Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A Novel Functionalized Pillar[5]arene for Forming a Fluorescent Switch and a Molecular Keypad

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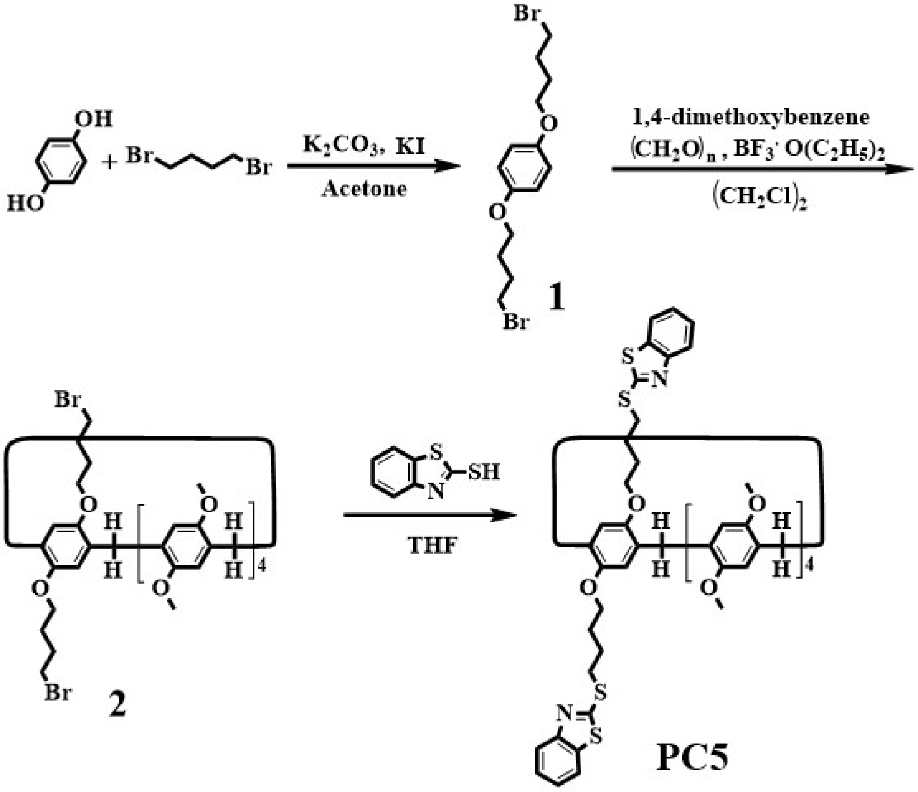
1. Materials and methods

1, 4−Dimethoxybenzene, boron trifluoride ethyl ether complex, 1,4−dibromobutane, and was reagent grade and used as received. Solvents were either employed as purchased or dried by $CaCl_2$. ^{1}H 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.

2. Synthesis of Functionalized Pillar[5]arene PC5



Scheme 1 Synthesis of functionalized Pillar[5]arene **PC5.**

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 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(6.0 g, 80%). Mp 83−85°C. ^{1}H 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).

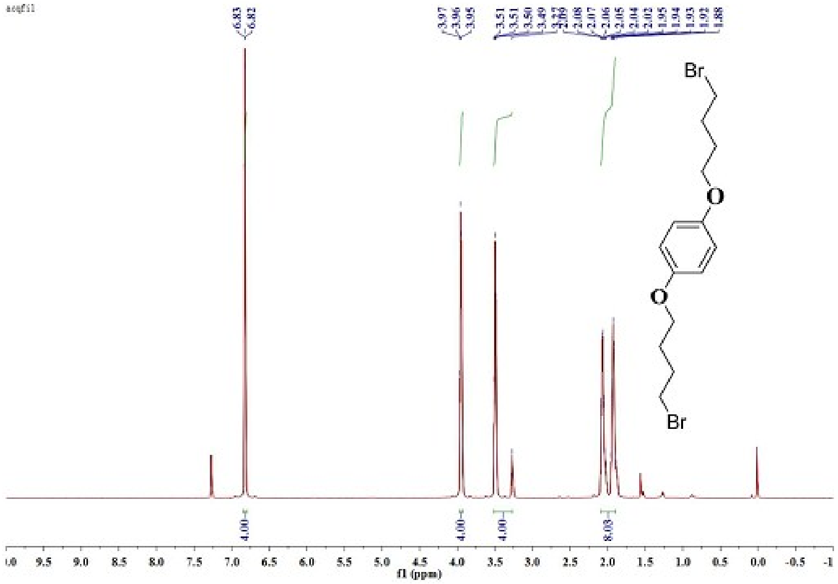


Figure S1 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of 1,4–bis (4–bromobutoxyl) benzene **1**.

Synthesis of a copillar[5]arene 2: 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 **2**(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 151.21–150.05 (m), 128.28 (s), 114.43–113.26 (m), 67.27–66.80 (m), 55.66 (s), 33.49 (s), 29.55 (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.

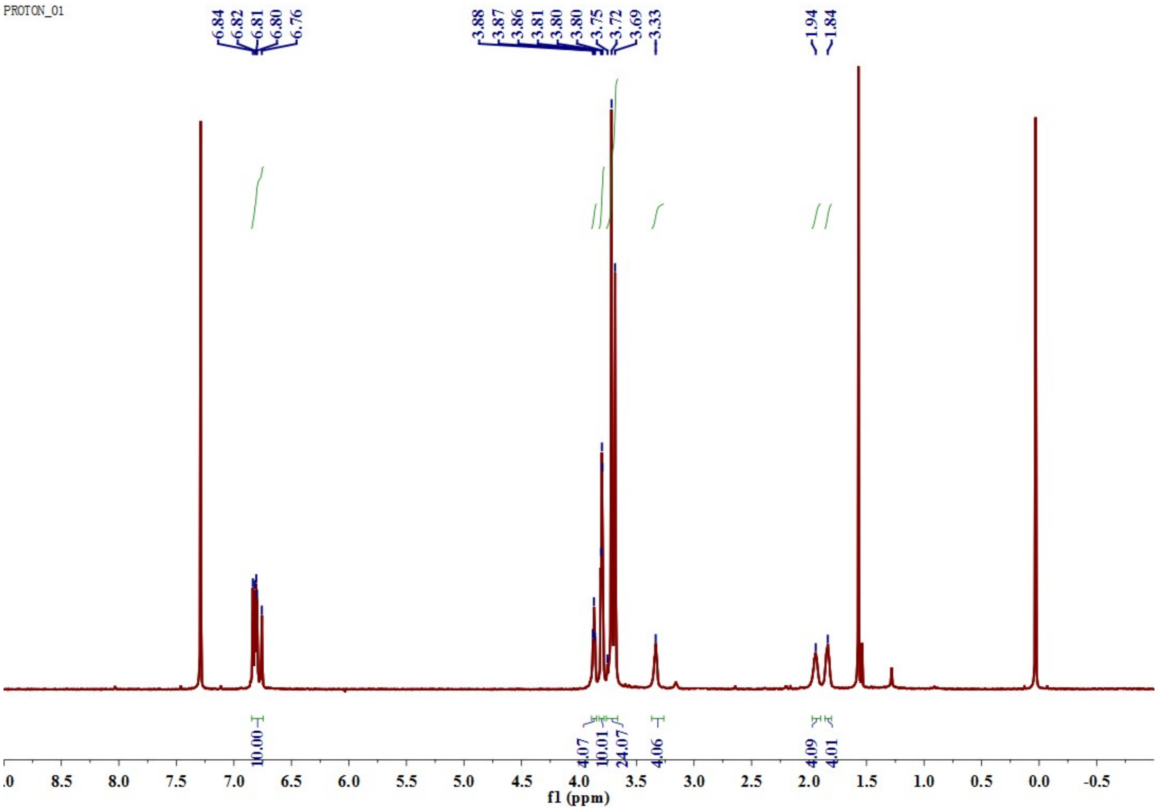


Figure S2 ^{1}H NMR spectra(600 MHz, $CDCl_3$) of a copillar[5]arene **2**.

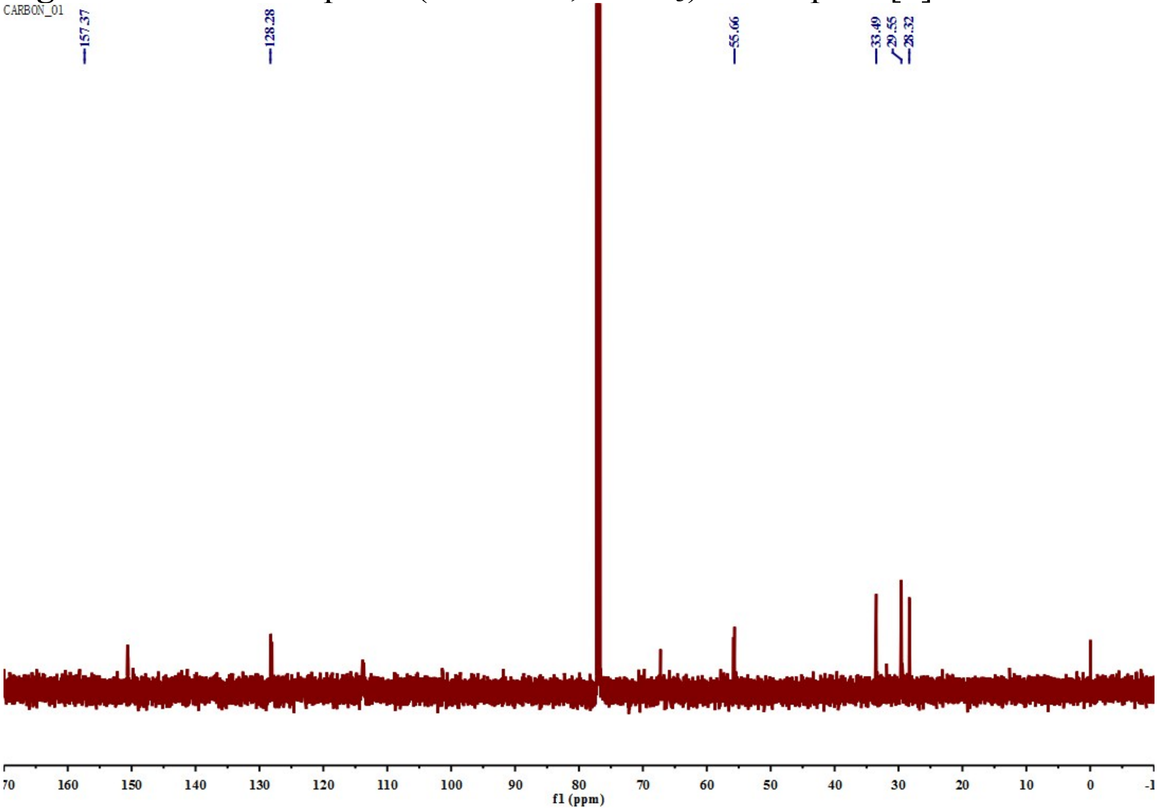


Figure S3 ^{13}C NMR spectra(151 MHz, $CDCl_3$) of a copillar[5]arene **2**.

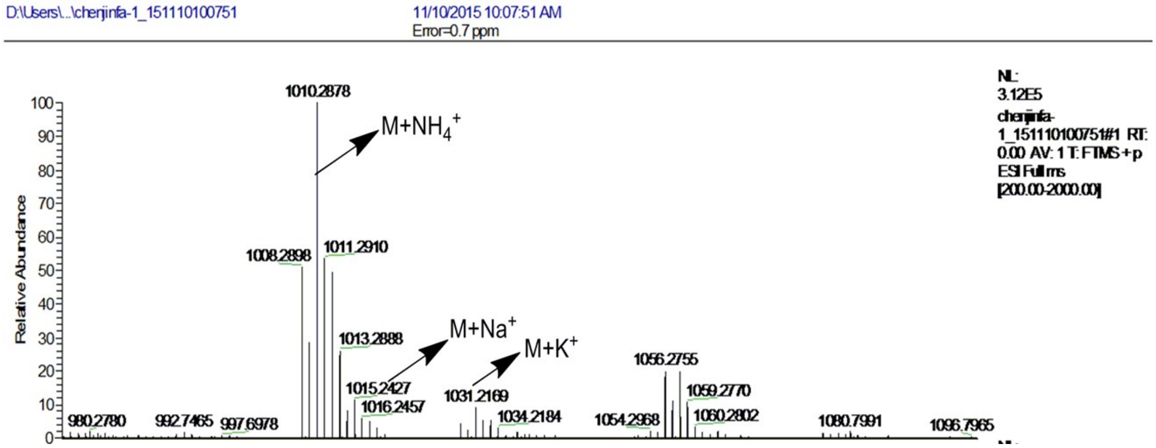


Figure S4 High resolution mass data of a copillar[5]arene **2**.

Synthesis of functionalized pillar[5]arene PC5: Copillar[5]arene **2** (0.4 g, 0.4 mmol), and 2−mercaptobenzothiazole (0.334 g , 2 mmol) was dissolved in THF (80 mL) . KOH (0.112 g, 2 mmol) was added and the reaction mixture was stirred at 65°C reflux for 8 hour. The solvent was evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (10 : 1, *v*/*v*) to give **PC5** (0.37 g, 80%) as a slightly yellow solid. Mp 55−57 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J*= 8.0 Hz, 2H), 7.75 (d, *J*= 7.7 Hz, 2H), 7.41 (t, *J*= 7.8 Hz, 4H), 6.75 (dd, *J*= 13.3, 9.0 Hz, 10H), 3.87 (s, 4H), 3.76 (d, *J*= 8.0 Hz, 10H), 3.64 (s, 12H), 3.61 (d, *J*= 4.5 Hz, 12H), 3.43 (t, *J*= 7.0 Hz, 4H), 2.05 (s, 4H), 1.95 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.79 (s), 153.27 (s), 135.14 (s), 128.16 (s), 126.01 (s), 124.17 (s), 121.45 (s), 120.91 (s), 114.16 (s), 67.67 (s), 55.78 (s), 33.28 (s), 28.80 (s), 26.25 (s). ESI−MS m/z: $(M+H)^+$ Calcd for $C_{65}H_{69}O_{10}N_2S_4$ 1165.3830; Found 1165.3804.

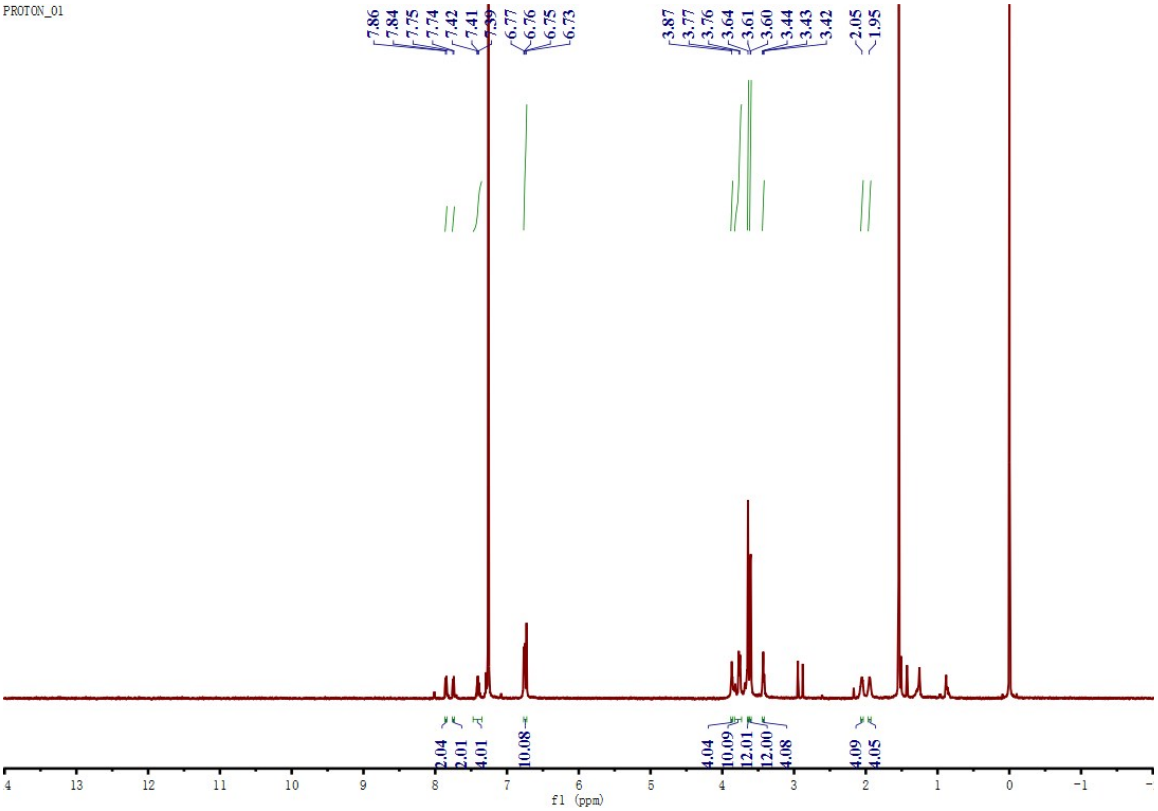


Figure S5 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of **PC5**.

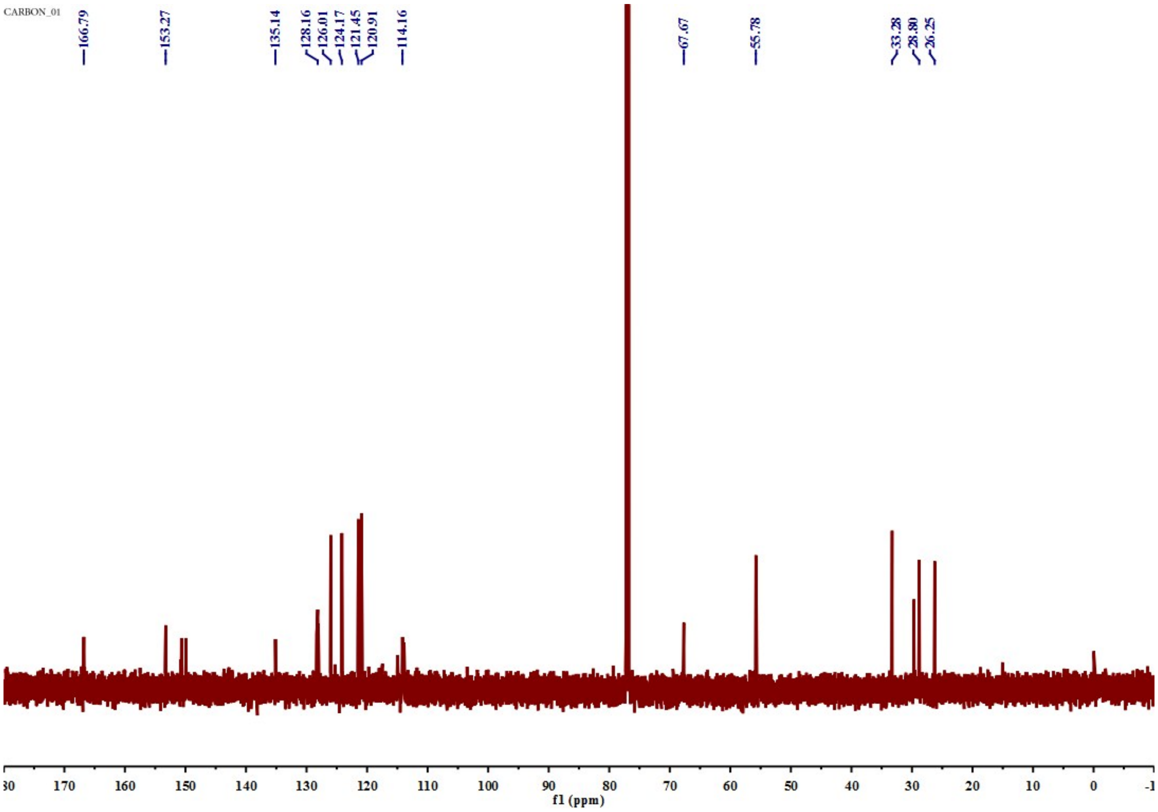


Figure S6 ^{13}C NMR spectra (151 MHz, $CDCl_3$) of **PC5**.

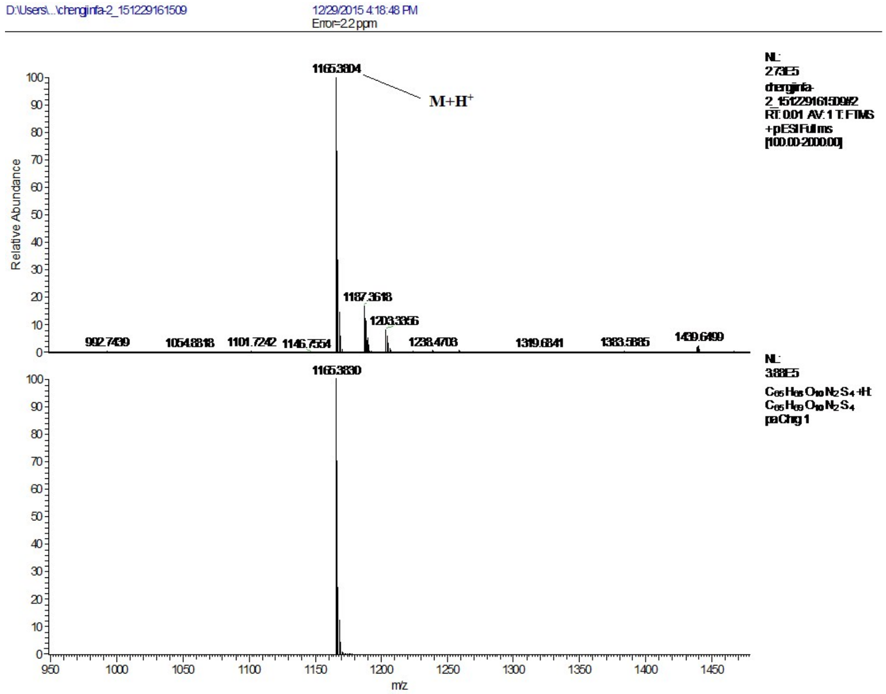
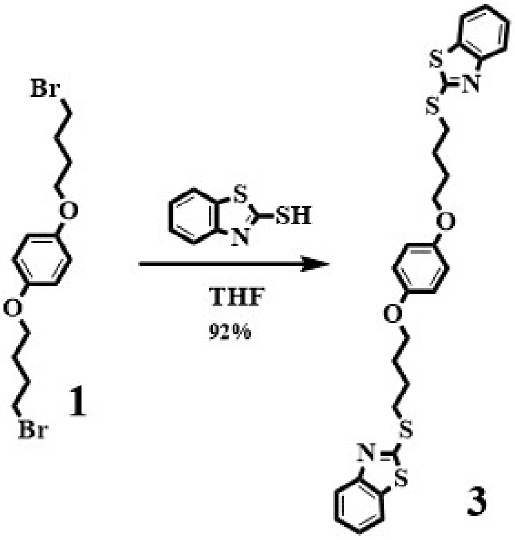


Figure S7 High resolution mass data of **PC5**.

3. Synthesis of compound 3:



Scheme 2 Synthesis of acyclic monomeric analog **3.**

Synthesis of compound 3: 1,4–bis(4–bromobutoxyl) benzene(0.19 g, 0.5 mmol), and 2−mercaptobenzothiazole (0.334 g, 2 mmol) was dissolved in THF (80 mL). KOH(0.112g , 2 mmol) was added and the reaction mixture was stirred at 65°C reflux for 8 hour. The solvent was evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (10 : 1, *v*/*v*) to give **3** (0.25 g, 92%) as a white solid. Mp 108−110 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.86 (d, *J*= 8.1 Hz, 2H), 7.76 (d, *J*= 7.9 Hz, 2H), 7.42 (t, *J*= 7.7 Hz, 2H), 7.30 (d, *J*= 7.1 Hz, 2H), 6.82 (s, 4H), 3.98 (t, *J*= 6.1 Hz, 4H), 3.45 (t, *J*=7.2 Hz, 4H), 2.06–2.03 (m, 4H), 1.99–1.95 (m, 4H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 166.93, 153.29, 153.08, 135.18, 125.98, 124.14, 121.46, 120.91, 115.45, 67.81, 33.24, 28.39, 26.10.

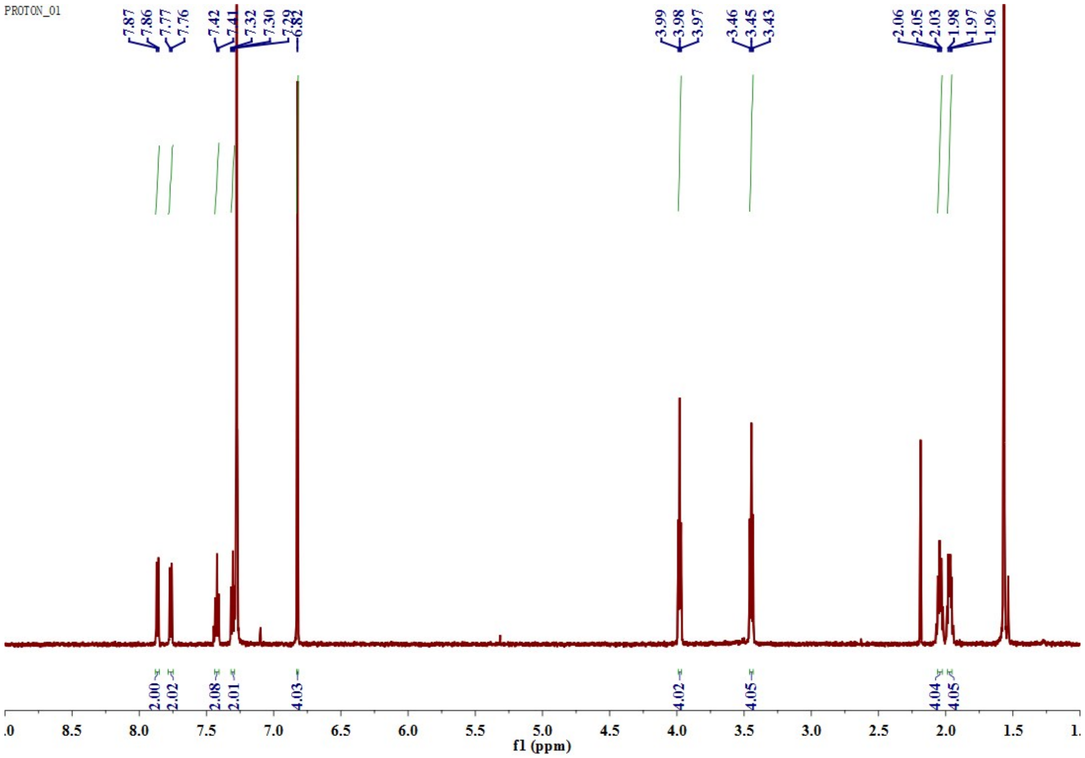


Figure S8 ^{1}H NMR spectra (600 MHz, CDCl$_3$) of **3**.

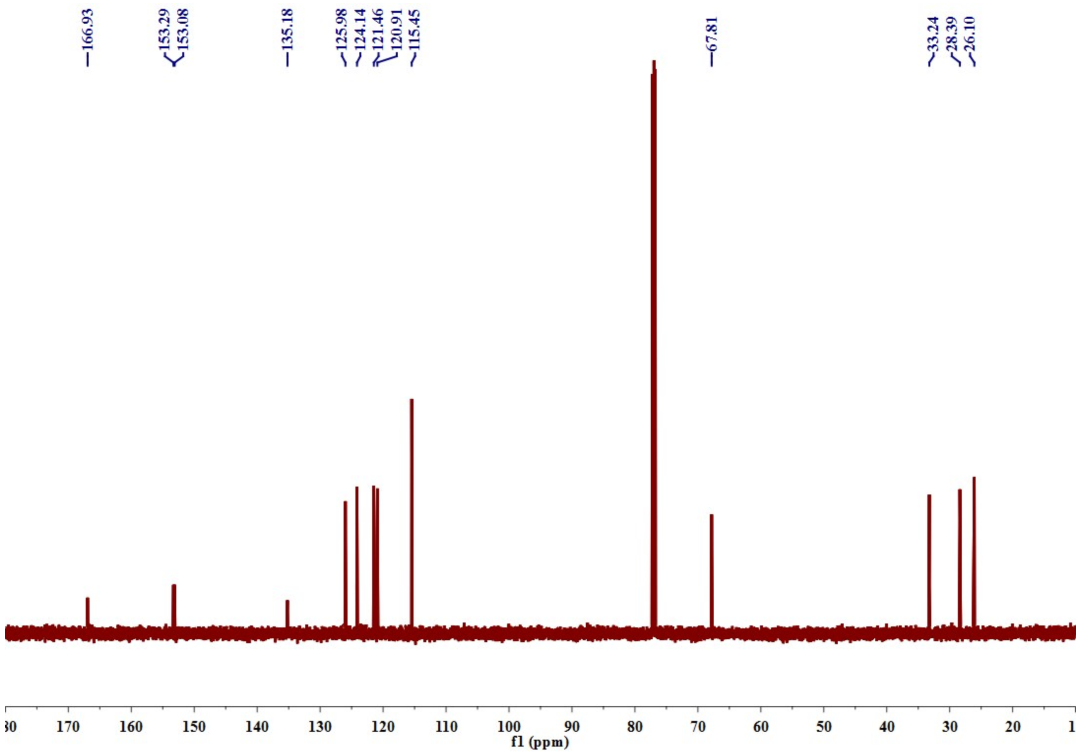


Figure S9 ^{13}C NMR spectra (151 MHz, $CDCl_3$) of **3**.

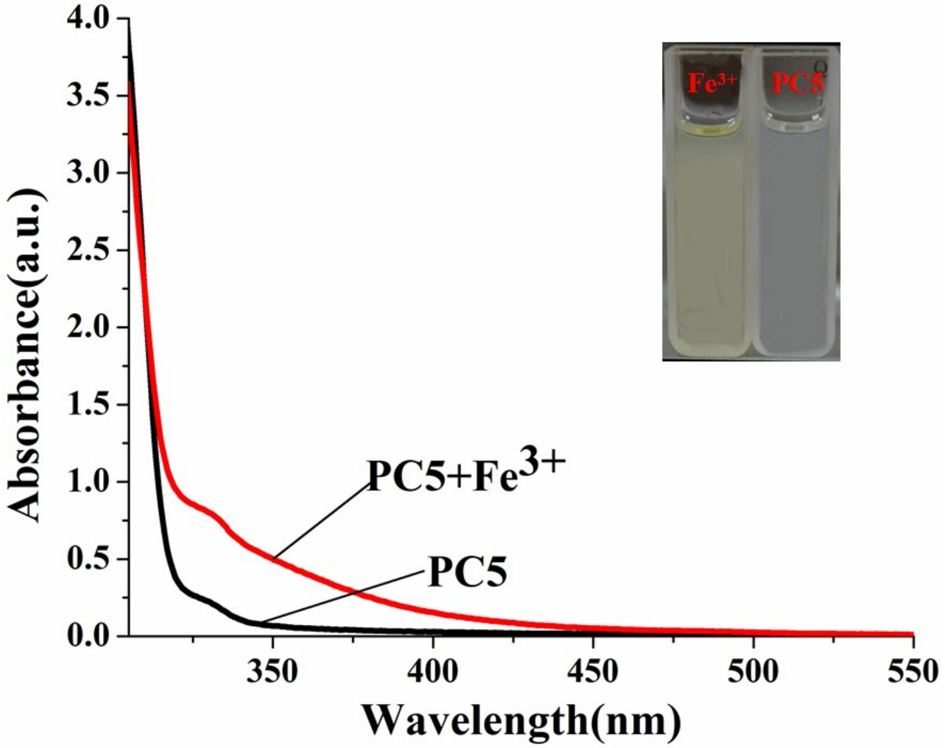


Figure S10 Absorbance spectra of **PC5** and **PC5+Fe^{3+}** in DMSO/THF (1 : 4, v/v) at the concentration of 2×10^{-4} mM. Inset: photograph shows the color of **PC5** and **PC5+Fe^{3+}** in DMSO/THF (1 : 4, v/v).

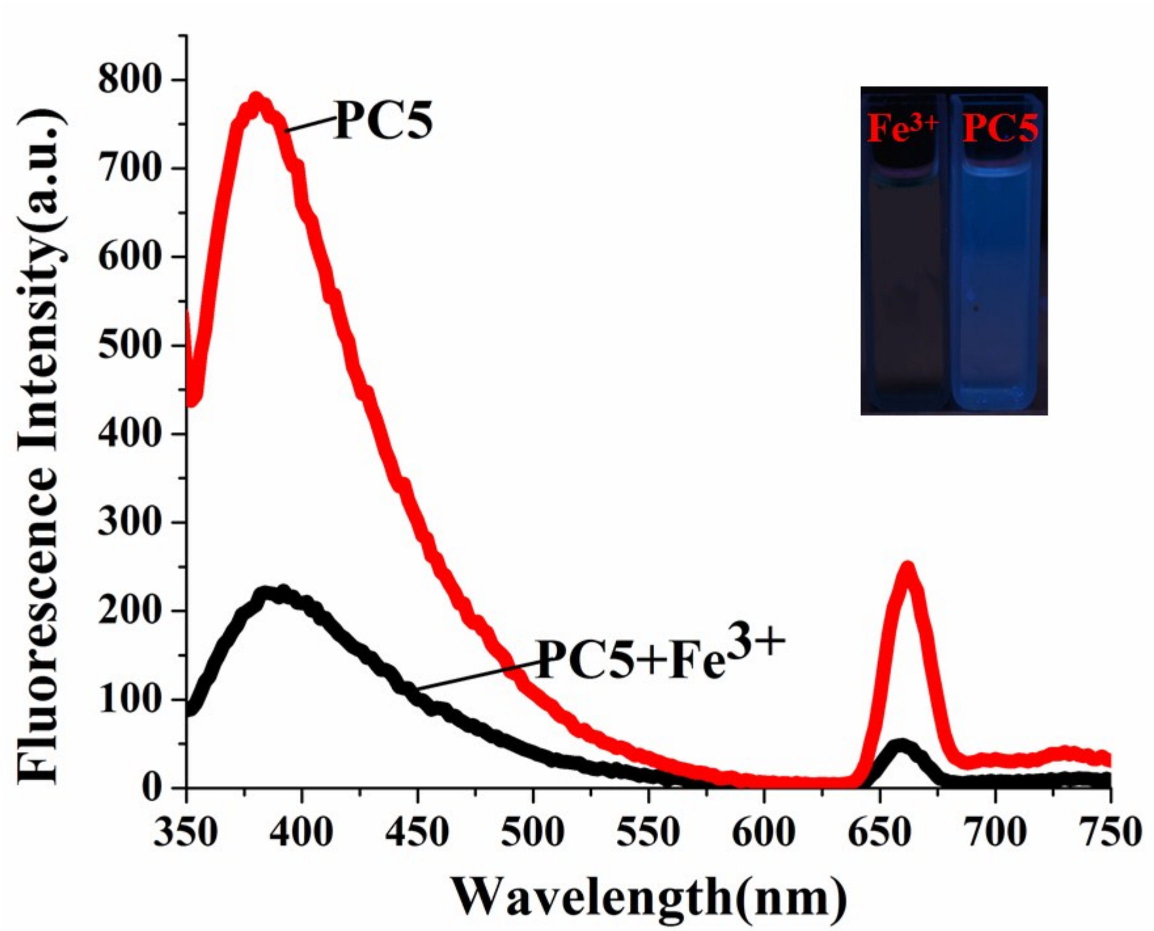
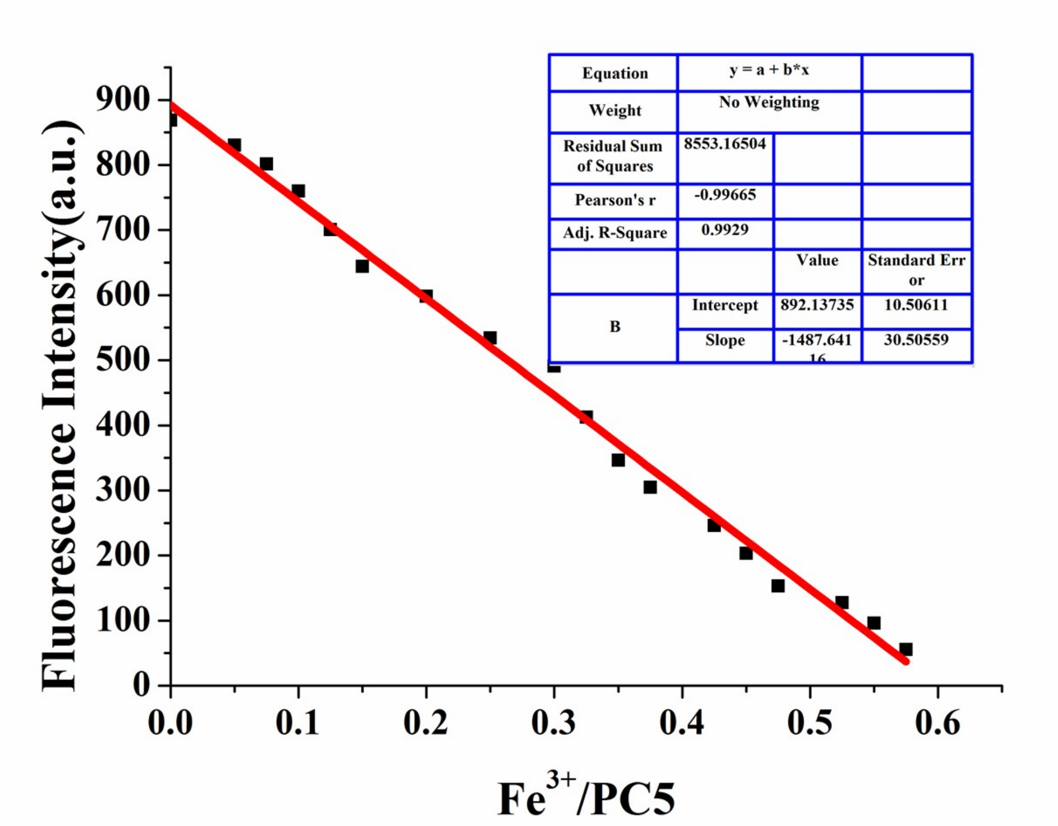


Figure S11 Fluorescence spectral response of **PC5** (2×10^{-4} M) in DMSO/THF (1 : 4, v/v) upon addition of 2 equiv. of Fe^{3+} (λ_{ex} = 330 nm). Inset: photograph of **PC5** (2×10^{-4} M) upon addition of 2 equiv. of Fe^{3+}, which was taken under a UV−lamp (365 nm).

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	8553.16504		
Pearson's r	-0.99665		
Adj. R-Square	0.9929		
		Value	Standard Error
B	Intercept	892.13735	10.50611
	Slope	-1487.64116	30.50559

Figure S12 The photograph of the linear range.

Linear Equation: Y=−1487.64116X+892.13735 R^2=0.9929

S=1487.64×10^6

$$\delta = \sqrt{\frac{\sum_{i=1}^{n}(X_i - \overline{X})^2}{n-1}} = 6.21(n = 30)$$

K=3

LOD =K×δ/S= 1.25 ×10^{-8}M

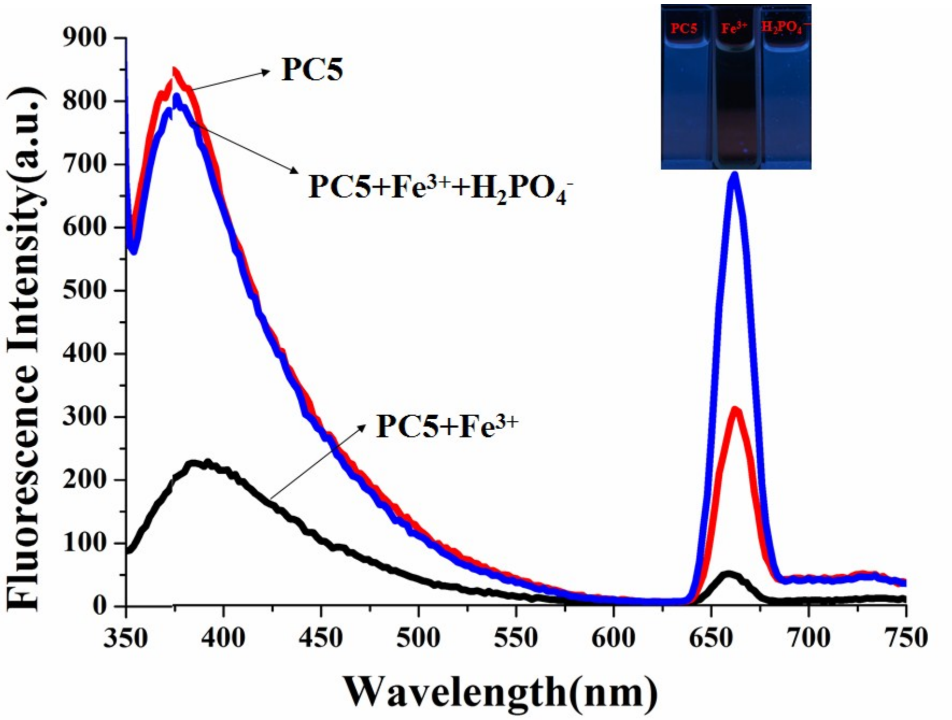


Figure S13 Fluorescence spectral response of **PC5** (2×10^{-4} M) in DMSO/THF (1 : 4, v/v) upon addition of 2 equiv. of Fe^{3+} (λ_{ex} = 330 nm), upon addition $H_2PO_4^-$ to the solution of **PC5** and Fe^{3+}, the strong brilliant blue fluorescence of **PC5** at 380nm emerged again. Inset: photograph of **PC5** (2×10^{-4} M) upon addition of 2 equiv. of Fe^{3+} , which was taken under a UV−lamp (365 nm).

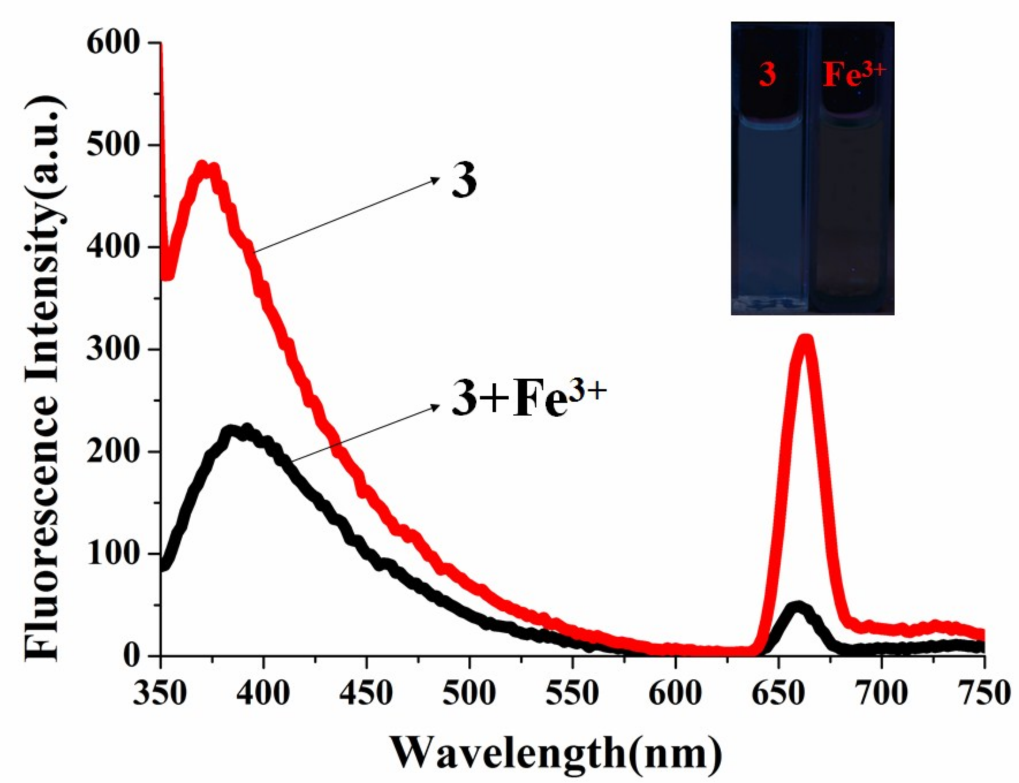


Figure S14 Fluorescence spectral response of **3** (2×10^{-4} M) in DMSO/THF (1 : 4, v/v) upon addition of 2 equiv. of Fe^{3+} (λ_{ex} = 330 nm). Inset: photograph of **3** (2×10^{-4} M) upon addition of 2 equiv. of Fe^{3+} , which was taken under a UV−lamp (365 nm).

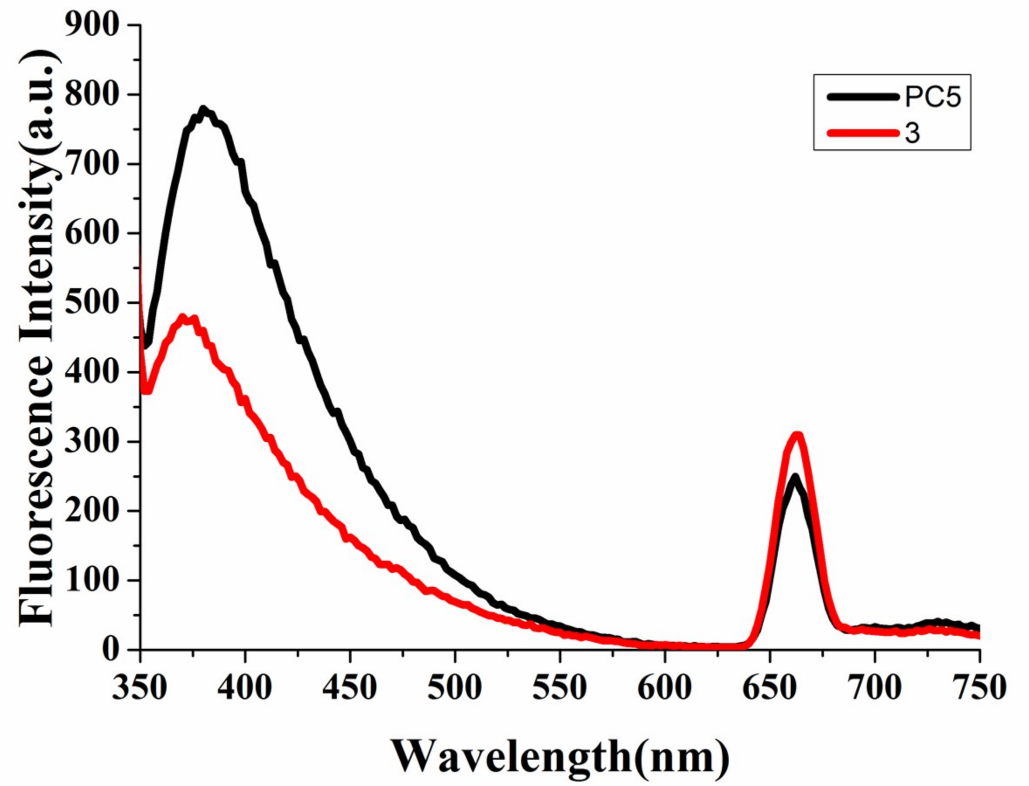


Figure S15 Fluorescence spectral response of **3** (2×10^{-4} M) and **PC5** (2×10^{-4} M) in DMSO/THF (1 : 4, v/v) , λ_{ex} = 330 nm.

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