

Supporting Information

In Situ Formation Hg²⁺-Coordinated Fluorescent Nanoparticles through Supramolecular Polymer Network, An Efficient Way for Hg²⁺ Sensing and Separation

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1. Experiment

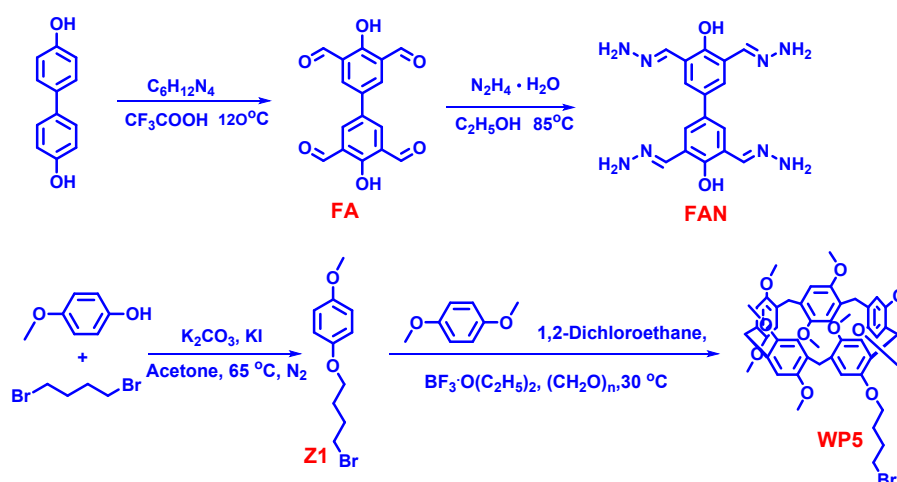
1.1 Materials

All reagents and starting materials were obtained from commercial suppliers and used as received unless otherwise noted. All cations were used as the perchlorate salts, which were purchased from Alfa Aesar and used as received. Fresh double distilled water was used throughout the experiment.

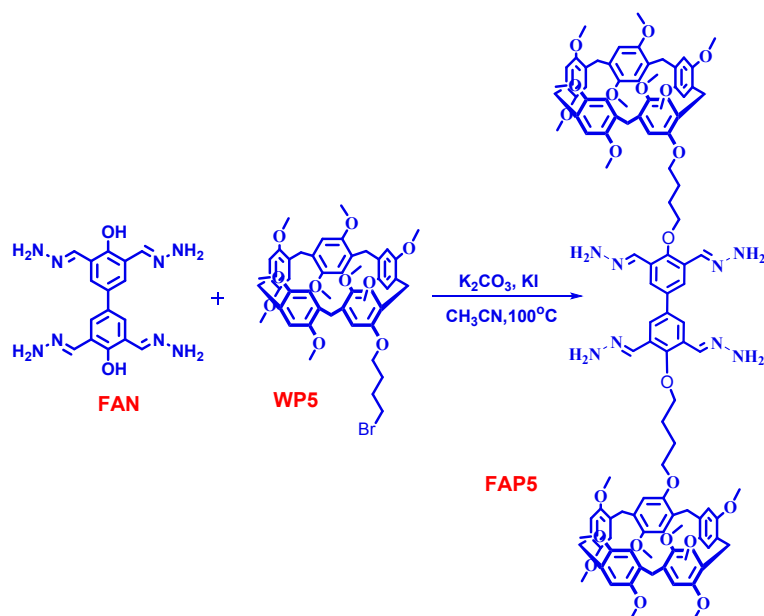
1.2 Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on Varian Mercury 400 and Varian Inova 600 instruments. Mass spectra were recorded on a Bruker Esquire 6000 MS instrument. The morphologies of the **FAP5** were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8kV. Tecani G2 F20 Field emission (FEI, American) transmission electron microscope (TEM). The fluorescent information of the supramolecular polymer was characterized using Laser Scanning Confocal Microscope (LSCM, Olympus Fluoview FV1200). Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

2. Characterization spectra of compound **FAN**, **FAP5**.



Scheme S1. Synthesis of compound **FA**, **FAN**.



Scheme S2. Synthesis of compound **FAP5**.

Synthesis of FA: 4,4'-biphenol (0.84 g, 5.0 mmol) was added to a mixture of hexamethylenetetramine (5.6 g, 40.0 mmol) in CF_3COOH (60 mL), and the reaction mixture was stirred reflux 72 h. After reaction was finished, the solution mixture was cooled and poured into 4M HCl , after decompression and filtration, the crude yellow solid product was obtained. Then the solid crude product was poured into the hot DMSO solution and the yellow compound **FA** was obtained. (1.49 g, 58 %). Mp: $> 280^\circ C$. 1H NMR (400 MHz, $DMSO-d_6$). δ (ppm): 11.68 (s, 2H), 10.34-10.33 (d, 4H), 8.43-8.42 (d, 4H). ^{13}C NMR ($DMSO-d_6$ 151 MHz). δ (ppm): 124.57, 135.05, 161.92, 193.09. ESI-MS m/z: $[M - H]^-$ Calcd for $C_{16}H_{10}O_6$ 298.04, found 297.0405.

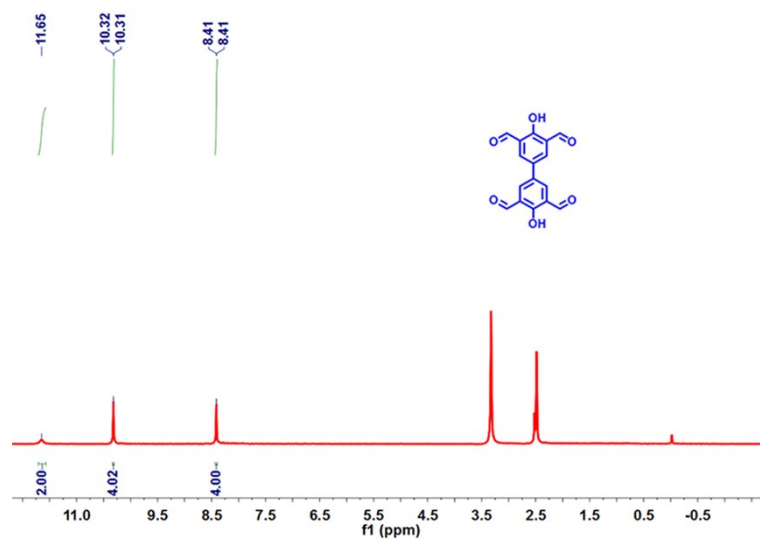


Figure S1 ¹H NMR Spectrum of FA (DMSO-*d*₆, 400 MHz, 298 K).

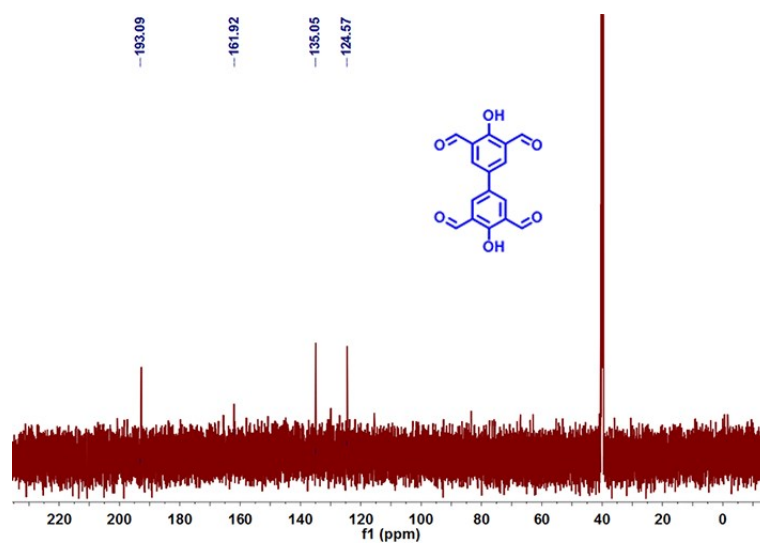


Figure S2 ¹³C NMR Spectrum of FA (DMSO-*d*₆, 151 MHz, 298 K).

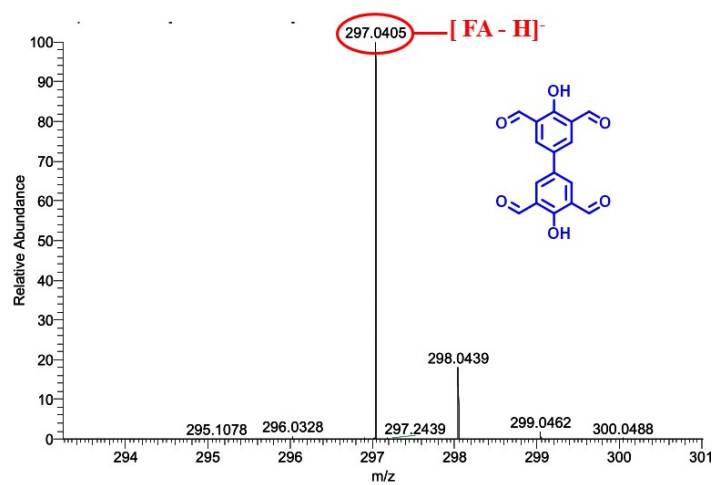


Figure S3. HR-MS Spectrum of FA.

Synthesis of FAN: Compound **FA** (0.98 g, 1.0 mmol) was added to a mixture of compound Hydrazine hydrate (0.40 g, 8 mmol) in C₂H₅OH (50 mL), and the resulting mixture was stirred for 36 h. The solid was filtered and the solvent was removed. The crude product was washed and purified by ethanol to give **FAN** as a white solid. Mp: > 280 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 12.10 (s, 2 H), 8.02 (s, 4 H), 7.56 (s, 4 H), 6.92 (s, 8 H). ¹³C NMR (DMSO-*d*₆ 151 MHz). δ (ppm): 127.12, 128.34, 135.86, 143.4, 158.43. ESI-MS m/z: [M + H]⁺ Calcd for C₁₆H₁₈N₈O₂ 354.16, found 355.1616.

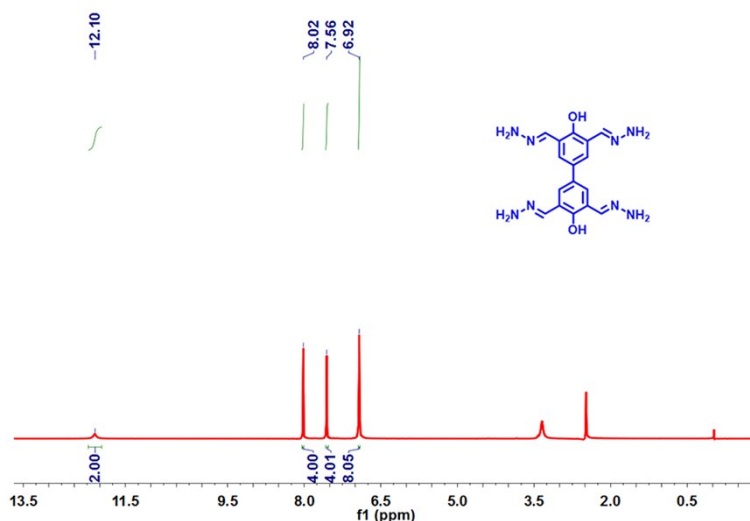


Figure S4. ¹H NMR Spectrum of **FAN** (DMSO-*d*₆, 400 MHz, 298 K).

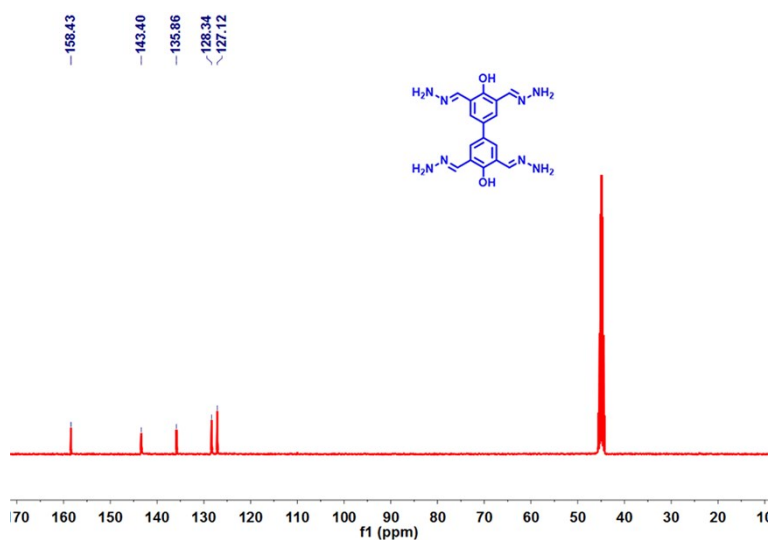


Figure S5. ¹³C NMR Spectrum of **FAN** (DMSO-*d*₆, 151 MHz, 298 K).

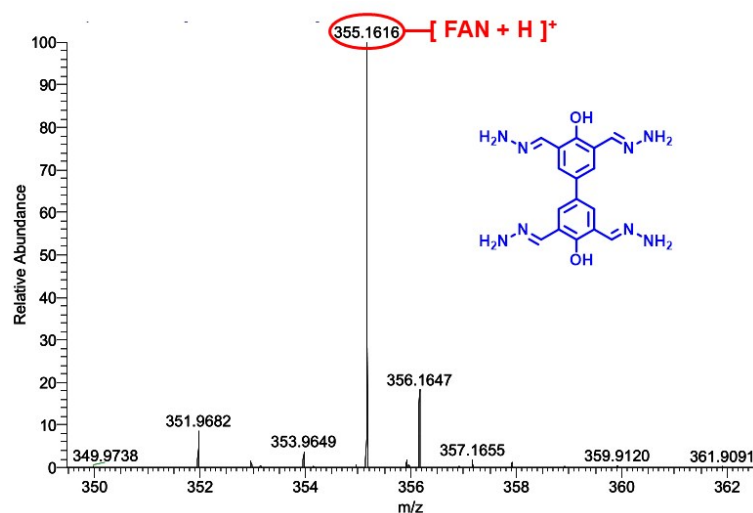


Figure S6. HR-MS Spectrum of **FAN**.

Synthesis of Z1: 4-Methoxyphenol (0.1241 g, 1 mmol) and KI (0.6641 g, 4 mmol) were added to a solution of K_2CO_3 (0.1381 g, 1 mmol) and 1,4-dibromobutane (0.8560 g, 4 mmol) in acetone (150 mL). The mixture was heated under nitrogen atmosphere at reflux at 60 °C for 72 h. The solid was filtered off and the solvent was removed. The residue was recrystallized in dichloromethane and petroleum ethers. The product **Z 1** was collected by filtration, and dried under vacuum (0.2321 g, 94.3 %). Mp: 45°C. 1H NMR (400 MHz, $DMSO-d_6$). δ (ppm): 6.84-6.81 (m, 4H), 3.90-3.88 (m, 2H), 3.67 (s, 3H). 3.56-3.54 (m, 1H), 1.80-1.76 (m, 2H), 1.75-1.72 (m, 2H).

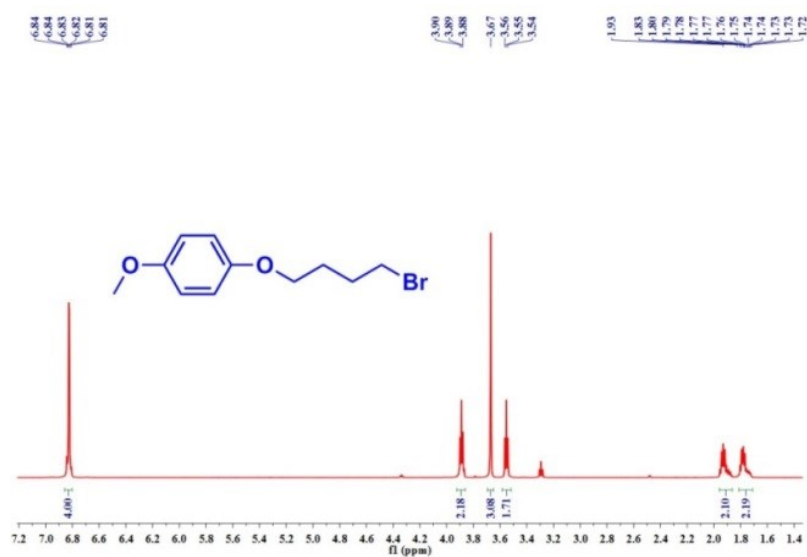


Figure S7. 1H NMR Spectrum of **Z1** ($DMSO-d_6$, 400 MHz, 298 K).

Synthesis of WP5: To a solution of 1,4-dimethoxybenzene (2.7652 g, 20 mmol) and **Z1** (1.225 g, 5 mmol) in 1,2-dichloroethane (200 mL) was added paraformaldehyde (0.7503 g, 25 mmol). Then, boron trifluoride diethyl etherate ($\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$, 4.5 mL, 36 mmol) was added to the solution, and the mixture was stirred at 30°C for 20 min. The solution was poured into water (100 mL) to quench the reaction. The mixture was filtered and the solvent was removed. The residue was dissolved in dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was isolated by column chromatography using ethyl acetate/petroleum ether (v/v 1:30) to give WP5 as a white solid (1.8276 g, 42%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$). δ (ppm): 6.81-6.79 (m, 10H), 3.86-3.85 (m, 2H), 3.68 (m, 37H), 3.51 (m, 2H), 1.84-1.83 (m, 4H). ESI-MS m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{48}\text{H}_{55}\text{O}_{10}\text{Br}$ 870.296, found 870.2961.

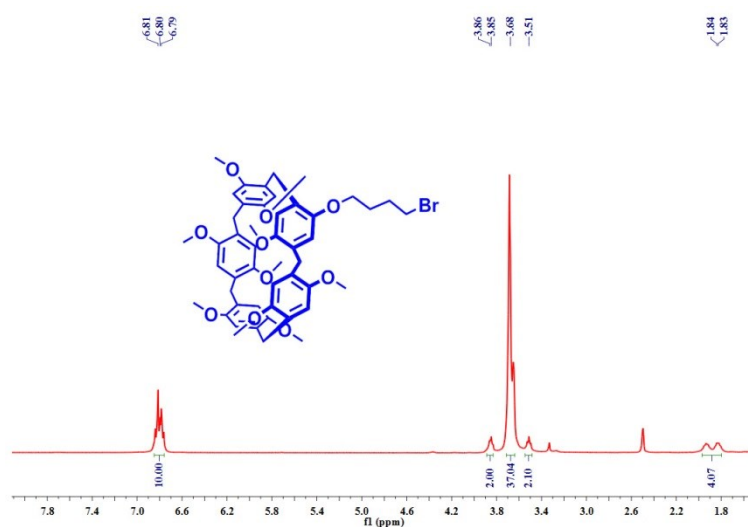


Figure S8. ^1H NMR Spectrum of **WP5** ($\text{DMSO}-d_6$, 400 MHz, 298 K).

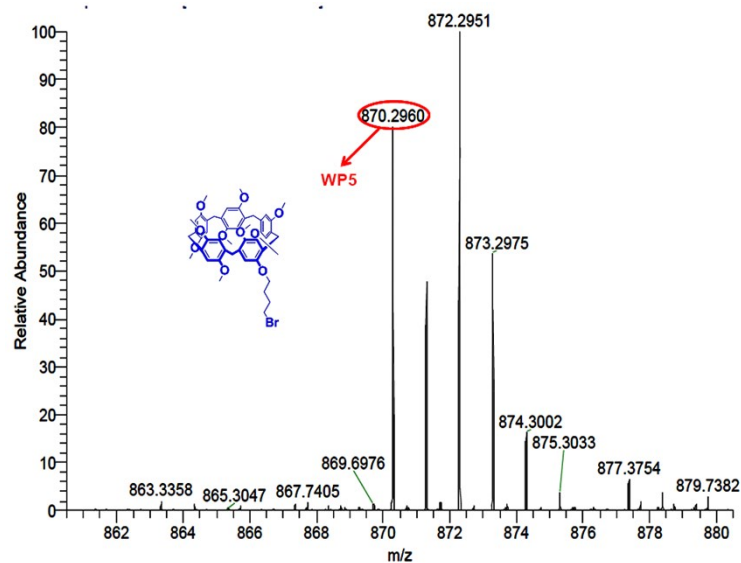


Figure S9. HR-MS Spectrum of **WP5**.

Synthesis of FAP5: Compound FAN (0.3543 g, 1 mmol) and KI (0.3320 g, 2 mmol) were added to a solution of K_2CO_3 (0.2762 g, 2 mmol) and compound WP5 (2.5237 g, 3.5 mmol) in acetonitrile (60 mL), and the resulting mixture was stirred for 48 h. The solid was filtered and the solvent was removed. The crude product was washed and purified by acetonitrile to give FAP5 as a orange solid (1.3941 g, 72%). Mp: $> 280\text{ }^{\circ}C$. 1H NMR (400 MHz, $DMSO-d_6$). δ (ppm): 9.05-8.98(m, 4H), 8.07-8.02(m, 8H), 7.57-7.55 (m, 4H), 6.91-6.76 (m, 20H), 3.84-3.63 (m, 24H), 3.49-3.45 (m, 54H), 2.05-2.03 (m, 4H), 1.26-1.01(m, 8H). ^{13}C NMR ($DMSO-d_6$ 151 MHz). δ (ppm): 29.64, 31.25, 56.32, 67.73, 113.93, 114.69, 117.89, 126.80, 127.96, 128.17, 135.58, 145.28, 147.93, 149.84, 150.55, 162.95. ESI-MS m/z: $[M - H]^-$ Calcd for $C_{112}H_{126}N_8O_{22}$ 1933.93, found 1933.9319.

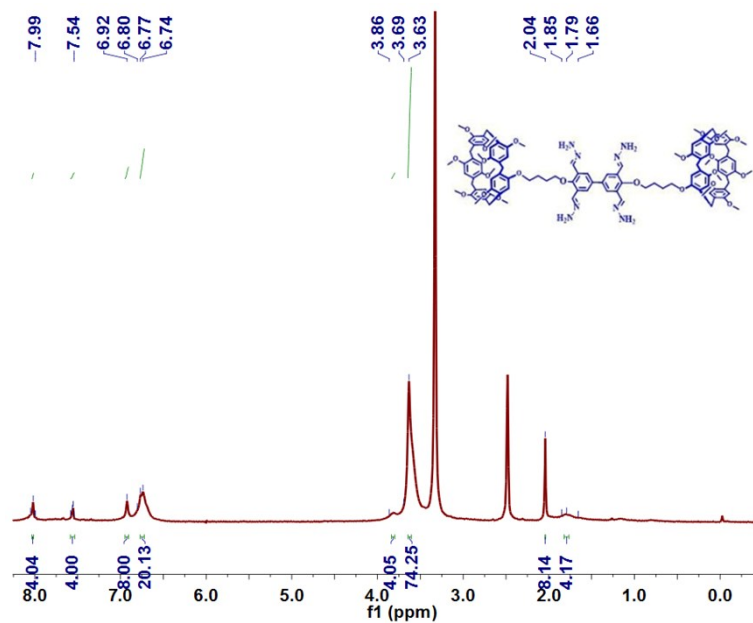


Figure S10. ¹H NMR Spectrum of **FAP5** (DMSO-*d*₆, 400 MHz, 298 K).

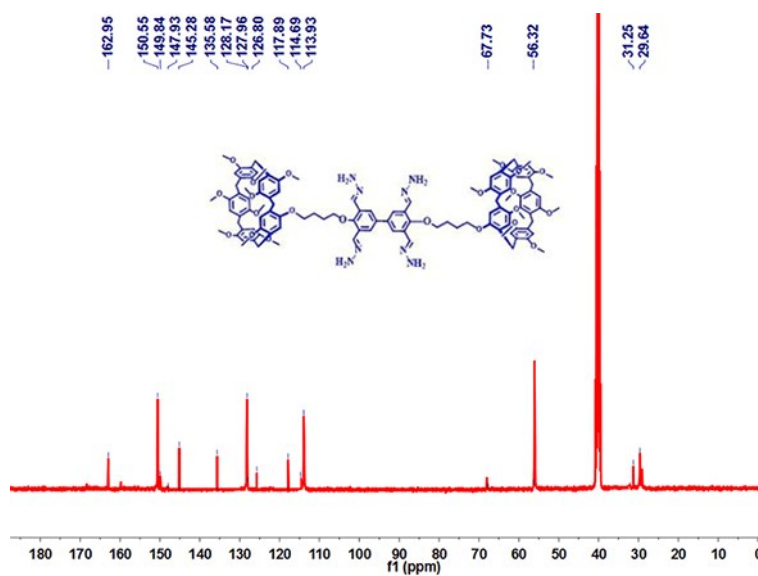


Figure S11. ¹³C NMR Spectrum of **FAP5** (DMSO-*d*₆, 151 MHz, 298 K).

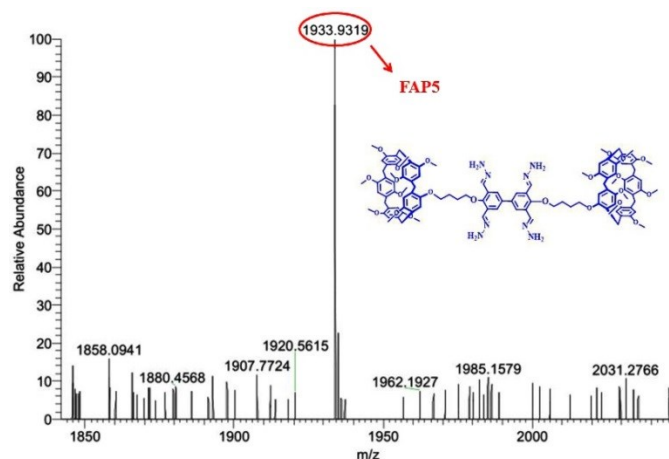
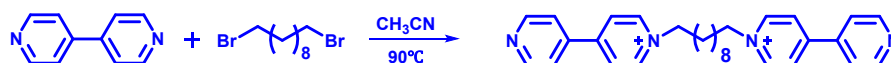


Figure S12. HR-MS Spectrum of **FAP5**.

3. Characterization spectra of compound **BN**.



Synthesis of BN: A solution of 1,10-dibromodecane (1.500 g, 5 mmol) in CH_3CN (25 mL) was added dropwise into a stirred solution of 4,4'-bipyridine (2.186 g, 14 mmol) in CH_3CN (50 mL) and refluxed over night. After it cooled, the suspension was filtered. The solid was washed with CH_3CN and then dried in an oven to afford a pale green solid **BN** (1.946 g, 86%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$). δ (ppm): 9.26-9.25(d, 4H), 8.85-8.84(m, 4H), 8.64-8.63 (m, 4H), 8.04-8.03 (m, 4H), 4.64-4.62 (m, 4H), 1.93-1.95 (m, 4H), 1.28-1.24 (m, 12H). ^{13}C NMR ($\text{DMSO}-d_6$ 151 MHz). δ (ppm): 25.87, 28.84, 29.15, 31.22, 60.67, 122.39, 125.83, 141.31, 145.77, 151.36, 152.56. ESI-MS m/z : $[\text{M}]^{2+}$ Calcd for $\text{C}_{30}\text{H}_{46}\text{N}_4^{2+}$ 226.146, found 226.1464.

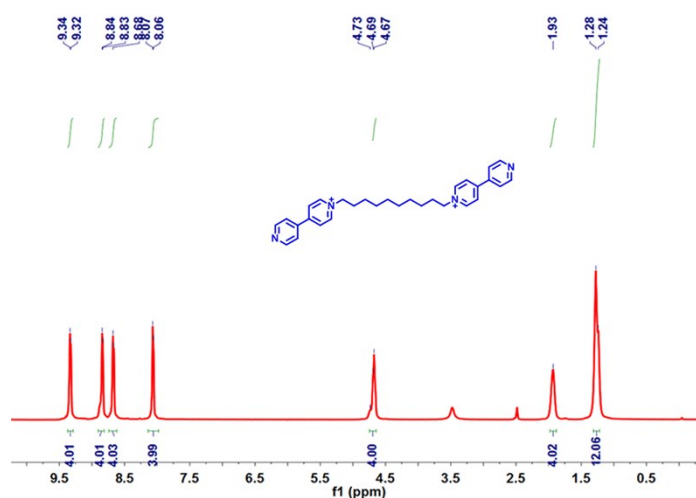


Figure S13. ^1H NMR Spectrum of **BN** ($\text{DMSO}-d_6$, 400 MHz, 298 K).

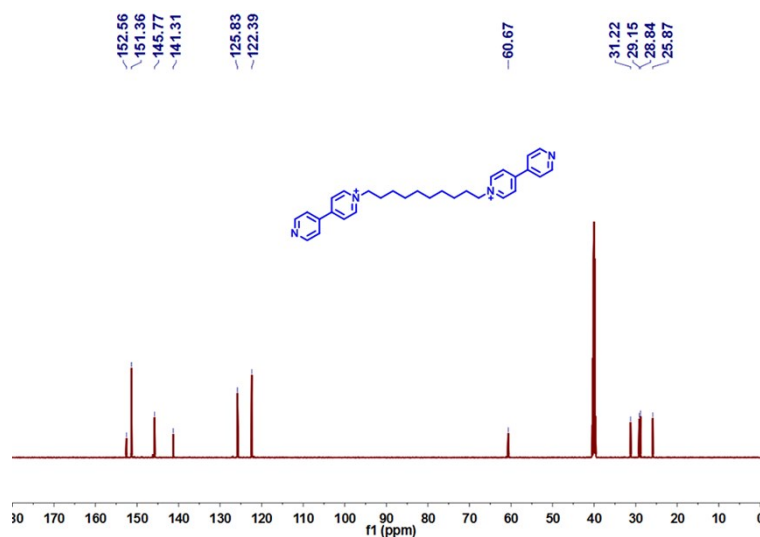


Figure S14. ¹³C NMR Spectrum of BN (DMSO-*d*₆, 151 MHz, 298 K).

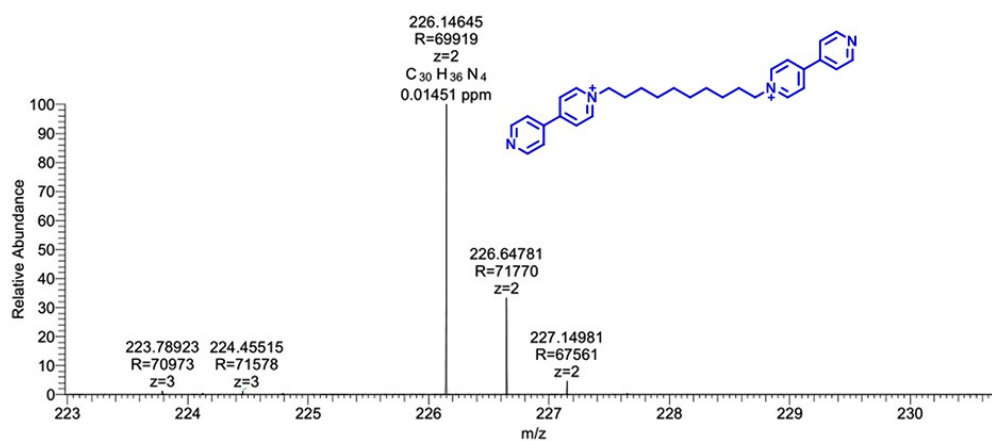


Figure S15. HR-MS Spectrum of BN.

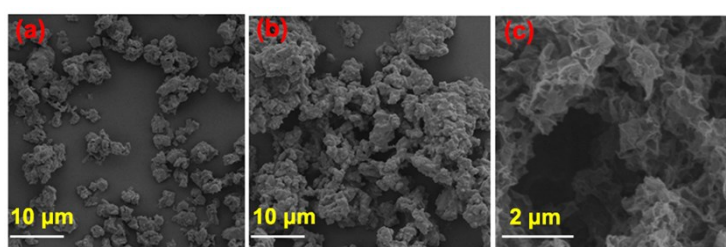


Figure S16. Representative SEM images showing the morphology of (a) FAP5, (b) BN, (c) FAP5-BN.

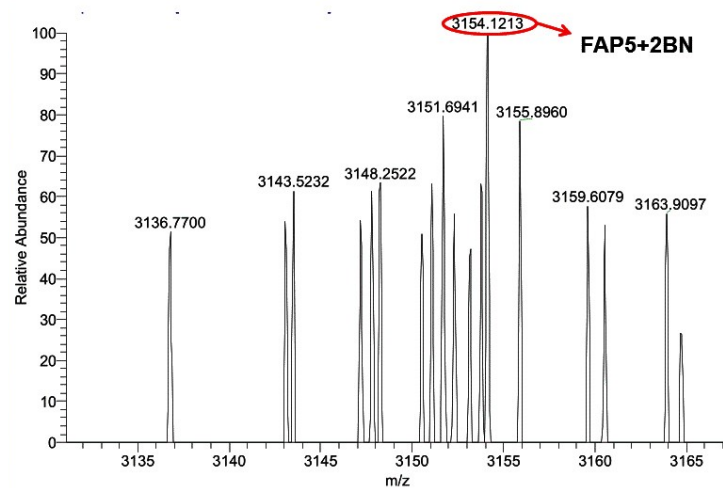


Figure S17. ESI-MS spectrum of the complex formed between **FAP5** and **BN**.

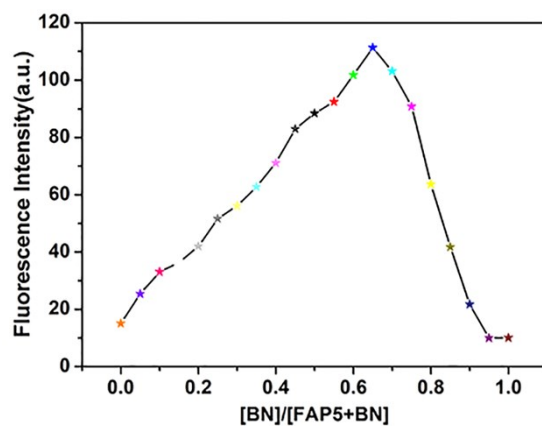
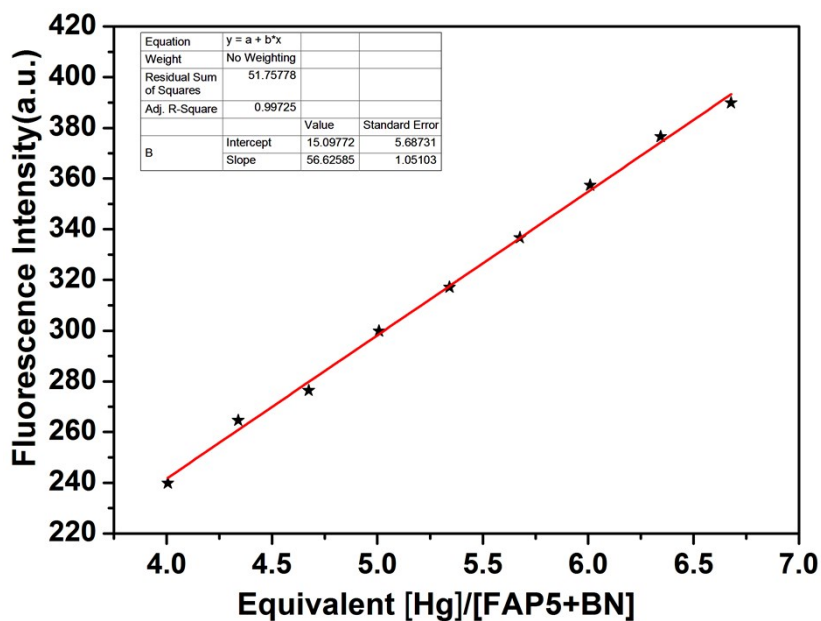


Figure S18. The Job plot showed a 2:1 stoichiometry between **BN** and **FAP5**.

$$\varphi_f = \frac{n_f^2}{n_s^2} \frac{A_s D_f}{A_f D_s} \varphi_s \quad (A \leq 0.05)$$

Figure S19. Fluorescence quantum yield expression of **FAP5-BN-Hg**.



Linear Equation: $Y = 56.6259 X + 15.0977$ $R^2 = 0.9972$

$$S = 5.6626 \times 10^7 \quad \delta = \sqrt{\frac{\sum(F - \bar{F})^2}{(N - 1)}} = 1.9503 \quad (N = 20) \quad K = 3$$

$$LOD = K \times \delta / S = 1.033 \times 10^{-7} \text{ M}$$

Figure S20. Plot of the fluorescence intensity at 400 nm for a mixture of the sensor FAP5-BN and Hg^{2+} in DMSO:H₂O (3:7 v/v) solution.

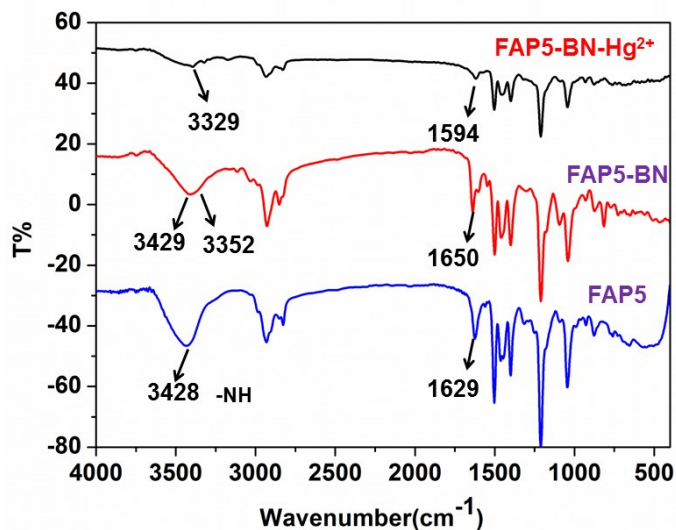


Figure S21. IR spectra of FAP5, FAP5-BN and FAP5-BN-Hg.

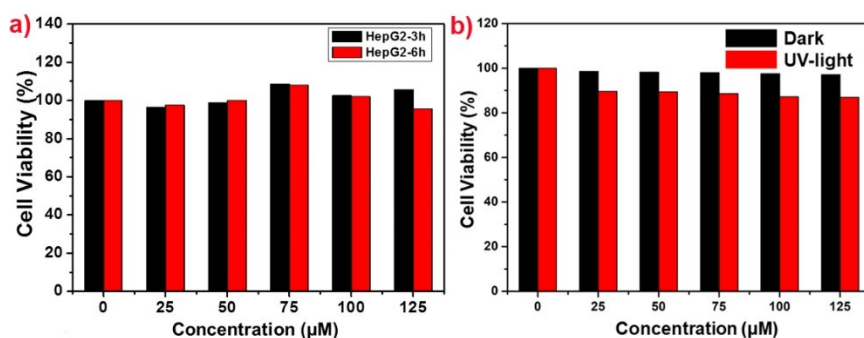


Figure S22. Cell viabilities (a) and light-cytotoxicity (b) of HepG2 cells treated with different concentrations of **FAP5-BN** by MTT assay.

$$\text{PIF} = \text{EC}_{50} (-\text{UVA}) / \text{EC}_{50} (+\text{UVA})^{[6]}$$

$$\text{PIF} = 1.83$$

The host **FAP5** and guest **BN** are dissolved in DMSO solution so that host and guest compounds are assembled into a supramolecular polymer network in solution. Then, removal of the solvent to obtain **FAP5-BN** solid powder. The **FAP5-BN** powder (1.10 mg) was added to the dilute aqueous solution of Hg^{2+} ($c = 1 \times 10^{-4}$ M). Then, the mixtures were stirred at room temperature for 24 h, the precipitates were separated by centrifugation (1000 r min^{-1} , 5 min). Finally, by the Inductively Coupled Plasma (ICP) analysis, the residual concentration of Hg^{2+} in water was about 0.412 ppm (Table S1). ICP analysis confirmed that the separation rate of the **FAP5-BN** for Hg^{2+} about was 99.1%.

Table S1. The ICP date of **FAP5-BN** with Hg^{2+}

Ion	Initial concentration (M)	Residual concentration (M)	Absorbing rate %
Hg^{2+}	1.0×10^{-4}	9.0×10^{-7}	99.1%

Table S2. Comparison of the LODs and adsorption rates of different organic materials for Hg^{2+}

Refs	Solvent	LOD (nM)	adsorping rate %
1	HEPES buffer	150	--
2	$\text{CH}_3\text{CN/PBS}$	770	--

3	CH ₃ CN-H ₂ O (1:1)	1770	--
4	MeCN-H ₂ O (8:2)	2160	--
5	Chloroform/acetone (1;4)	300	90%
This Work	Aqueous solution	103	99.1%

Notes and references

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