Electronic Supplementary Material

A novel iodization triggered competitive coordination mechanism: indirect detection of Hg^{2+} and I^- using a simple copillar[5]arene-based fluorometric sensor

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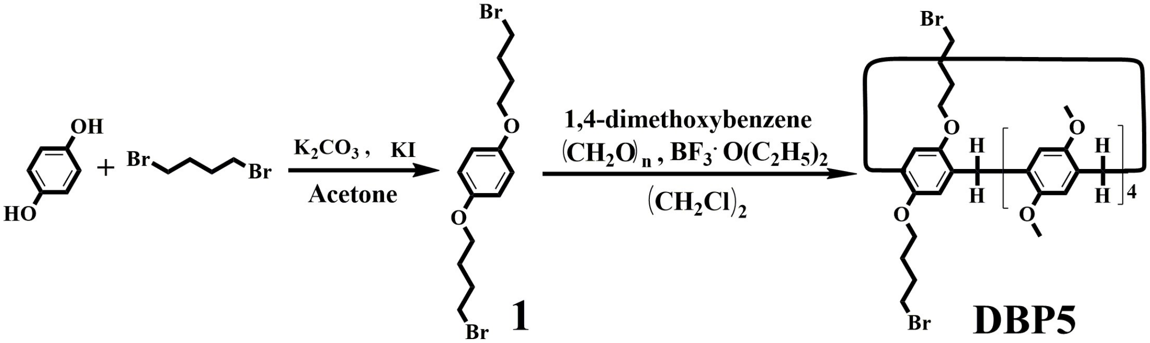
1. Materials and methods

1, 4−Dimethoxybenzene, boron trifluoride ethyl ether complex and 1,4−dibromobutane were analytical grade, which were purchased from Alfa Aesar and used as received. Solvents were either employed as purchased or dried by $CaCl_2$. ^1H NMR spectra were recorded on a Mercury−600BB spectrometer at 600 MHz and ^{13}C NMR spectra were recorded on a Mercury−600BB spectrometer at 150 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Melting points were measured on an X−4 digital melting−point apparatus (uncorrected). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker−FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

2. Synthesis of copillar[5]arene DBP5



Scheme S1 Synthesis of copillar[5]arene **DBP5.**

Synthesis of 1,4−bis(4−bromobutoxy)benzene 1: Hydroquinone (2.3 g, 20.0 mmol), K_2CO_3 (16.6 g, 120 mmol), KI (6.6 g, 40 mmol), 1,4−dibromobutane (34.6 g, 160 mmol) and acetone (400.0 mL) were added in a 500 mL round–bottom flask stirred at room temperature. The reaction mixture was stirred at reflux for 2.5 days. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CH_2Cl_2. Column chromatography (silica gel; petroleum ether : CH_2Cl_2 = 10 : 1) afforded a white solid (6.0 g, 80%). Mp 83−85°C. ^1H NMR (600 MHz, $CDCl_3$) δ 6.83 (d, J = 0.8 Hz, 4H), 3.96 (t, J = 6.0 Hz, 4H), 3.52–3.25 (m, 4H), 2.10–1.88 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.07 (s), 115.49 (d, J = 28.1 Hz), 67.35 (d, J = 30.2 Hz), 33.52 (s), 29.50 (s), 28.00 (s). ESI−MS m/z: M^+ Calcd for $C_{14}H_{20}O_2Br_2$ 379.9804; Found 379.9799.

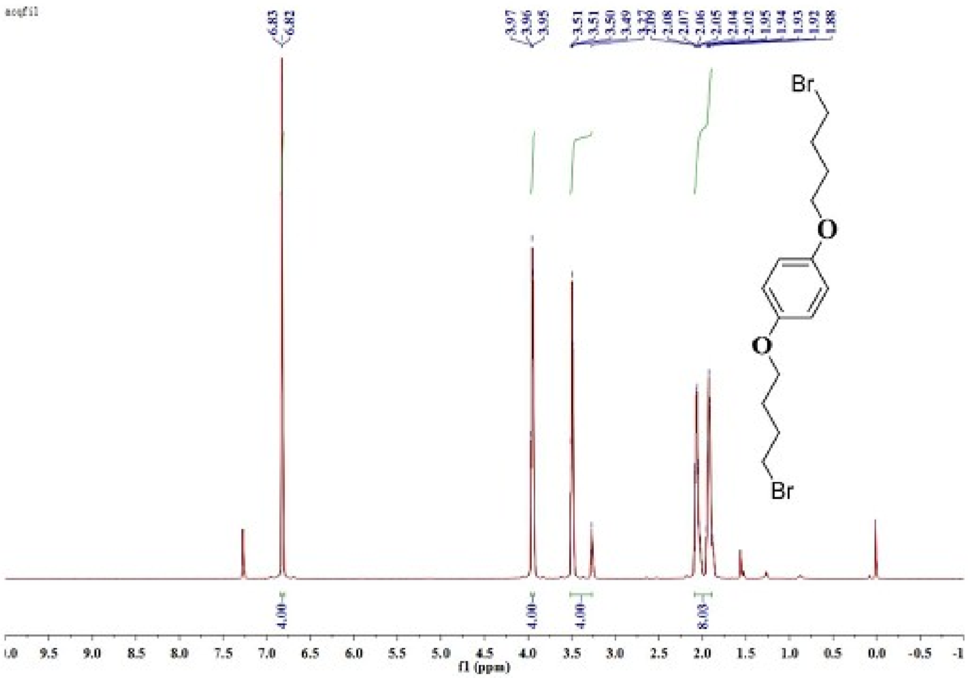


Fig. S1 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of 1,4–bis (4–bromobutoxyl) benzene **1**.

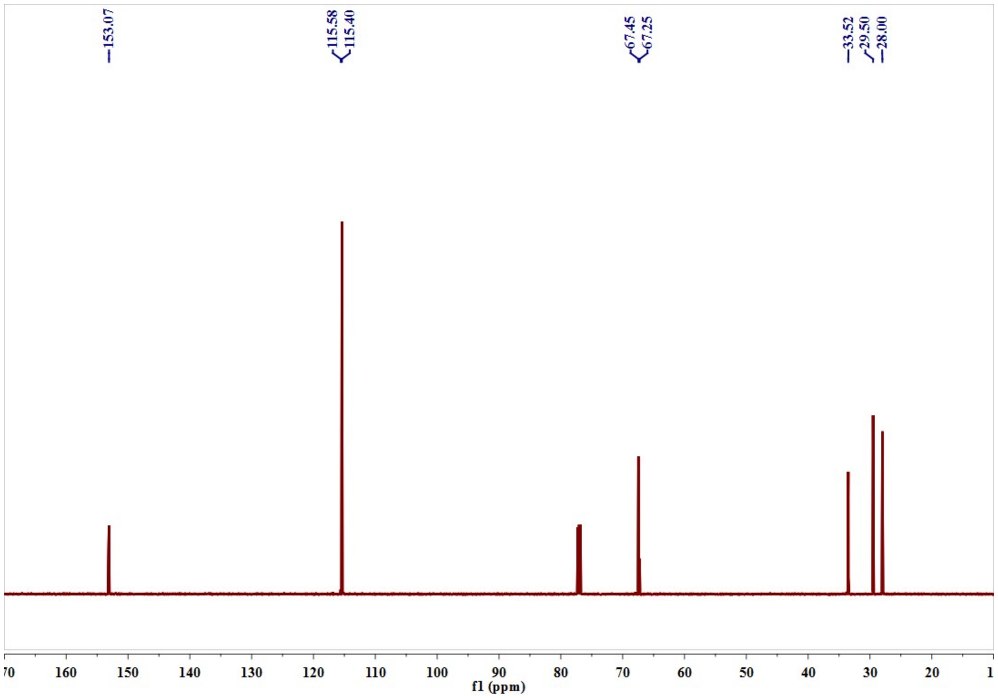


Fig. S2 ^{13}C NMR spectra(151 MHz, $CDCl_3$) of 1,4–bis (4–bromobutoxyl) benzene **1**.

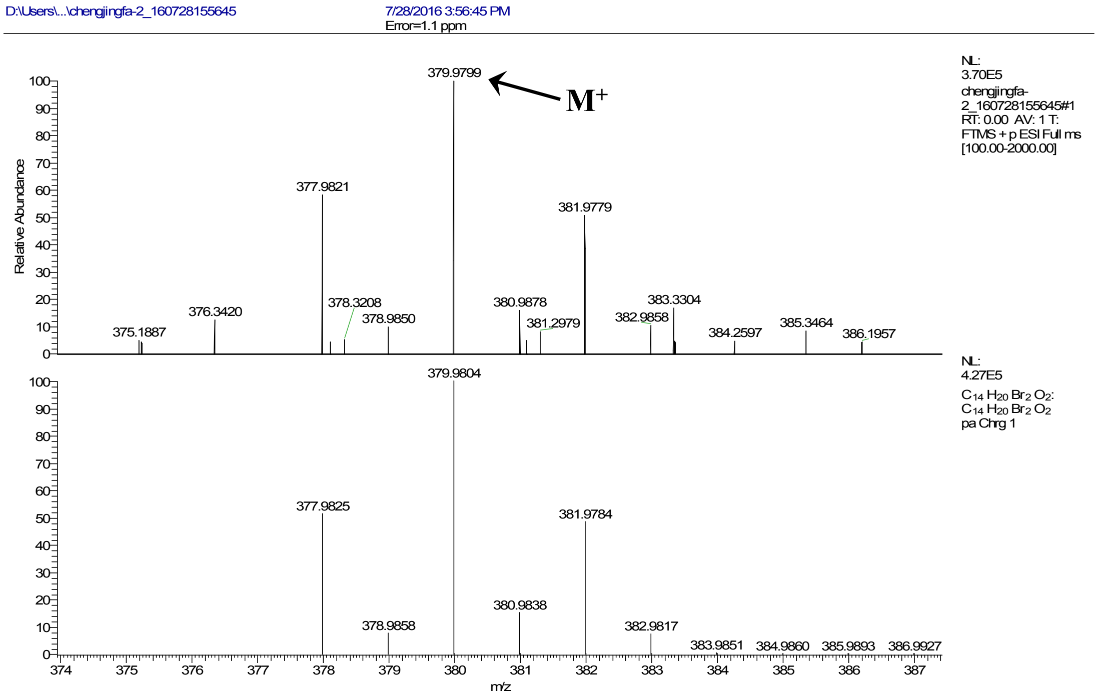


Fig. S3 High resolution mass data of 1,4–bis (4–bromobutoxyl) benzene **1**.

Synthesis of a copillar[5]arene DBP5: To a solution of 1,4−bis (4−bromobutoxy) benzene (1.9 g, 5.0 mmol) and 1,4−dimethoxybenzene (2.76 g, 20.0 mmol) in 1, 2−dichloroethane (200 mL), paraformaldehyde (0.75 g, 25.0 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (6.75 mL, 25 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h and concentrated by rotary evaporation. The resultant oil was dissolved in CH_2Cl_2 and washed twice with H_2O. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (20 : 1, *v*/*v*) to give **DBP5** (1.69 g, 34%) as a white solid. Mp 187−189 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84–6.74 (m, 10H), 3.87 (t, J = 5.9 Hz, 4H), 3.83–3.78 (m, 10H), 3.72 (t, J = 19.9 Hz, 24H), 3.33 (s, 4H), 1.94 (s, 4H), 1.84 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.80 (s), 150.75 (s), 150.70 (s), 150.58 (s), 149.84 (s), 128.44 (s), 128.30 (s), 128.08 (s), 114.89 (s), 114.15 (s), 113.92 (s), 113.71 (s), 67.32 (s), 55.95 (d, J = 3.6 Hz), 55.76 (s), 55.70 (s), 33.34 (s), 30.55 (s), 29.75 (s), 29.48 (d, J = 5.2 Hz), 29.19 (s), 28.32 (s). ESI−MS m/z: $(M+NH_4)^+$ Calcd for $C_{51}H_{64}O_{10}Br_2N$ 1010.2871; Found 1010.2878.

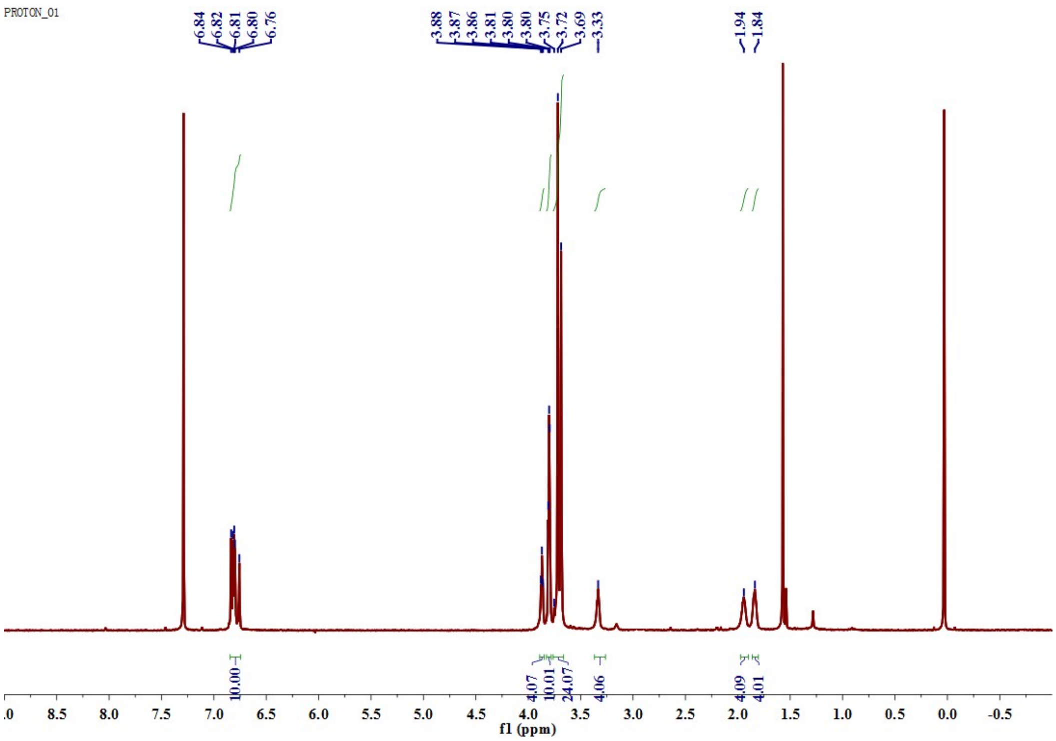


Fig. S4 ^{1}H NMR spectra(600 MHz, $CDCl_3$) of a copillar[5]arene **DBP5**.

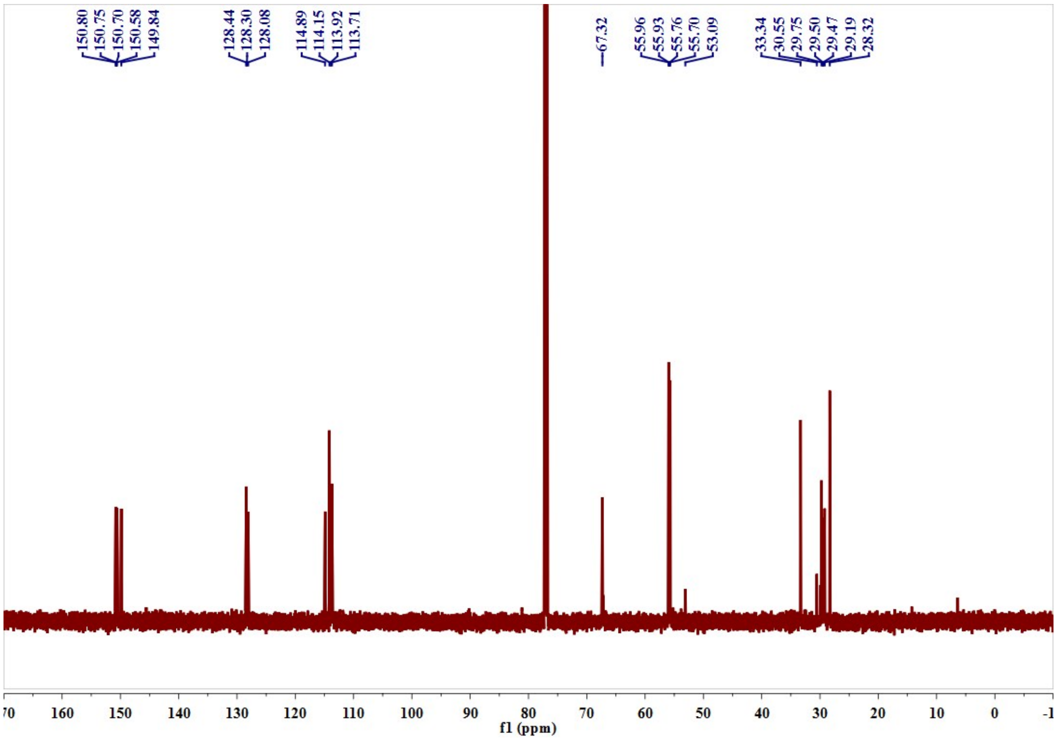


Fig. S5 ^{13}C NMR spectra(151 MHz, $CDCl_3$) of a copillar[5]arene **DBP5**.

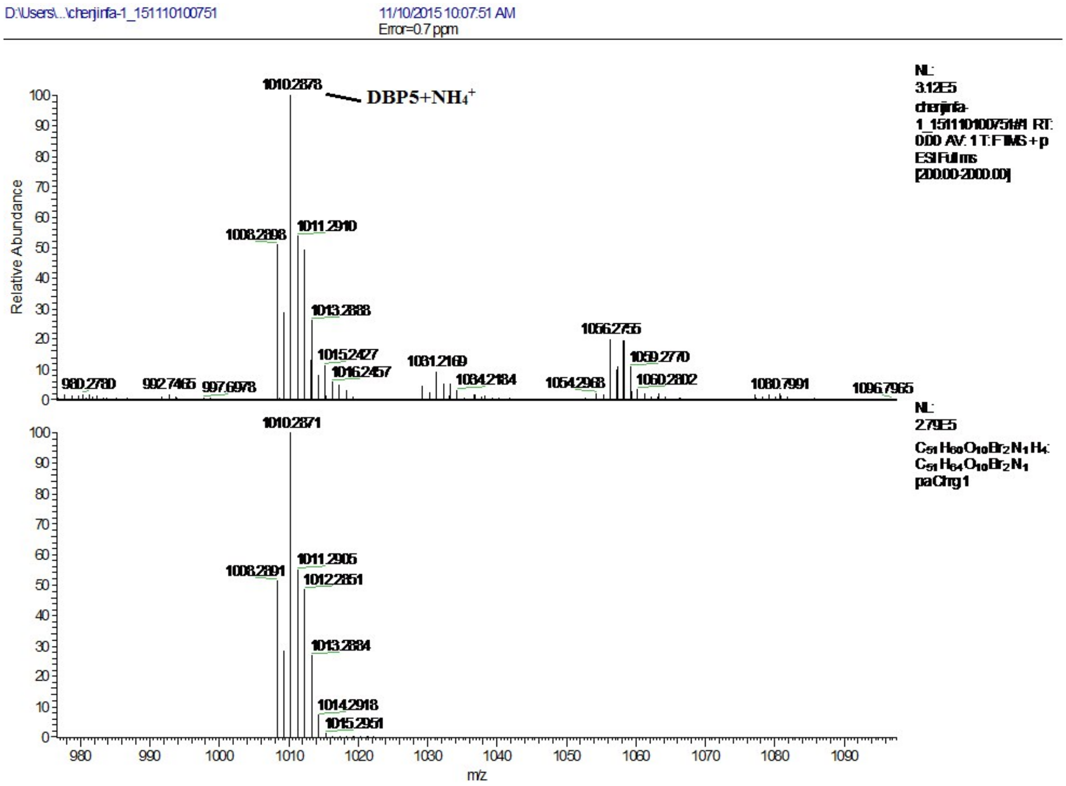


Fig. S6 High resolution mass data of a copillar[5]arene **DBP5**.

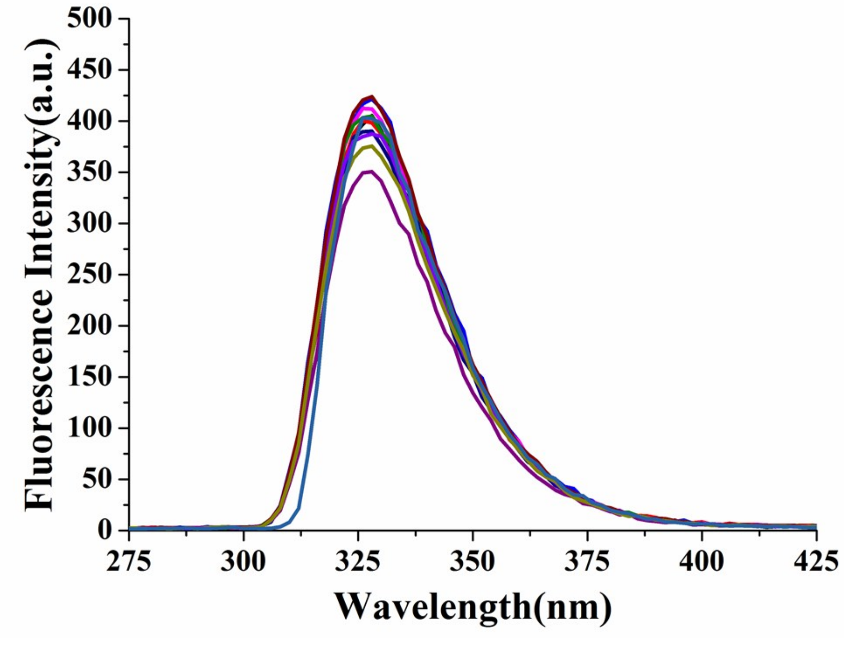


Fig. S7 Fluorescence spectral response of **DBP5** (2×10^{-4} M) in H_2O/DMSO (1 : 9 , v/v) solution upon addition of 2.5 equiv. of anions (λ_{ex} = 295 nm).

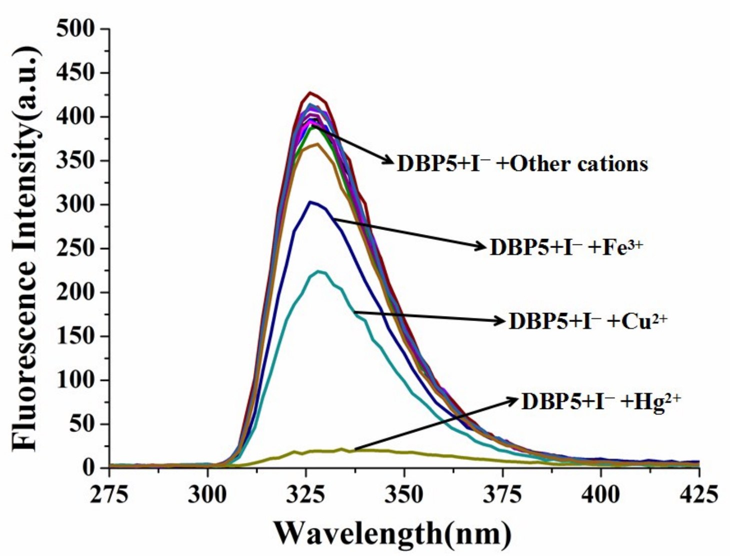


Fig. S8 Fluorescence spectral response of **DBP5I** ([**DBP5**]/[I^-] = 1 : 2.5, [**DBP5**]= 2×10^{-4} M) in H_2O/DMSO (1 : 9 , v/v) solution upon addition of 0.25 equiv. of different cations (λ_{ex} = 295 nm).

Determination of the detection limit

We use the 3δ way to figure out the detection limit. The process of the analysis as follows.

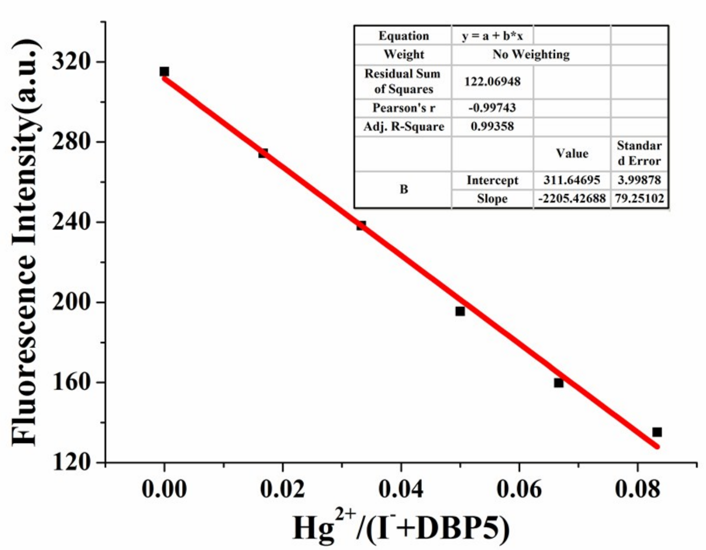


Fig. S9 The photograph of the linear range.

Linear Equation: Y=−2205.42688X+311.64695 R^2=0.99358

S=2205.427×10^6

$$\delta=\sqrt{\frac{\sum(x_i-\bar{x})^2}{n-1}}=27.42(n=30)$$

LOD =3δ/S= 3.73×10^{-8} M

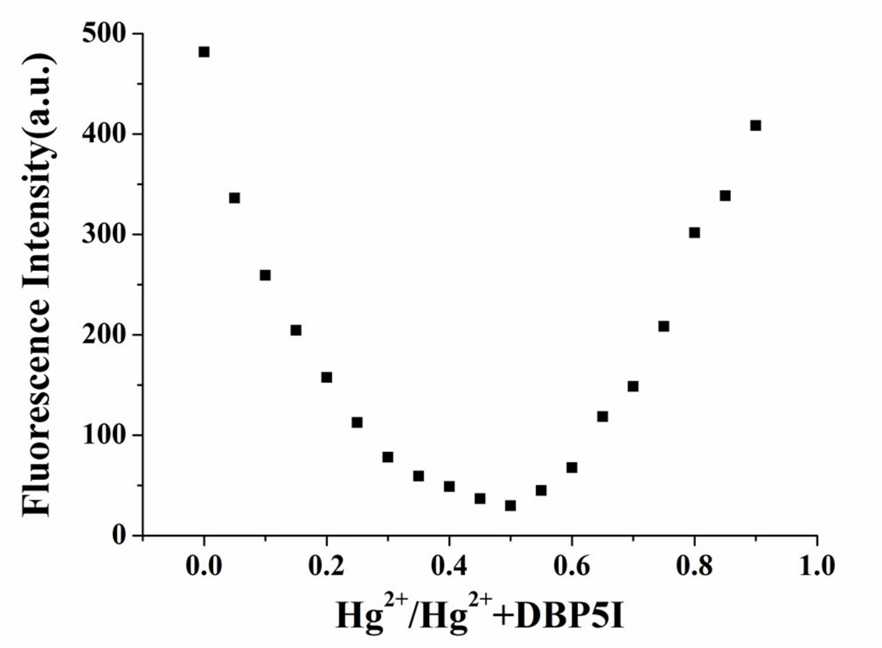


Fig. S10 The Job's plot examined between Hg^{2+} and **DBP5I**, indicating the 1 : 1 stoichiometry, which was carried out by fluorescence spectra (λ_{ex} = 295 nm).

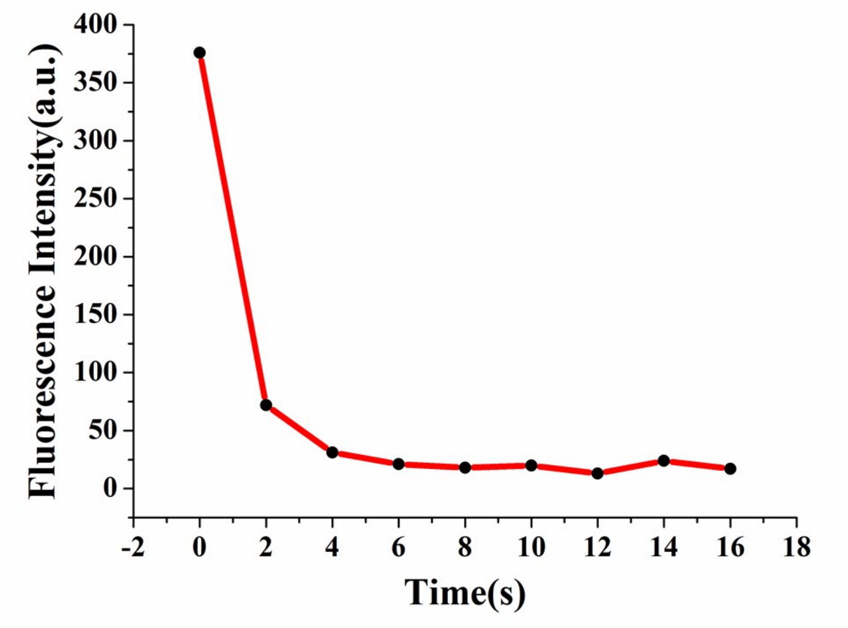


Fig. S11 Time-dependent of **DBP5I** (2×10^{-4} M) upon addition of Hg^{2+} (0.25 equiv.) in H_2O/DMSO (1 : 9 , v/v) with a plot of the fluorescence intensity that is estimated as the peak height at 328 nm.

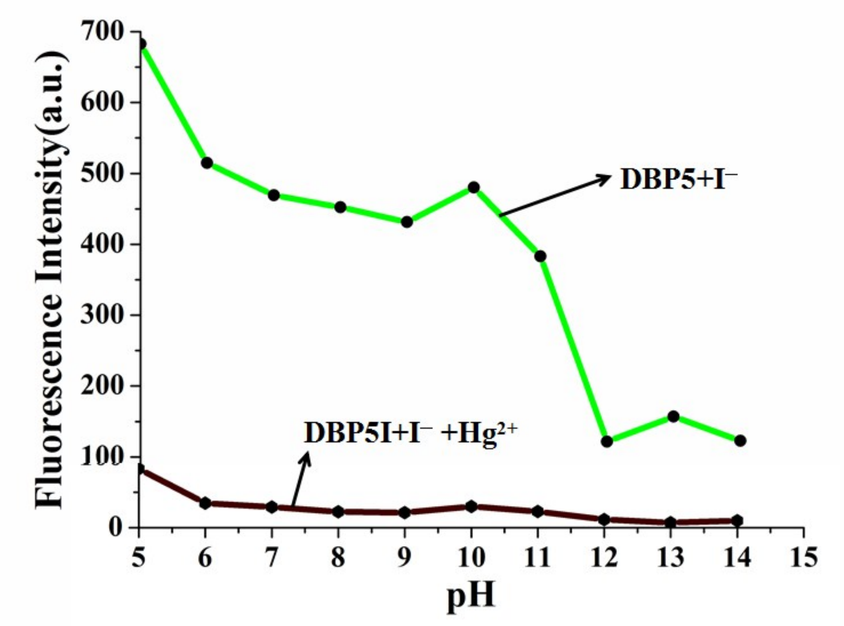


Fig. S12 Influence of pH on the fluorescence of **DBP5I** (2×10^{-4} M) with Hg^{2+} (0.25 equiv.) in H_2O/DMSO (1 : 9 , v/v).

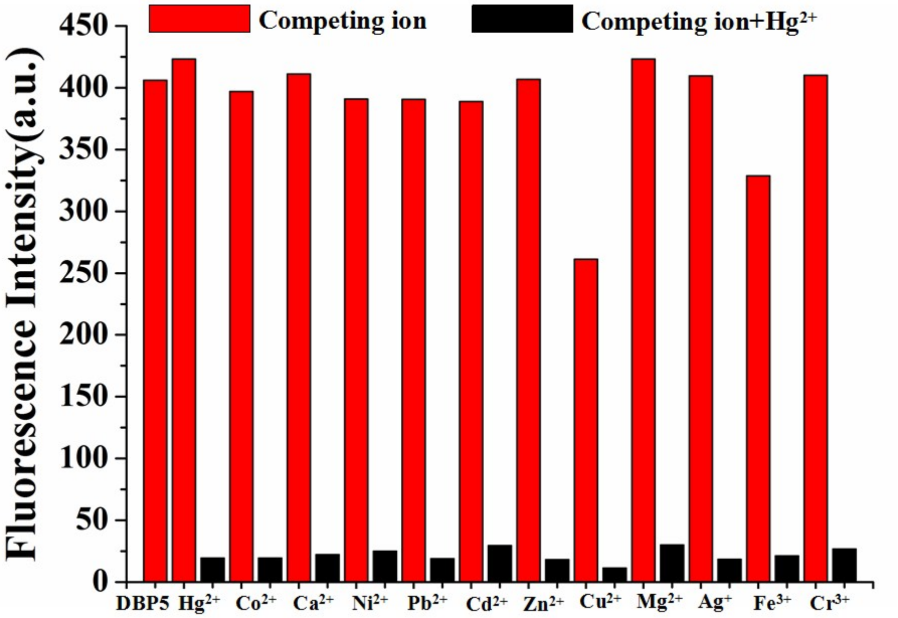


Fig. S13 Fluorescence of **DBP5I** at 328 nm with addition of 0.4 equiv. of Hg^{2+} in the presence of 0.4 equiv. of other cations in H_2O/DMSO (1 : 9 , v/v) solution.

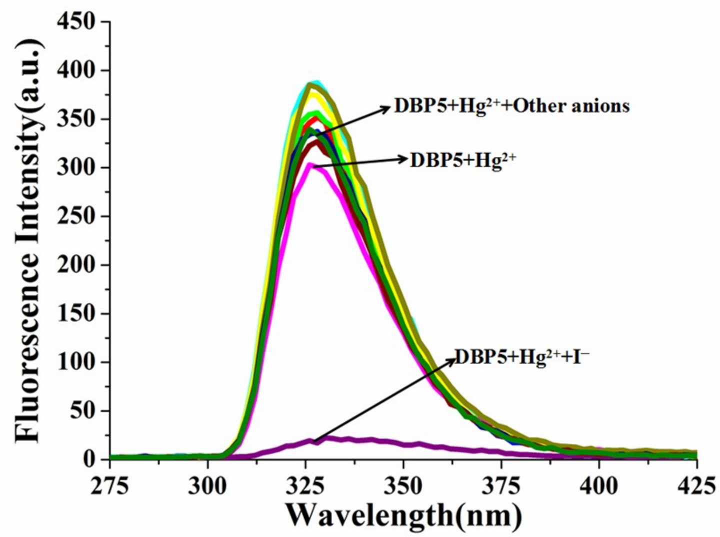
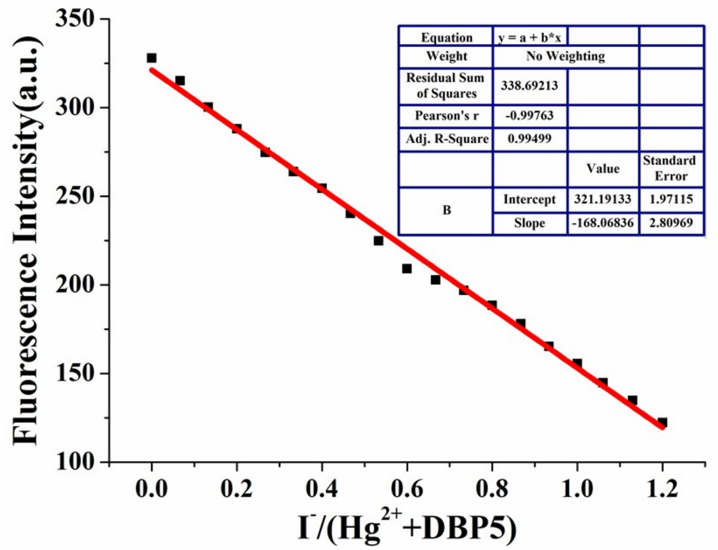


Fig. S14 Fluorescence spectral response of **DBP5**–Hg^{2+} system ([**DBP5**]/[Hg^{2+}] = 1 : 1, [**DBP5**]= 2×10^{-4} M) in H_2O/DMSO (1 : 9 , v/v) solution upon addition of 2.0 equiv. of different anions (λ_{ex} = 295 nm).

Determination of the detection limit

We use the 3δ way to figure out the detection limit. The process of the analysis as follows.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	338.69213		
Pearson's r	-0.99763		
Adj. R-Square	0.99499		
		Value	Standard Error
B	Intercept	321.19133	1.97115
	Slope	-168.06836	2.80969

Fig. S15 The photograph of the linear range.

Linear Equation: Y=−168.06836X+321.19133 R^2=0.99499

S=168.06836×10^6

$$\delta=\sqrt{\frac{\sum(x_i-\bar{x})^2}{n-1}}=19.66(n=30)$$

LOD =3δ/S= 3.51 ×10^{-7} M

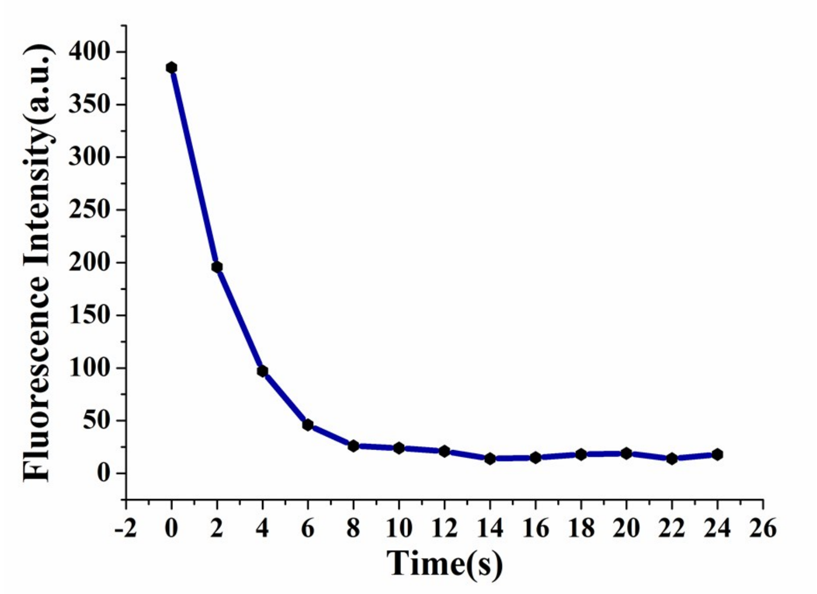


Fig. S16 Time-dependent of **DBP5**−Hg^{2+} (2×10^{-4} M) system upon addition of I^- (2.0 equiv.) in H_2O/DMSO (1 : 9 , v/v) with a plot of the fluorescence intensity that is estimated as the peak height at 328 nm.

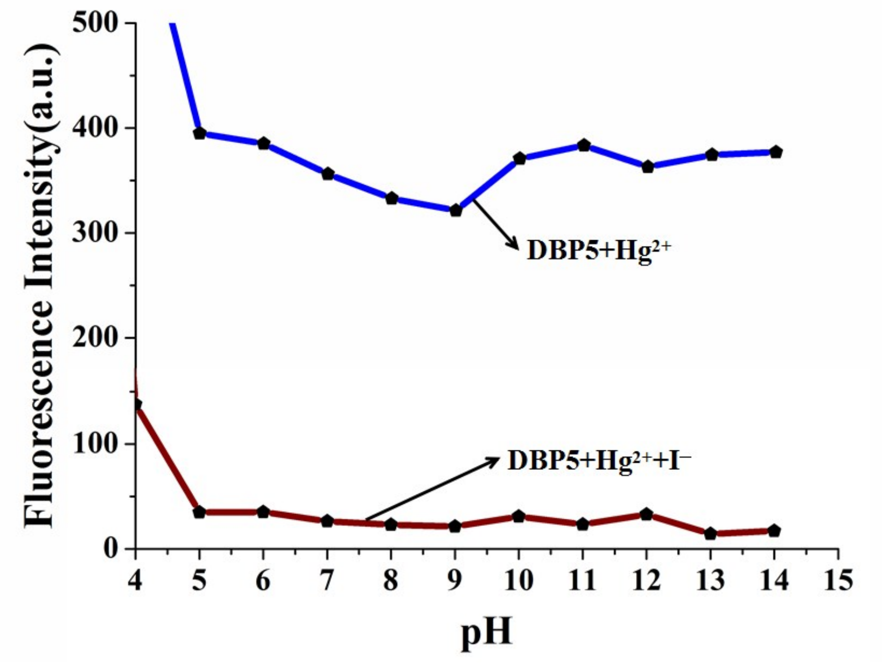


Fig. S17 Influence of pH on the fluorescence of **DBP5**−Hg^{2+} (2×10^{-4} M) system with I^- (2.0 equiv.) in H_2O/DMSO (1 : 9 , v/v).

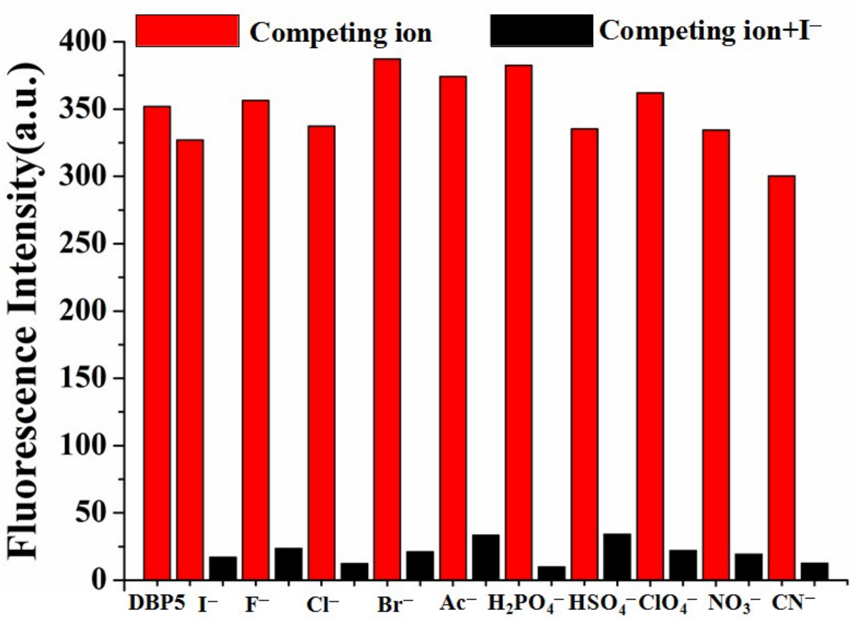


Fig. S18 Fluorescence of **DBP5**−Hg^{2+} system at 328 nm with addition of 2.0 equiv. of I^- in the presence of 2.0 equiv. of other anions in H_2O/DMSO (1 : 9 , v/v) solution.

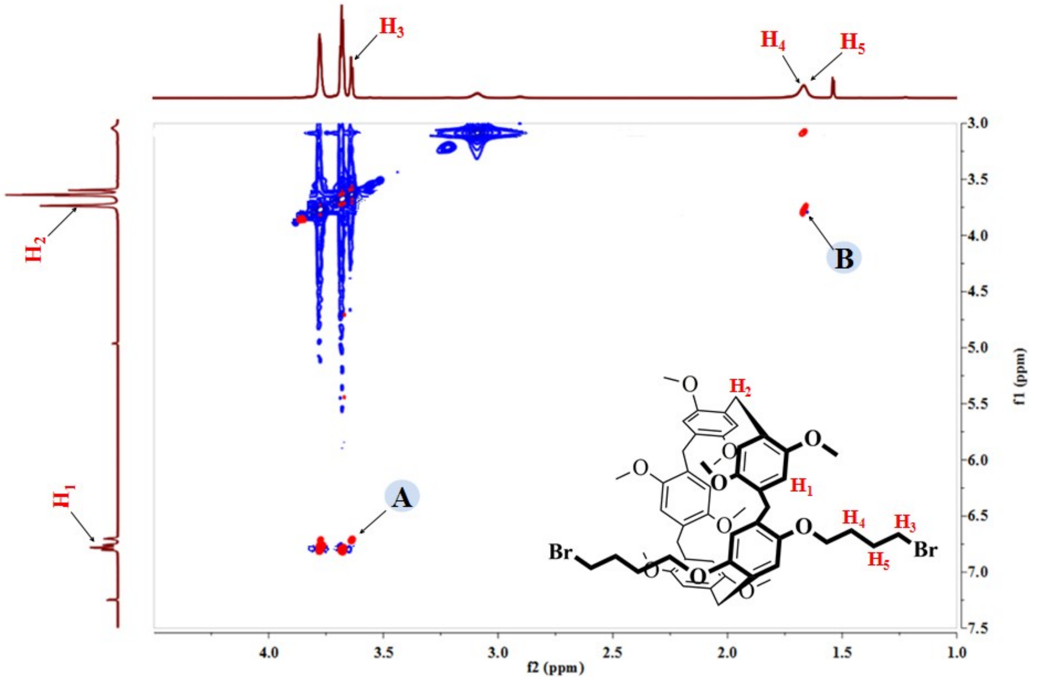


Fig. S19 The 2D NOESY spectrum of (600 MHz, $CDCl_3$, 298 K) of **DBP5** at 50.0 mM.

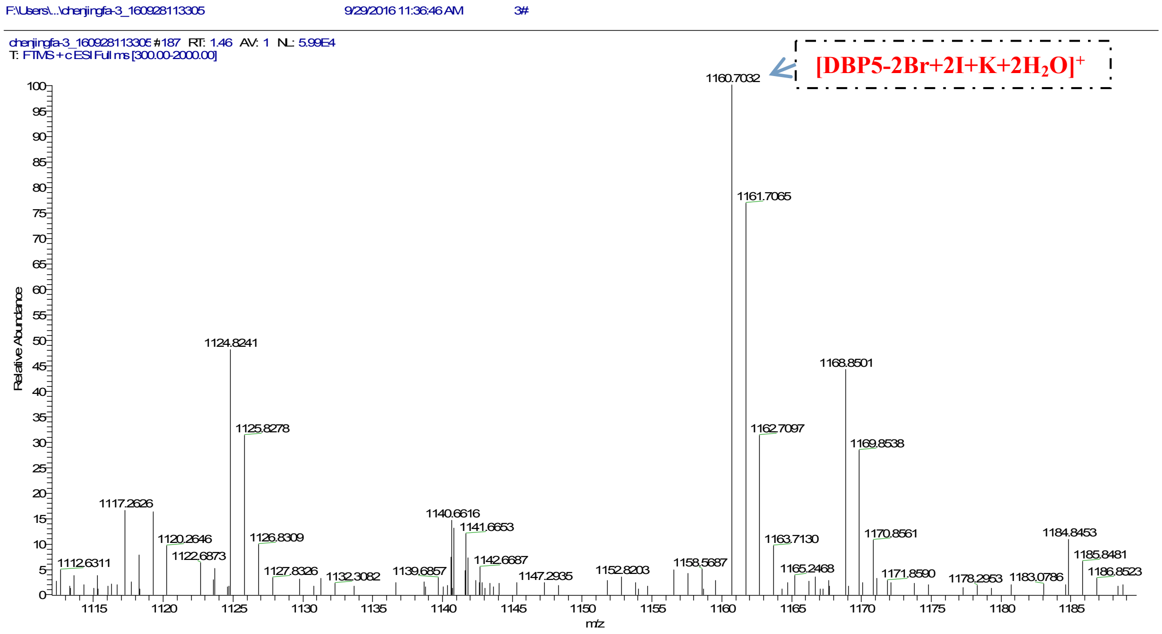


Fig. S20 High resolution mass data of the system of **DBP5** and I$^-$.

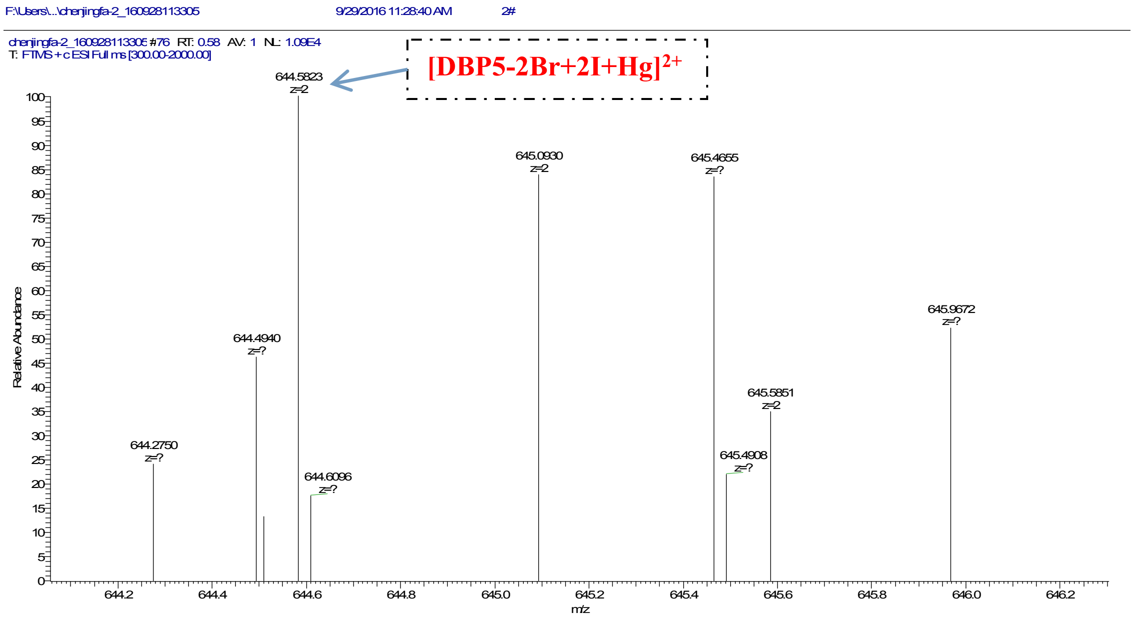
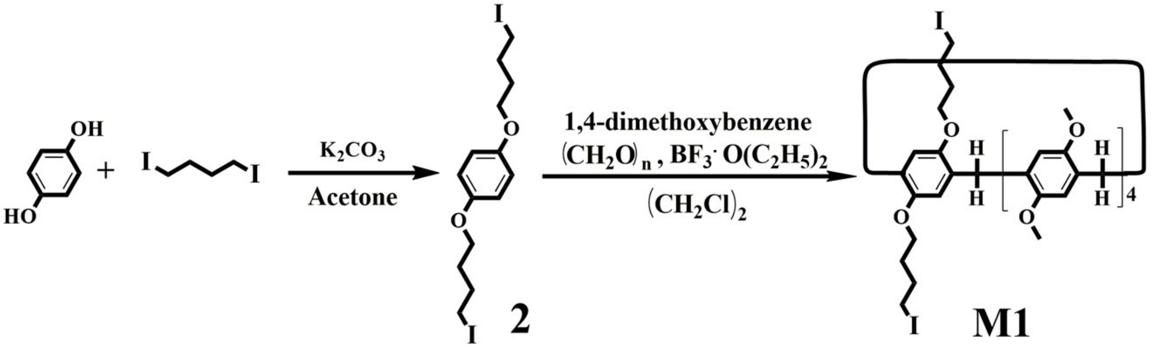


Fig. S21 High resolution mass data of the complex of **DBP5**–I$^-$ system and Hg^{2+}.

3. Synthesis of the model compound M1



Scheme S2 Synthesis of the model compound **M1.**

Synthesis of 1,4−bis(4−iodobutoxy)benzene 2: Hydroquinone (0.55 g, 5.0 mmol), K_2CO_3 (5.5 g, 40 mmol), 1,4−diiodobutane (12.4 g, 40 mmol) and acetone (200.0 mL) were added in a 250 mL round–bottom flask stirred at room temperature. The reaction mixture was stirred at reflux for 1.5 days. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CH_2Cl_2. Column chromatography (silica gel; petroleum ether : CH_2Cl_2 = 10 : 1) afforded a white solid (1.8 g, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 (s, 4H), 3.93 (t, J = 6.1 Hz, 4H), 3.25 (t, J = 6.9 Hz, 4H), 2.08–1.97 (m, 4H), 1.93–1.80 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.06 (s), 115.39 (s), 67.25 (s), 30.22 (d, J = 7.0 Hz), 6.51 (s).

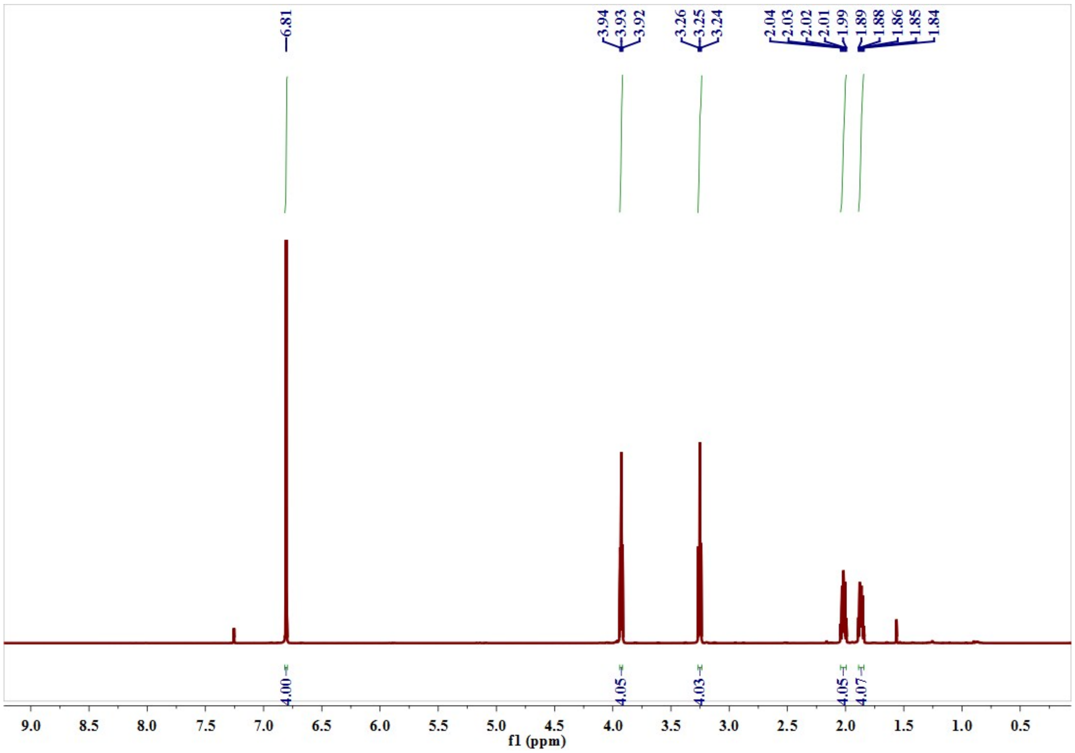


Fig. S22 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of 1,4–bis (4–iodobutoxyl) benzene **2**.

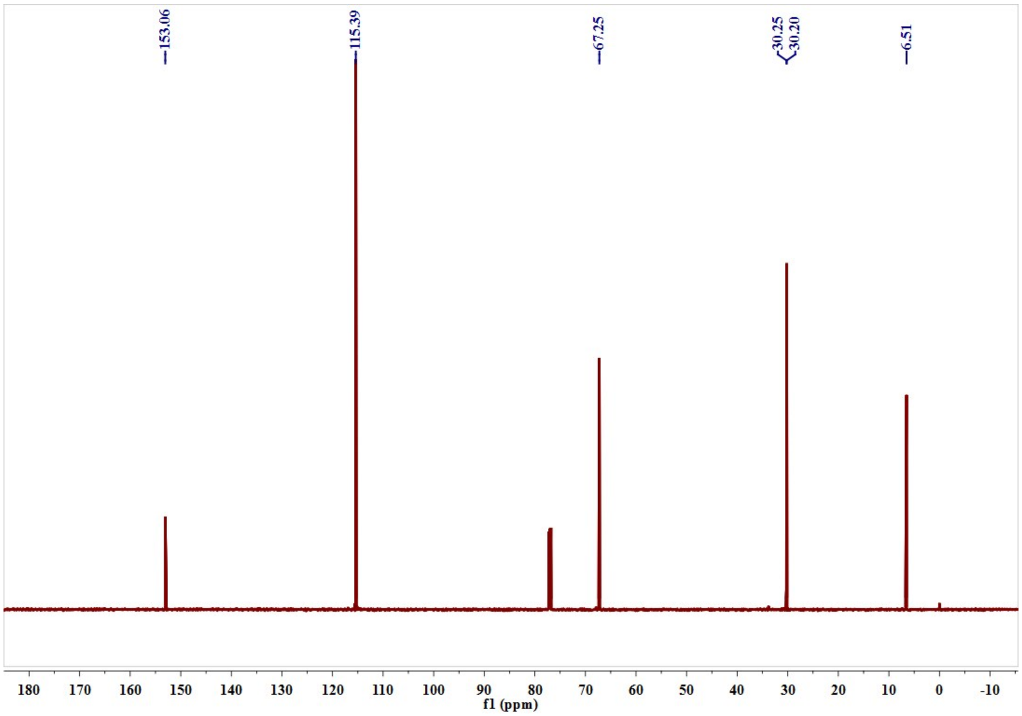


Fig. S23 ^{13}C NMR spectra (151 MHz, $CDCl_3$) of 1,4–bis (4–iodobutoxyl) benzene **2**.

Synthesis of the model compound M1: To a solution of 1,4−bis (4−iodobutoxy)benzene (0.95 g, 2.0 mmol) and 1,4−dimethoxybenzene (1.38 g, 10.0 mmol) in 1, 2−dichloroethane (150 mL), paraformaldehyde (0.36 g, 12.0 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (3.24 mL, 12 mmol) was added to the solution and the mixture was stirred at room temperature for 1 h and concentrated by rotary evaporation. The resultant oil was dissolved in CH_2Cl_2 and washed twice with H_2O. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (20 : 1, *v*/*v*) to give **M1** (0.46 g, 21%) as a white solid. ^1H NMR (600 MHz, $CDCl_3$) δ 6.81 (t, *J* = 9.4 Hz, 10H), 3.78 (d, *J* = 2.9 Hz, 10H), 3.77 (s, 4H), 3.69 (d, *J* = 6.0 Hz, 24H), 3.65 (s, 4H), 1.65 (s, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.74–149.00 (m), 128.23 (dd, *J* = 31.5, 22.0 Hz), 114.17 (dd, *J* = 101.1, 71.0 Hz), 67.15 (s), 55.86 (dd, *J* = 36.1, 15.3 Hz), 29.94 (dd, *J* = 101.1, 61.1 Hz), 6.41 (s). ESI−MS m/z: $(M+Na)^+$ Calcd for $C_{51}H_{60}I_2NaO_{10}$ 1109.2168; Found 1109.2160.

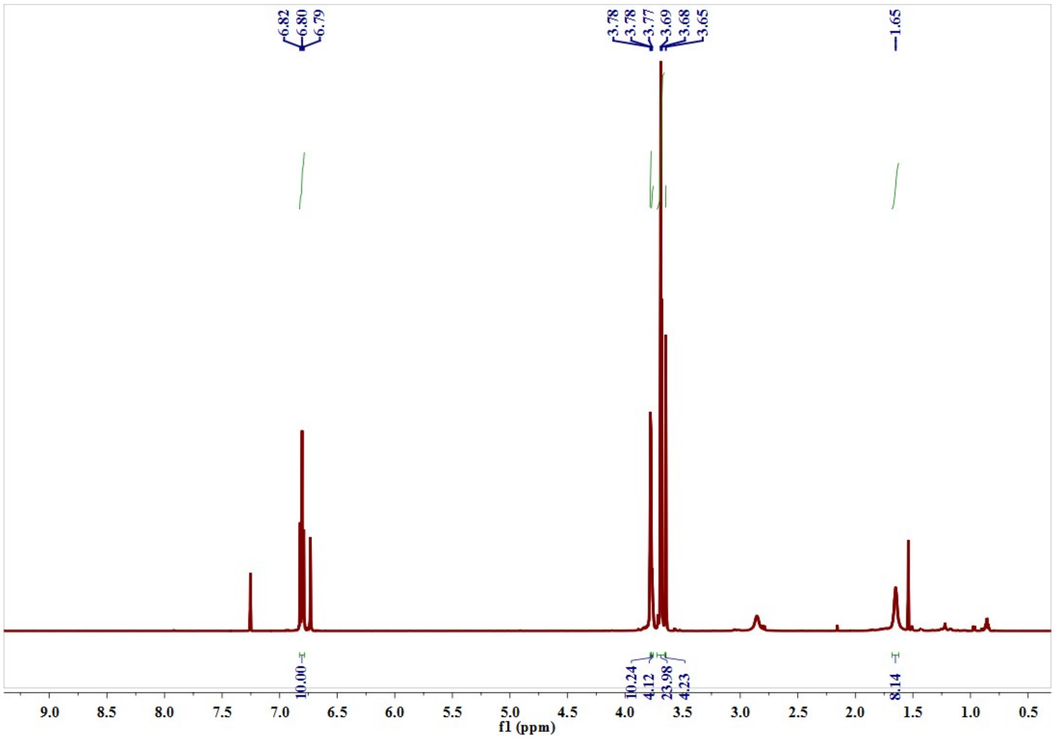


Fig. S24 ^1H NMR spectra (600 MHz, $CDCl_3$) of the model compound **M1**.

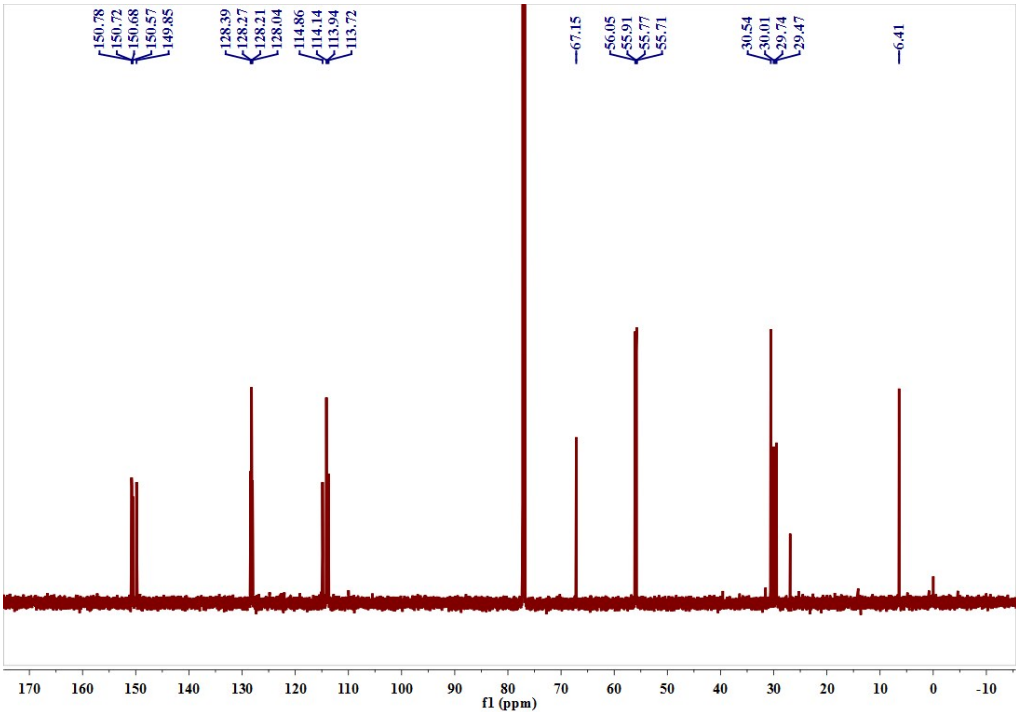
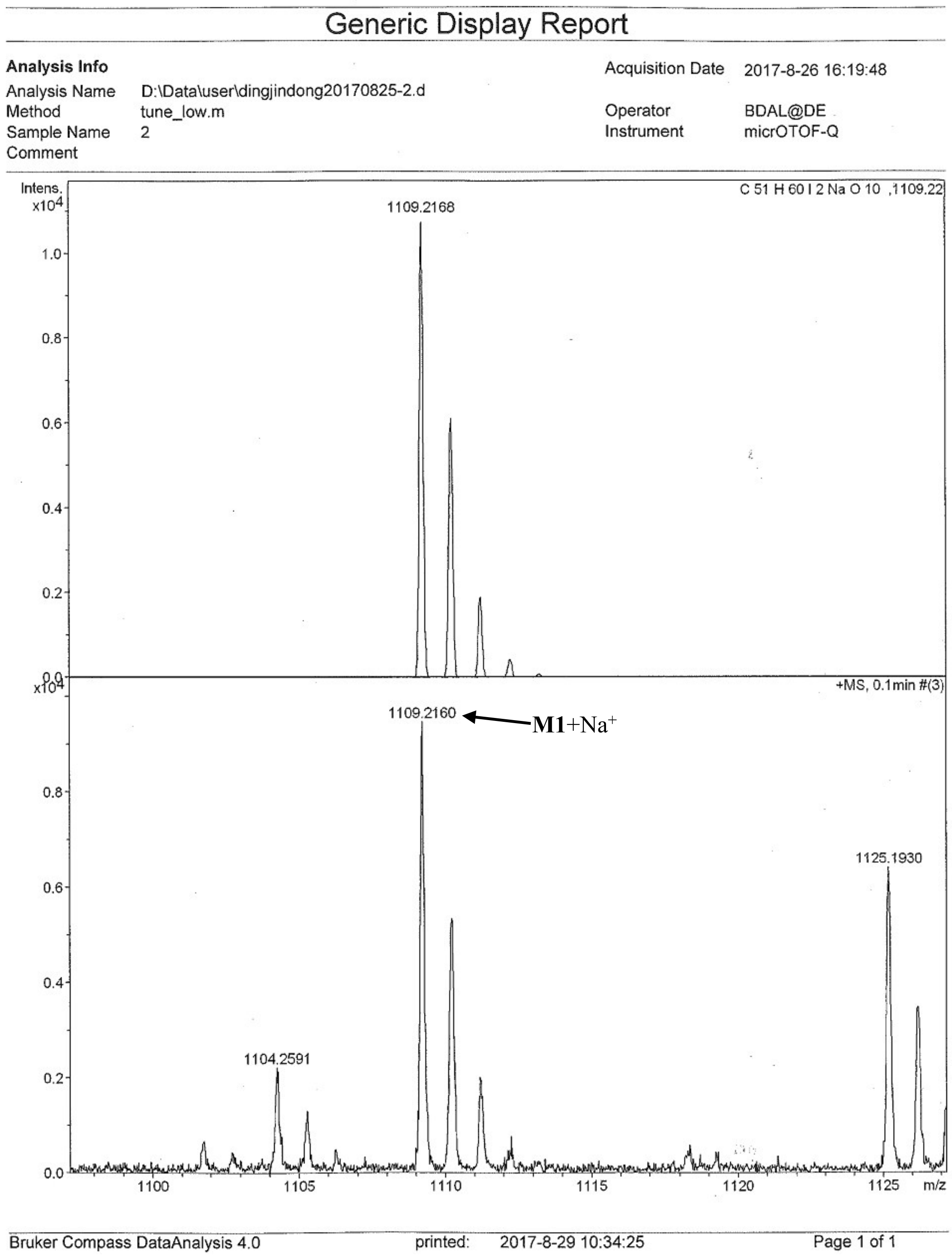


Fig. S25 ^{13}C NMR spectra (151 MHz, $CDCl_3$) of the model compound **M1**.



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Bruker Compass DataAnalysis 4.0 printed: 2017-8-29 10:34:25 Page 1 of 1

Fig. S26 High resolution mass data of the model compound **M1**.

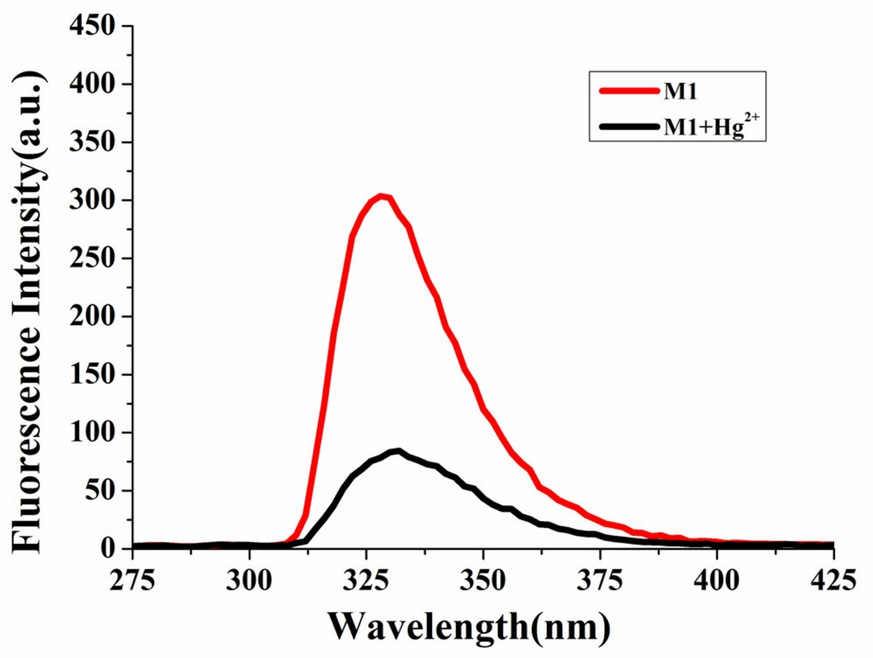

Fig. S27 Fluorescence spectral response of **M1** (2×10^{-4} M) in H_2O/DMSO (1 : 9 , v/v) solution upon addition of 2.0 equiv. of Hg^{2+} (λ_{ex} = 295 nm).

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