Electronic Supplementary Information

Pillar[5]arene and naphthalimide constructed novel supramolecular sensor for successive detection Fe³⁺ and F⁻ in

water

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Synthesis and characterizations of compound B1.



Scheme S1 The synthesis of compound B1.



Fig. S1 ¹H NMR spectrum of B1 in DMSO- d_6 .



Fig. S2 ESI-MS spectrum of B1.

Synthesis and characterizations of compound P5.



Scheme S2 The synthesis of compound P5.

Synthesis of compound 1.

Hydroquinone (2.2 g, 20.0 mmol), K₂CO₃ (13.8 g, 100 mmol), KI (0.83 g, 5 mmol), 1,4-Dibromobutane (17.28 g, 80.0 mmol) and acetone (200.0 mL) were added in a 250 mL round-bottom flask. The reaction mixture was stirred at reflux for 5 days. Then 200 mL of cold water was added to the reaction mixture, where compound **1** precipitated as a white solid. The compound **1** was purified by column chromatography on silica gel with petroleumether/ethyl acetate (5:1 ν/ν) as the eluent to get a white powder (6.5 g, 86 %). m.p. = 86 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.79 (t, *J* = 6.0 Hz, 4H), 4.00 - 3.83 (m, 4H), 3.46 (t, *J* = 6.6 Hz, 4H), 2.12 - 1.81 (m, 8H). ¹³C NMR (151 MHz, CDCl₃) δ :76.65 (s), 67.46 (s), 33.46 (s), 29.52 (s), 28.02 (s). MS: ESI (Fig. S5) *m/z* for **1** C₁₄H₂₁Br₂O₂, found: 380.9882, calcd: 380.9888.



Fig. S3 ¹H NMR (400 MHz, 298K) spectra of compound 1 in CDCl₃.



Fig. S4 ¹³C NMR (151 MHz, 298K) spectra of compound 1 in CDCl₃.



Fig. S5 High resolution electrospray ionization mass spectrum of compound 1.

Synthesis of compound 2.

A solution of compound **1** (3.8 g, 10.0 mmol) in 1, 2-dichloroethane (200 mL), paraformaldehyde (0.686 g, 20.0 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (BF₃·O(C₂H₅)₂, 1.42 g, 10.0 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h. A green solution was obtained. After the solvent was removed, the obtained solid was purified by column chromatography on silica gel with petroleumether/dichloromethane (1:1 v/v) as the eluent to get a white powder compound **2** (1.57 g, 40 %). m.p. = 124-126 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.86 (s, 10H), 3.96 (s, 20H), 3.76 (d, *J* = 8.0 Hz, 10H), 3.50 (s, 10H), 3.29 (s, 10H), 2.12 (s, 20H), 1.99 (s, 20H). ¹³C NMR (151 MHz, CDCl₃) δ 149.79, 128.33, 114.77, 67.58, 67.44, 33.74, 31.12, 30.80, 30.49, 30.27, 29.83, 29.70 and 28.53. MALDI-TOF-MS: m/z calcd for C₇₅H₁₀₁Br₁₀O₁₀, 1960.9, found 1960.7.



Fig. S6 ¹H NMR (400 MHz) spectra of compound 2 in CDCl₃.



Fig. S7 ¹³C NMR (151 MHz, 298K) spectra of compound 2 in CDCl₃.



Fig. S8 MALDI-TOF-MS of 2.



Fig. S10 13 C NMR (151 MHz, 298K) spectra of product P5 in D₂O.



Fig. S11 High resolution electrospray ionization mass spectrum of P5.



Fig. S12 High resolution electrospray ionization mass spectrum of P5B1.



Fig. S13 Fluorescence intensity changes of P5 water solution (2.0 × 10⁻⁵ mol L⁻¹) upon addition of different amounts of B1 (λ_{ex} = 380 nm).

I is the observed the fluorescence intensity of P5 at the fixed concentrations of B1.

 I_{max} and I_{min} are the corresponding maximum and minimum, respectively.

$$\log \frac{\mathbf{I} - \mathbf{I}_{\min}}{\mathbf{I}_{\max} - \mathbf{I}} = \log \mathbf{K} \mathbf{a} + \log [\mathbf{B}\mathbf{1}]$$

 $K = 3.46 \times 10^9 \text{ M}^{-2}$.



Fig. S14 2D NOESY NMR spectrum (600 MHz, D_2O , 298 K) of P5 : B1 = 1 : 1. (P5 = 20.0 mM.).



Fig. S15 Fluorescent emission ($\lambda_{ex} = 380 \text{ nm}$) spectra of P5B1 ($2.0 \times 10^{-5} \text{ M}$) to Fe³⁺ (10 equiv.) in the presence of various competing cations in water (buffered with HEPES, pH = 7.2). Form 1 to 16: P5B1, P5B1 + Fe³⁺ + Ca²⁺, P5B1 + Fe³⁺ + Mg²⁺, P5B1 + Fe³⁺ + Zn²⁺, P5B1 + Fe³⁺ + Cu²⁺, P5B1 + Fe³⁺ + Co²⁺, P5B1 + Fe³⁺ + Ni²⁺, P5B1 + Fe³⁺ + Cd²⁺, P5B1 + Fe³⁺ + Cd²⁺, P5B1 + Fe³⁺ + Ag⁺, P5B1 + Fe³⁺ + Cr³⁺, P5B1 + Fe³⁺ + Cr³⁺, P5B1 + Fe³⁺ + Cr³⁺, P5B1 + Fe³⁺ + Ct³⁺, P5B1 + Ft³⁺, P5B1 + Ft³⁺,



Fig. S16 Fluorescence spectra of supramolecular sensor P5B1 water solution (2×10^{-5} mol L⁻¹) in the presence of different concentrations of Fe³⁺ ($\lambda_{ex} = 380$ nm).



Fig. S17 Plot of the intensity at 490 nm for a mixture of the sensor **P5B1** (20 μ M) and Fe³⁺ in water (buffered with HEPES, pH = 7.2) in the range 0.00 to 10.0 equiv. (λ ex = 380 nm). The result of the analysis as follows:

Linear Equation:
$$Y = -24.8311X + 403.0438$$
 $R^2 = 0.98387$
 $S = 2.48311 \times 10^7$ $\delta = \sqrt{\frac{\Sigma(A_0 - A_1)^2}{N - 1}} = 4.14679$ (N=20) K = 3

 $LOD = K \times \delta/S = 5.01 \times 10^{-7}$

 A_0 is the absorbance intensity of **P5B1**; A_1 is the average of the A_0 .



Fig. S18 Fluorescence spectra of supramolecular sensor P5B1Fe water solution (2 × 10⁻⁵ mol L⁻¹) in the presence of different concentrations of F⁻ (λ_{ex} = 380 nm).



Fig. S19 Plot of the intensity at 490 nm for a mixture of the sensor **P5B1Fe** (20 μ M) and F⁻ in water (buffered with HEPES, pH = 7.2) in the range 0.00 to 3.2 equiv. (λ ex = 380 nm). The result of the analysis as follows:

Linear Equation:
$$Y = 65.4675X + 148.7782$$
 $R^2 = 0.99834$
 $S = 6.54675 \times 10^6$ $\delta = \sqrt{\frac{2(A_0 - A_0)^2}{N-1}} = 8.88175$ (N=20) $K = 3$

 $LOD = K \times \delta/S = 4.07 \times 10^{-6}$

 A_0 is the absorbance intensity of **P5B1Fe**; A_1 is the average of the A_0 .



Fig. S20 The fluorescence spectra of (a) **P5** and **P5Fe**; (b) **B1Fe** and **B1Fe** + **F**⁻; (c) **P5** and **P5** + **F**⁻; (d) **B1** and **B1** + **F**⁻; (e) **P5B1Fe** and **P5B1Fe** + **F**⁻ ($\lambda_{ex} = 380$ nm).



Fig. S21 The fluorescence spectra of P5B1, P5B1 + Fe²⁺ and P5B1 + Fe³⁺ ($\lambda_{ex} = 380$ nm).



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