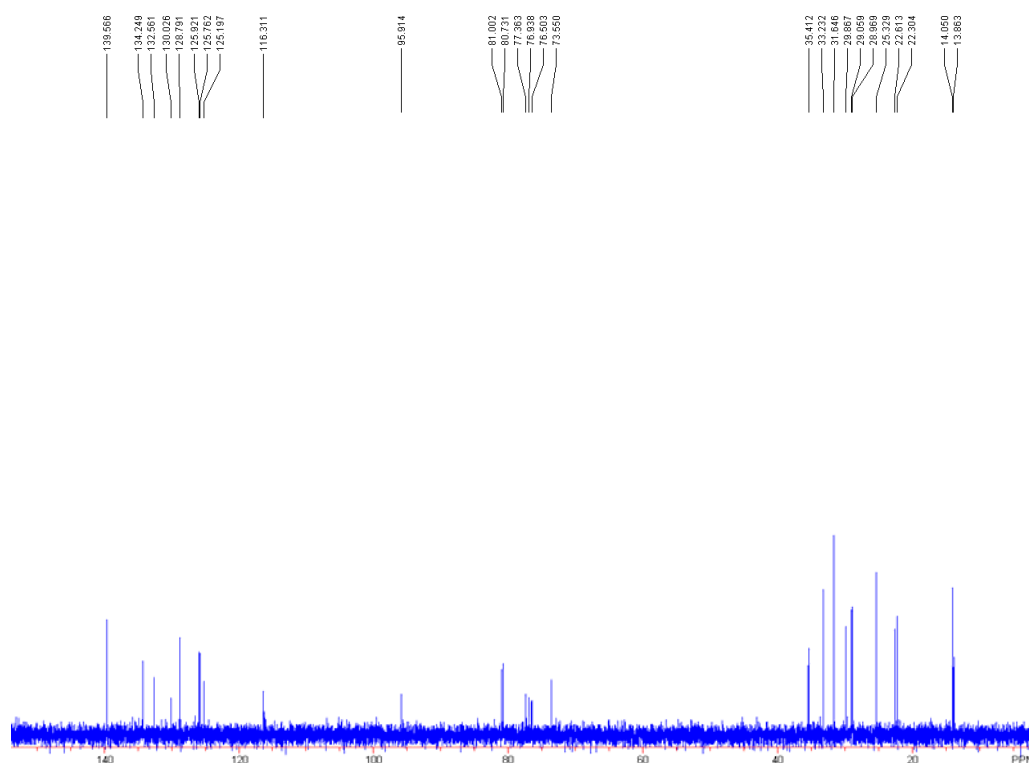
A mixture of **2** (2.17 g, 2.5 mmol), Pd(PPh₃)₄ (55 mg, 0.05 mmol), CuI (18.3 mg, 0.10 mmol) and trimethylsilyl acetylene (1.0 mL, 7.5 mmol) was dissolved in the mixed solvents of 10 mL toluene and 10 mL Et₃N. The reaction mixture was stirred at 80°C for 2 days under a N₂ atmosphere. The solution was then cooled to room temperature and the solvent was removed under reduced pressure, the residue was extracted with CH₂Cl₂. The organic layer was washed with water (25 mL × 3) and brine (30 mL), dried over anhydrous Na₂SO₄, and evaporated under vacuum to dryness. The crude product was dissolved in 30 mL of methanol. 0.8g NaOH was added to the above

solution. The solution was stirred at room temperature for 4 h. After the removal of solvent under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) (10:1, v/v) to give (*R*)-6,6'-dibutyl-3,3'-diethynyl-2,2'-bis(octoxy)-1,1'-binaphthyl (1.36 g, 82.0%) as a yellow oil. $[\alpha]_D^{25} = +20.9$ (*c* 0.45, THF). ^1H NMR (300 MHz, CDCl_3): δ 8.10 (s, 2H), 7.60 (s, 2H), 7.14 (dd, 2H, $J = 8.7$ Hz, 1.5 Hz), 7.09 (d, 2H, $J = 8.7$ Hz), 4.03-3.96 (m, 2H), 3.74-3.69 (m, 2H), 3.31 (s, 2H), 2.74 (t, 4H, $J = 7.8$ Hz), 1.72-1.62 (m, 4H), 1.43-1.36 (m, 4H), 1.32-1.22 (m, 11H), 1.14-0.87 (m, 25H). ^{13}C NMR (75 MHz, CDCl_3): δ 139.6, 134.2, 132.6, 130.0, 128.8, 125.9, 125.8, 125.2, 116.3, 95.9, 81.0, 80.7, 73.6, 35.4, 33.2, 31.6, 29.9, 29.0, 28.9, 25.3, 22.6, 22.3, 14.0, 13.9. FT-IR (KBr, cm^{-1}): 3312, 2955, 2927, 2856, 2106, 1591, 1496, 1463, 1438, 1375, 1354, 1239, 1114, 1023. MS (EI, m/z): 671 (4.8%), 670 (29%), 447 (12%), 446 (100%), 403 (62%), 57 (14%), 43 (50%), 41 (15%). Anal. calcd for $\text{C}_{48}\text{H}_{62}\text{O}_2$: C, 85.92; H, 9.31. Found: C, 86.14; H, 9.55.

^1H NMR of *R*-M-1 in CDCl_3



^{13}C NMR of *R*-M-3 in CDCl_3



1,4-Diazidobenzene ^[2]

1,4-phenylene-bis(diazonium tetrafluoroborate): In a 100-mL three necked round bottom flask were placed 11.3 mL of distilled water and 2.7 g (25mmol) of sodium tetrafluoroborate. The mixture was stirred until all solid was dissolved, and then 11.3 mL of conc. hydrochloric acid was added. The flask was placed in a -20°C cold bath and the solution was kept stirring. In a separate flask containing 18.7 mL of distilled water were placed 1.0g (9.2mmol) of *para*-phenylenediamine and 1.4g(20mmol) of sodium nitrite (minimal heating was used to dissolve solids). The solution of *p*-phenylenediamine was added dropwise to the reaction flask with stirring. The temperature was kept at -20°C to 15°C during the addition. The mixture was stirred for an additional 30 min. The precipitate was collected by filtration, washed with water followed by ethyl ether, and air dried to give 1.92(68%) of dark solid which was used as is in the next step.

In a 200-mL round-bottom flask was placed a solution of 1.0 g (15 mmol) of sodium azide in 77

mL of distilled water. The flask was placed in an ice bath, treated with 1.9 g (6.3mmol) of 1,4-phenylenebis(diazonium tetrafluoroborate), and stirred for 30 min. The resultant precipitate was collected by filtration, washed with water, then dissolved in ethyl ether. The ether solution was dried over magnesium sulfate and treated with decolorizing charcoal. The solvent was evaporated to give 0.7 g (70%) of light yellow/orange powder with mp 80-81 °C. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.03 (s, Ar-H).

Responsive behavior of Polymer on various metal ions

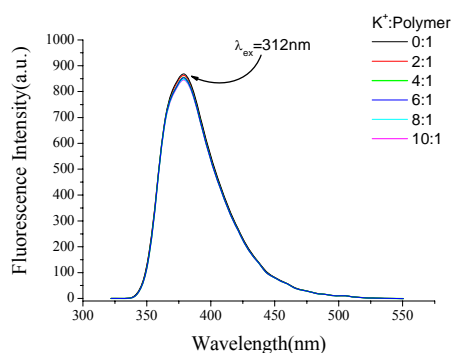


Figure S1(a)

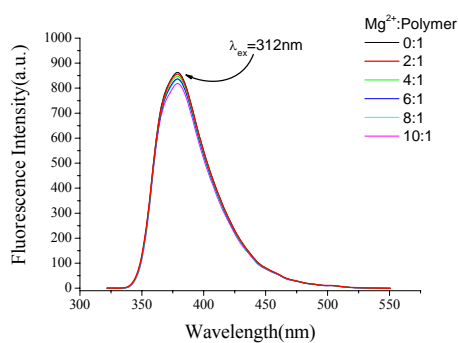


Figure S1(b)

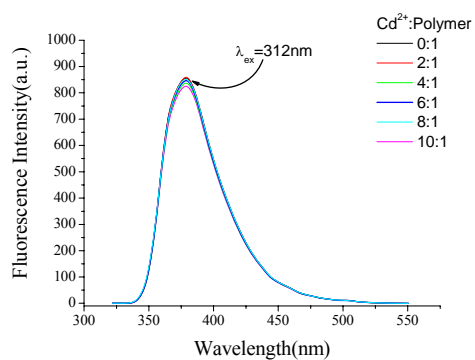


Figure S1(c)

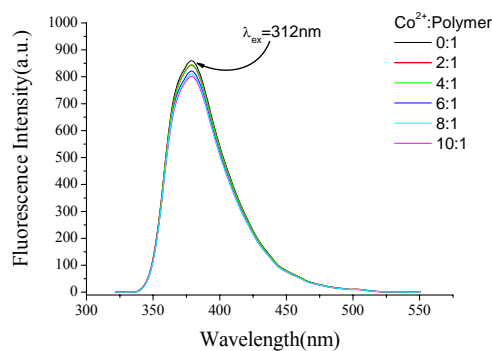


Figure S1(d)

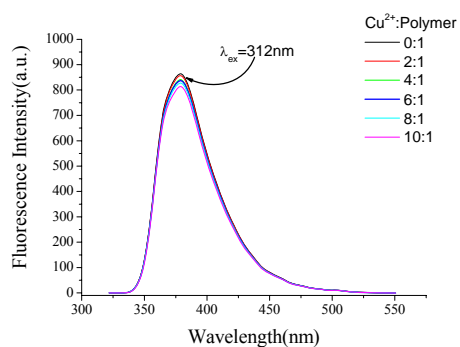


Figure S1(e)

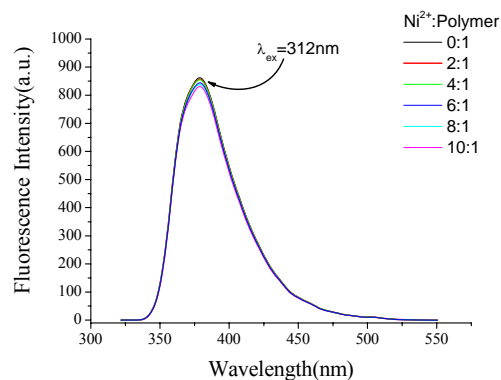


Figure S1(f)

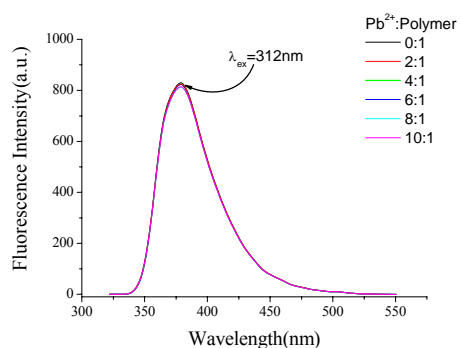


Figure S1(g)

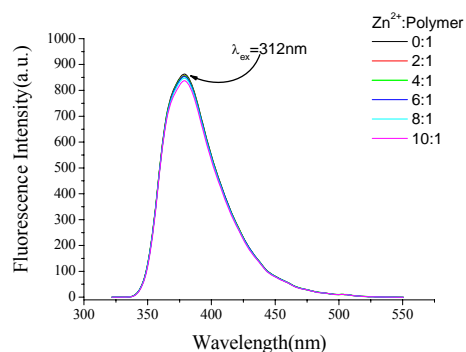


Figure S1(h)

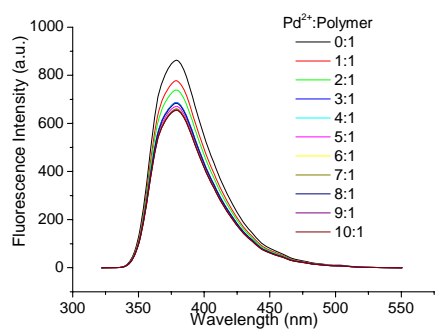


Figure S1(i)

Figure S1. Fluorescence response of **polymer** ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) upon addition of various metal ions.

The fluorescence spectra change profiles of polymer with Hg^{2+} in the absence or presence of selected metal ions

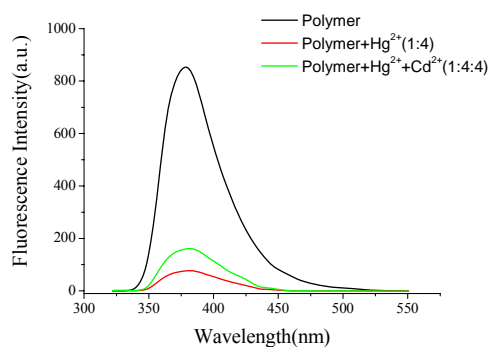


Figure S2(a).

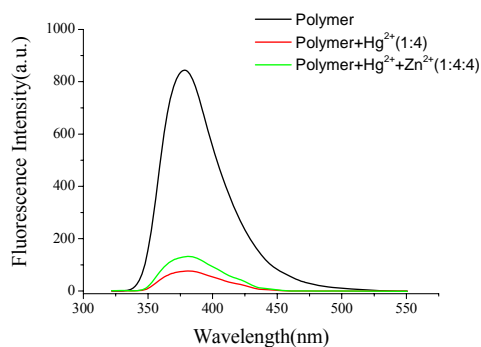


Figure S2(b).

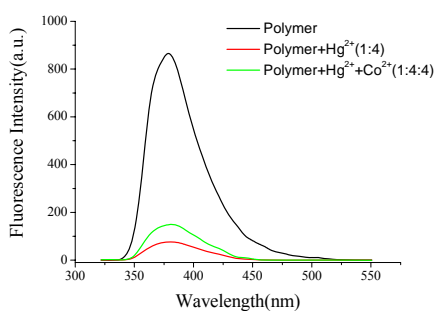


Figure S2(c).

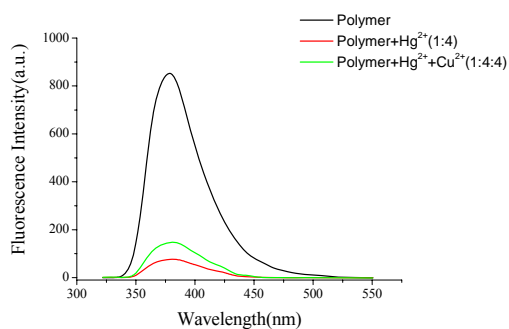


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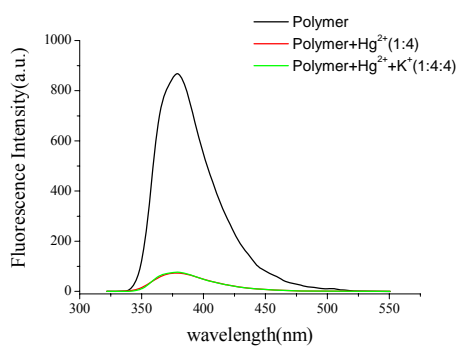


Figure S2(e).

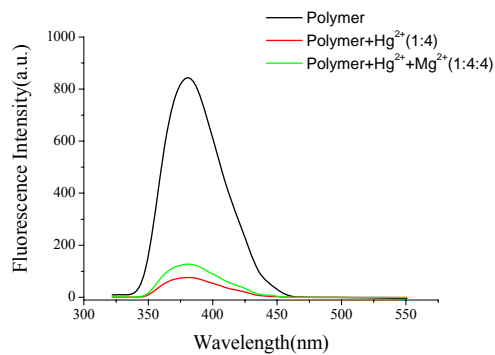


Figure S2(f).

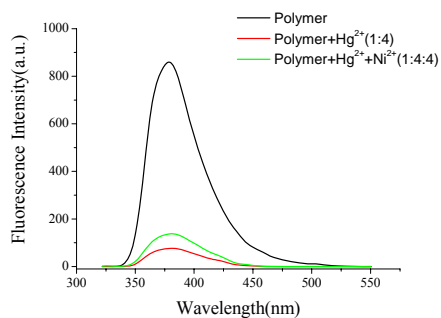


Figure S2(g).

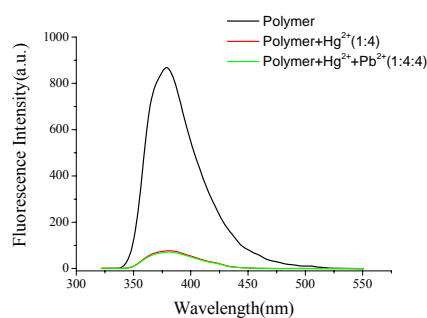


Figure S2(h).

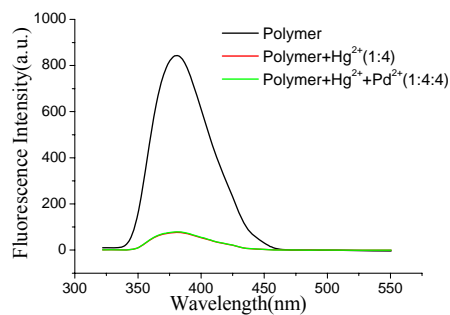


Figure S2(i).

Figure S2. The fluorescence spectra change profiles of **polymer** ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) with Hg^{2+} ($4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) in the absence or presence of various metal ions ($4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$). $\lambda_{\text{ex}} = 312 \text{ nm}$

Thermal analysis of the polymer

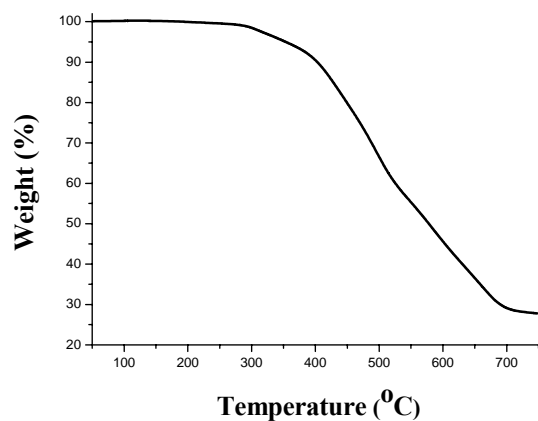
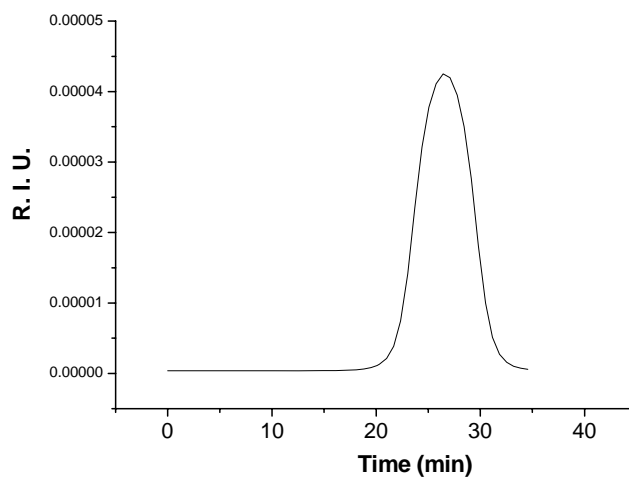


Figure S3. TGA curve of polymer

GPC curve of the polymer



References

- [1] X. Huang, Y. Xu, Q. Miao, L. Zong, H. Hu, Y. Cheng, *Polymer* **2009**, *50*, 2793.
- [2] M. Minato, P. M. Lahti, *J. Am. Chem. Soc.* **1997**, *119*, 2187.