

Supporting Information

Efficient sensing F⁻ in water using a novel water soluble self-assembled supramolecular sensors based on pillar[5]arene

Qi Lin *, Feng Zheng, Lu Liu, Peng-Peng Mao, You-Ming Zhang, Hong Yao and Tai-Bao Wei *
*Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China,
Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical
Engineering, Northwest Normal University, Lanzhou, Gansu, 730070, P. R. China.*

Corresponding author: linqi2004@126.com, weitaibao@126.com.

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Experimental section

1.1 Materials and physical methods.

All anions were used as the sodium salts while all cations were used as the perchlorate salts, which were purchased from Alfa Aesar and used as received. Other reagents used in the study were analytical grade. Fresh double distilled water was used throughout the experiment. All other reagents and solvents were commercially available at analytical grade and were used without further purification. ^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). Low-resolution mass spectra were recorded on a Bruker Esquire 6000 MS instrument. The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

1.2 General procedure for fluorescence experiments

Fluorescence spectroscopy was carried out keeping the host concentration constant in ethanol solution on a Shimadzu RF-5301PC spectrofluorophotometer.

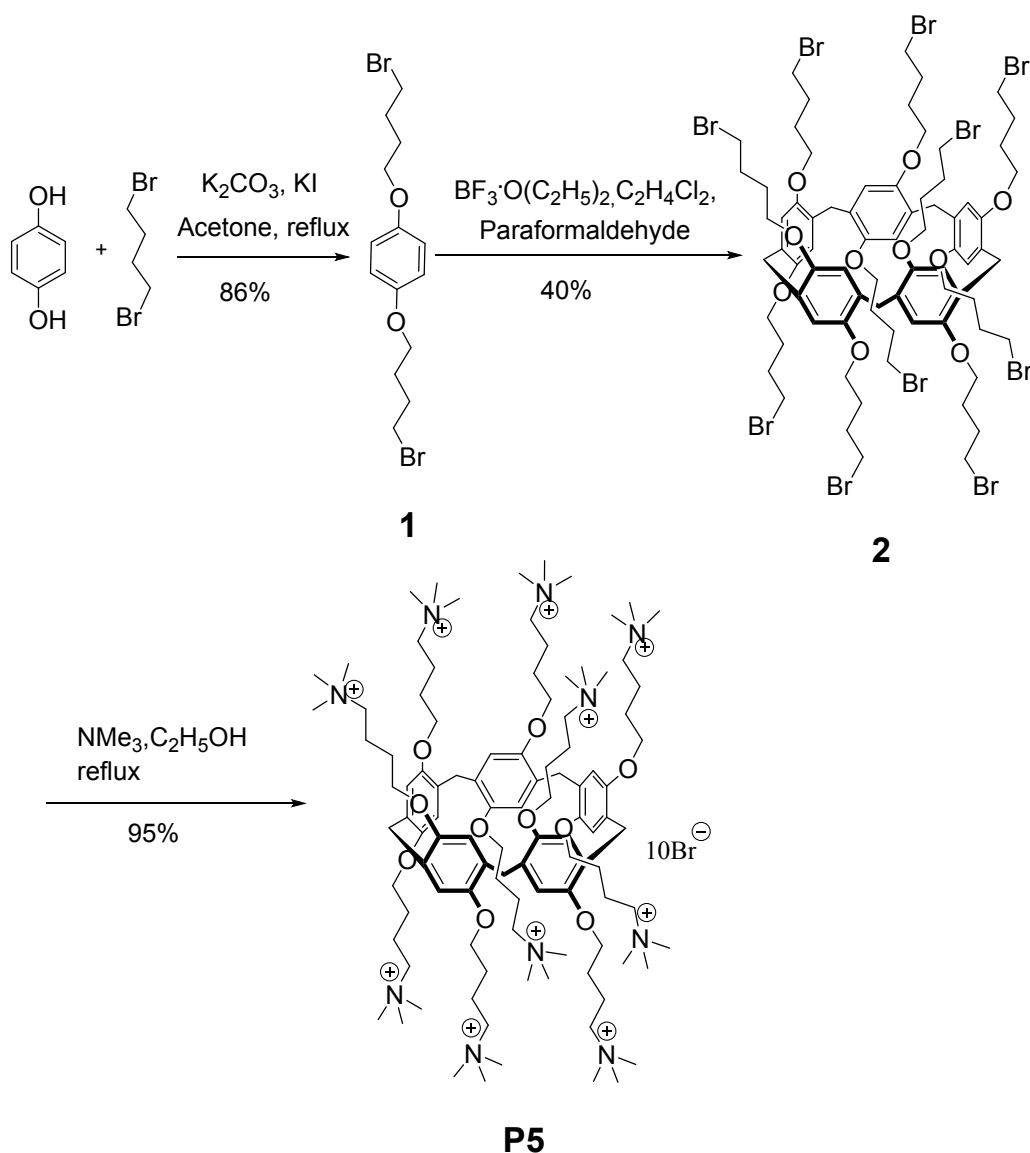
1.3 General procedure for ^1H NMR titrations

For ^1H NMR titrations, three stock solutions were prepared: one of them contained the host only in D_2O , the second one contained an appropriate concentration of guest in D_2O . The third one contained an appropriate concentration of host and guest in

D₂O. Aliquots of the two solutions were mixed directly in NMR tubes.

1.4 General procedure for concentration-dependent ¹H NMR measurements

The concentration-dependent ¹H NMR was carried out by gradually increasing the concentration of the D₂O solution of **N1**. The initial concentration of the **N1** is 1.0 mM, the concentration was adjusted by directly addition right amount of powdery **N1** into the D₂O solution.



Scheme S1. Synthesis of P5.

2. Synthesis of P5.

2.1 Synthesis of compound 1.

Hydroquinone (2.2 g, 20.0 mmol), K_2CO_3 (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 petroleum ether/ethyl acetate (5:1 v/v) as the eluent to get a white powder (6.5 g, 86 %). m.p. 86 °C. ¹H NMR (600 MHz, CDCl₃, Fig. S14) 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, Fig. S15) δ: 76.65 (s), 67.46 (s), 33.46 (s), 29.52 (s), 28.02 (s). MS: ESI (Fig. S16) *m/z* for **1** C₁₄H₂₁Br₂O₂, found: 380.9882, calcd : 380.9888.

2.2 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 petroleum ether/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 (600 MHz, CDCl₃, Fig. S17) 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, Fig. S18) δ 149.55, 128.15, 67.33, 33.83, 32.09, 30.12 and 28.57. MS: ESI (Fig. S19) *m/z* for **2** C₇₅H₁₀₄K₂Br₁₀O₁₀Na₆, found: 2180.89, calcd : 2180.82.

2.3 Synthesis of P5.

The compound **2** (1.00 g, 0.51 mmol) and trimethylamine (33 % in ethanol, 6.89 mL, 25.5 mmol) were added to ethanol (50 mL). The solution was refluxed over night. Then the solvent was removed by evaporation, deionized water (20 mL) was added.

After filtration, a clear solution was obtained. Then the water was removed by evaporation to obtain **P5** as a white solid (1.28 g, 95 %). m.p.218-220 °C. ¹H NMR (600 MHz, D₂O, Fig. S20) δ 6.78 (s, 11H), 3.82 (d, *J* = 38.2 Hz, 31H), 3.25 (s, 21H), 2.97 (s, 90H), 1.78 (s, 41H). The ¹³C NMR spectrum of **P5** is shown in Fig. S21. ¹³C NMR (151 MHz, D₂O) δ 150.12, 129.22, 116.81, 68.46, 65.87, 52.87, 25.78 and 19.46. HRESIMS (Fig. S22) *m/z* for **P5** [M-3Br+9Na+2NH₄]³⁺ C₁₀₅H₁₉₈Br₇N₁₂Na₉O₁₀, found 848.9418, calcd 848.9554.

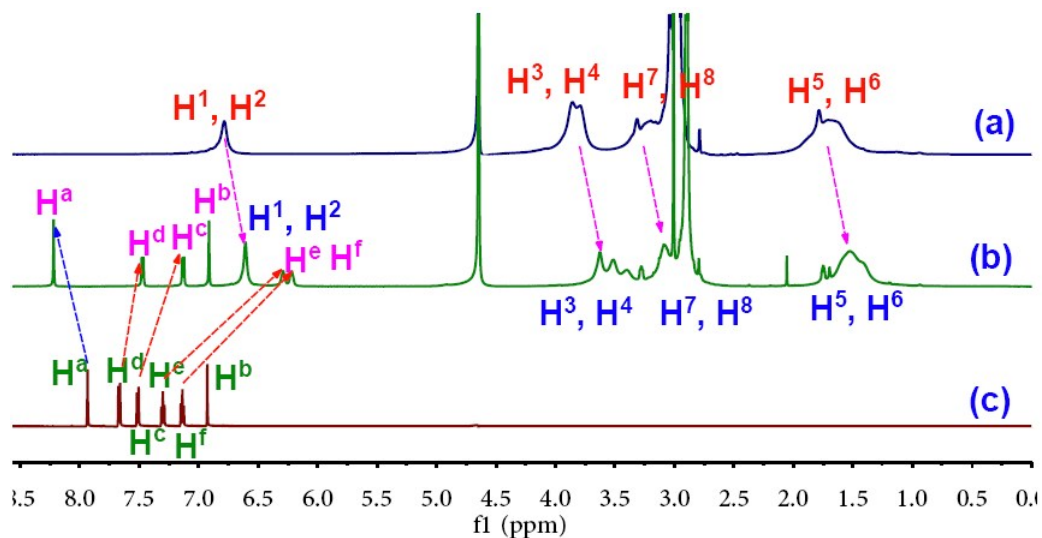


Fig. S1 Partial ^1H NMR spectra (600 MHz, 298 K) of (a) **P5** (1×10^{-3} mol L^{-1}); (b) equimolar mixture of **P5** and **N1** (1 : 2); (c) **N1** (2×10^{-3} mol L^{-1}) in D_2O .

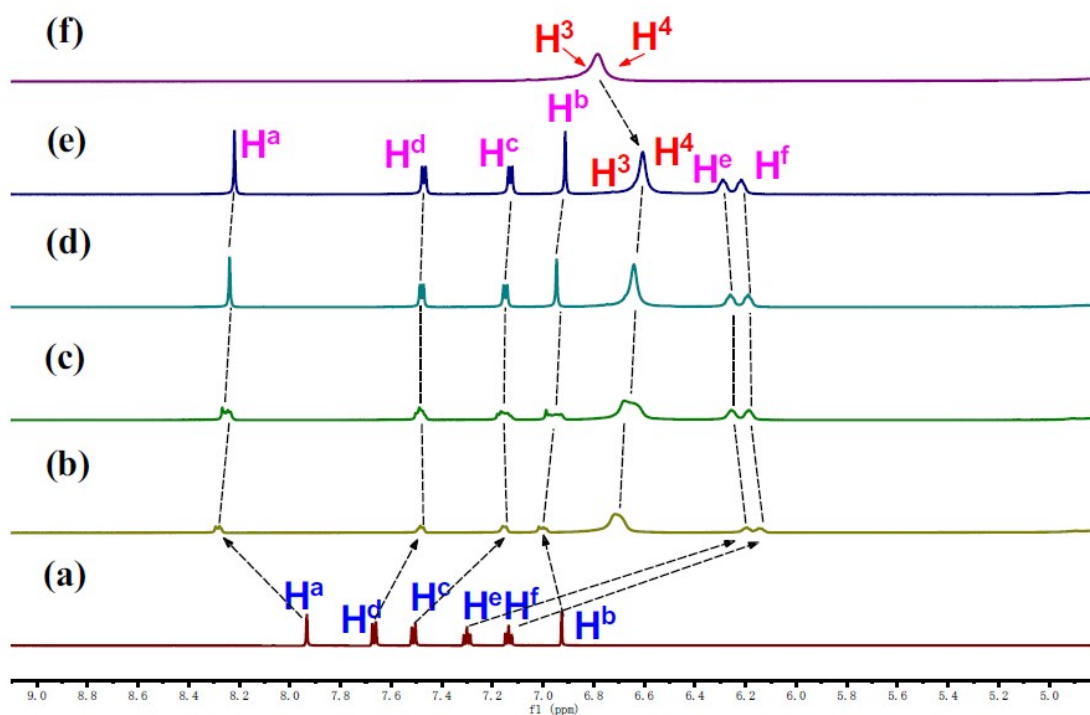


Fig. S2 Partial ^1H NMR spectra of **P5** (1×10^{-3} mol L^{-1} , D_2O) and in the presence of varying amounts of **N1**: (a) free **N1**; (b) **P5** : **N1** = 1 : 0.5; (c) **P5** : **N1** = 1 : 1; (d) **P5** : **N1** = 1 : 1.5; (e) **P5** : **N1** = 1 : 2; (f) free **P5** in D_2O .

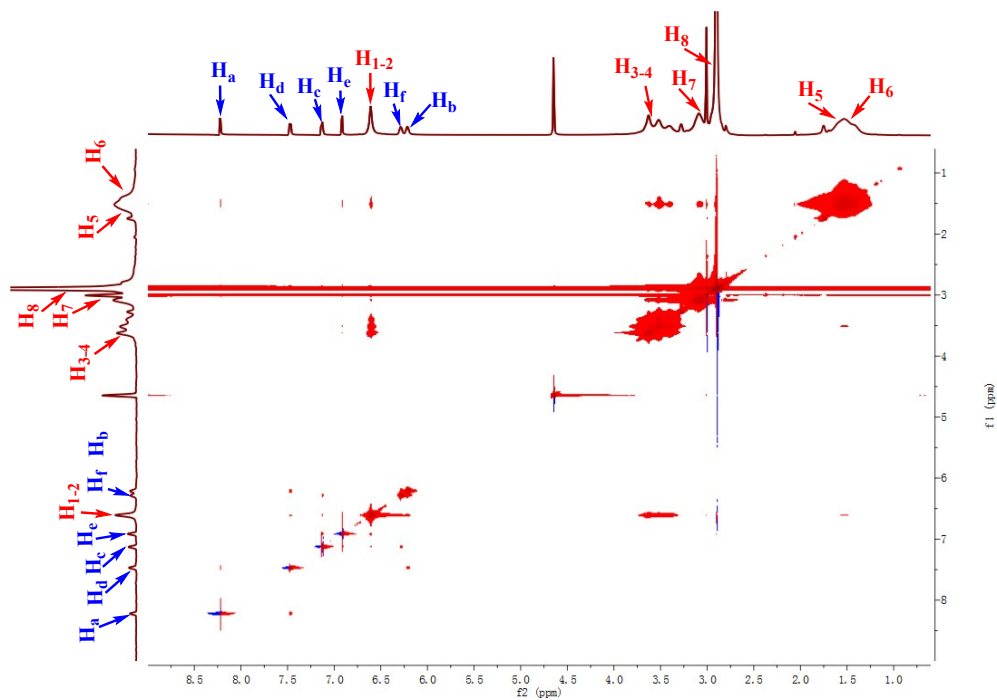


Fig. S3 NOESY NMR spectrum (600 MHz, D₂O, 298 K) of **P5 : N1 = 1 : 2**. (P5 = 20.0 mM.)

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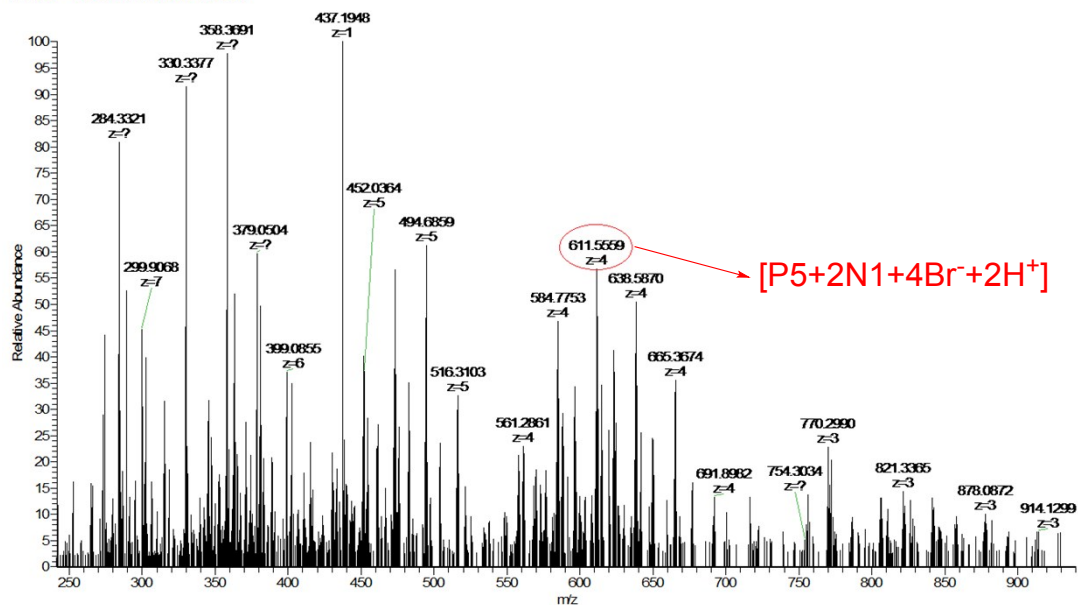


Fig. S4 High resolution electrospray ionization mass spectrum of **P5N1**.

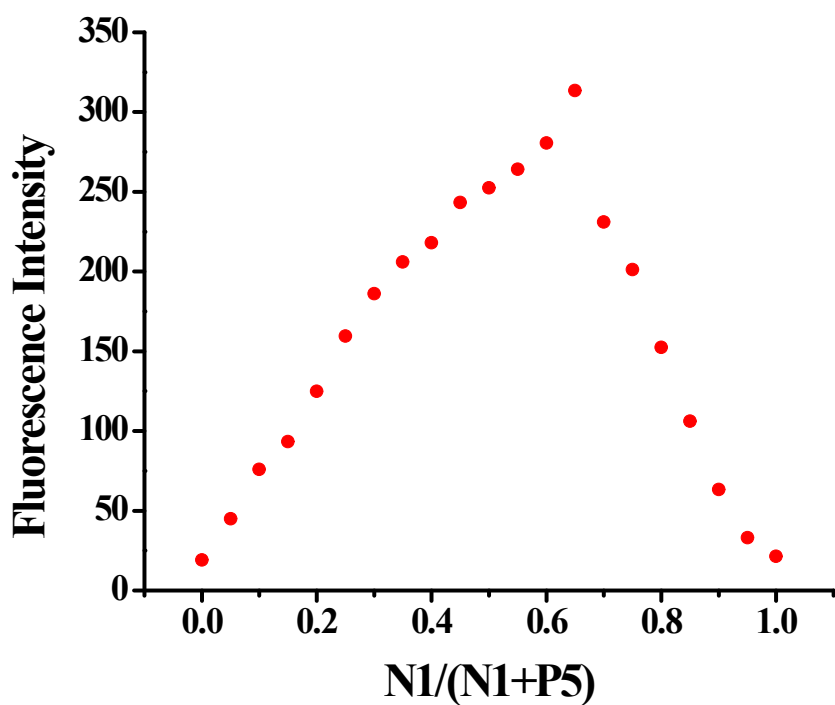


Fig. S5 Job plot for complexation of sensor **P5** with **N1** in H_2O , indicating the 1: 2 stoichiometry.

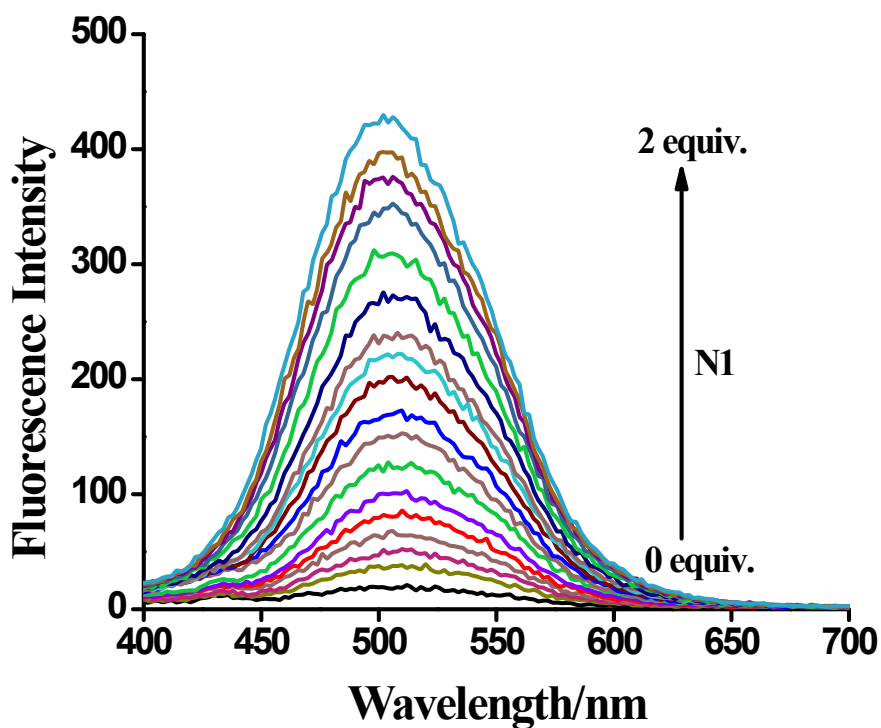


Fig. S6 Fluorescence intensity changes of **P5** water solution ($1 \times 10^{-5} \text{ mol L}^{-1}$) upon addition of different amounts of **N1** ($\lambda_{\text{ex}} = 376 \text{ nm}$).

I is the observed the fluorescence intensity of **P5** at the fixed concentrations of **N1**.

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

$$\log \frac{I - I_{\min}}{I_{\max} - I} = \log K + 2\log[\mathbf{N1}]$$

$$K = 9.94 \times 10^9 \text{ M}^{-1}$$

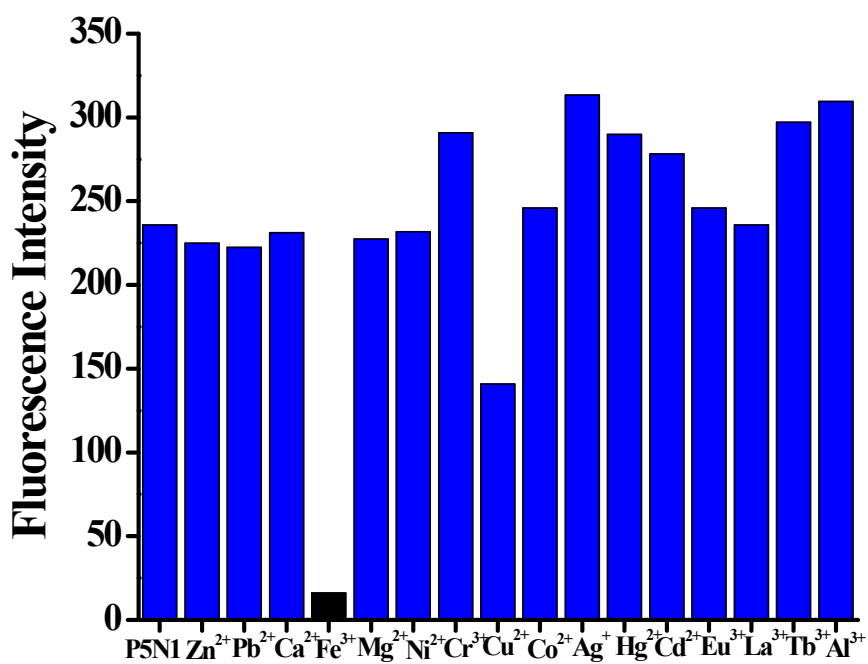


Fig. S7 Histogram of fluorescence emission of supramolecular sensor **P5N1** in the presence of various cations (10 equiv.) in water ($\lambda_{\text{ex}} = 376\text{nm}$).

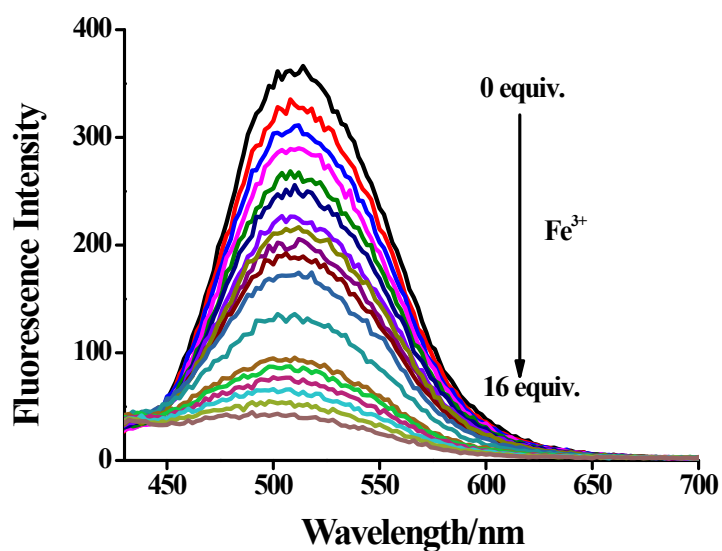


Fig. S8 Fluorescence spectra of supramolecular sensor **P5N1** water solution (1×10^{-5} mol L⁻¹) in the presence of different concentrations of Fe³⁺ ($\lambda_{\text{ex}} = 376$ nm).

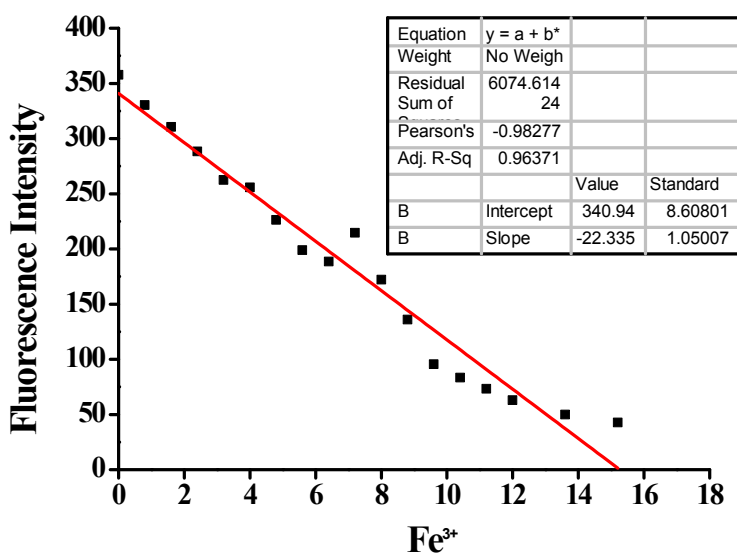


Fig. S9 The photograph of the linear range.

Linear Equation: $Y = -22.3356X + 340.946$ $R^2 = 0.96371$

$$S = 2.23356 \times 10^7 \quad \delta = \sqrt{\frac{\Sigma(F_i - F_0)^2}{N - 1}} \quad K = 3$$

$$\delta = 6.20044 \quad \text{LOD} = K \times \delta / S = 8.328 \times 10^{-7} \text{M}$$

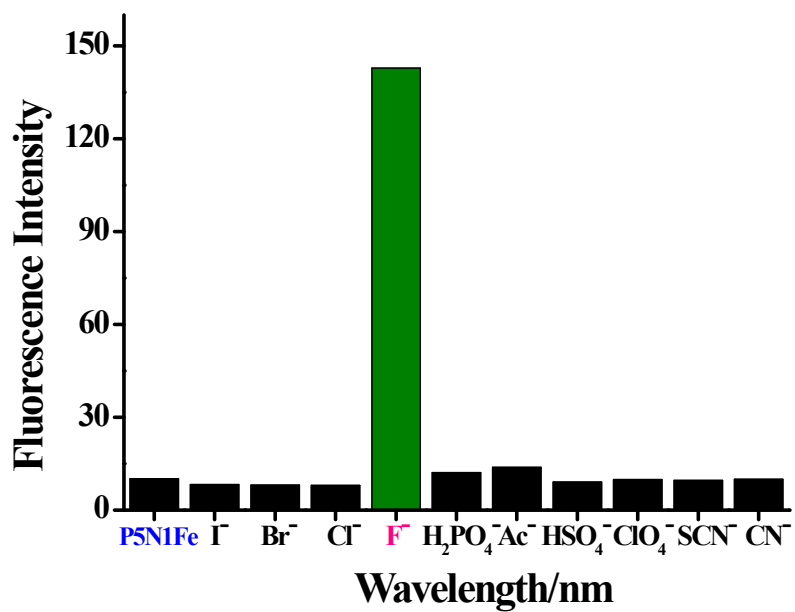


Fig. S10. Histogram of fluorescence emission of supramolecular sensor **P5N1Fe** in the presence of various anions (2 equiv.) in water ($\lambda_{\text{ex}} = 376\text{nm}$).

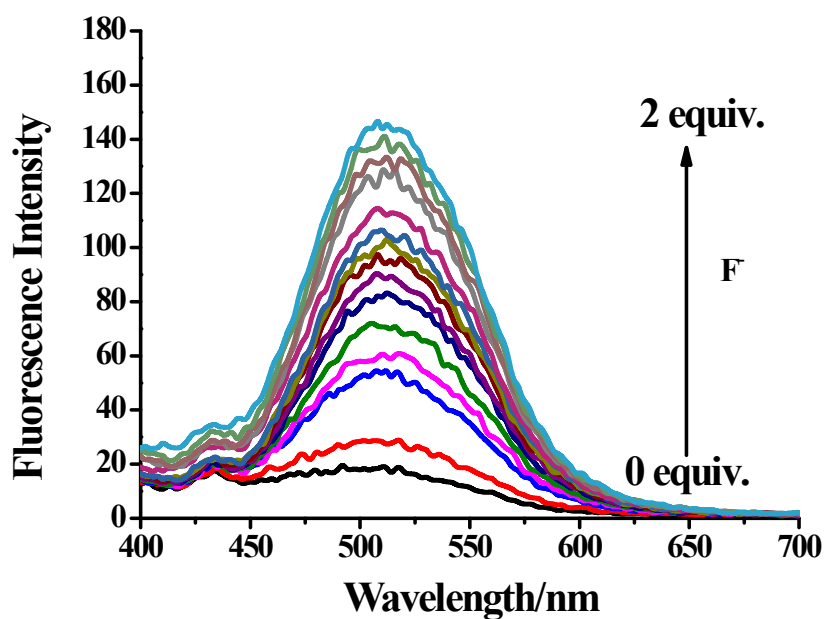


Fig. S11 Fluorescence spectra of supramolecular sensor **P5N1Fe** water solution ($1 \times 10^{-5} \text{ mol L}^{-1}$) in the presence of different concentrations of F^- ($2 \times 10^{-4} \text{ mol L}^{-1}$, $\lambda_{\text{ex}} = 376 \text{ nm}$).

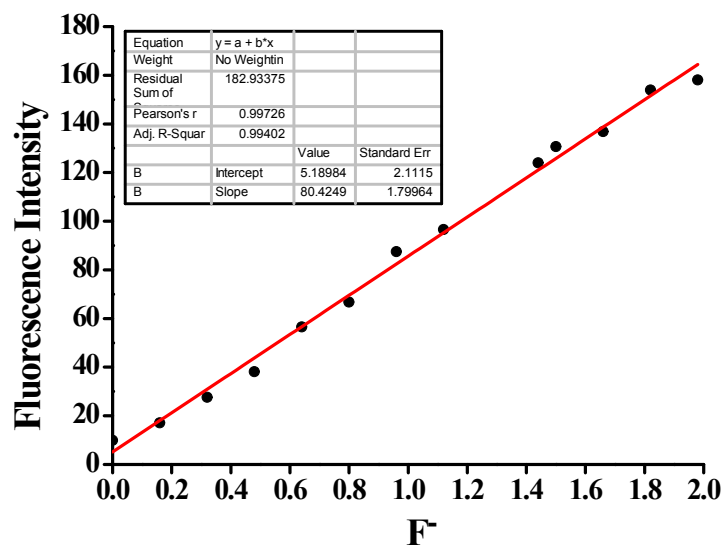


Fig. S12 The photograph of the linear range.

Linear Equation: $Y=80.4249X+5.18984$ $R^2=0.99402$ $K=3$

$\delta=1.09325$
($N=20$)



$LOD = K \times \delta/S = 4.07 \times 10^{-8}M$

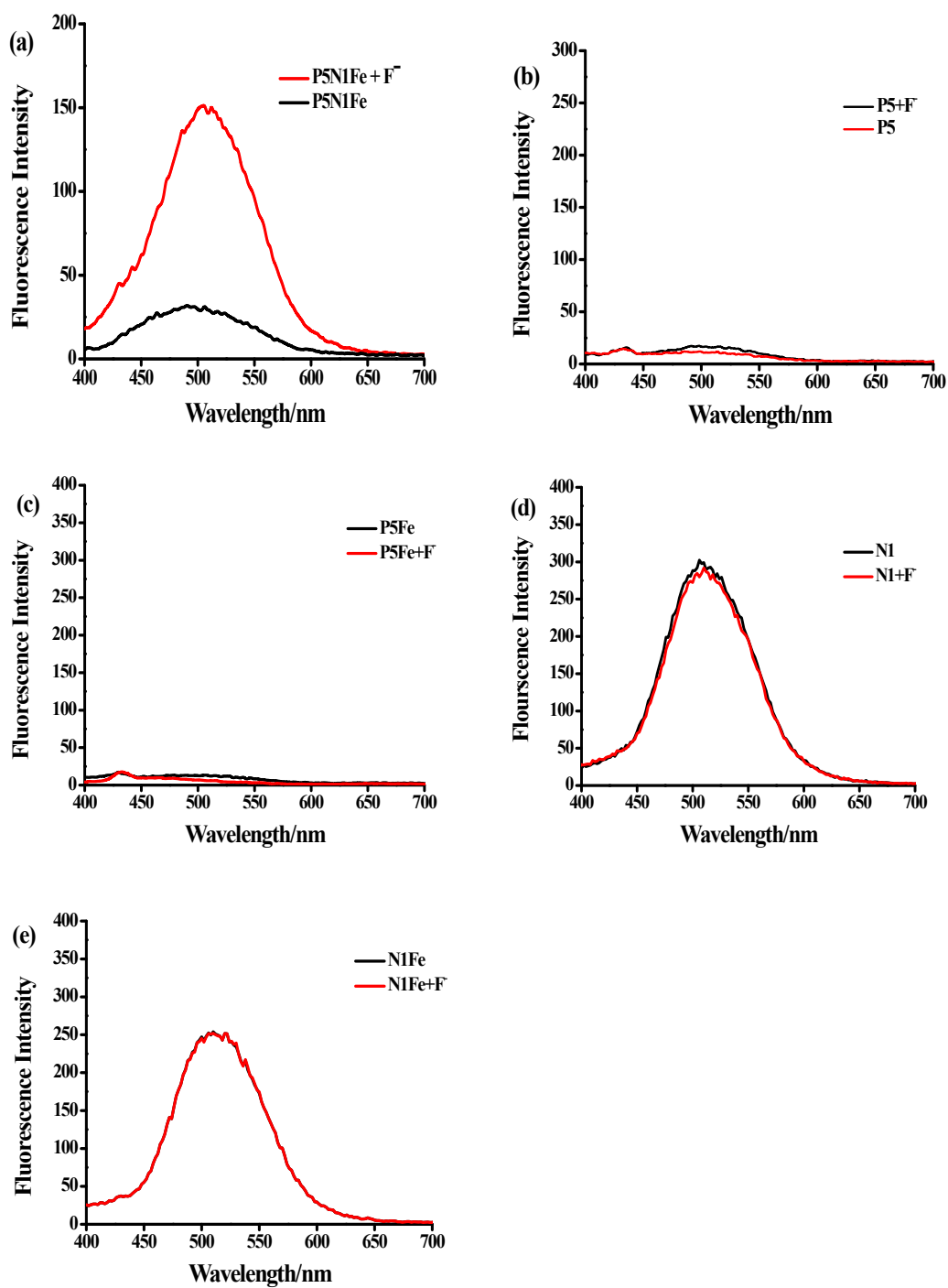


Fig. S13 The fluorescence spectra of (a) **P5N1Fe** and **P5N1Fe + F⁻**; (b) **P5** and **P5 + F⁻**; (c) **P5Fe** and **P5Fe + F⁻**; (d) **N1** and **N1 + F⁻**; (e) **N1Fe** and **N1Fe + F⁻** ($\lambda_{ex} = 376$ nm).

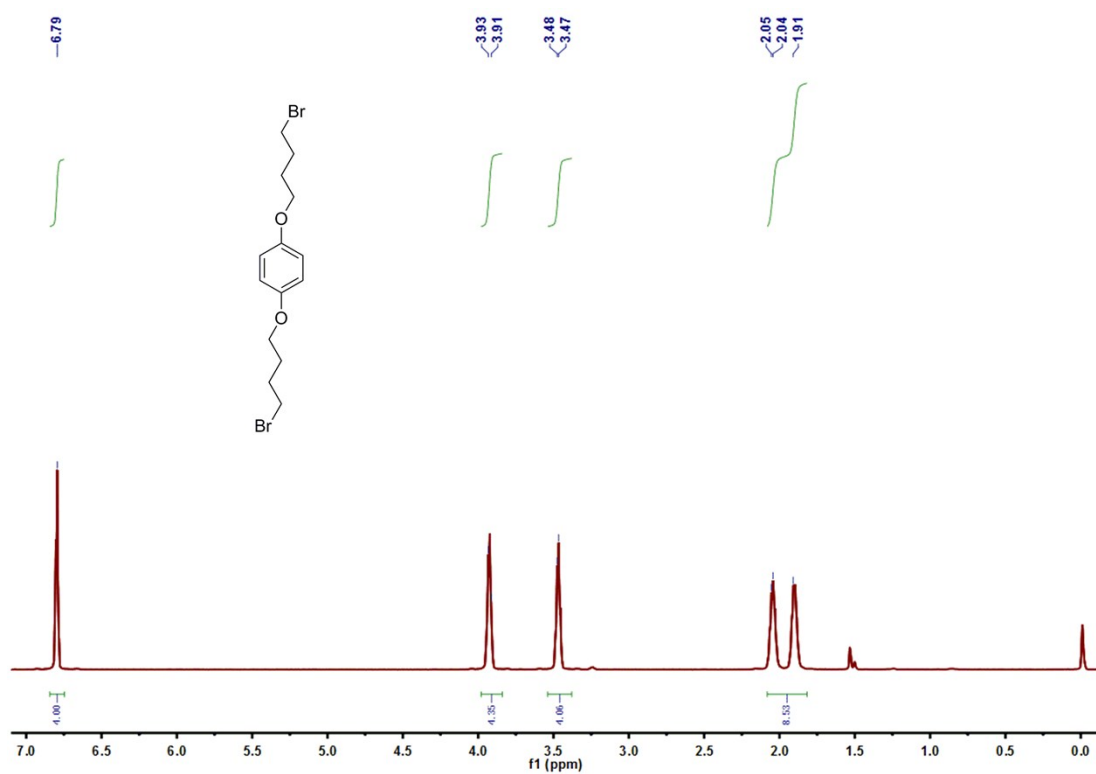


Fig. S14 ¹H NMR (600 MHz, 298K) spectra of compound **1** in CDCl₃.

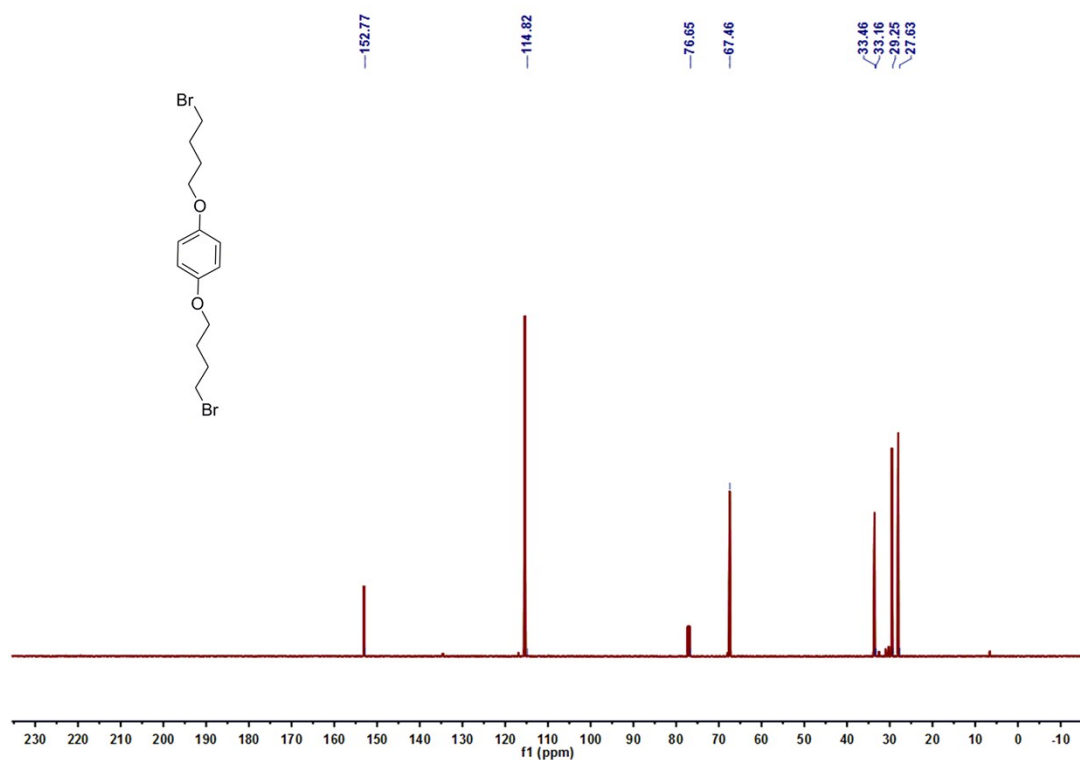


Fig. S15 ¹³C NMR (150 MHz, 298K) spectra of compound **1** in CDCl₃.

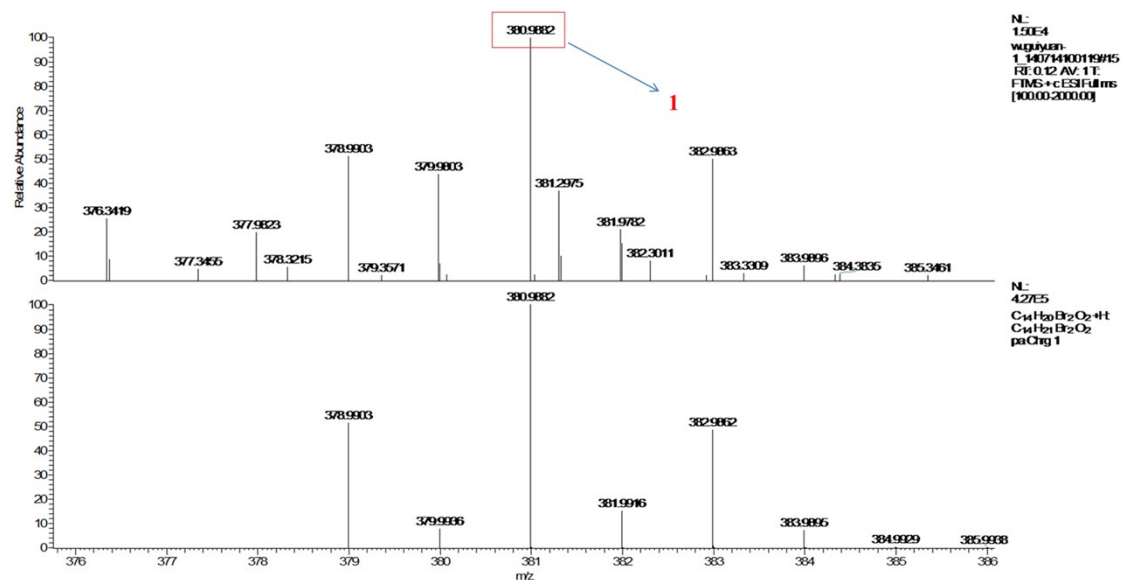


Fig. S16 High resolution electrospray ionization mass spectrum of compound 1.

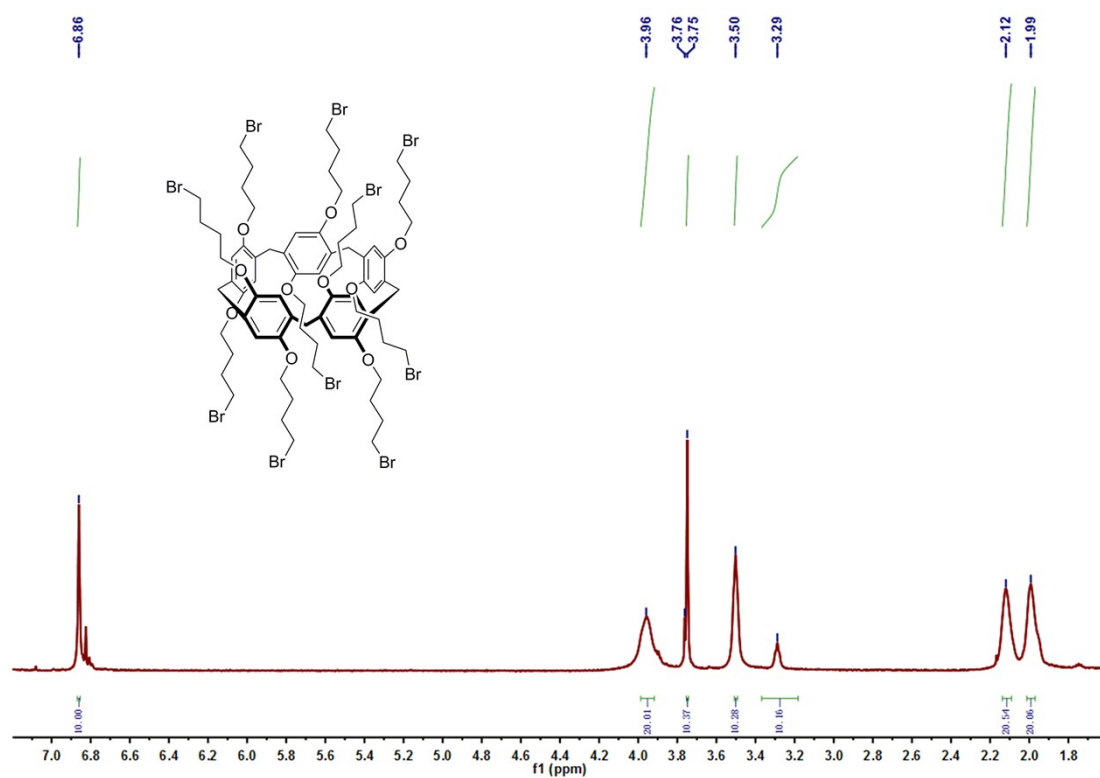


Fig. S17 ¹H NMR (600 MHz) spectra of product 2 in CDCl₃.

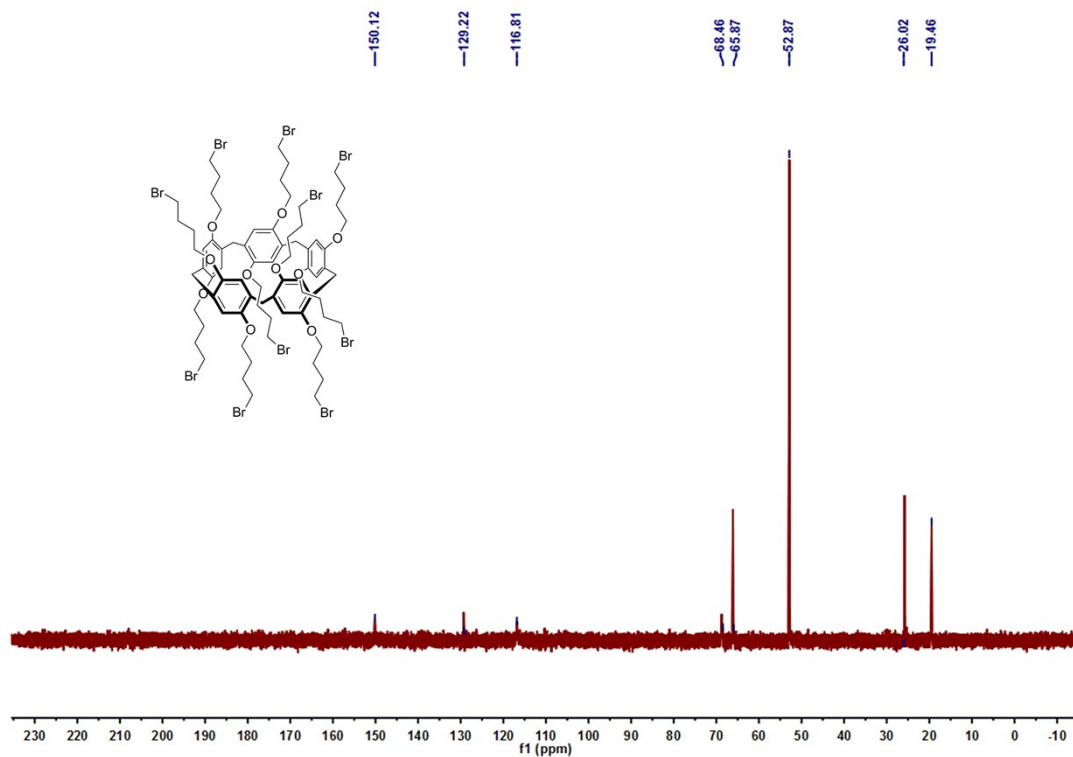


Fig. S18 ^{13}C NMR (150 MHz, 298K) spectra of product **2** in CDCl_3 .

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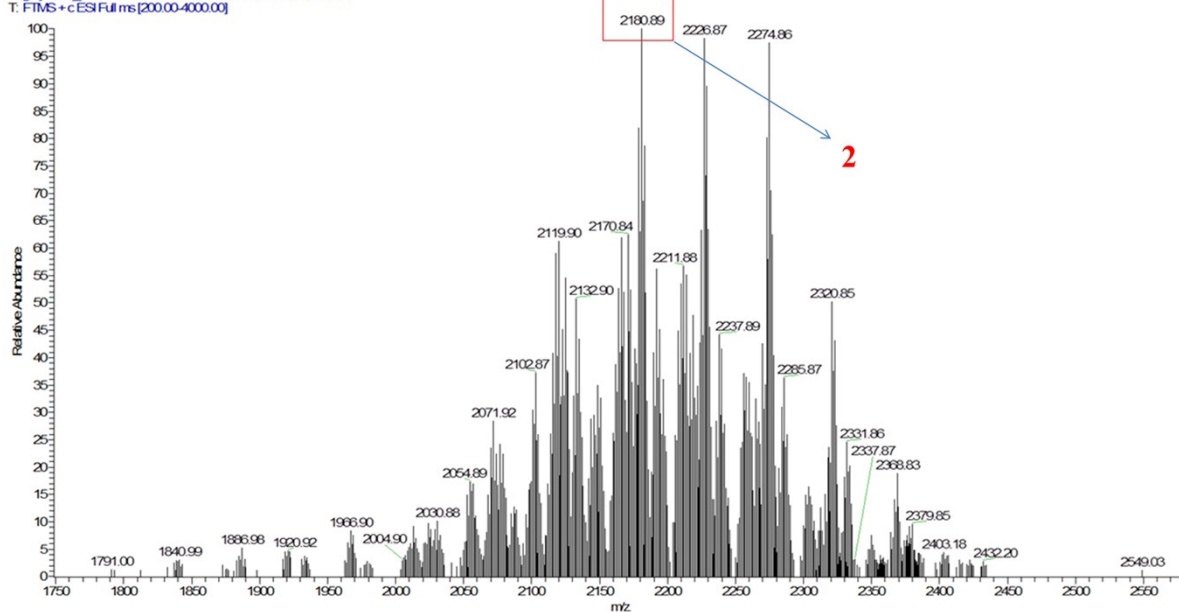


Fig. S19 Electrospray ionization mass spectrum of compound **2**.

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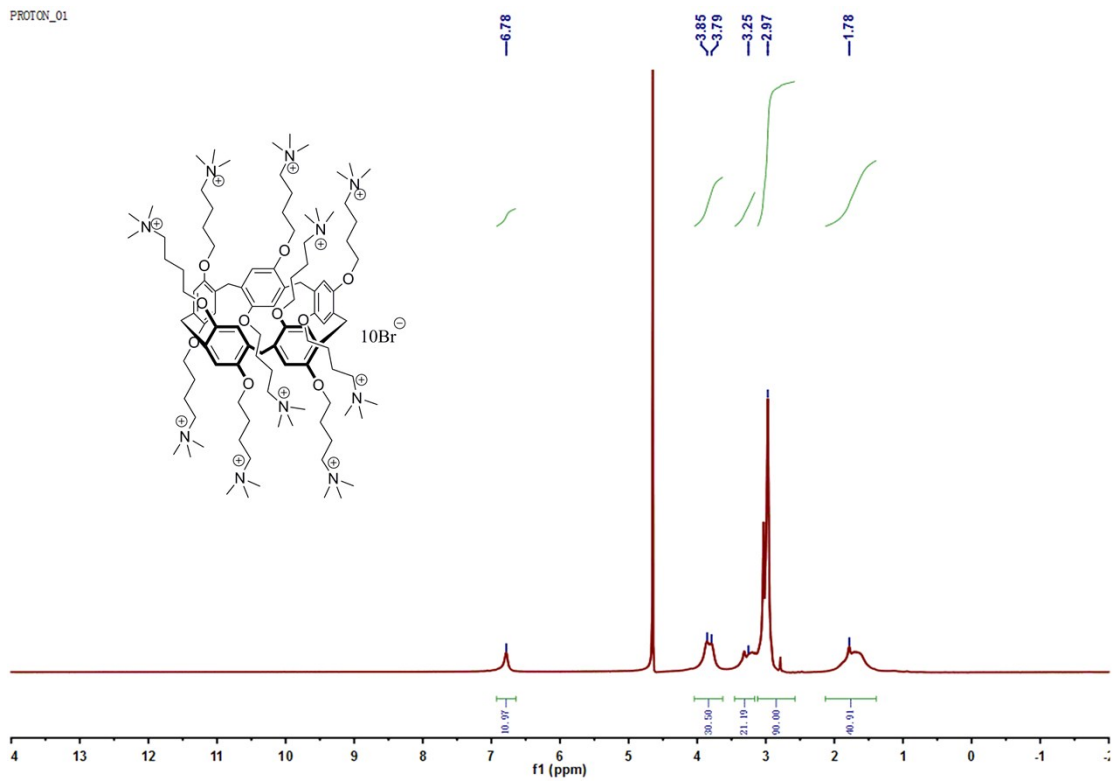


Fig. S20 ^1H NMR (600 MHz, 298K) spectra of product **P5** in D_2O .

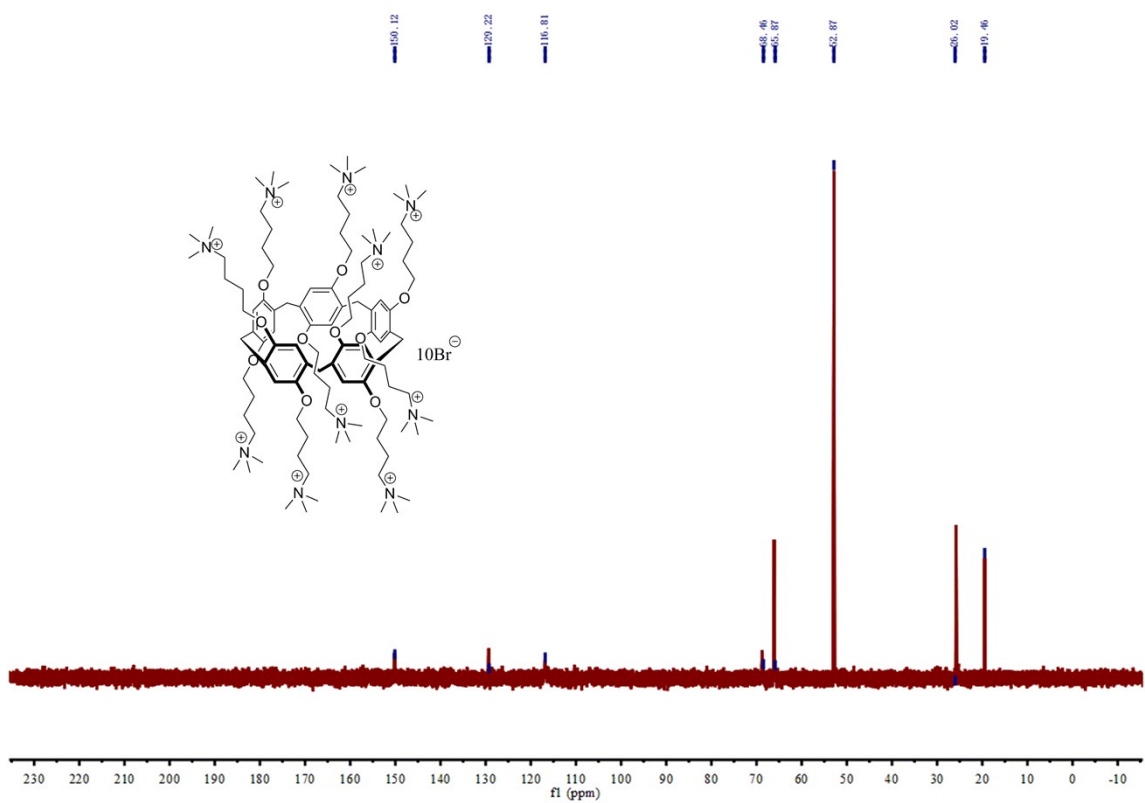


Fig. S21 ^{13}C NMR (150MHz, 298K) spectra of product **P5** in D_2O .

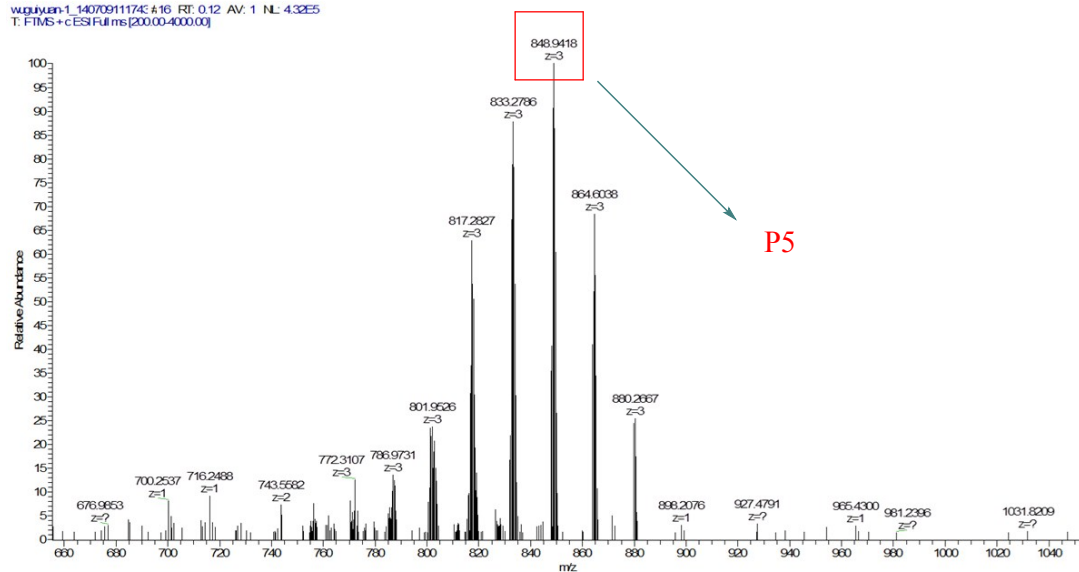
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Fig. S22 High resolution electrospray ionization mass spectrum of P5.