Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Material

A Novel Functionalized Pillar[5]arene: Synthesis, Assembly and Application in Sequential Fluorescent Sensing for Fe^{3+} and F^{-} in Aqueous Media

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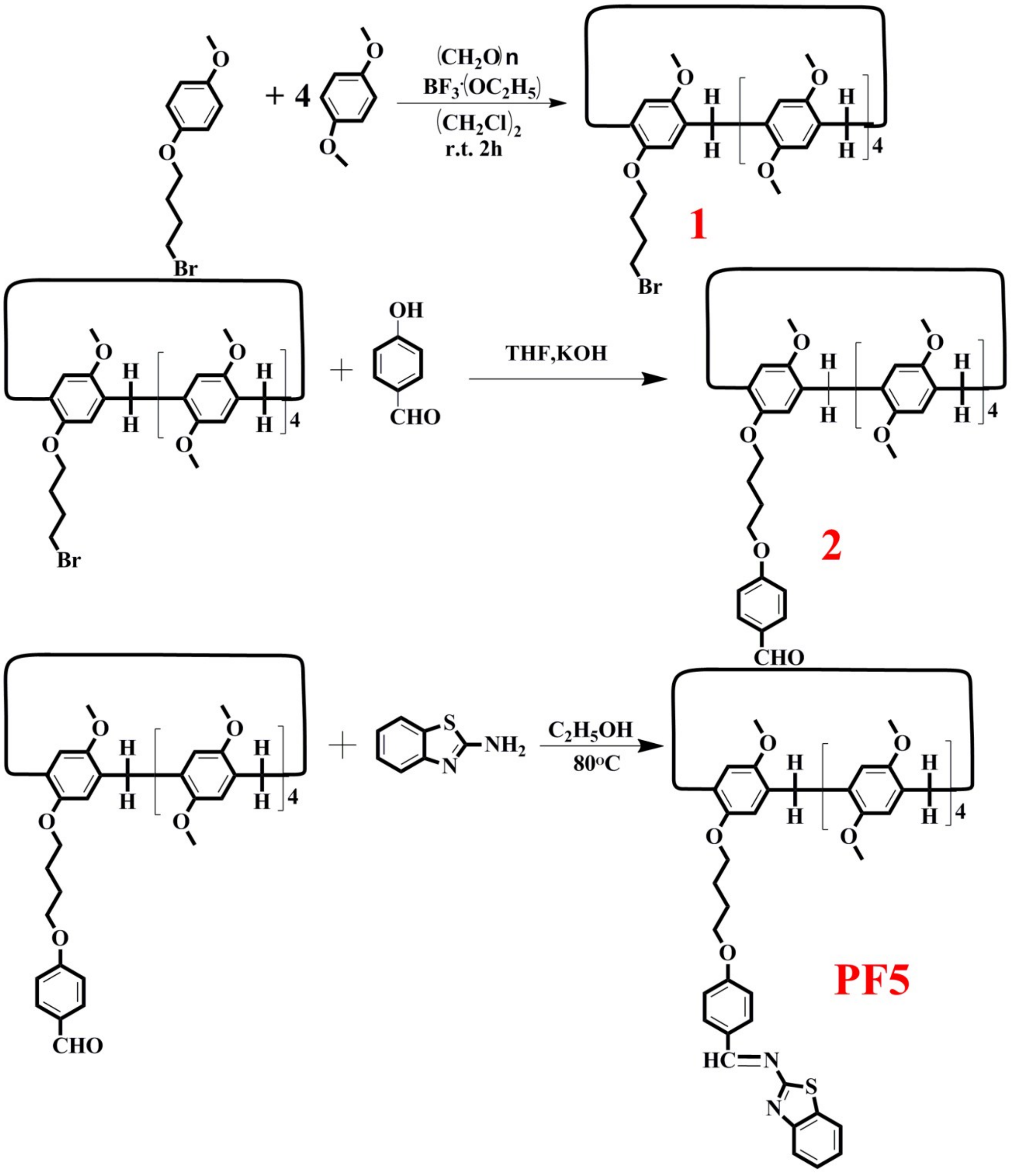
1, 4−Dimethoxybenzene, boron trifluoride ethyl ether complex, 1,4−dibromobutane, and was reagent grade and used as received. Solvents were either employed as purchased or dried by $CaCl_2$. ^{1}H NMR spectra were recorded on a Mercury−600BB spectrometer at 600 MHz and ^{13}C NMR spectra were recorded 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.

The association constants (Ka) were also determined based on the absorbance titration curve using the equation as follows: where A and A_0 represent the absorbance of host in the presence and absence of ions, respectively, A_{max} is the saturated absorbance of host in the presence of excess amount of ions; [G] is the concentration of ions added.

$$\frac{1}{A_{max} - A_0} = \frac{1}{A_1 - A_0}\left[\frac{1}{K[G]^2} + 1\right]$$

1. Synthesis of compound PF5 and model compound DMP5 and G



Scheme S1 Synthesis of the functionalized pillar[5]arene **PF5**.

Synthesis of 1−(4-bromobutoxyl)−4−methoxybenzene: In a 500 mL round–bottom flask, 4−Methoxyphenol (2.48 g, 20.0 mmol), K_2CO_3 (8.4 g, 60 mmol), KI (3.3 g, 20mmol), 1,4−dibromobutane (17.3 g, 80 mmol) and acetone (400.0

mL) were added. The reaction mixture was stirred at reflux for 2 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 : ethyl acetate=50:1) afforded a white solid (3.4 g，65%), m.p.45 ℃. ^{1}H NMR (600MHz, $CDCl_3$) δ 6.83 (s, 4H), 3.94 (t, J=6.1Hz, 2H), 3.83–3.69(m, 3H), 3.48(t, J=6.7Hz, 2H), 2.11–2.00(m, 2H), 1.97–1.84(m, 2H).

Synthesis of copillar[5]arene 1: To a solution of 1−(4−bromobutoxyl)−4−methoxybenzene (1.32 g, 5 mmol) and 1, 4−dimethoxybenzene (2.76 g, 20 mmol) in 1, 2–dichloroethane (80 mL), paraformaldehyde (0.75 g, 25 mmol) was added. Then, boron trifluoride diethyl etherate (3.2 mL, 25 mmol) was added to the solution and the mixture was stirred at room temperature for 1 h. The solution was poured into methanol and the resulting precipitate was collected by filtration. The solid was dissolved in $CHCl_3$ (150 mL) and the insoluble part was filtered off. The resulting solid dissolved in $CHCl_3$ and washed twice with H_2O (100 mL). 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 (50:1). The fractions containing the product were combined and concentrated under vacuum to give copillar[5]arene (30%) as a white solid, m.p. 116~119 °C. The proton NMR spectrum of copillar[5]arene. ^{1}H NMR(600MHz, $CDCl_3$) δ 6.93–6.63 (m, 10H), 3.89(d, J=6.5Hz, 1H), 3.83(t, J=6.0Hz, 1H), 3.81–3.75(m, 10H), 3.75–3.55(m, 27H), 3.42(d, J=130.4Hz, 2H), 1.92(s, 1H), 1.81(s, 1H), 1.25(s, 2H).

Synthesis of compound intermediate 2: copillar[5]arene 1 (0.71 g ,1mmol), and 4–Hydroxybenzaldehyde (0.122g , 1mmol) was dissolved in THF (80 mL). KOH (0.056 , 1mmol) was added and the reaction mixture was stirred at room temperature for 3 days. The solvent was evaporated and the residue was dissolved in CH_2Cl_2. The resultant solution was washed with H_2O , after the solid was filtered afforded a white solid 2 (0.49 g， 60%). ^1H NMR (600 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.01–6.55 (m, 14H), 3.79 (s, 10H), 3.71–3.64 (m, 27H), 3.34 (d, J = 6.8 Hz, 4H), 1.89 (d, J = 56.8 Hz, 4H).

Synthesis of PF5: intermediate 2 (0.912g, 1mmol), and 2–aminobenzothiazole (0.15g, 1mmol) was dissolved in C_2H_5OH (60 mL). and the reaction mixture was stirred at 80 ℃ for 2 days. After the solvent was evaporated, you can precipitate and filtration afforded a white solid (0.74g, 70%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 6.92–6.60 (m, 18H), 3.77 (s, 10H), 3.66 (d, J = 6.3 Hz, 27H), 3.49 (s, 2H), 3.22 (s, 2H), 1.80 (s, 4H). 13C NMR (101 MHz, $CDCl_3$) δ 150.83, 128.41, 114.00, 67.62, 55.88, 29.71, 27.35. ESI–MS m/z: $[M+H]^+$ Calcd for 1044; Found 1045.49.

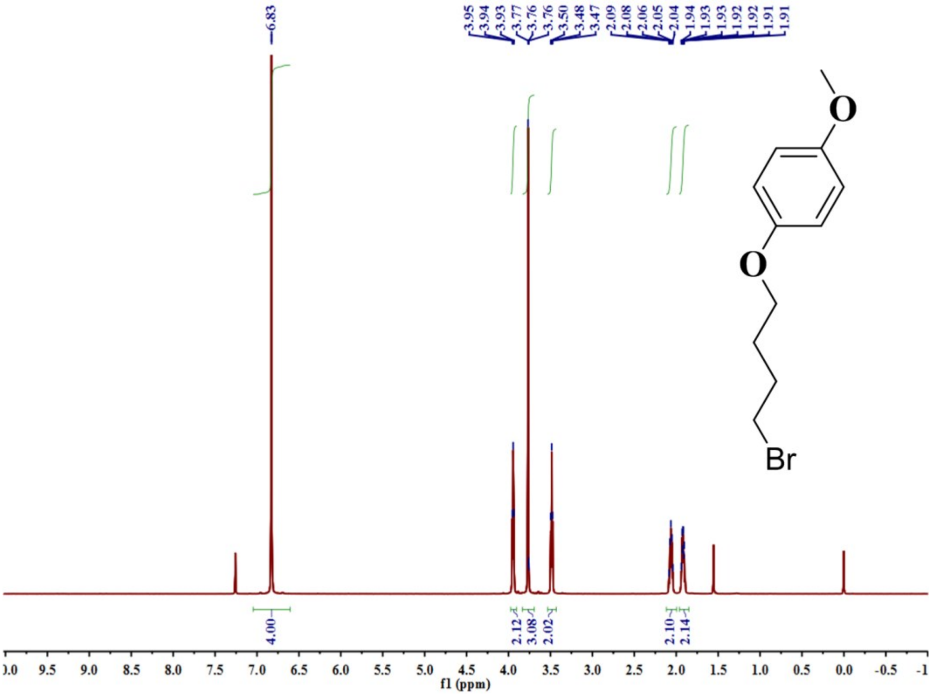


Figure S1 ^{1}H NMR spectra of 1–(4–bromobutoxyl)–4– methoxybenzene.

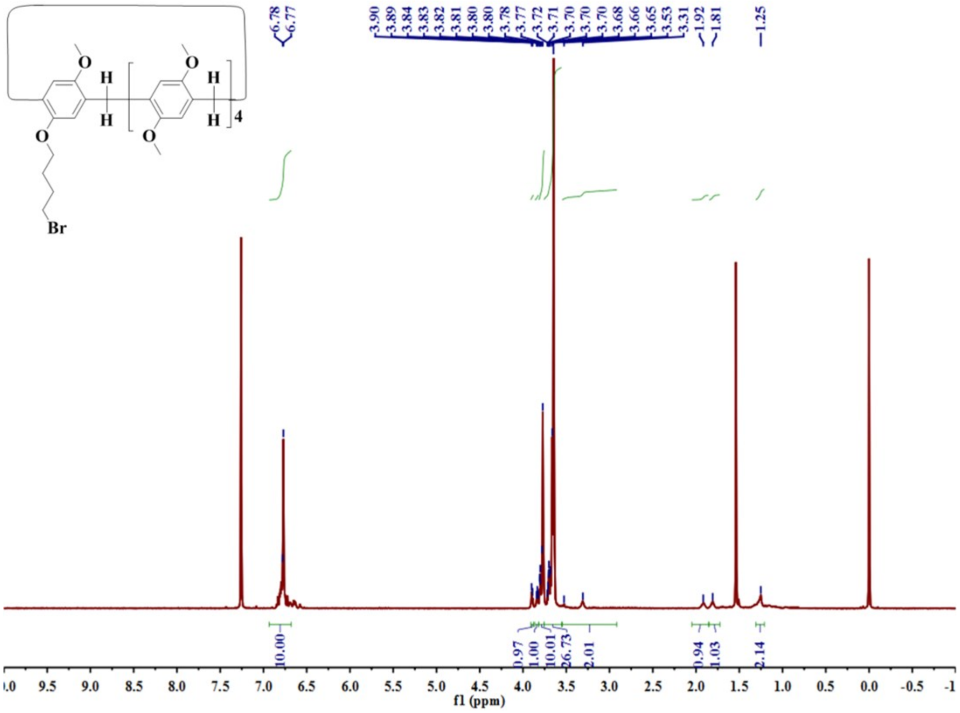


Figure S2 ^{1}H NMR spectra (600MHz, $CDCl_3$, 298K) of copillar[5]arene **1**.

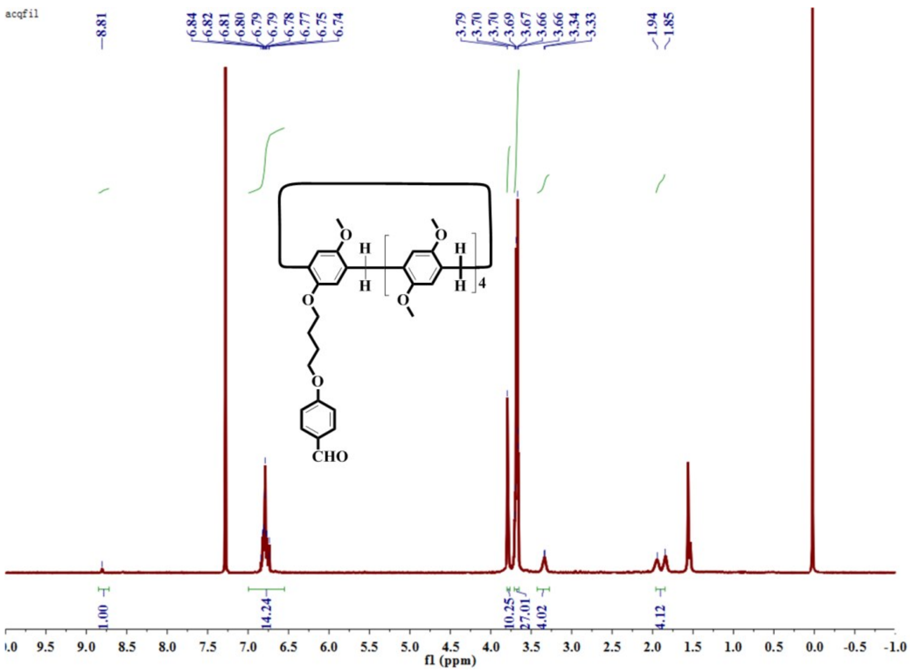


Figure S3 ^{1}H NMR spectra (600 MHz, CDCl$_3$, 298K) of **2**.

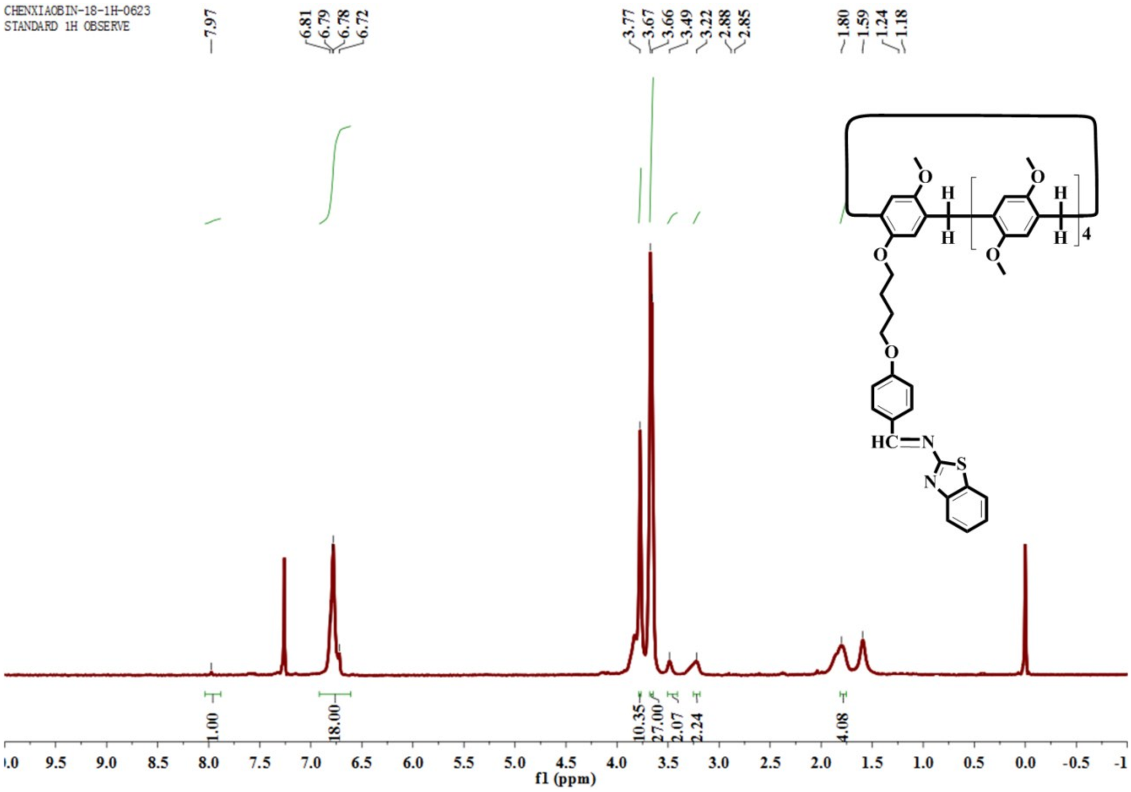


Figure S4 ^{1}H NMR spectra (400 MHz, CDCl$_3$, 298K) of **PF5**.

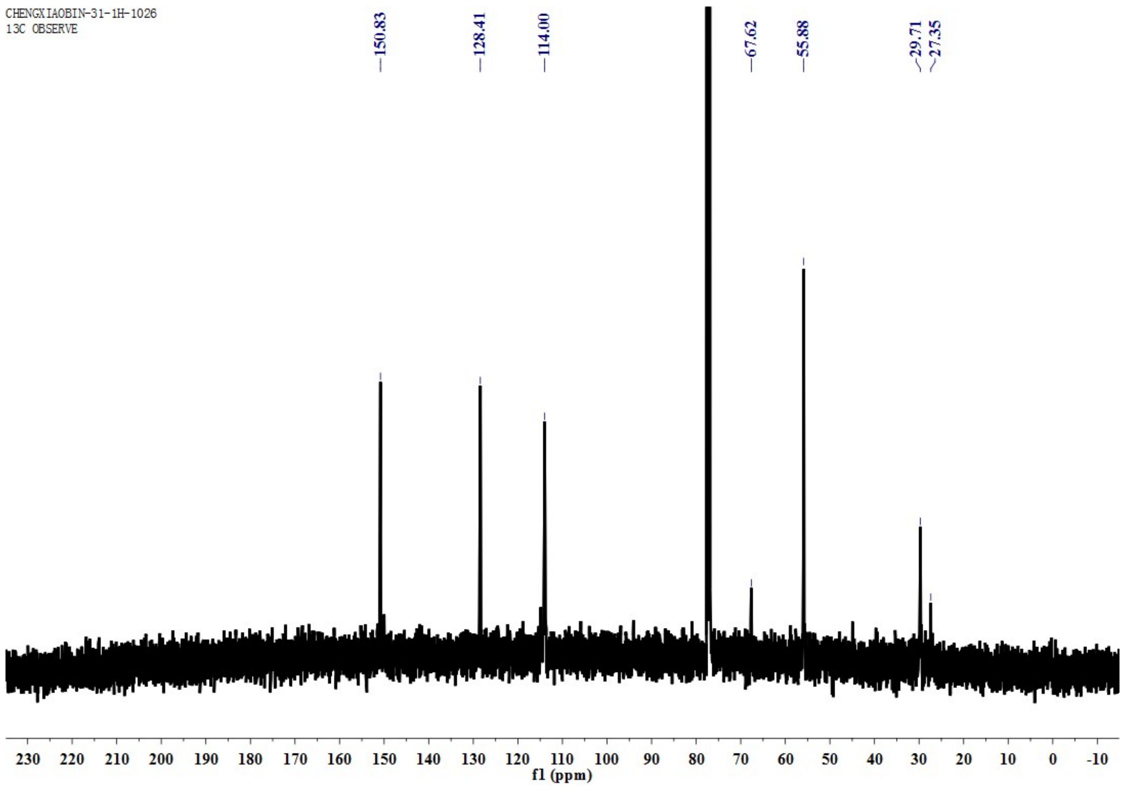


Figure S5 ^{13}C NMR spectra (101 MHz, $CDCl_3$, 298K) of **PF5**.

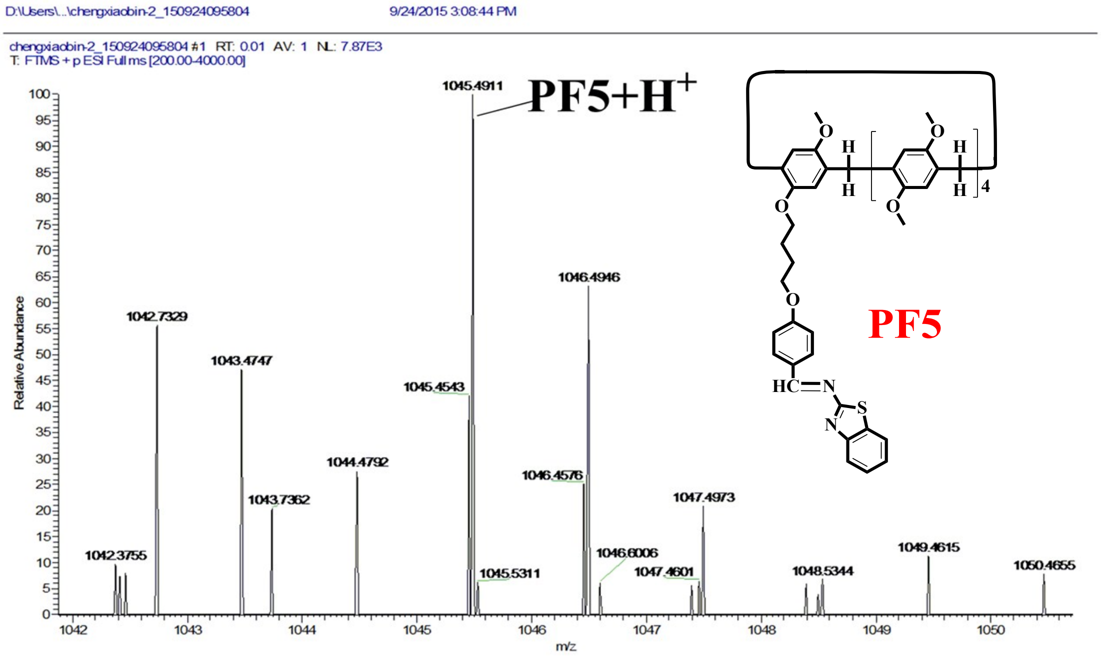
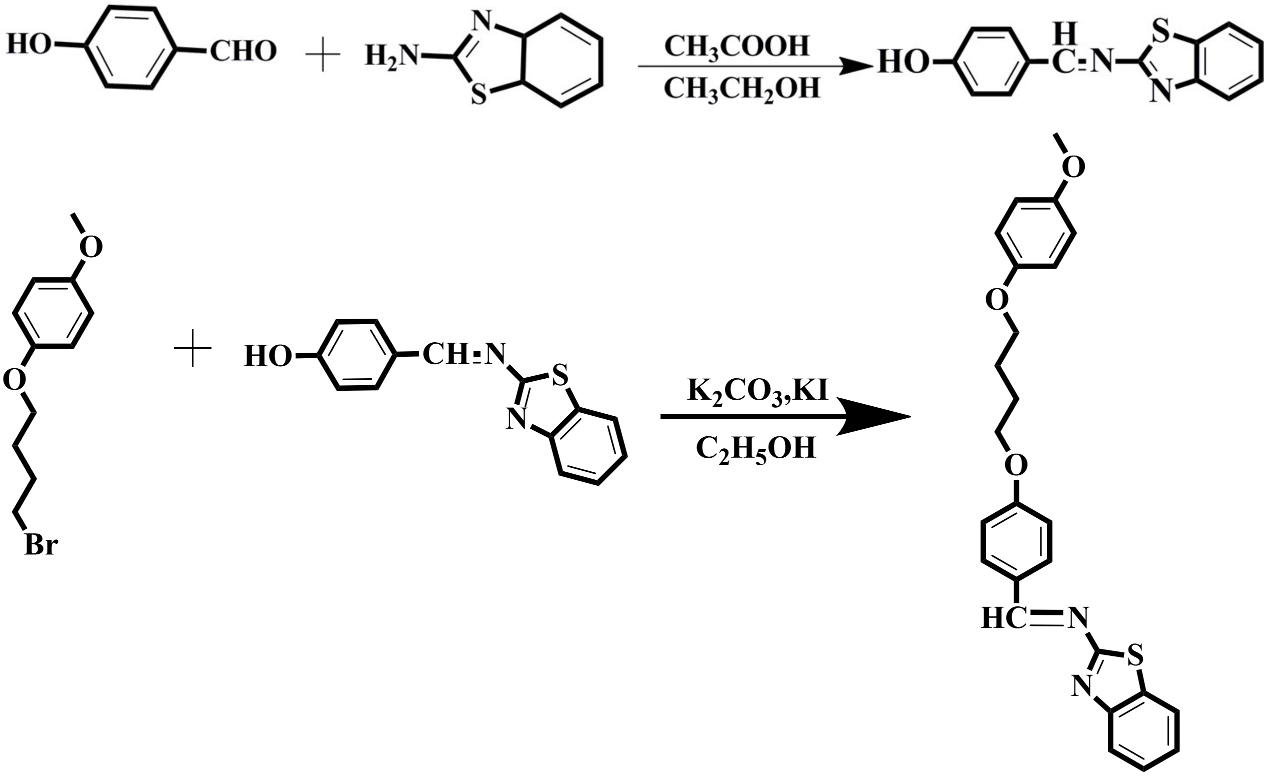


Figure S6 High resolution mass data of **PF5**.



Scheme S2. Synthetic route to compound G.

Synthesis compound intermediate of G: 4–Hydroxy benzaldehyde (0.61g, 5mmol), and 2–aminobenzothiazole (0.75g, 5mmol) was dissolved in C_2H_5OH (40 mL), then add 1mL glacial acetic acid. The reaction mixture was stirred at 80 ℃ for 12 hours. After the solvent was evaporated, you can precipitate and filtration afforded a yellow solid (1.29g, 95%). ^{1}H NMR (600 MHz, DMSO–d6) δ 10.77 (s, 1H), 9.09 (s, 1H), 8.13–7.80 (m, 4H), 7.56–7.40 (m, 2H), 7.02 (d, J = 7.9 Hz, 2H).

Synthesis of G: 1−(4−bromobutoxyl)−4−methoxybenzene (1.32g, 5mmol), and compound intermediate of G (1.27g, 5mmol) was dissolved in ethanol (30 mL). K_2CO_3 (0.69 g, 5 mmol), KI (0.825 g, 5mmol), was added and the reaction mixture was stirred at 80 ^{o}C for 12 hours for 24h. After the solvent was evaporated column chromatography (silica gel; petroleum ether : ethyl acetate=20:1) afforded a white solid (2.1g, 81%). 1H NMR (400 MHz, CDCl$_3$) δ 9.89 (s, 1H), 7.83 (d, J = 7.9 Hz, 3H), 6.92 (dd, J = 64.4, 4.6 Hz, 9H), 4.13 (t, J = 5.7 Hz, 2H), 4.00 (t, J = 5.6 Hz, 2H), 3.77 (d, J = 0.9 Hz, 3H), 2.02–1.96 (m, 4H).

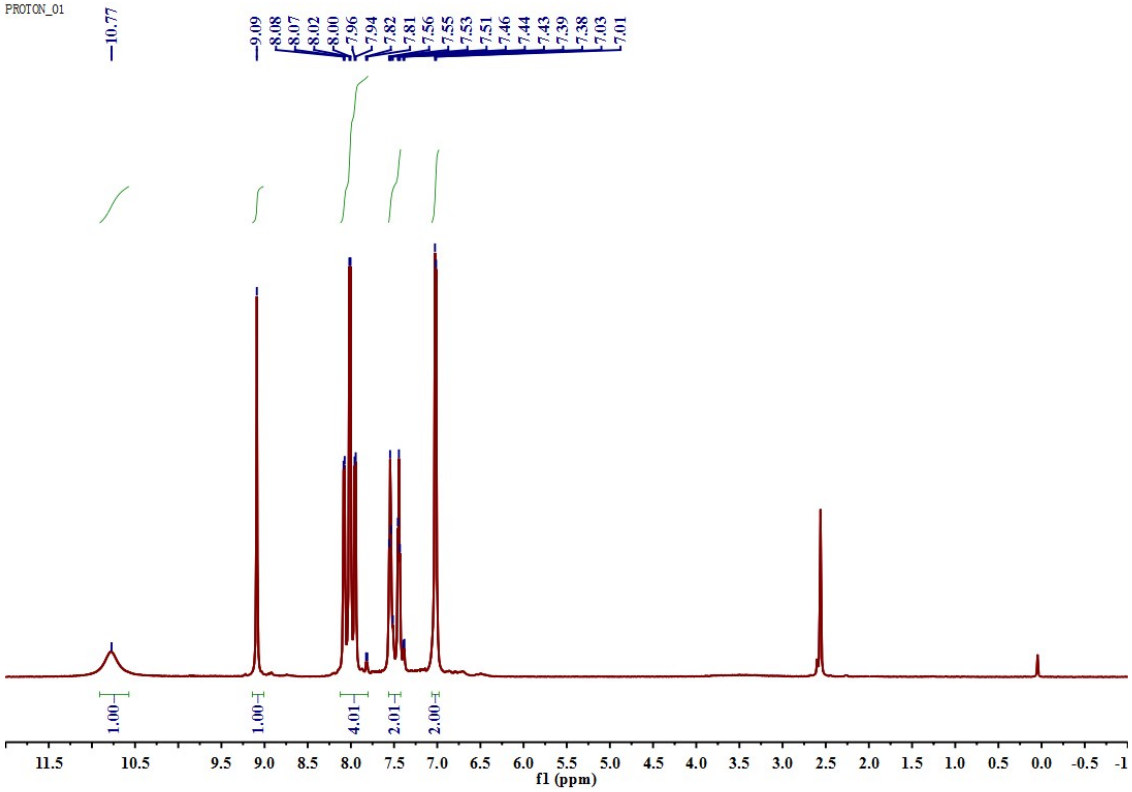


Figure S7 ^{1}H NMR spectra (600 MHz, DMSO–d_6, 298K) of compound intermediate of **G**.

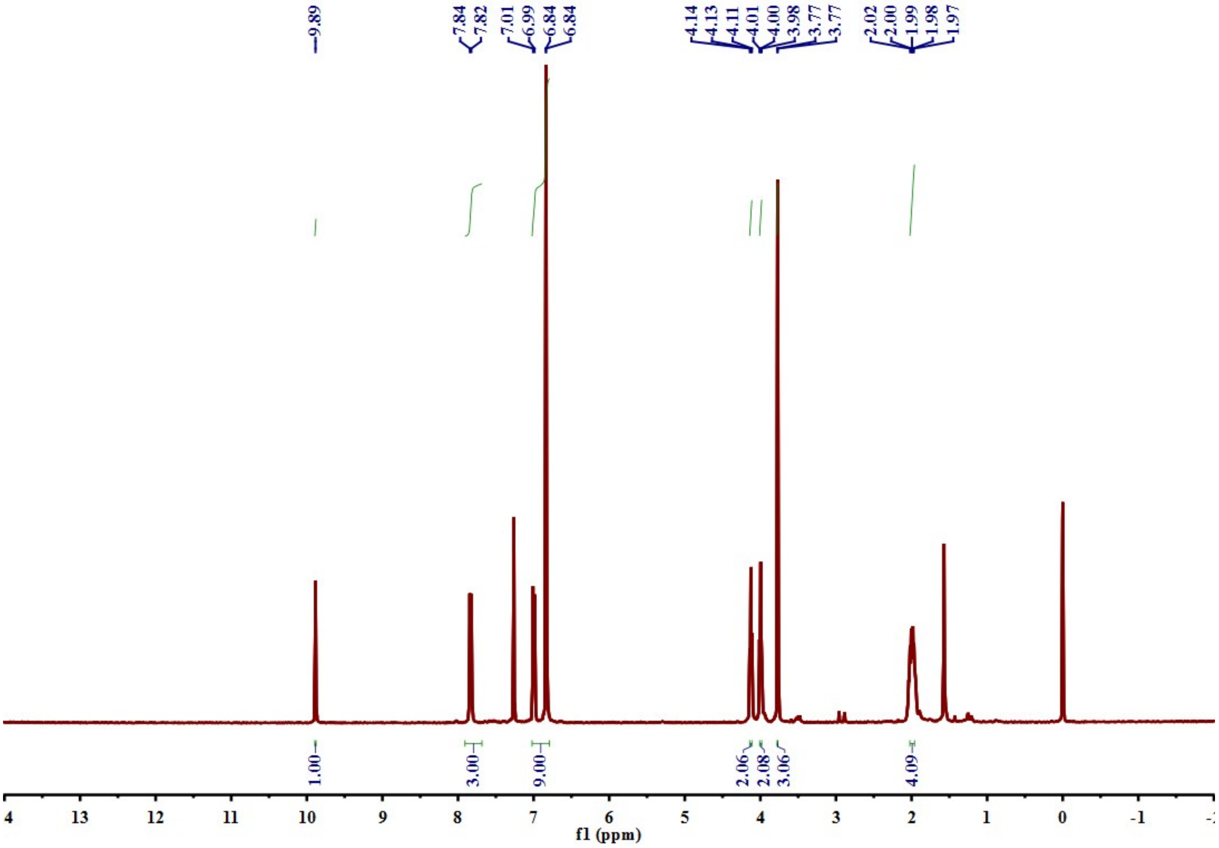


Figure S8 ^{1}H NMR spectra (400 MHz, CDCl$_3$, 298K) of **G**.

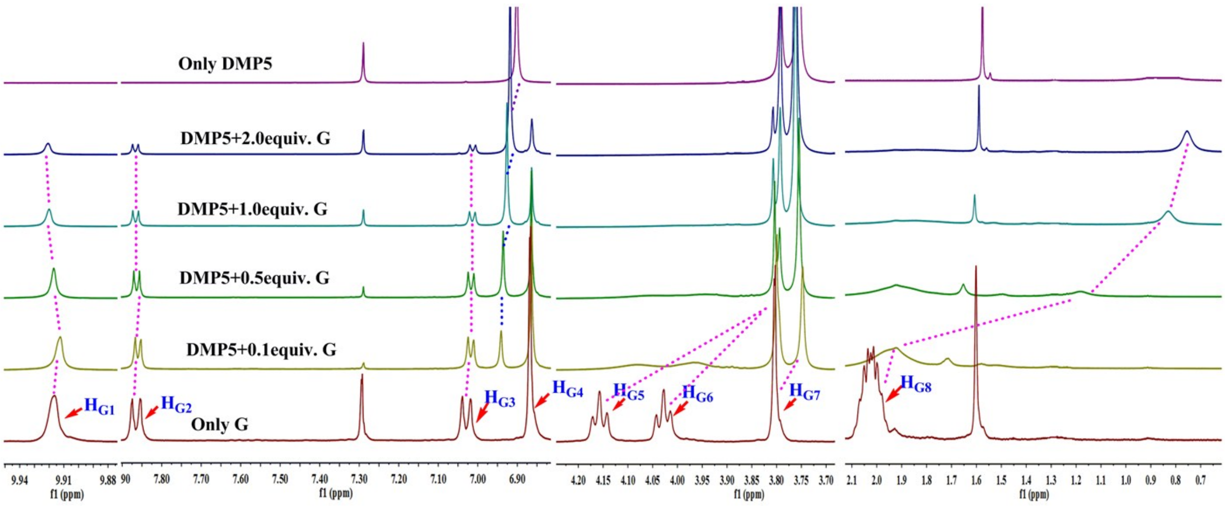


Figure S9 Partial ^{1}H NMR spectra (600 MHz, 298 K, CDCl$_3$) of **DMP5** (10 mM) with different equivalents of **G**.

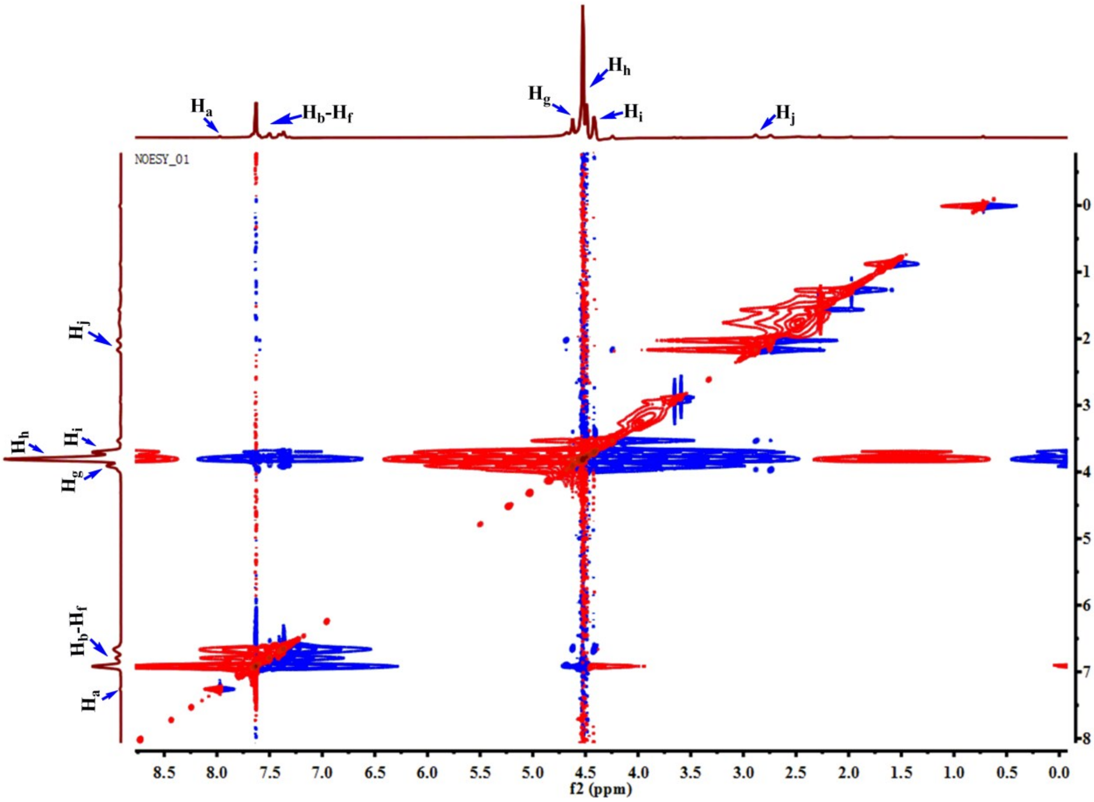


Figure S10. NOESY NMR spectrum (600 MHz, CDCl3, 298 K) of **PF5** at 50.0 mM.

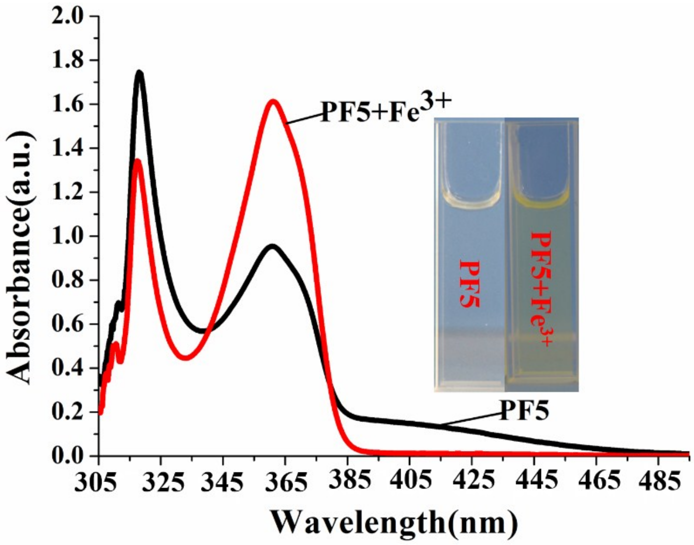


Figure S11. Absorption spectra of the DMSO/H_2O (8:2, v/v) solution of host **PF5** (1.0 mM) before and after the addition of 10 equiv. of Fe^{3+}.

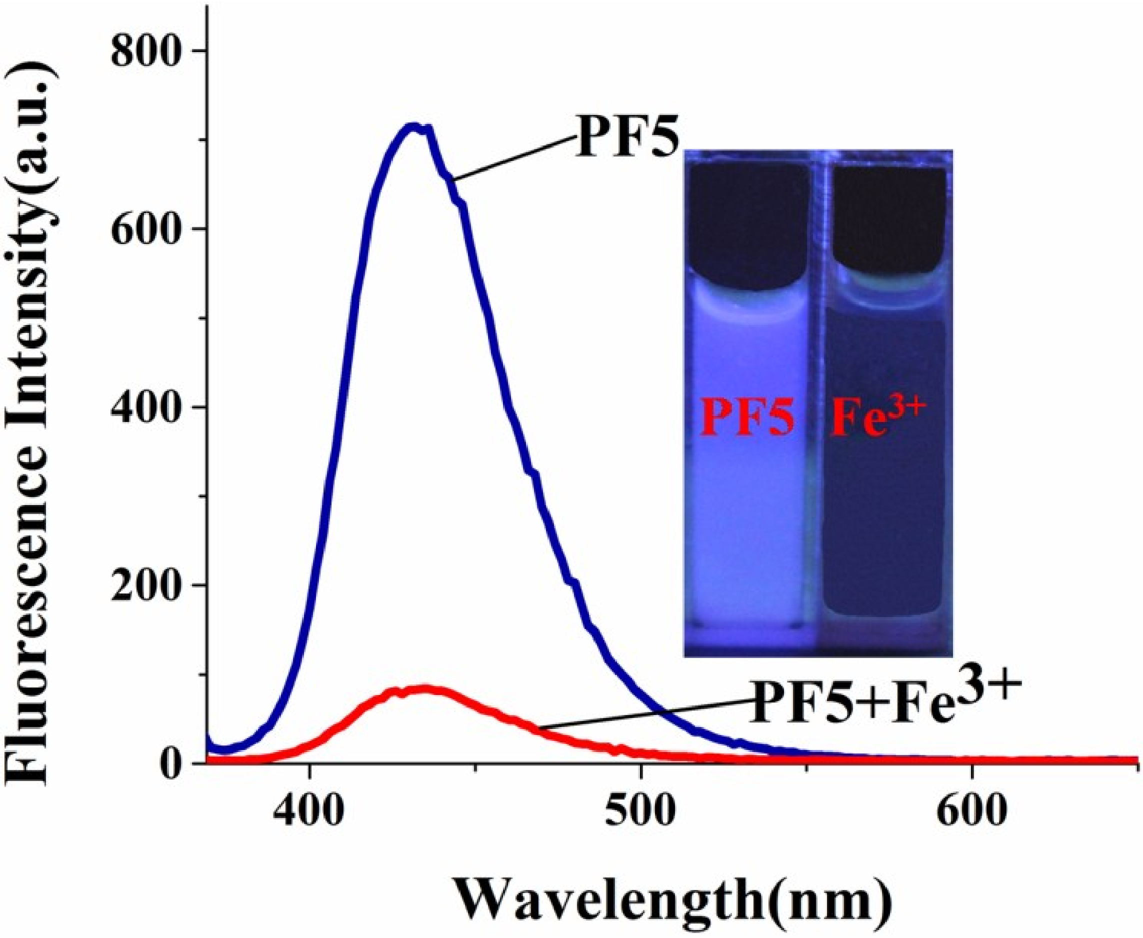


Figure S12. Fluorescence spectral response of **PF5** (1.0 mM) in DMSO/H_2O (8:2, v/v) upon addition of 10.0 equiv. of Fe^{3+} (λ_{ex} = 360 nm). Inset: photograph of **PF5** (1.0 mM) upon addition of 10.0 equiv. of Fe^{3+}, which was taken under a UV–lamp (365 nm).

Determination of the detection limit

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

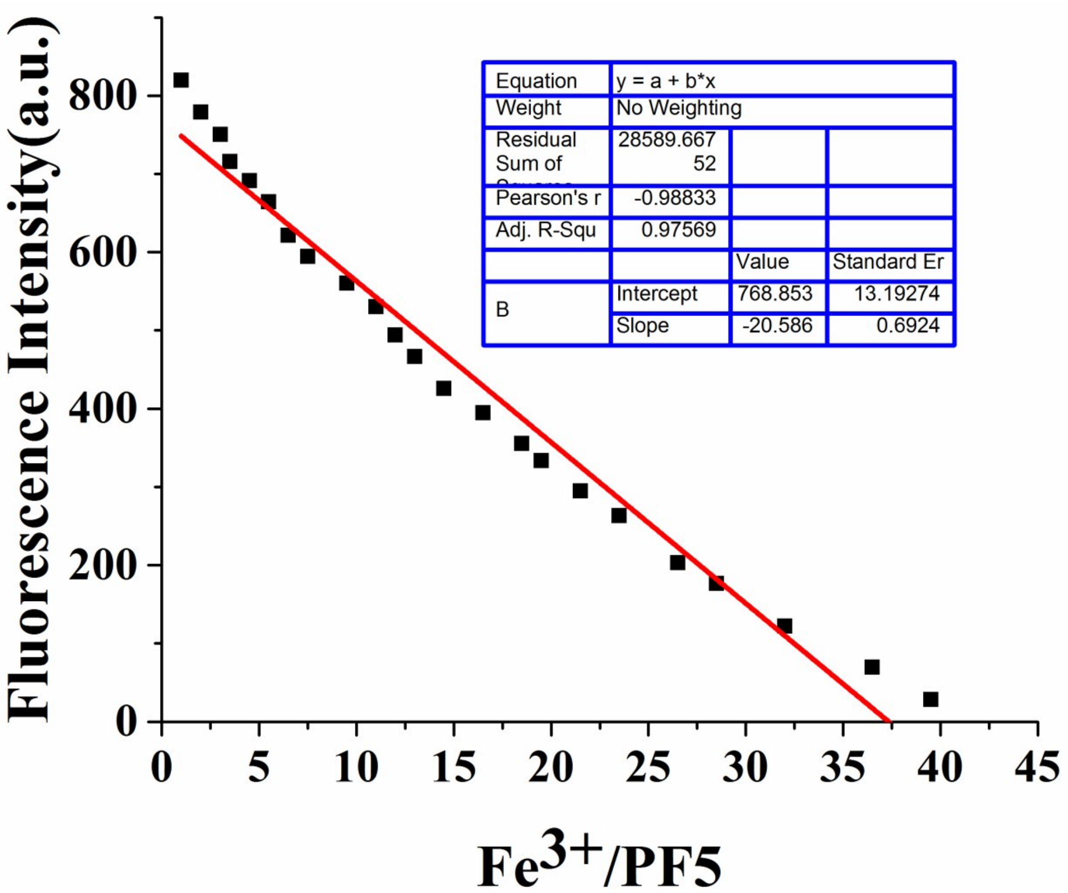


Figure S13 The photograph of the linear range

Linear Equation: $Y=-20.586X+768.853$

$R^2=0.97569$

$S=2.0586 \times 10^7$ $\delta = \sqrt{\frac{\Sigma(Fi - F0)^2}{N-1}} = 6.17$ (N=30) K=3

LOD $=K \times \delta/S = 9.0 \times 10^{-7}$M

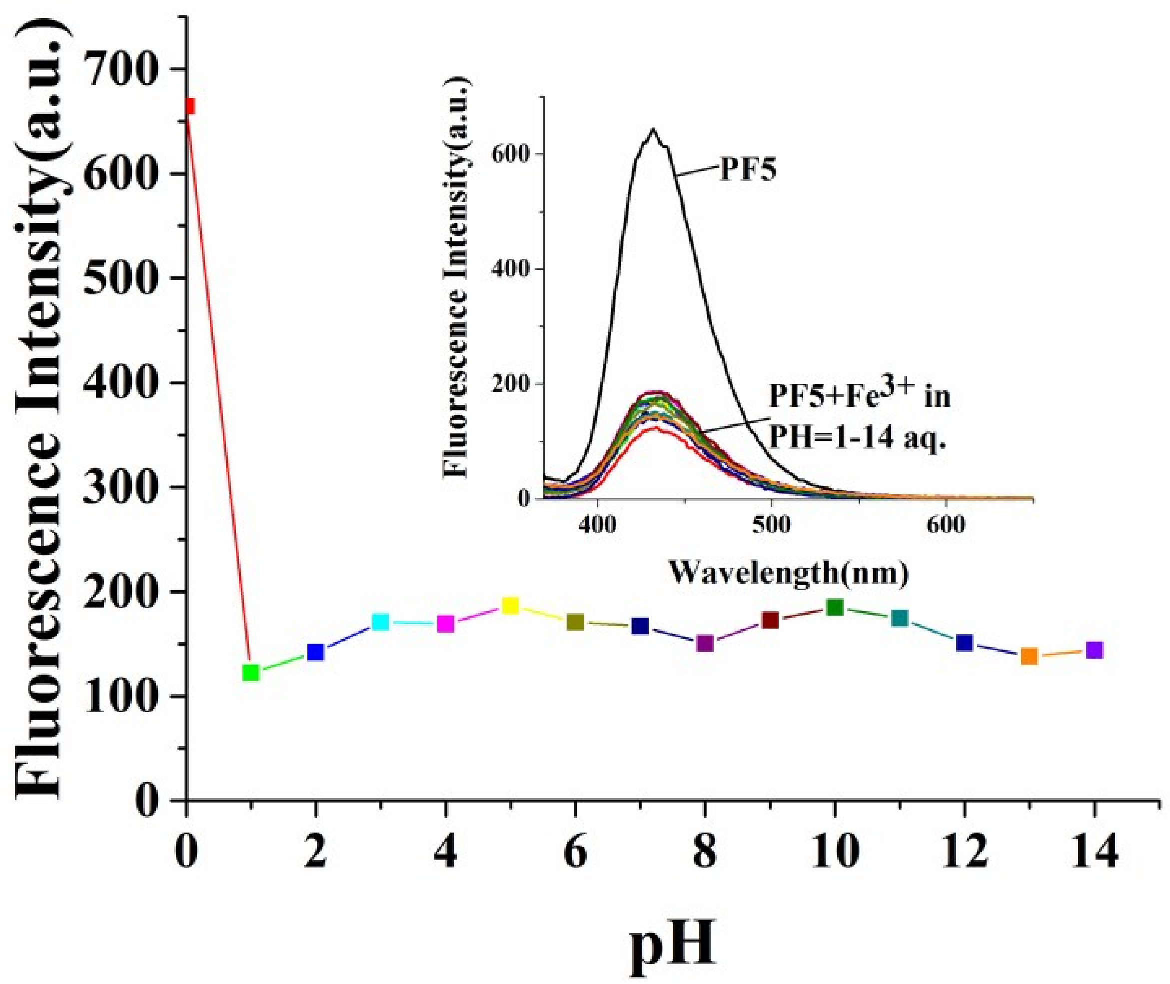


Figure S14 Influence of pH on the fluorescence of **PF5** and Fe^{3+} in DMSO/H_2O (v/v = 8:2). Inset: pH fluorescence of a full scan.

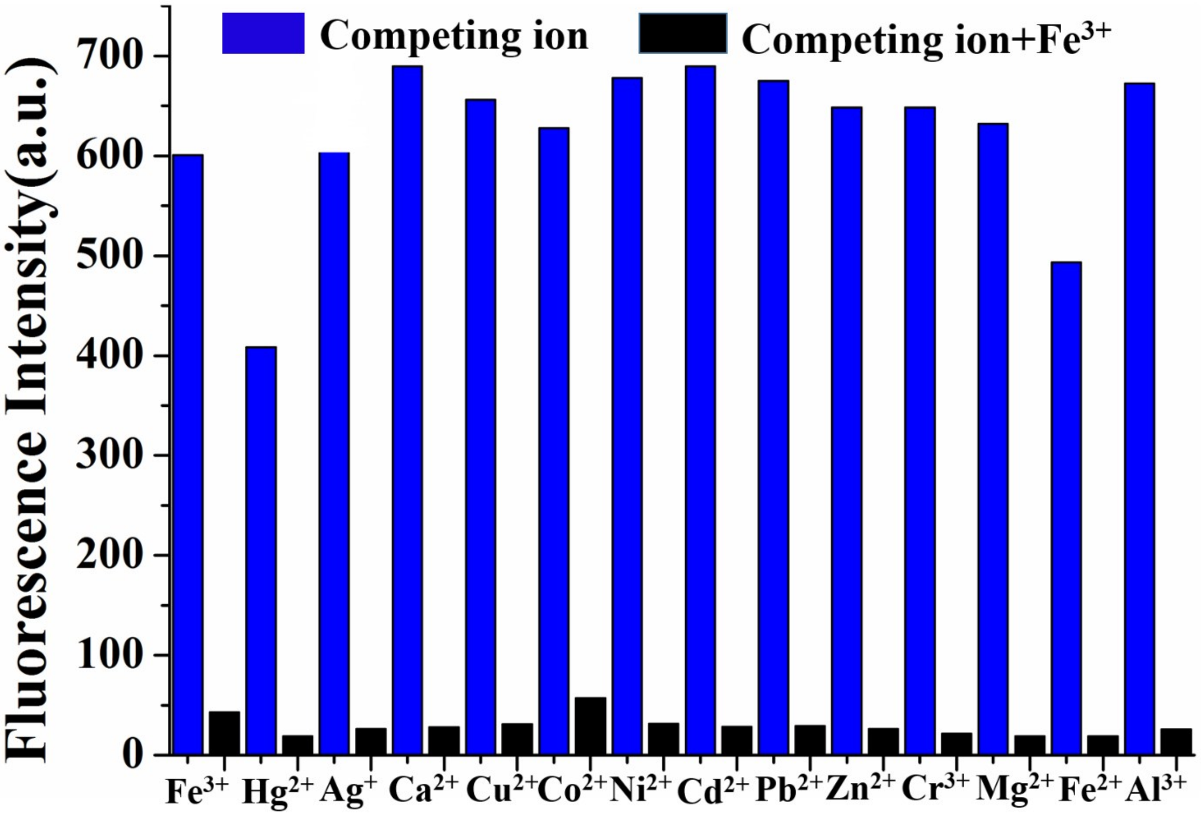


Figure S15 Fluorescence intensities of **PF5** (1.0 mM) in the presence of 20.0 equiv. of various ions containing 20.0 equiv. of Fe^{3+} in DMSO/H_2O (8:2, v/v) (λ_{ex} = 360 nm).

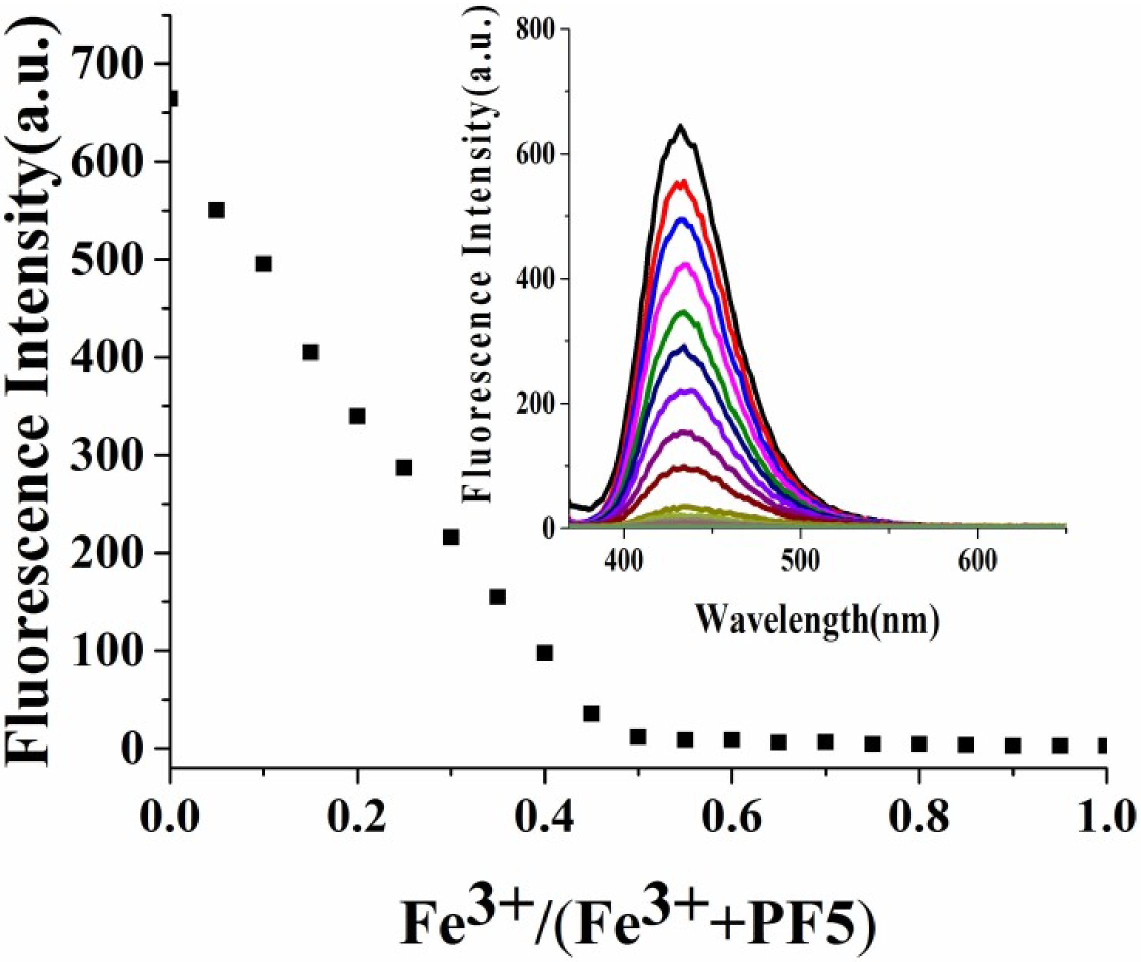


Figure S16 Job plot for complexation of sensor **PF5** with Fe^{3+} in DMSO/H_2O (8:2, v/v), indicating the 1:1 stoichiometry. Inset: Job plot fluorescence of a full scan.

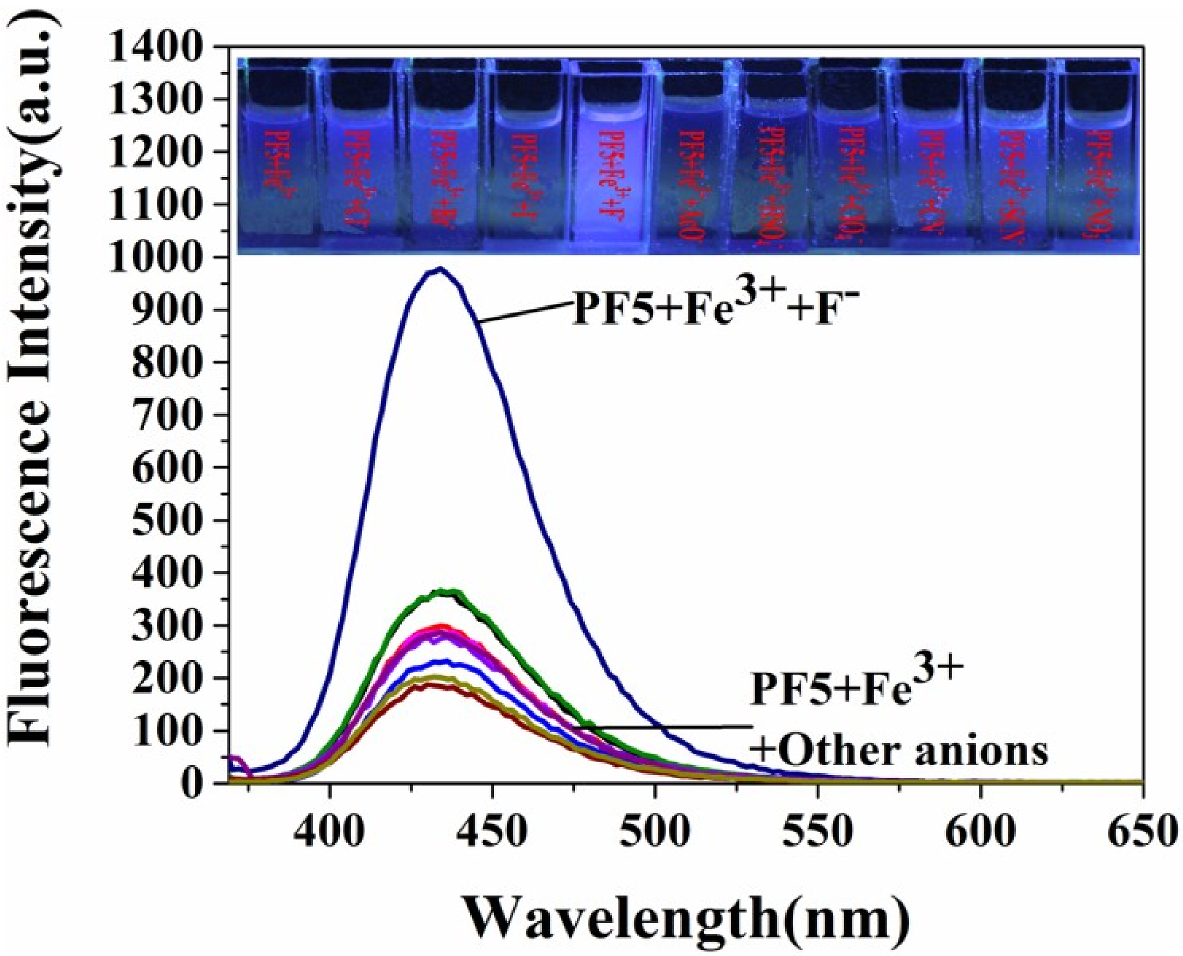
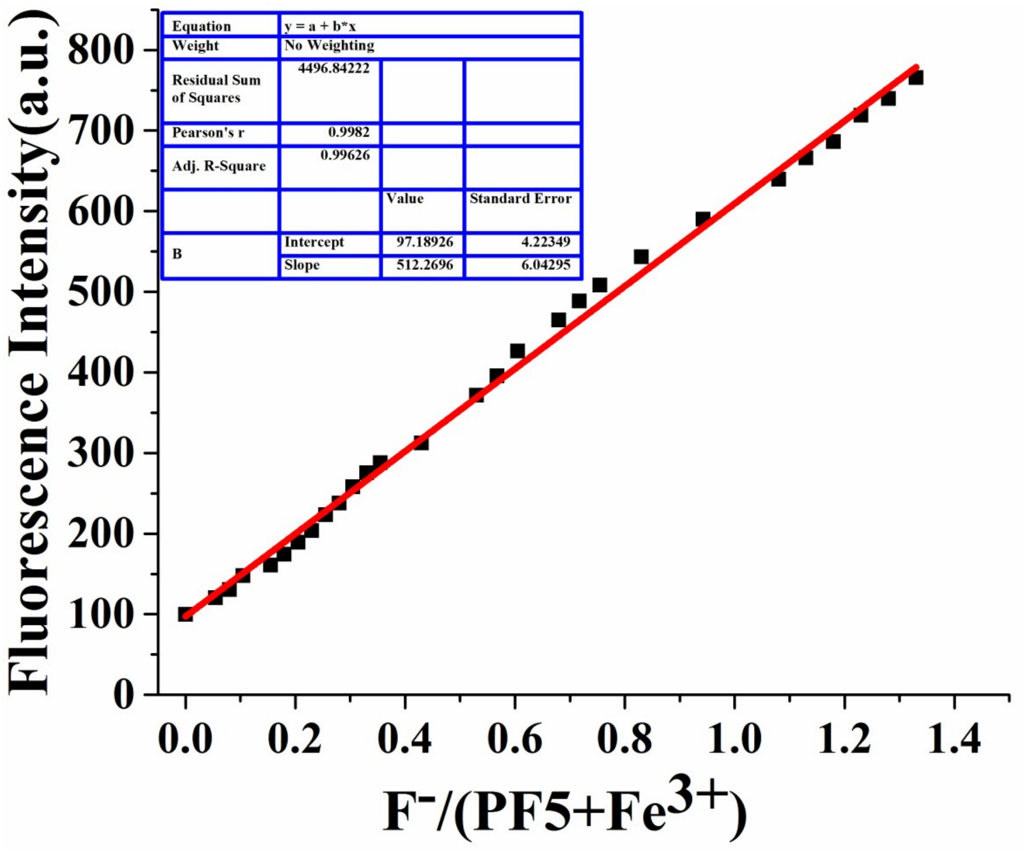


Figure S17 Fluorescence emission spectra of **PF5**–Fe^{3+} (10 mM) in the presence of various anions (1.5 equiv.) in a mixed aqueous medium (DMSO/H_2O (8:2, v/v); λ_{ex} = 360 nm). Inset: Photograph of **PF5**–Fe^{3+} (10 mM) upon adding 1.5 equiv. of various ions, which was observed under a UV–lamp (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	4496.84222		
Pearson's r	0.9982		
Adj. R-Square	0.99626		
		Value	Standard Error
B	Intercept	97.18926	4.22349
	Slope	512.2696	6.04295

Figure S18 The photograph of the linear range.

Linear Equation: $Y=512.2696X+97.18926$ $R^2=0.99626$

$S=5.12 \times 10^8$ $\delta = \sqrt{\frac{\Sigma(Fi - F0)^2}{N-1}} = 4.42$ $K=3$

LOD $=K \times \delta/S= 2.59 \times 10^{-8}$M

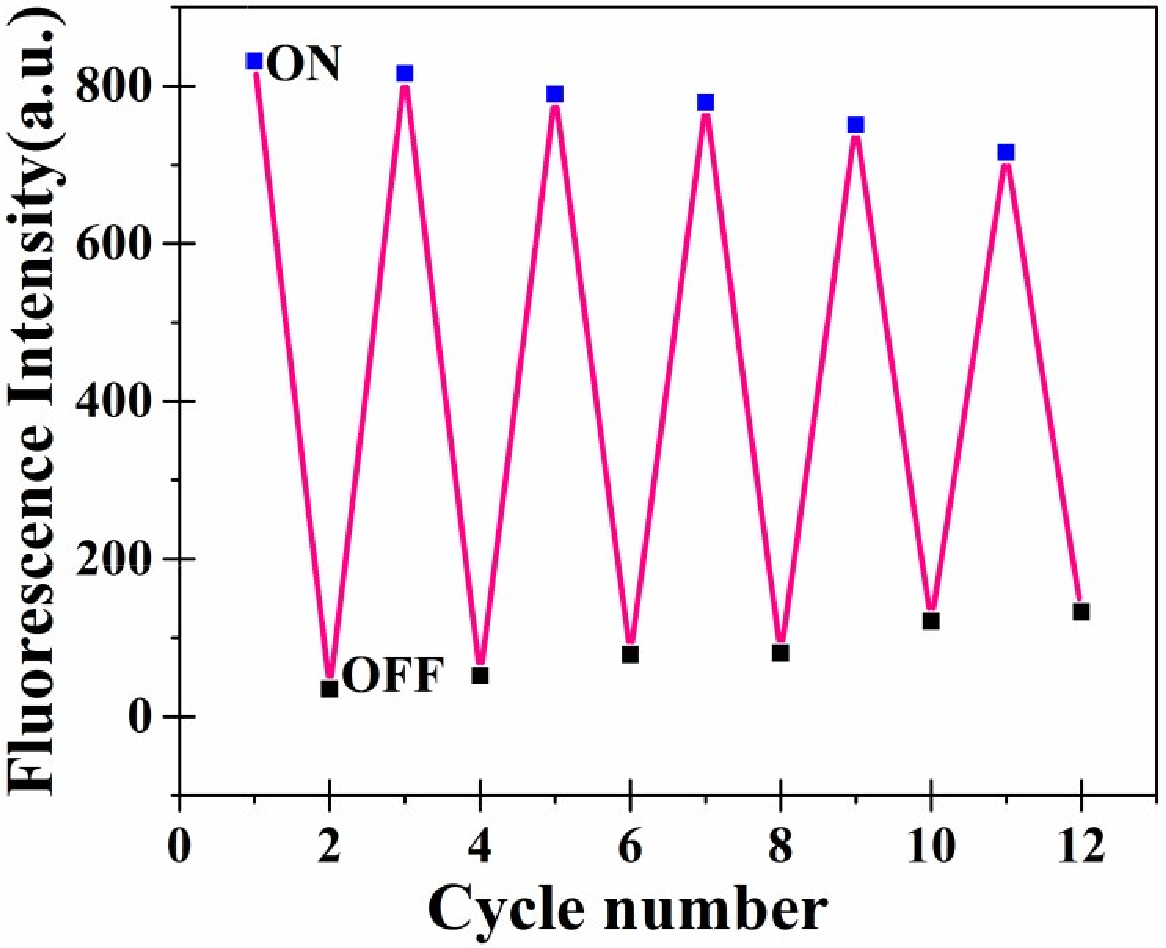


Figure S19 Fluorescence intensity changes of **PF5** (1.0 mM) at 432 nm in a mixed aqueous medium (DMSO/H_2O (8:2, v/v); λ_{ex} = 360 nm) as a function of cycles upon alternate addition of Fe^{3+} and F^{-}.

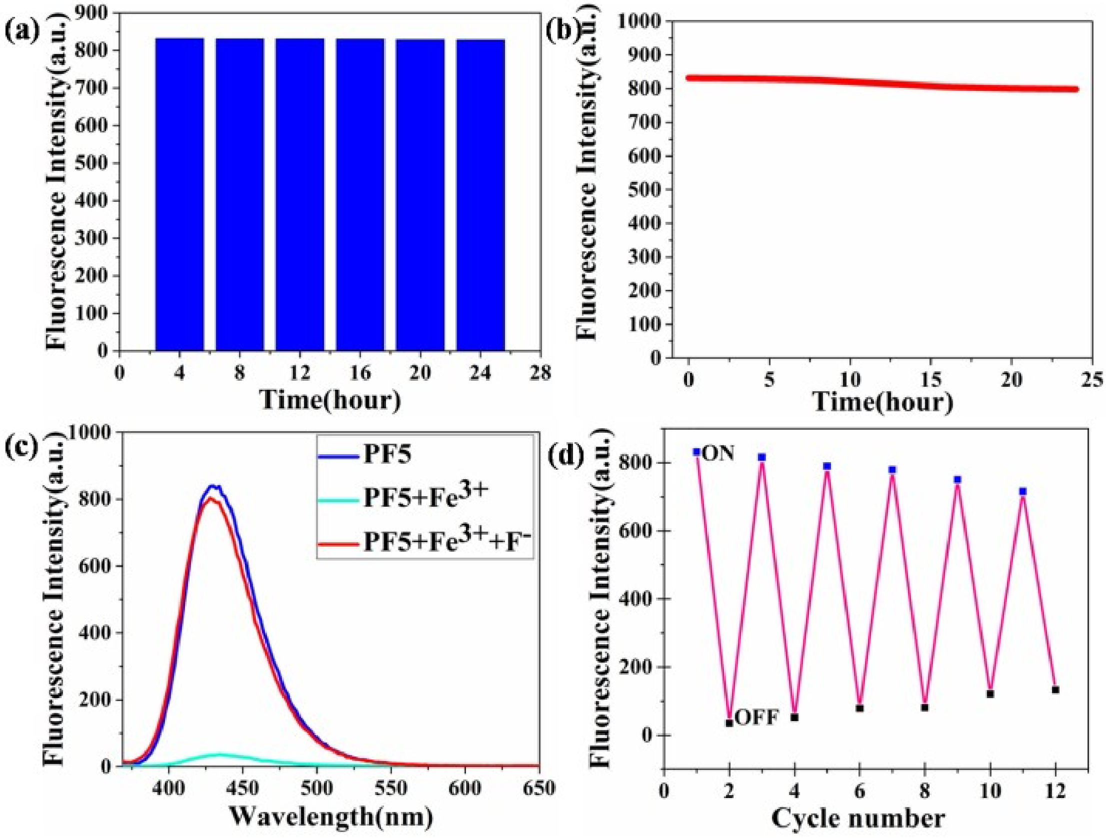


Figure S20 (a) time stability experiment, **PF5** showed excellent time stability after 24 hours; (b) photostability experiment, the fluorescence intensity of **PF5** has barely changed after irradiated by 365nm about 24 hours; (c) reversibility experiment, the fluorescence spectra of **PF5**, **PF5**+Fe^{3+} and **PF5**+Fe^{3+}+F^{-}, **PF5**+Fe^{3+} shows very weak fluorescence, however, the fluorescence of **PF5**+Fe^{3+}+F^{-} was dramatically enhanced, it showed good reversibility; (d) repeatability experiment, fluorescence intensity changed after addition of Fe^{3+} and F^{-}, demonstrating that this process was reversible.