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Supporting Information

Novel 2-(hydroxy)-naphthyl imino functionalized pillar[5]arene: A highly efficient supramolecular sensor for tandem fluorescence detection of Fe^{3+} and F^- and facile separation of Fe^{3+}

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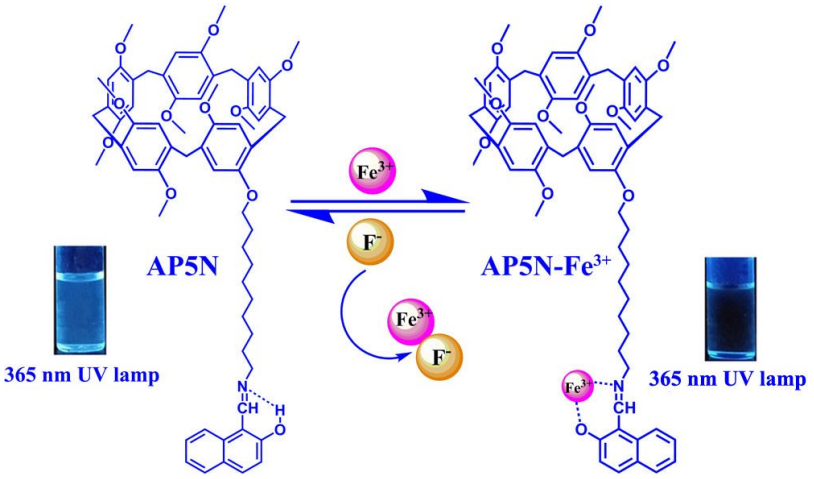
Table S1. The ICP Date of Supramolecular Sensor of **AP5N** with Fe^{3+}.



Scheme S1 Chemical structure of **AP5N** and proposed sensing mechanism of **AP5N** for Fe^{3+} and F^-.

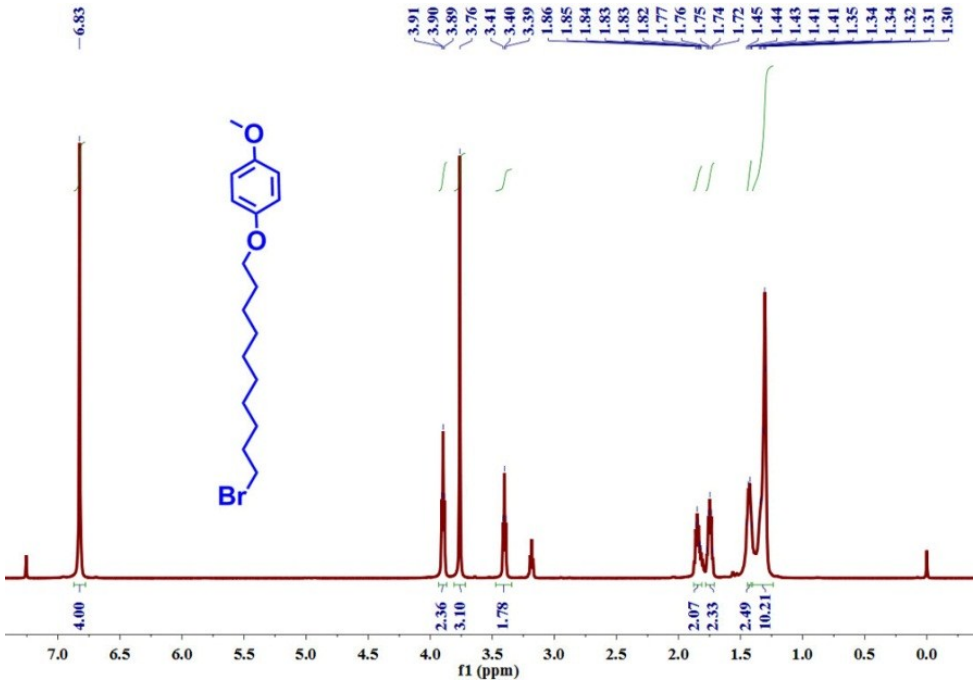


Fig. S1 ^{1}H NMR spectrum of compound **P** in $CDCl_3$.

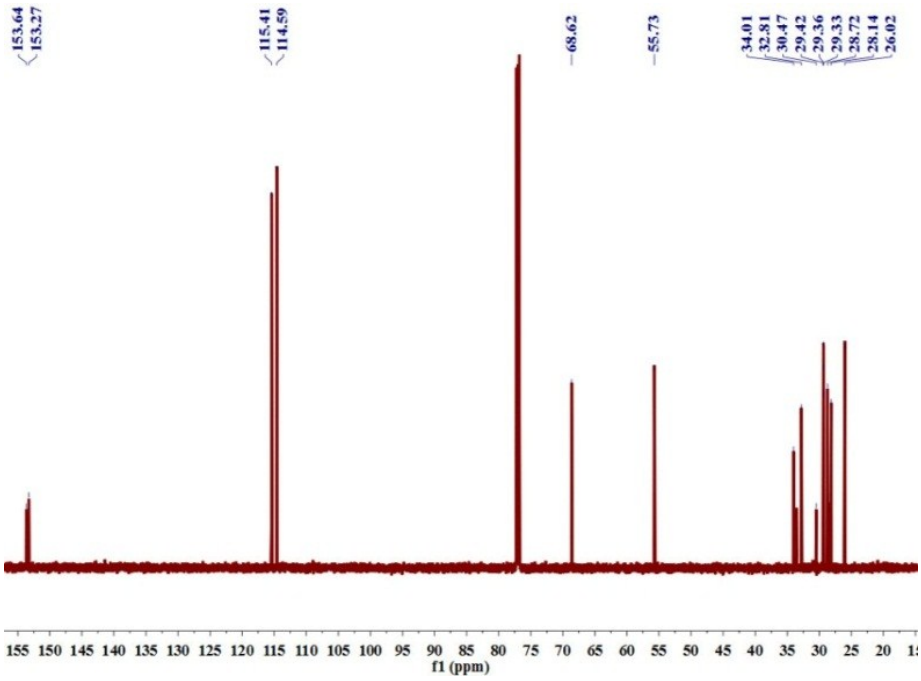


Fig. S2 ^{13}C NMR spectrum of compound **P** in $CDCl_3$.

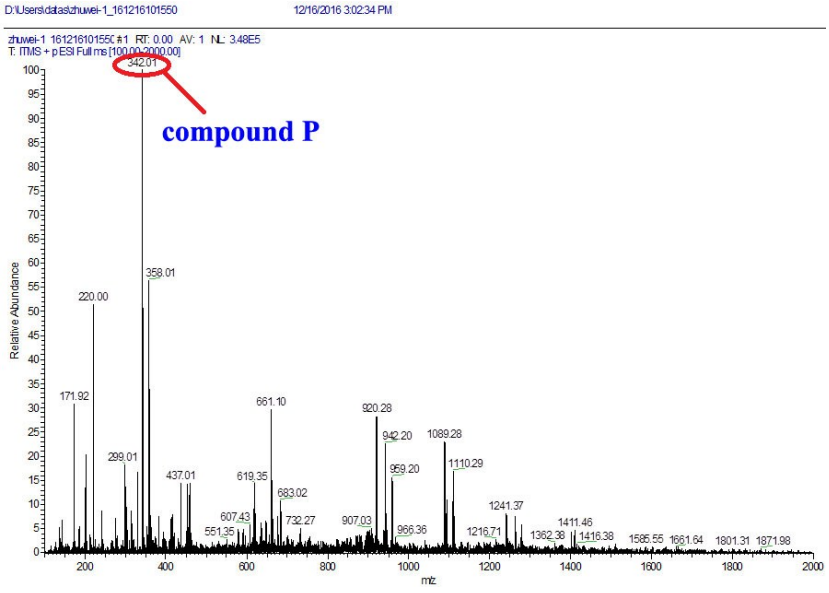


Fig. S3 High resolution ESI-MS data of compound **P**.

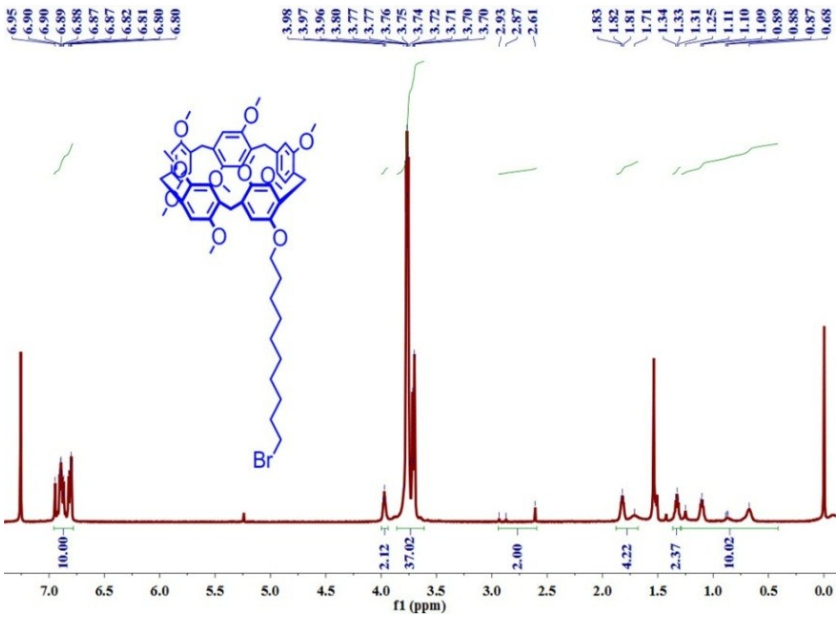


Fig. S4. ^{1}H NMR spectrum of compound **P5** in $CDCl_3$.

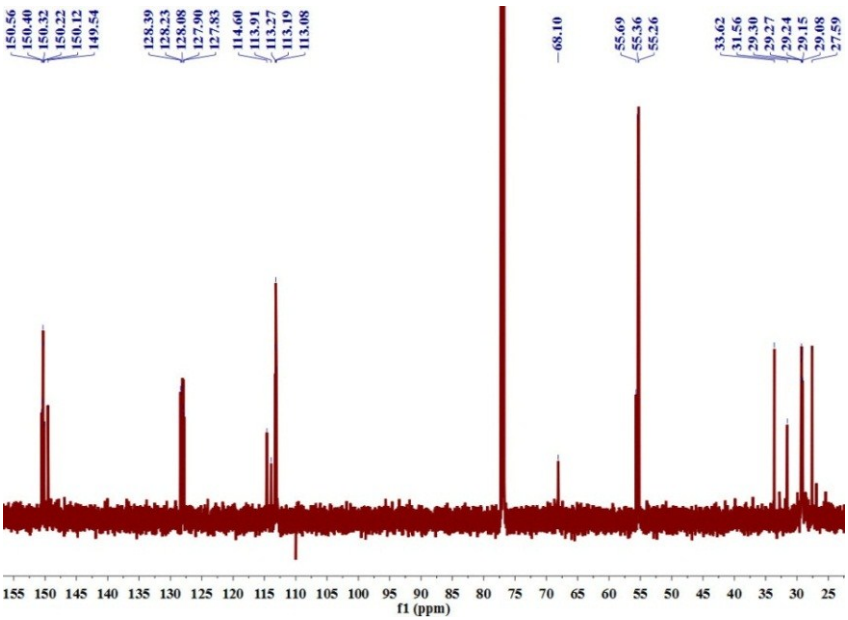


Fig. S5 ^{13}C NMR spectrum of compound **P5** in $CDCl_3$.

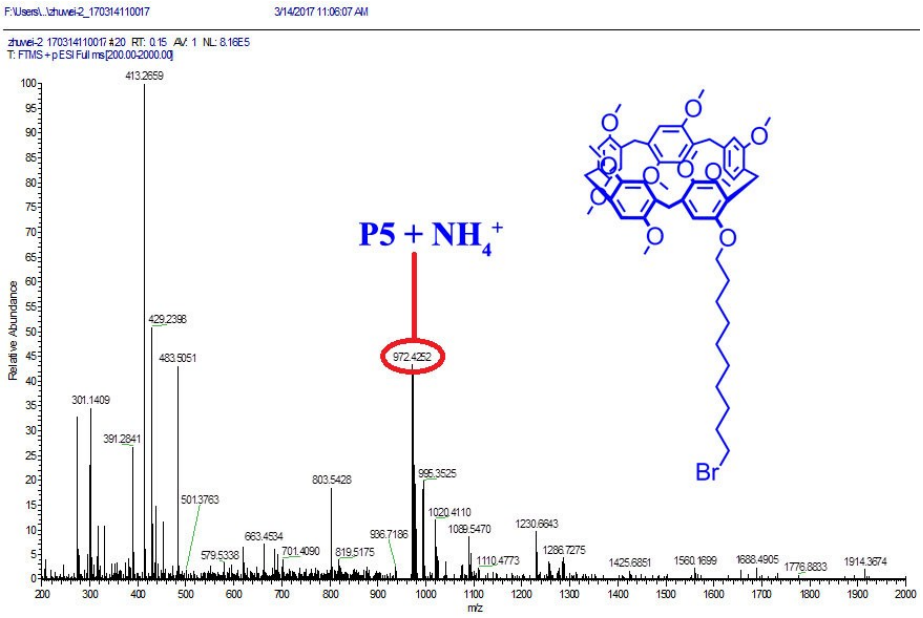


Fig. S6 High resolution ESI-MS data of compound **P5**.

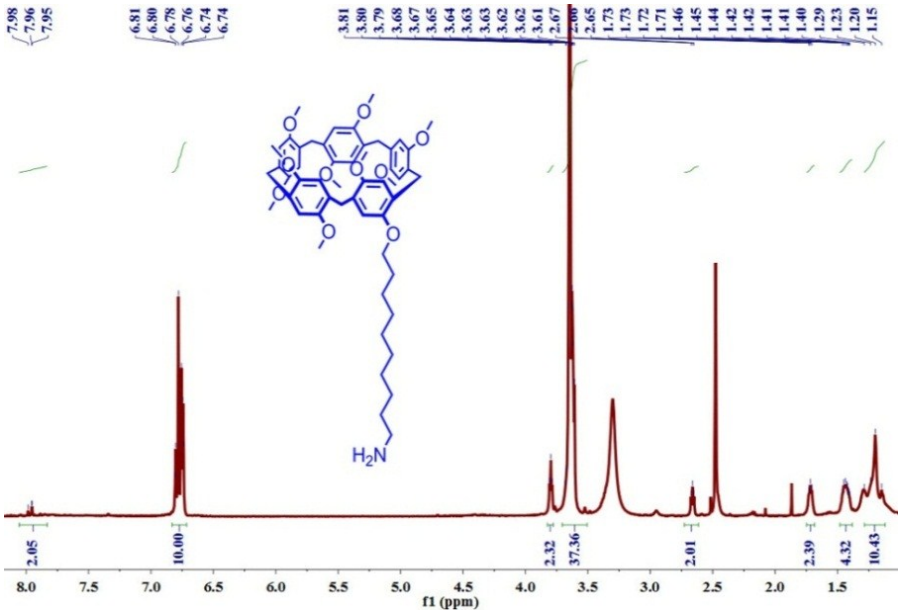


Fig. S7 ^{1}H NMR spectrum of compound **P5N** in DMSO-d_6.

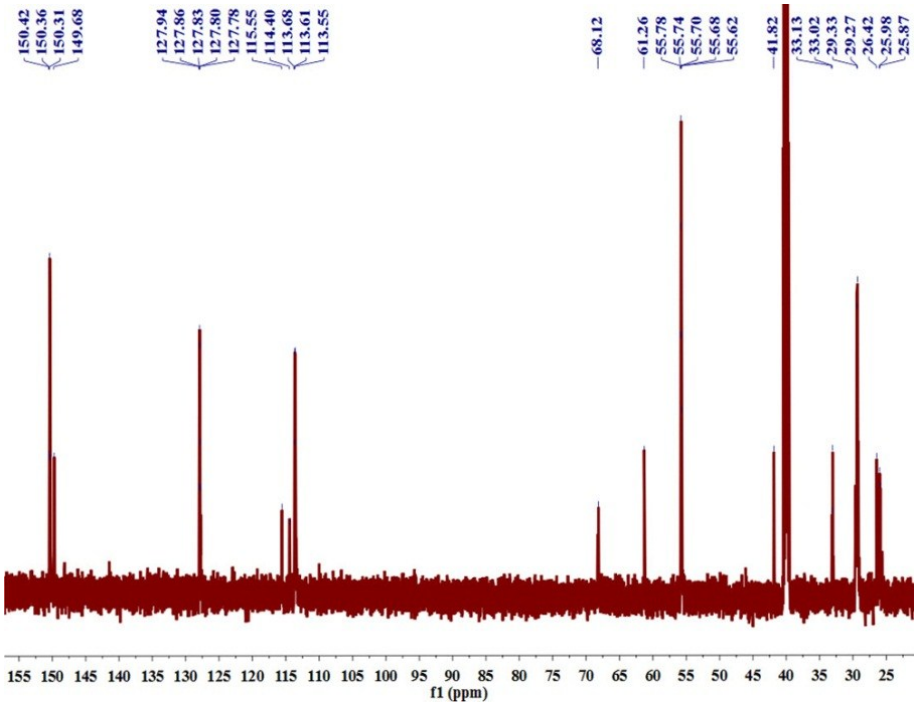


Fig. S8 ^{13}C NMR spectrum of compound **P5N** in DMSO-d_6.

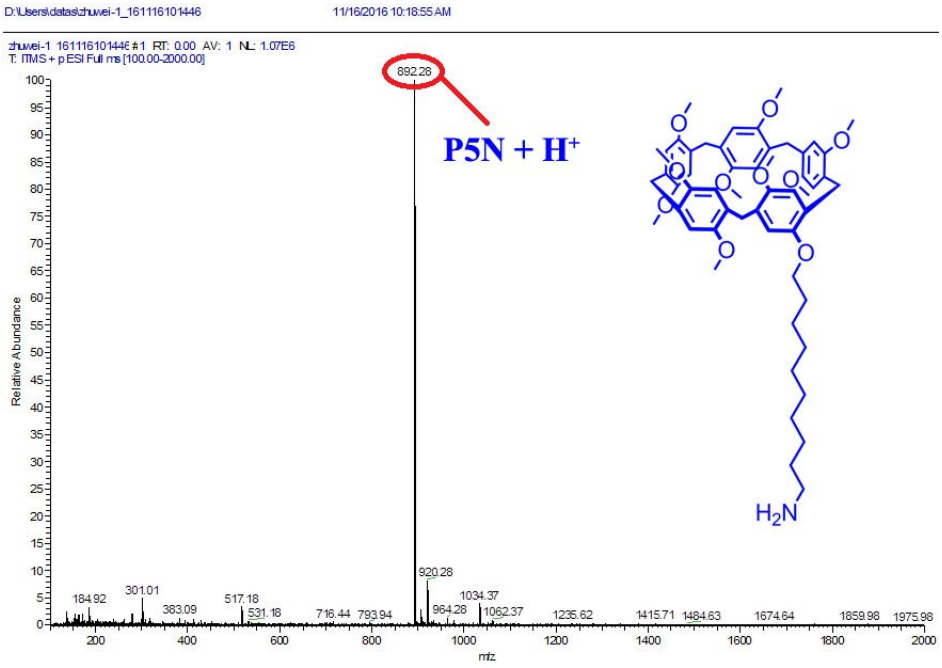


Fig. S9 High resolution ESI-MS data of compound **P5N**.

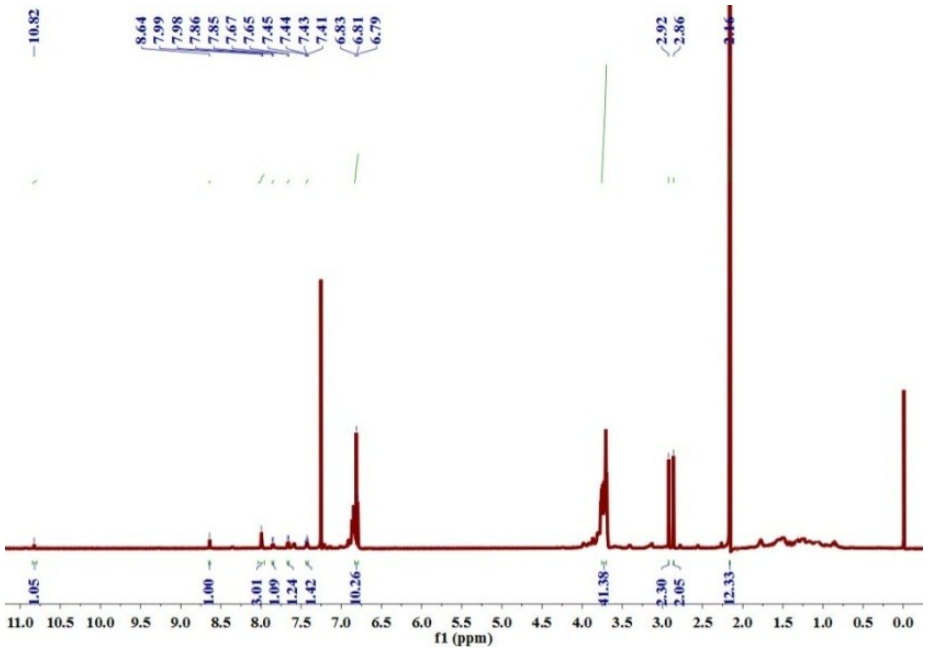


Fig. S10 ^{1}H NMR spectrum of compound **AP5N** in $CDCl_3$.

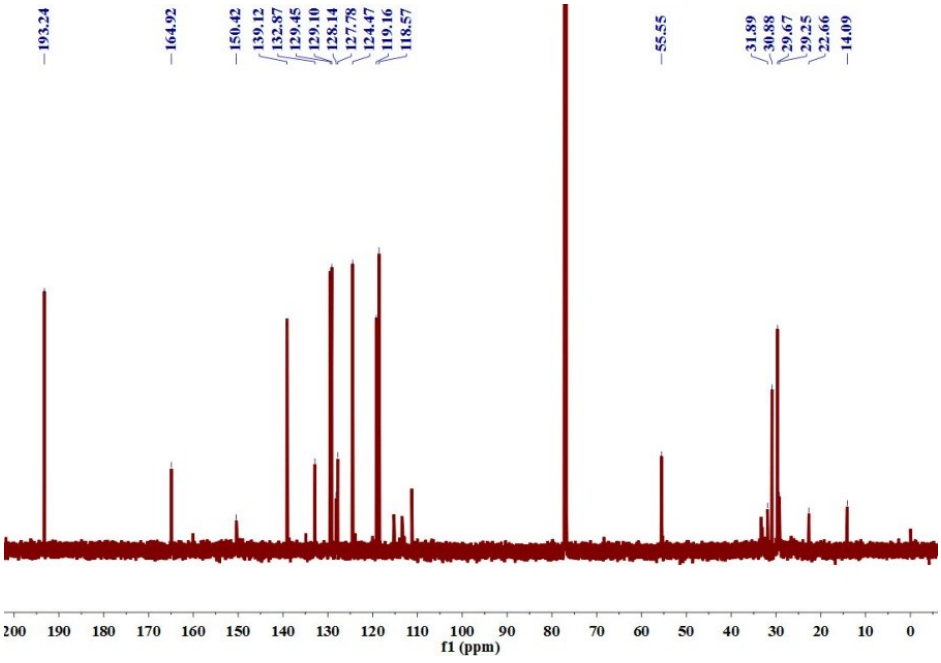


Fig. S11 ^{13}C NMR spectrum of compound A**P5N** in $CDCl_3$.

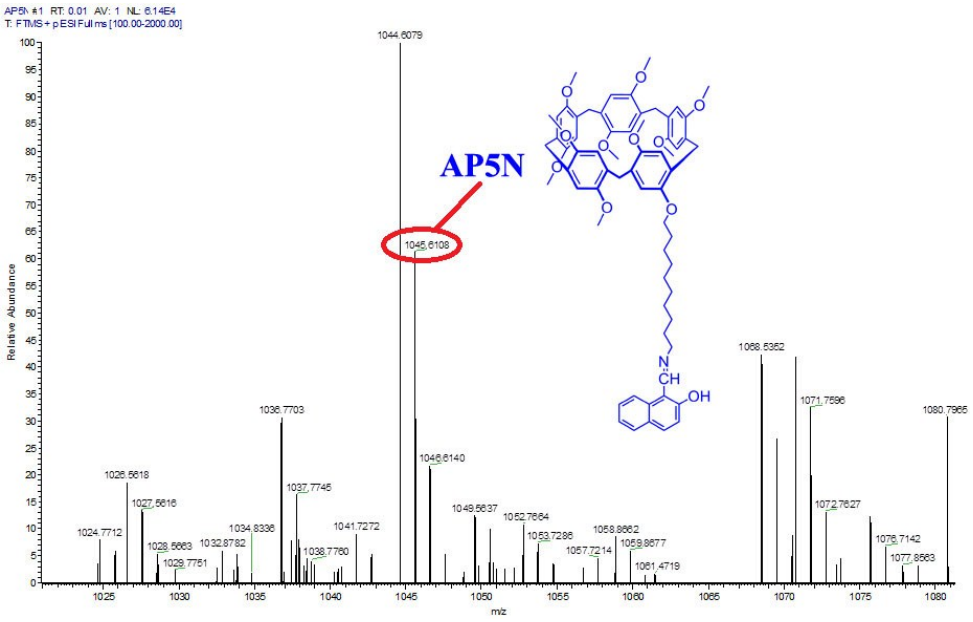
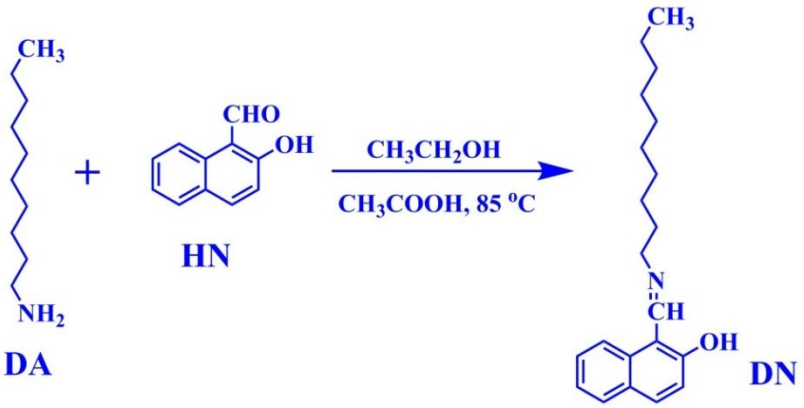


Fig. S12 High resolution ESI-MS data of compound **AP5N**.

Synthesis and characterization of **ND:**

To a 100 mL round bottom flask, compound **DN** (0.12 g, 1.2 mmol) and 2-hydroxy-1-naphthaldehyde (0.17 g, 1.0 mmol) were dissolved in 30 mL absolute ethanol. 3 mL acetic acid was then added dropwise with vigorous stirring at room temperature. After the addition, the reaction mixture was stirred under reflux for 12 h at 85℃. After completion of the reaction, the crude product was purified by column chromatography using petroleum ether/ethyl acetate (V/V = 40:1) as the eluent, the **DN** as a yellow solid (0.24g, yield 75%) was isolated. Mp: 60-62℃. ^{1}H NMR ($CDCl_3$, 600 MHz), δ/ppm: 13.15 (s, 1H), 10.82 (s, 1H), 8.36-8.34 (d, *J* = 8.5 Hz, 1H), 7.99-7.97 (d, *J* = 8.1 Hz, 1H), 7.81-7.79 (d, *J* = 8.1 Hz, 1H), 7.63-7.60 (m, 1H), 7.45-7.42 (m, 1H), 7.15-7.14 (d, *J* = 9.1 Hz, 1H), 4.11-3.63 (m, 2H), 2.31-1.74 (m, 2H), 1.52-0.87 (m, 14H), 0.07-0.06 (t, *J* = 3H). ^{13}C NMR ($CDCl_3$, 151 MHz), δ/ppm: 193.25, 164.93, 139.13, 132.88, 129.46, 129.10, 127.79, 124.48, 119.17, 118.58, 111.27, 29.90. ESI-MS m/z: calcd for $C_{21}H_{30}NO$ [**DN** + H]$^{+}$: 312.2327; found: 312.2314.



Scheme S2 Synthesis of compound **DN**.

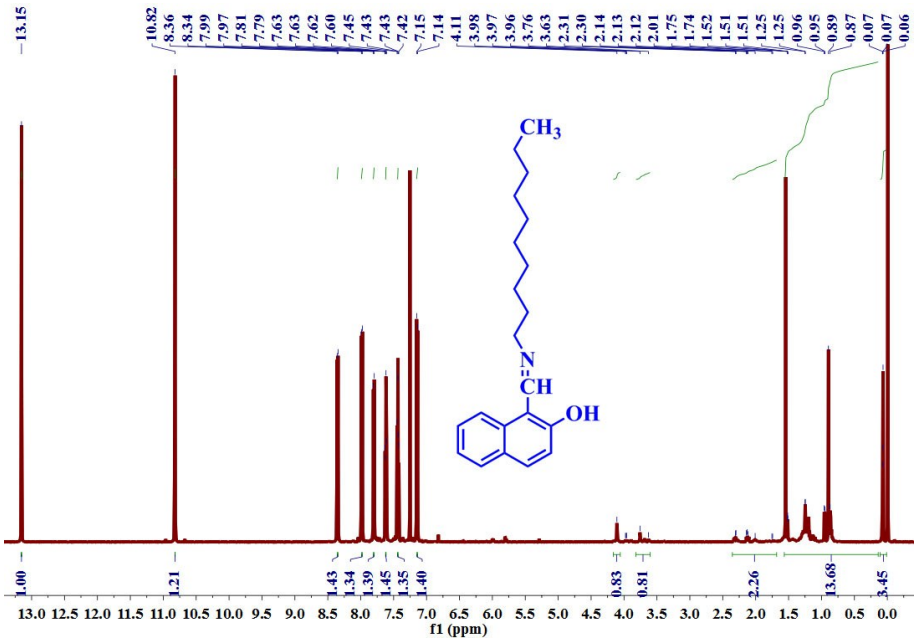


Fig. S13 ^{1}H NMR spectrum of compound **DN** in $CDCl_3$.

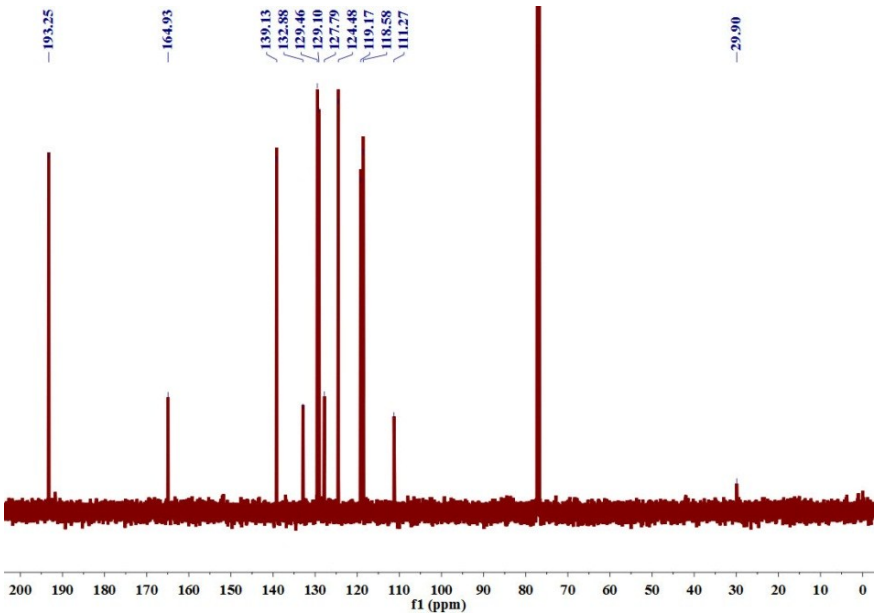


Fig. S14 ^{13}C NMR spectrum of compound **DN** in $CDCl_3$.

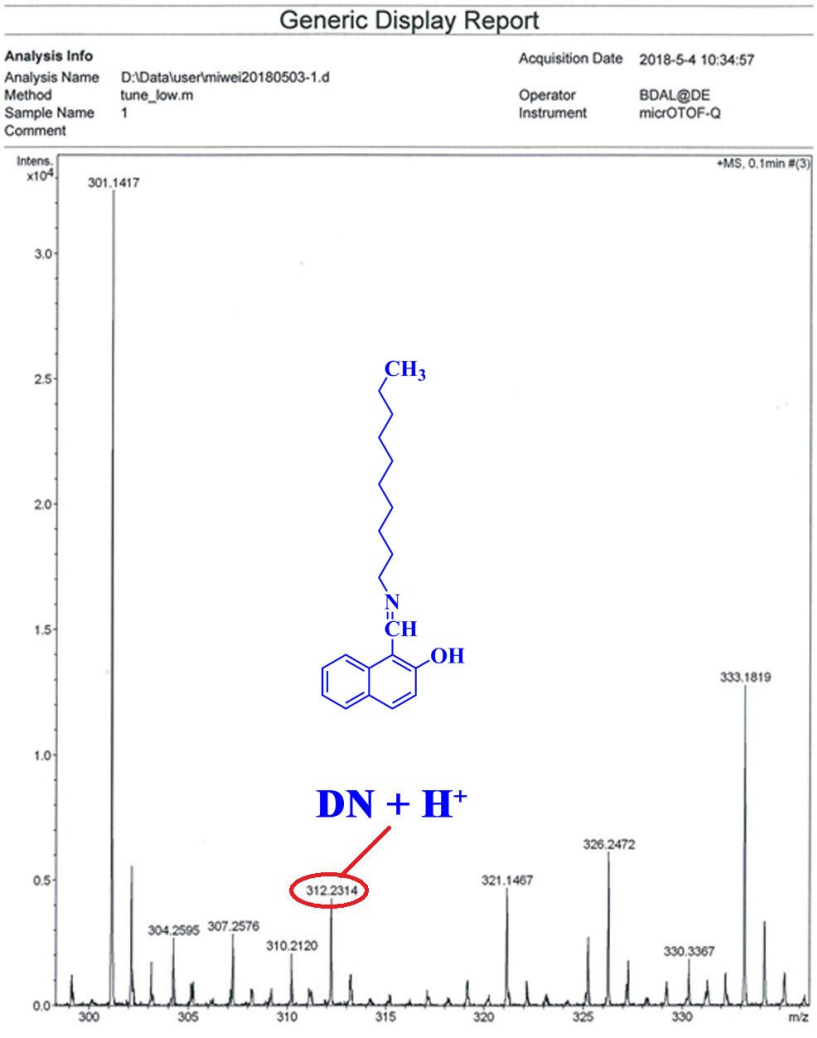


Fig. S15 High resolution ESI-MS data of compound **DN.**

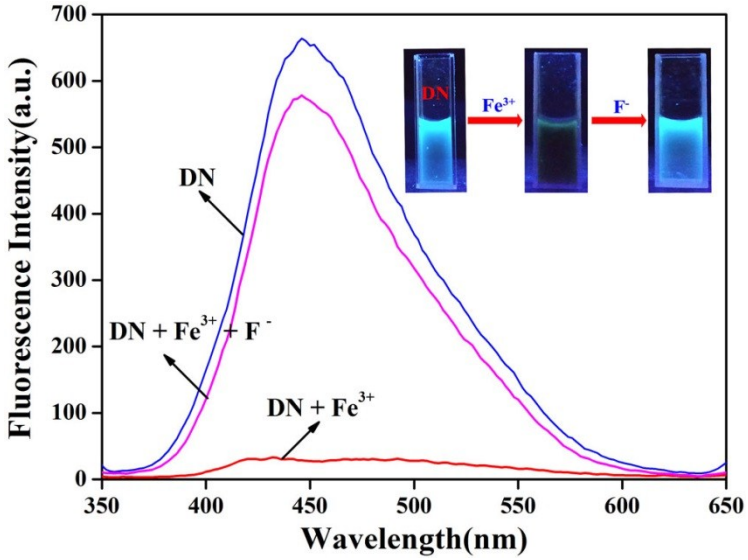


Fig. S16 Fluorescence emission spectra (λ_{ex} = 330 nm) of **DN** in the presence of Fe^{3+} (20 equiv.) and F^- (50 equiv.) in H_2O/DMSO (1/9, v/v) solution. Inset: photograph showing the change in color of the solution of **DN** in H_2O/DMSO (1/9, v/v) solution after addition of Fe^{3+} and F^-.

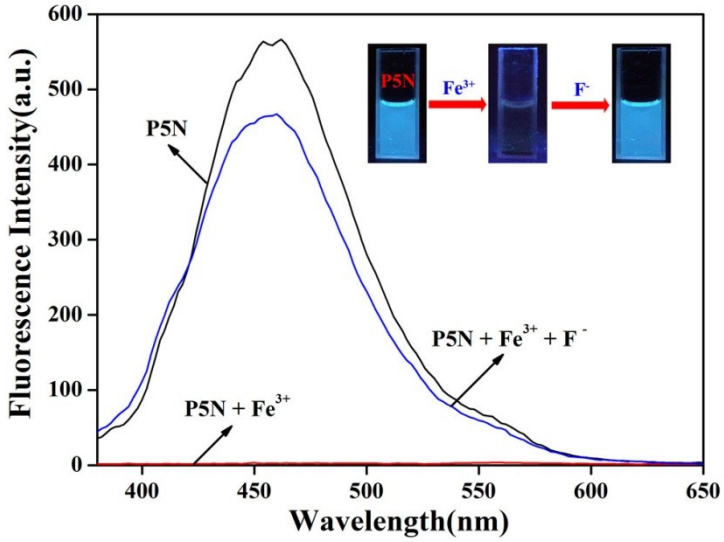


Fig. S17 Fluorescence emission spectra (λ_{ex} = 365 nm) of **P5N** in the presence of Fe^{3+} (20 equiv.) and F^- (50 equiv.) in H_2O/DMSO (1/9, v/v) solution. Inset: photograph showing the change in color of the solution of **P5N** in H_2O/DMSO (1/9, v/v) solution after addition of Fe^{3+} and F^-.

Calculation method of fluorescence emission quantum yield

Fluorescence quantum yield was calculated by the following equation:

$$\varphi_f = \frac{n_f^2}{n_s^2}\frac{A_s D_f}{A_f D_s}\varphi_s \quad (\varphi_s = 0.55\,, A \leq 0.05)$$

Where φ_f represents fluorescence quantum yield, A represents the absorbance, n represents the refractive index of the solution, and D represents the corrected fluorescence emission spectral integral area. Excitation was chosen at 395 nm, among which $n_f = n_s$.

(a) The fluorescence quantum yields for **AP5N**.

$$\varphi_f = 0.55 \times \frac{45.6261}{72.1573} \times \frac{0.014}{0.042} = 0.12$$

(b) The fluorescence quantum yields for **AP5N**-Fe^{3+}.

$$\varphi_f = 0.55 \times \frac{0.0043}{72.1573} \times \frac{0.014}{0.0023} = 0.0002$$

Determination of association constant

The association constants (K_a) were calculated based on the fluorescent titration curve of the supramolecular sensor **AP5N** to Fe^{3+}. Association constants were determined by a nonlinear least squares fit of the data with the following equation as referenced elsewhere. I is the observed the fluorescence intensity of **AP5N** at the fixed concentrations of Fe^{3+}. I_{max} and I_{min} are the corresponding maximum and minimum, respectively.

$$Iog\,\frac{I - I_{min}}{I_{max} - I} = Iog\,Ka + Iog\,[Fe^{3+}]$$

$K_a = 8.40 \times 10^7\ M^{-1}$

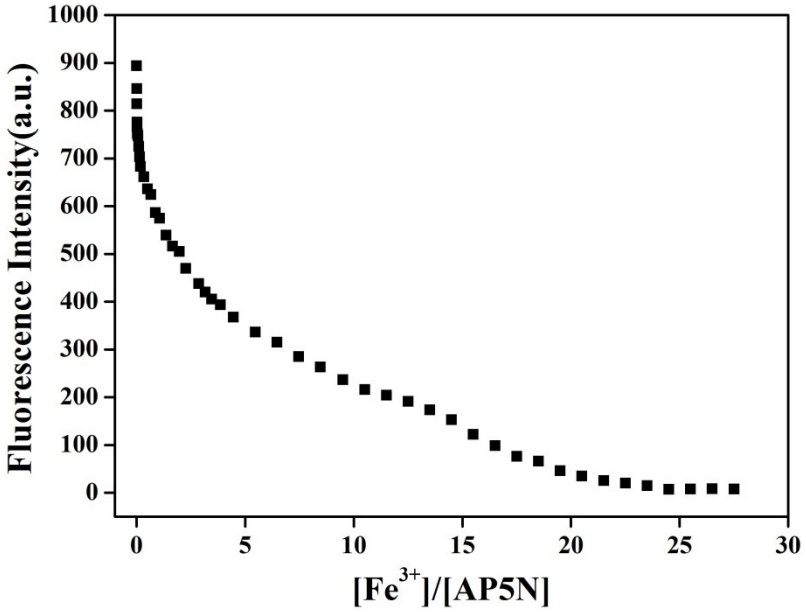


Fig. S18 A plot of emission at 456 nm versus number of equivalents of Fe^{3+}.

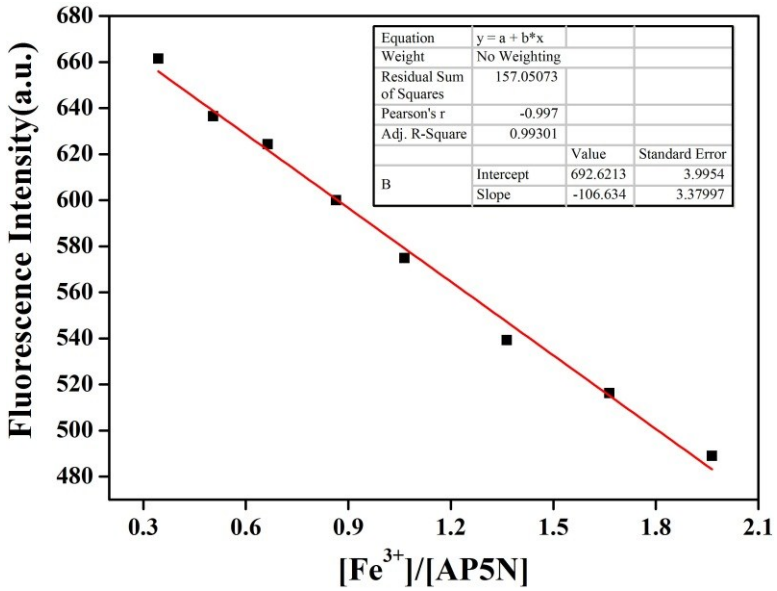


Fig. S19 The photograph of the linear range for Fe^{3+}.

The result of the analysis as follows:

Linear Equation: $Y = -106.634 \times X + 692.6213$ $R^2 = 0.99301$

$S = 1.066 \times 10^8$

$$\delta = \sqrt{\frac{\sum_{i=1}^{N}(F_i - \overline{F})^2}{N-1}} = 4.30 \qquad (N = 20) \qquad K = 3$$

$$LOD = K \times \delta / S = 1.21 \times 10^{-7}\ M$$

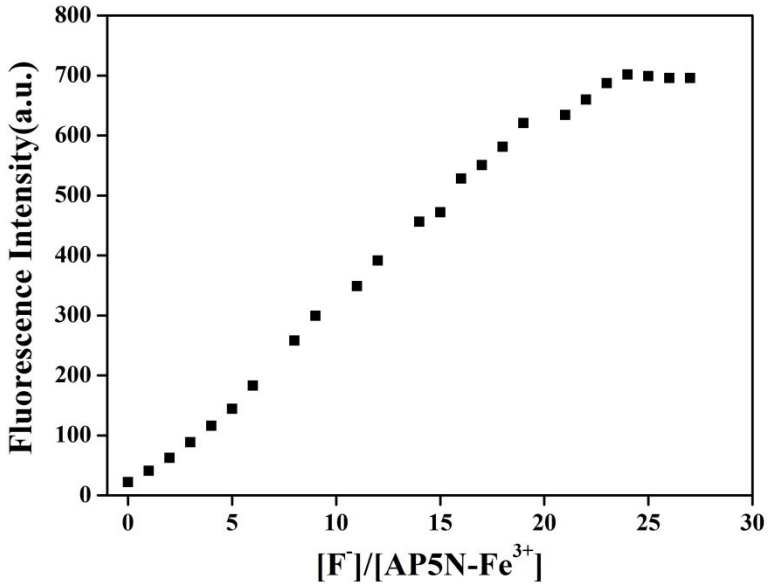


Fig. S20 A plot of emission at 456 nm versus number of equivalents of F^-.

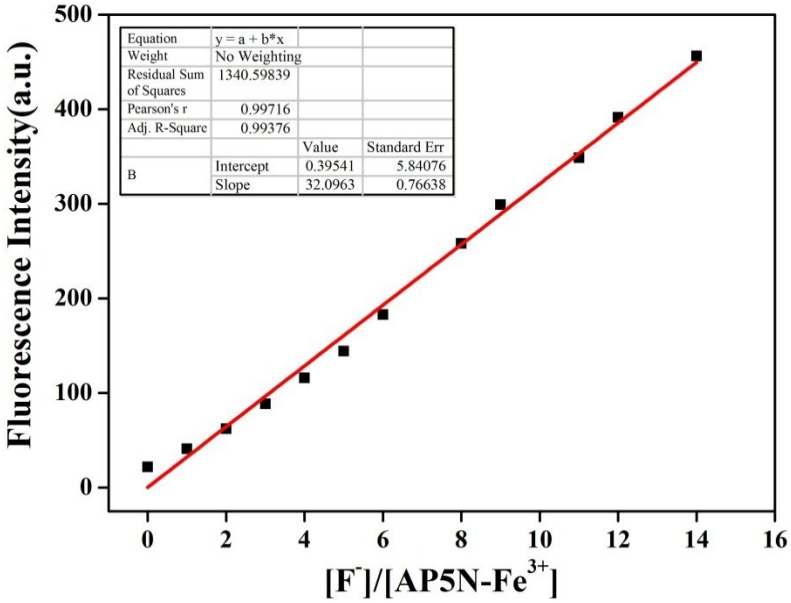


Fig. S21 The photograph of the linear range for F^-.

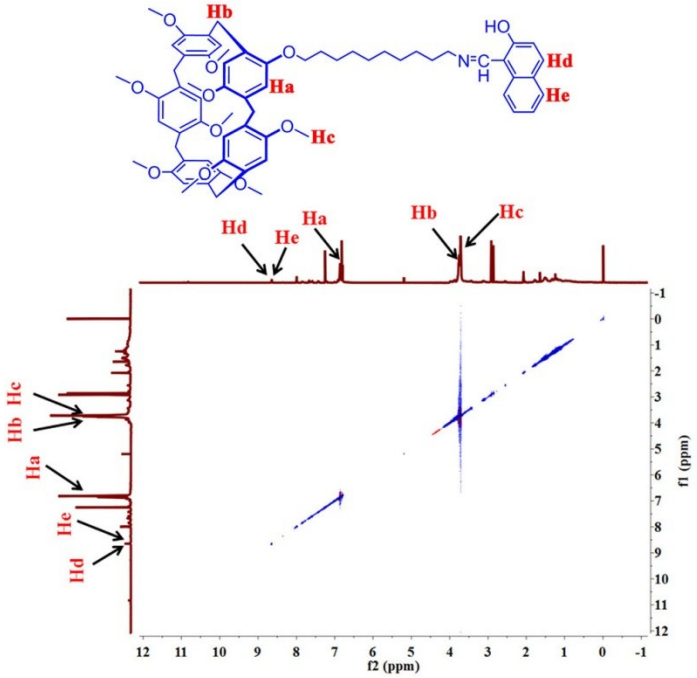
The result of the analysis as follows:

Linear Equation: $Y = 32.0963 \times X + 0.39541$ $\qquad R^2 = 0.99376$

$S = 3.20963 \times 10^7$

$$\delta = \sqrt{\frac{\sum_{i=1}^{N}(F_i - \overline{F})^2}{N-1}} = 1.43 \qquad (N = 20) \qquad K = 3$$

$LOD = K \times \delta / S = 1.34 \times 10^{-7}$ M



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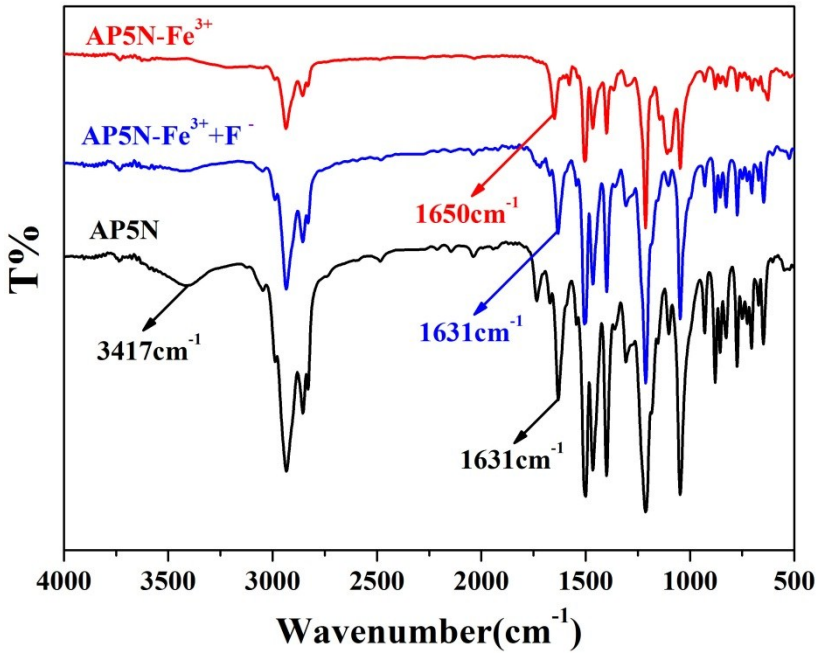

Fig. S23 FT-IR spectra of powdered **AP5N**, **AP5N**-Fe^{3+} and **AP5N**-Fe^{3+}+F^-.

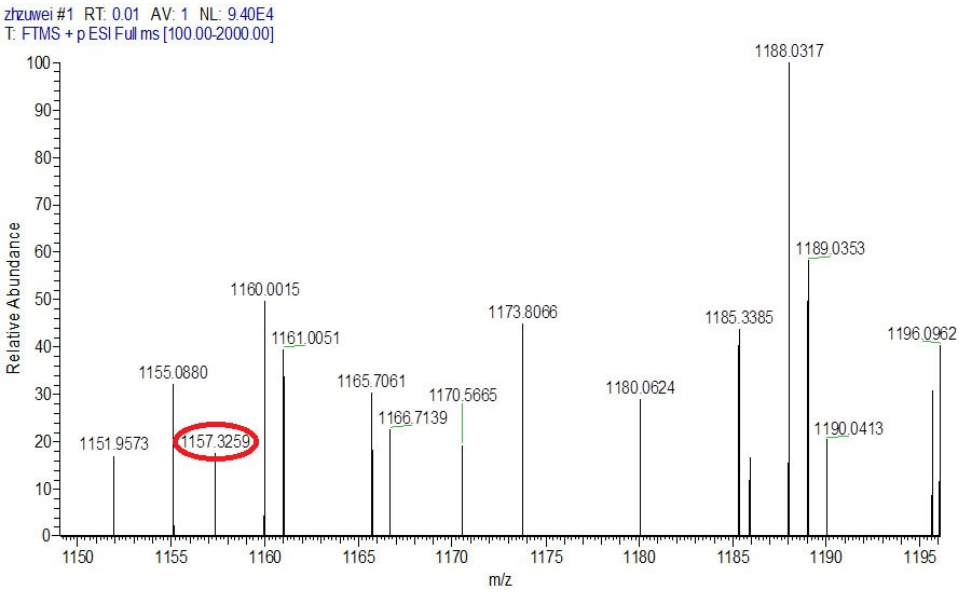

Fig. S24 High resolution ESI-MS data of [**AP5N**+Fe+Na+2OH-H]$^+$.

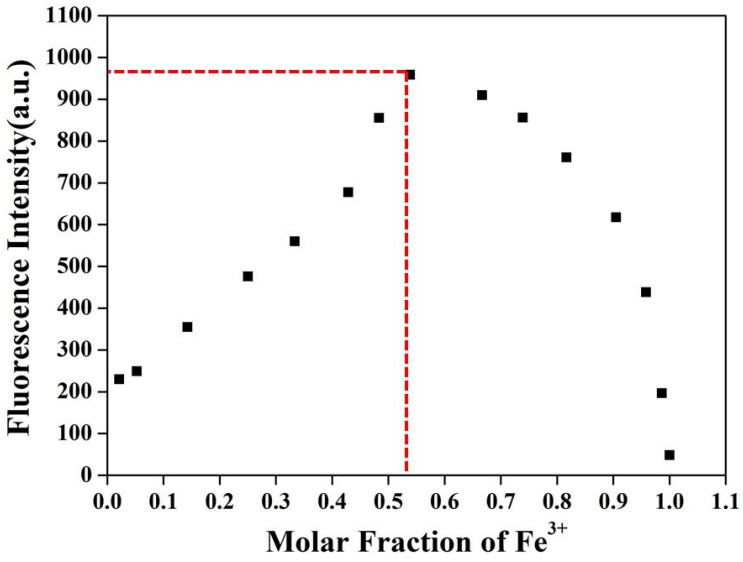

Fig. S25 Job's plot showing the 1:1 stoichiometry of the complexation between **AP5N** and Fe^{3+} in H_2O/DMSO (1/9, v/v) solution by plotting the fluorescence intensity at λ_{ex} = 395 nm.

Table S1. The ICP Date of Supramolecular Sensor of **AP5N** with Fe^3

Label	Solution Concentration	Unite	SD	%RSD	Int.(c/s)	Calculated Concentration
Fe 234.350	0.097936	mg/L	0.010273	10.5	81.9944	0.097936mg/L
Fe 259.940	0.083311	mg/L	0.018477	22.2	87.8443	0.083311mg/L
Fe 261.187	0.067991	mg/L	0.054203	79.7	52.1919	0.067991mg/L
Fe 238.204	0.080717	mg/L	0.010537	13.1	191.881	0.080717mg/L

Ion	Initial concentration (M)	Residual concentration (M)	Absorbing rate %
Fe^{3+}	1.0×10^{-4}	1.75×10^{-6}	98.25%