Electronic Supplementary Information

A novel pillar[5]arene-based supramolecular organic framework gel to achieve ultrasensitive response by introducing the competition of cation···π and π···π interactions

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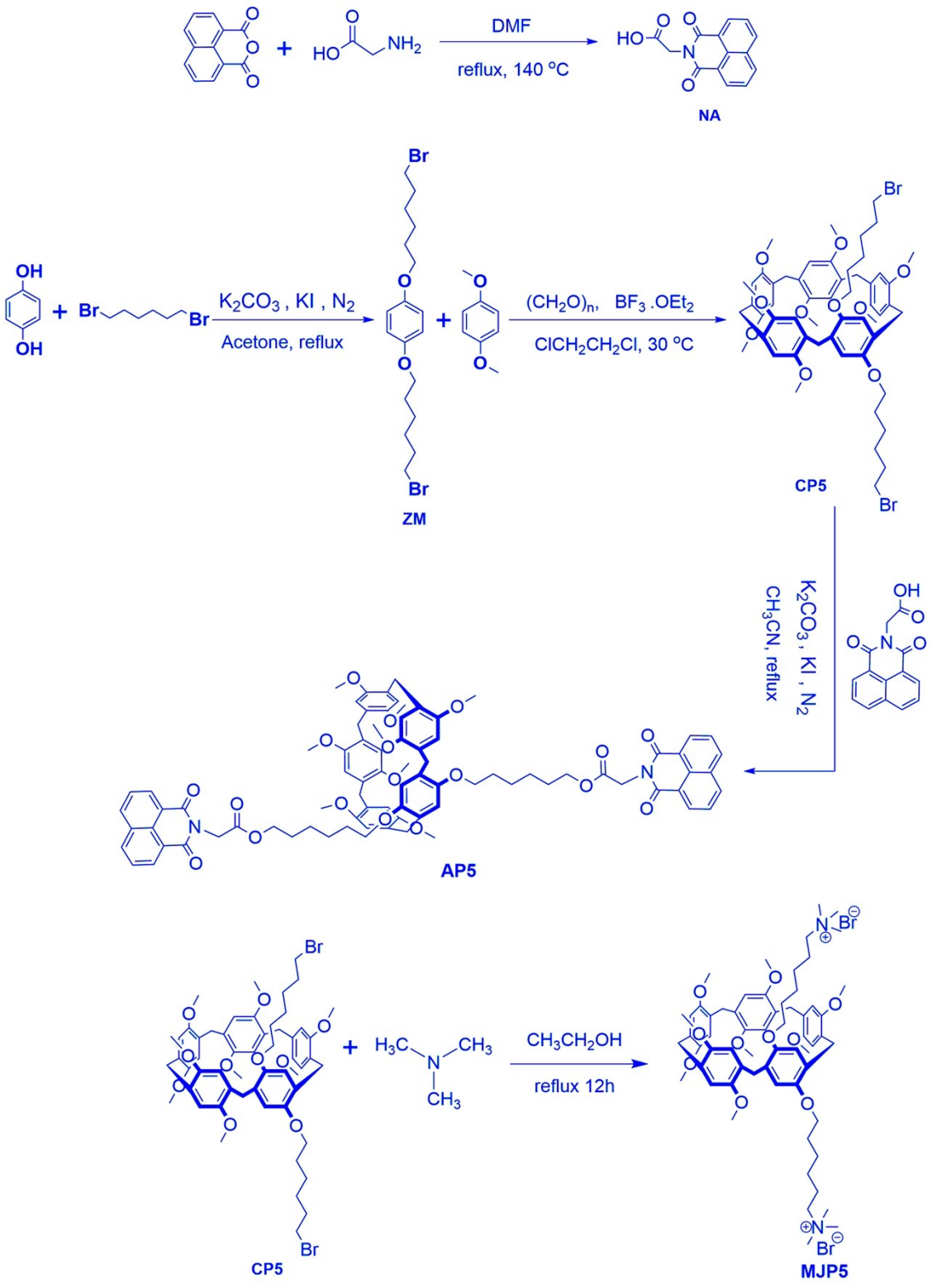
Materials and physical methods

All anions were used as tetrabutylammonium salts, which were purchased from Alfa Aesar and used as received. All metal ions were prepared from the perchlorate salts. Other reagents used in the study were of 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. ^{1}H NMR spectra were recorded on Mercury-400BB spectrometer (400MHz) and Bruker Digital RF spectrometer (300MHz). ^{1}H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, TM scale with the solvent resonances as internal standards). 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 X-ray diffraction analysis (XRD) was performed on a Rigaku D/Max-2400 X-Ray Diffractometer. The morphologies and sizes of the xerogels were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8 kV. 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.

2. Synthesis and characterizations of compound MJP5 and **AP5**.



Scheme S1 Synthesis of compound **MJP5** and **AP5**.

Synthesis of compound NA: A mixture of 1,8-naphthalenedicarboxylic anhydride (1.98 g, 10.0 mmol), glycine (1.13 g, 15.0 mmol) in anhydrous

DMF (20 mL) was stirred at 140 °C reflux for 24 h. After cooling to room temperature, add water and the precipitate was filtered, then with acetonitrile recrystallization get gray powder product NA. yield 65%; m.p. >300 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.06 (s, 1H),8.48 (m, 4H), 7.88 (t, 2H), 4.72 (s, 2H). ESI-MS m/z: [2(**NA**)+Na]$^+$ Calcd for $C_{28}H_{18}N_2NaO_8$, 533.0961; Found 533.09.

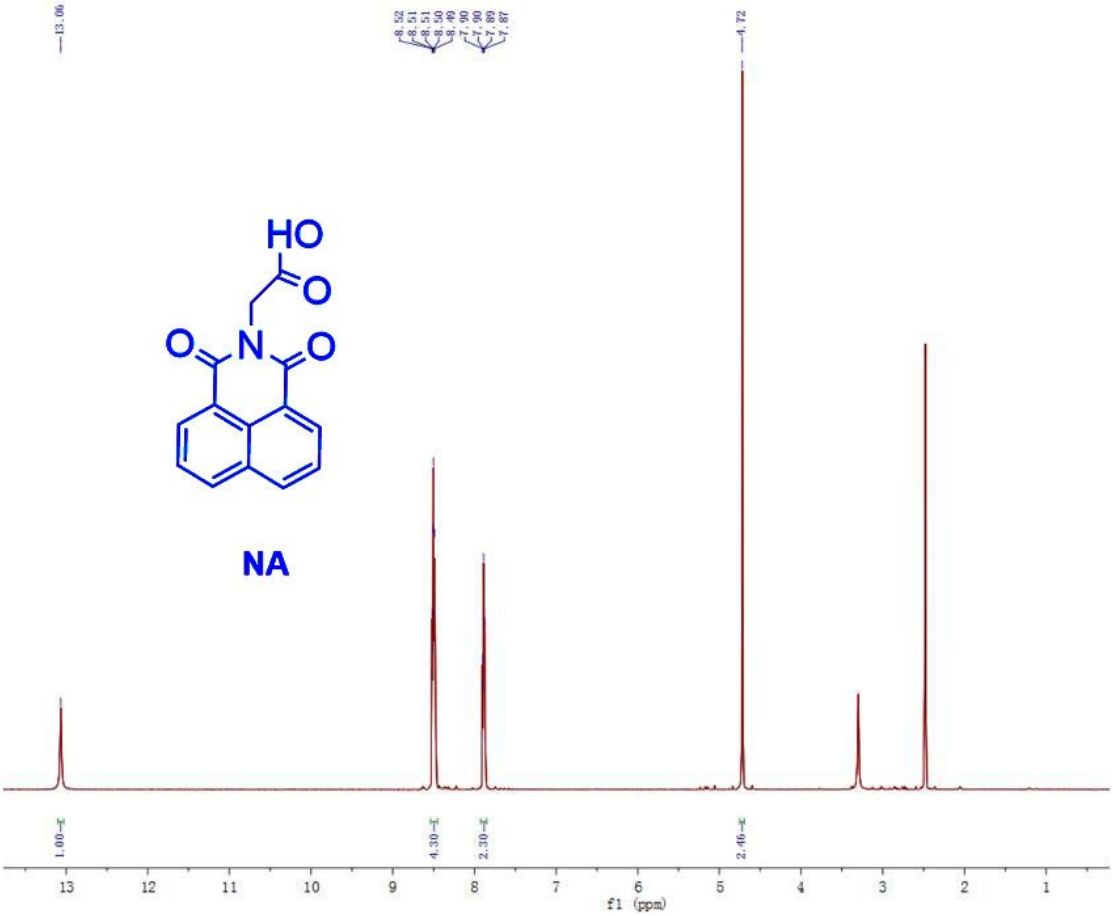


Fig. S1 ^{1}H NMR spectrum of **NA** in DMSO-d_6.

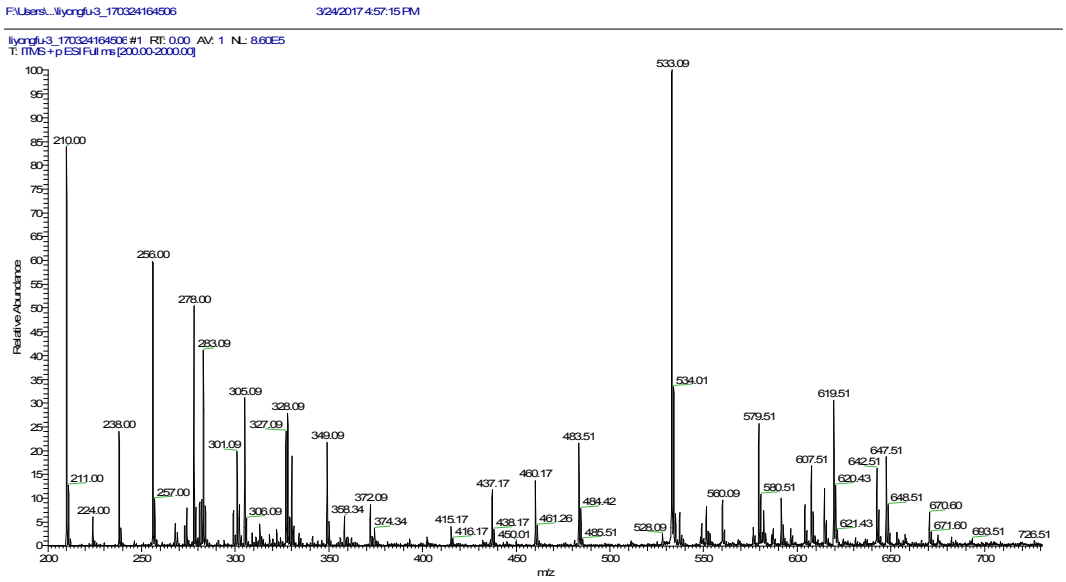


Fig. S2 ESI-MS spectrum of **NA**.

Synthesis of 1, 4-bis(4-bromohexyloxy)benzene ZM: Hydroquinone (2.3 g, 20.0 mmol), K_2CO_3 (16.6 g, 120 mmol), KI (6.6 g, 40 mmol), 1, 4-dibromobutane (34.6 g, 160 mmol) and acetone (400.0 mL) were added in a 500mL round bottom flask stirred at room temperature. The reaction mixture was stirred at reflux for 1.5 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: CH_2Cl_2 = 10:1) afforded a white solid (6.0 g yield 70%). m.p.: 87 ^oC. ^1H NMR (600 MHz, $CDCl_3$) δ 6.81 (s, 4H), 3.90 (t, 4H), 3.42 (t, 4H), 1.89 (m, 4H), 1.77 (m, 4H), 1.49 (m, 8H). ESI-MS m/z: $[ZM+H]^+$ Calcd for $C_{18}H_{29}Br_2O_2$, 437.05; Found 437.01.

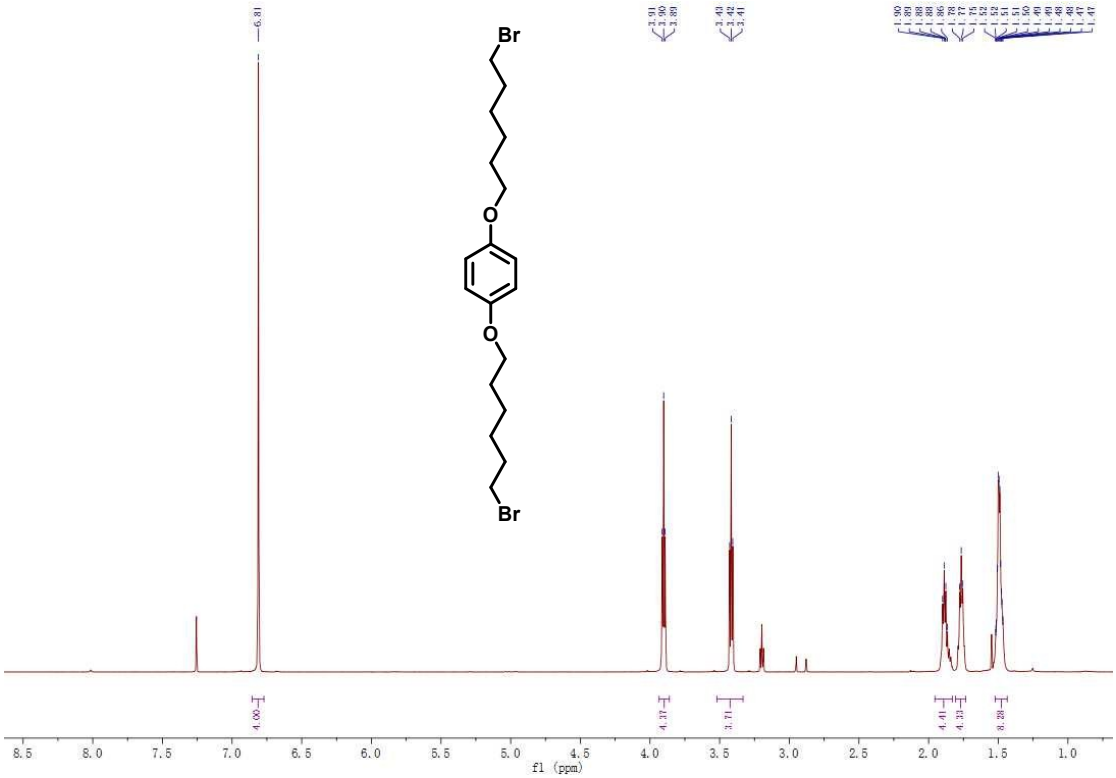


Fig. S3 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of **ZM**.

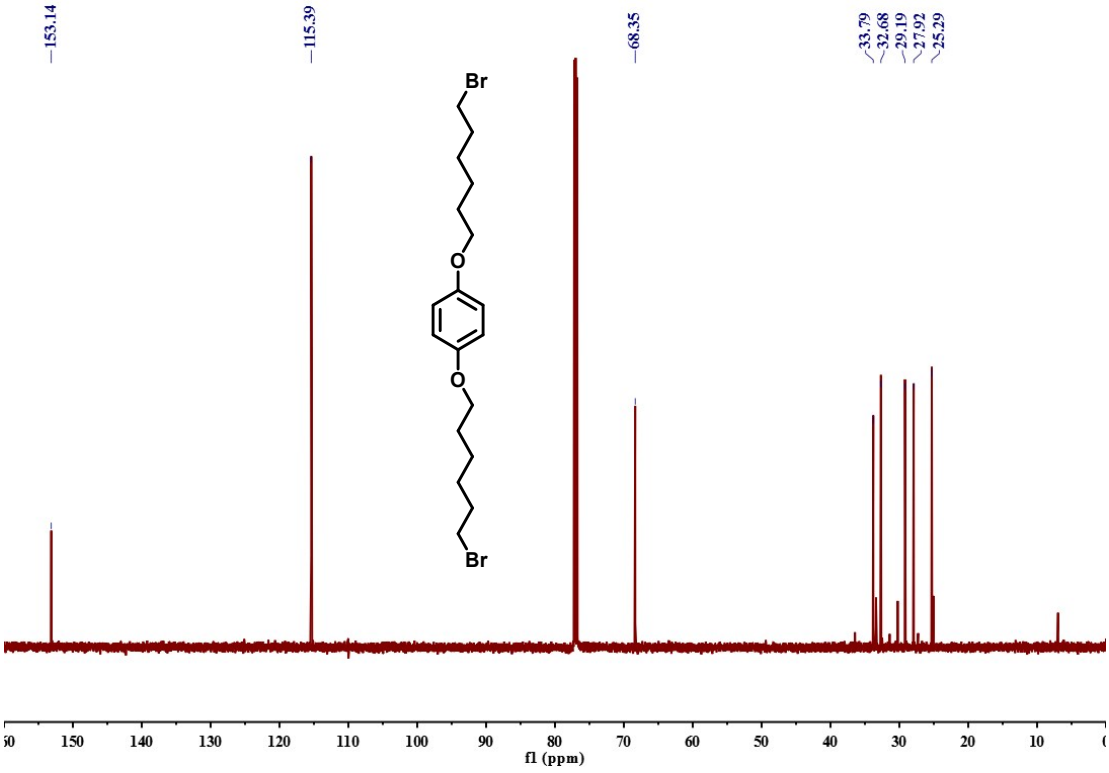


Fig. S4 ^{13}C NMR spectra (600 MHz, $CDCl_3$) of **ZM**.

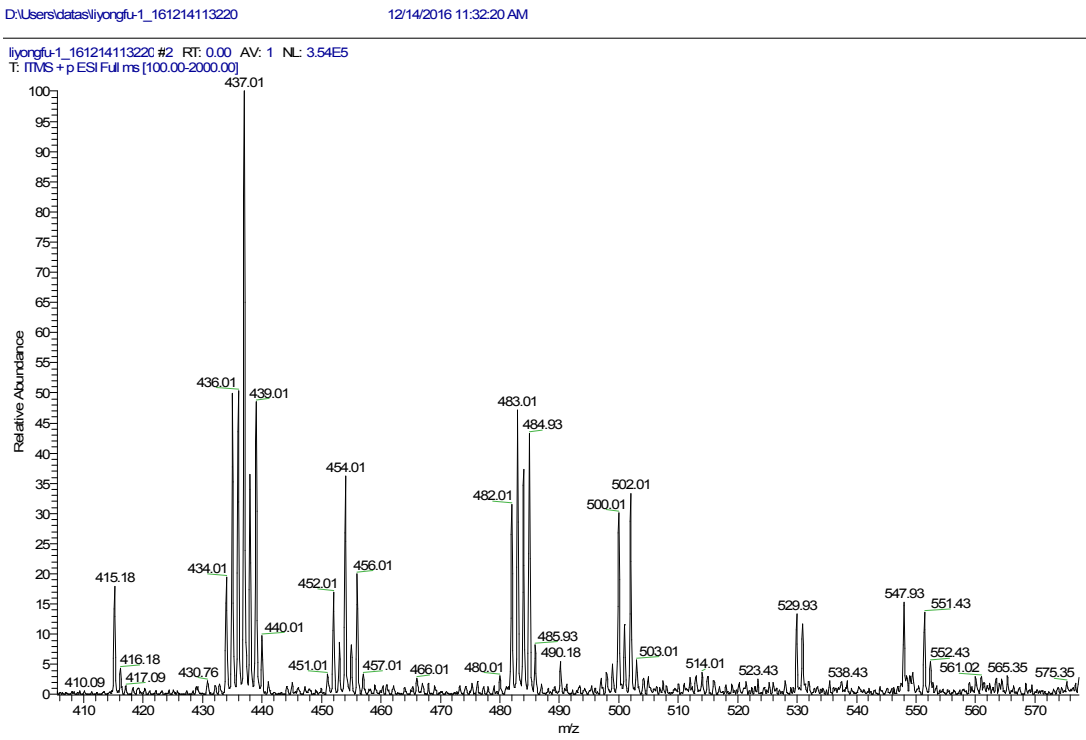


Fig. S5 ESI-MS spectrum of **ZM**.

Synthesis of Copillar[5]arene CP5. To a solution of 1, 4-bis (4-bromohexyoxy) benzene (1.9 g, 5.0 mmol) and 1,4-dimethoxybenzene (2.76 g, 20.0 mmol) in 1, 2-dichloroethane (200 mL), paraformaldehyde (0.75 g, 25.0 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (6.75 mL, 25 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h and concentrated by rotary evaporation. The resultant oil was dissolved in CH_2Cl_2 and washed twice with H_2O. 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 (20 : 1,v/v) to give CP5 2.0219 g (38.66%) as a white solid. m.p.:185-189 ^oC. ^1H NMR (600 MHz, $CDCl_3$, room temperature) δ (ppm): 6.93(m, 10H),

3.82(m, 34H), 3.69(s, 4H), 1.49(m,16H), 0.87(m, 4H). ESI-MS m/z: [$C_{55}H_{68}O_{10}Br_2 + NH_4^+$] Calcd for 1066.3493; Found 1066.3496.

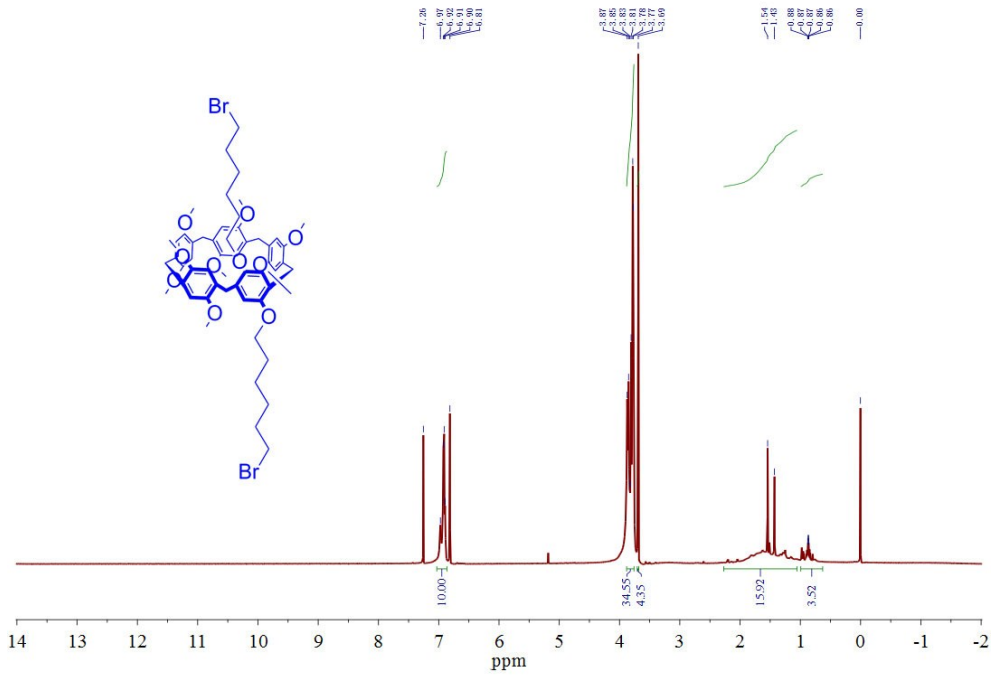


Fig. S6 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of **CP5**.

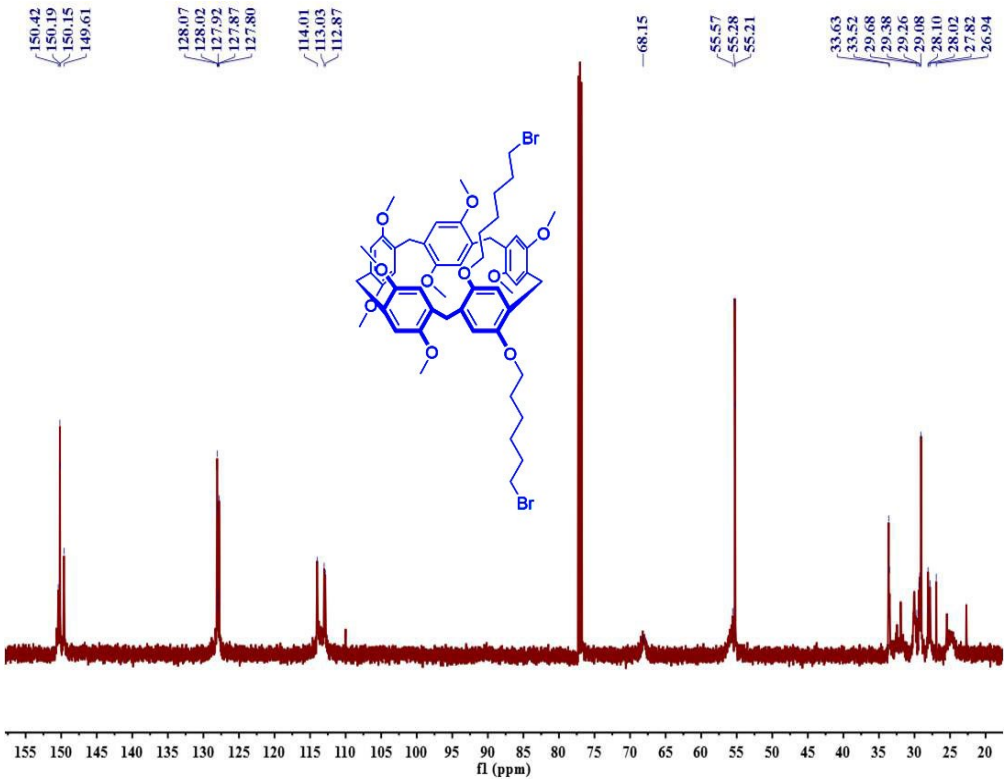


Fig. S7 ^{13}C NMR spectra (600 MHz, $CDCl_3$) of **CP5**.

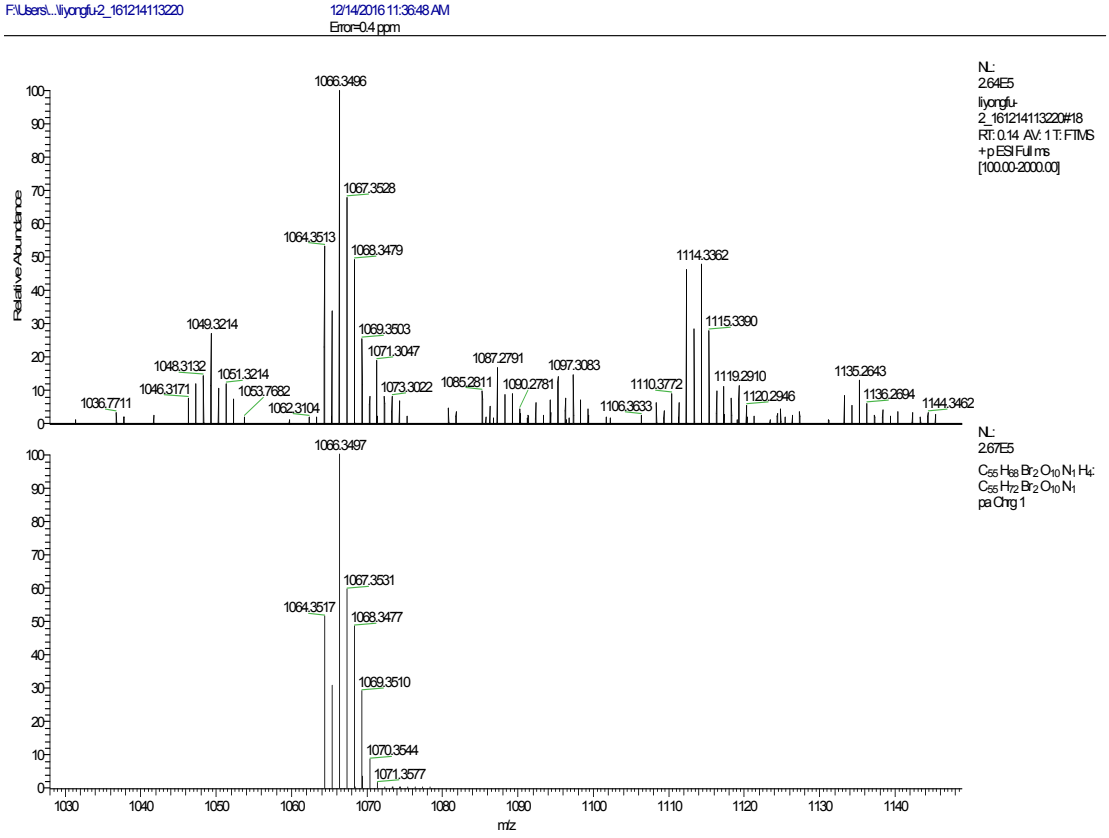


Fig. S8 High resolution mass data of compound **CP5**.

Synthesis of guest compound MJP5: Copillar[5]arene **2** (0.5 g, 0.5 mmol) and trimethylamine (33 % in ethanol, 1.0 mL, 3.7 mmol) were added to ethanol (80 mL). The solution was refluxed overnight. Then the solvent was removed by evaporation, you can afford a white solid. After white solid was washed by diethyl ether to obtain **MJP5** as a white solid (0.52 g, 93 %). Mp 176−178 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.00 – 6.67 (m, 10H), 3.95 (d, J = 70.8 Hz, 4H), 3.83 – 3.53 (m, 34H), 3.43 (t, J = 7.0 Hz, 4H), 3.07 (d, J = 6.1 Hz, 18H), 1.71 (s, 8H), 1.56 (s, 4H), 1.40 – 1.29 (m, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 150.34, 149.61, 128.04, 113.77, 68.08, 65.68, 55.99, 55.93, 55.91, 55.84, 52.61, 36.16, 31.18, 29.48, 26.17, 25.83, 22.54.

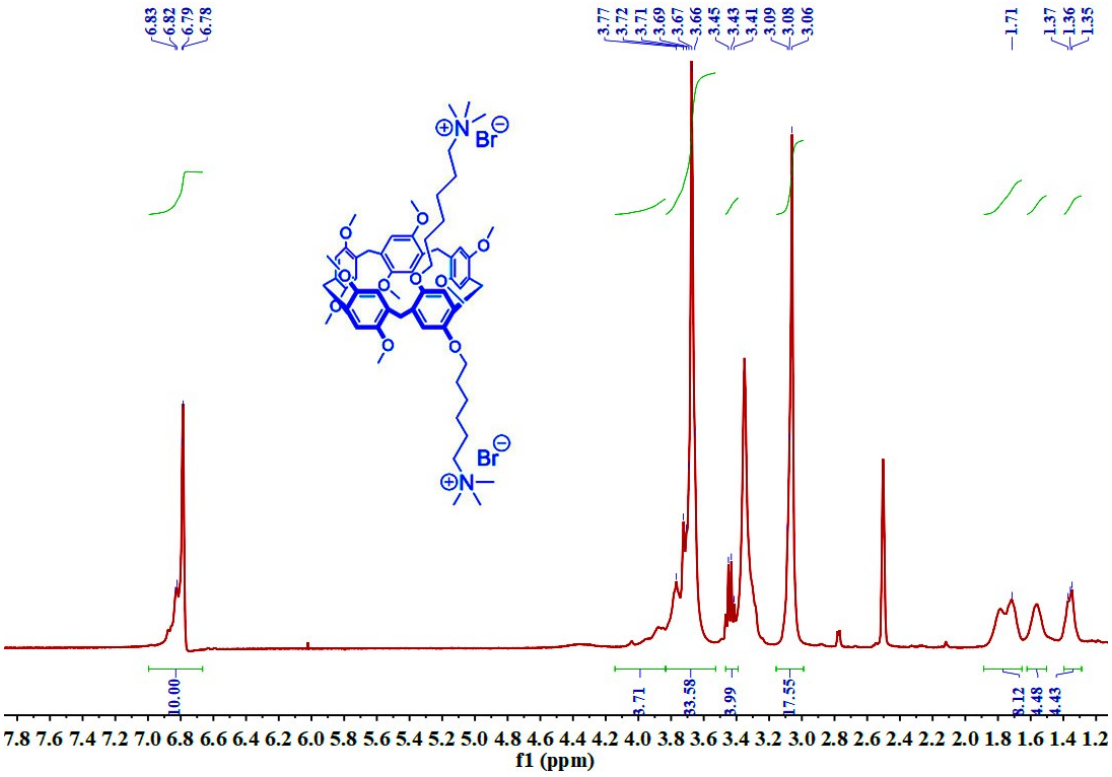


Fig. S9 ^{1}H NMR spectra (400 MHz, DMSO-d_6) of **MJP5**.

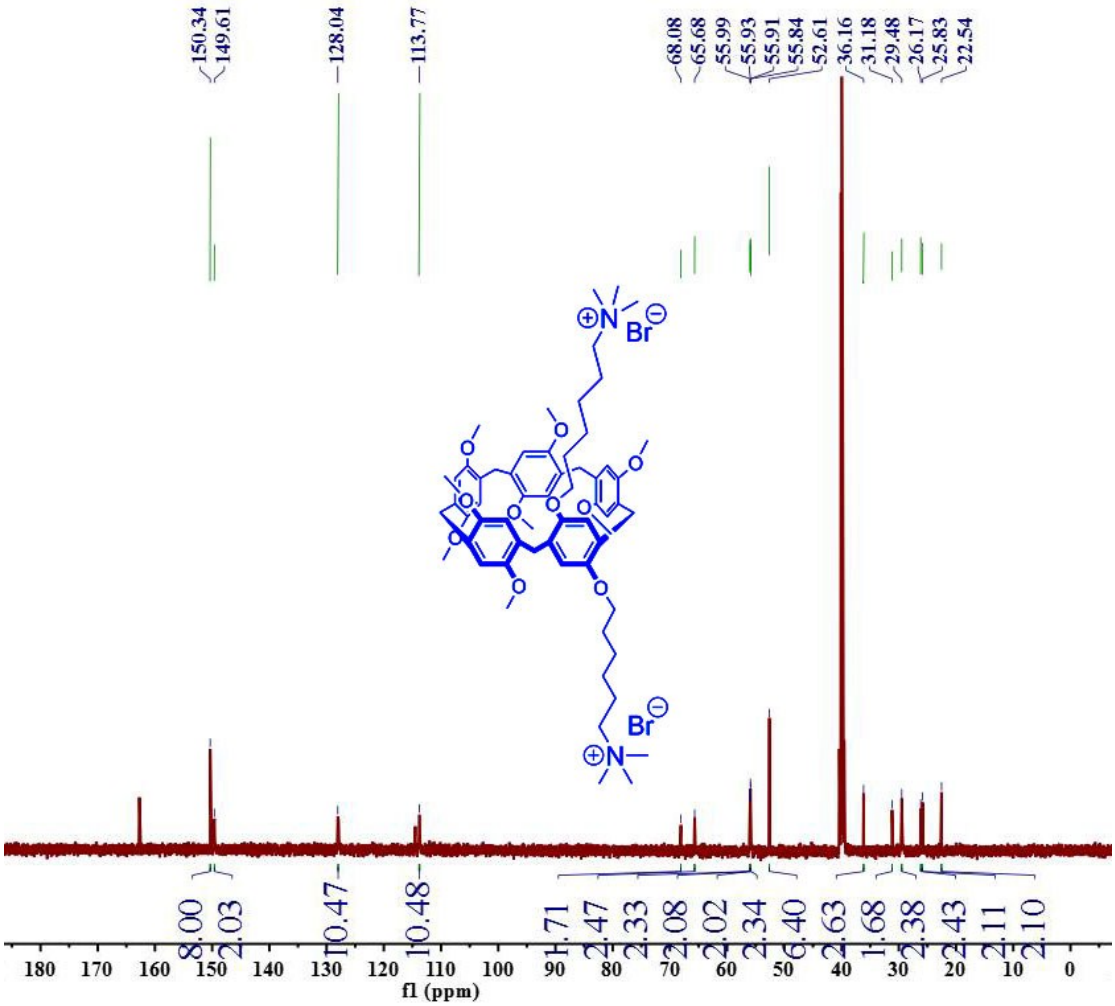


Fig. S10 ^{13}C NMR spectra (151 MHz, DMSO-d_6) of **MJP5**.

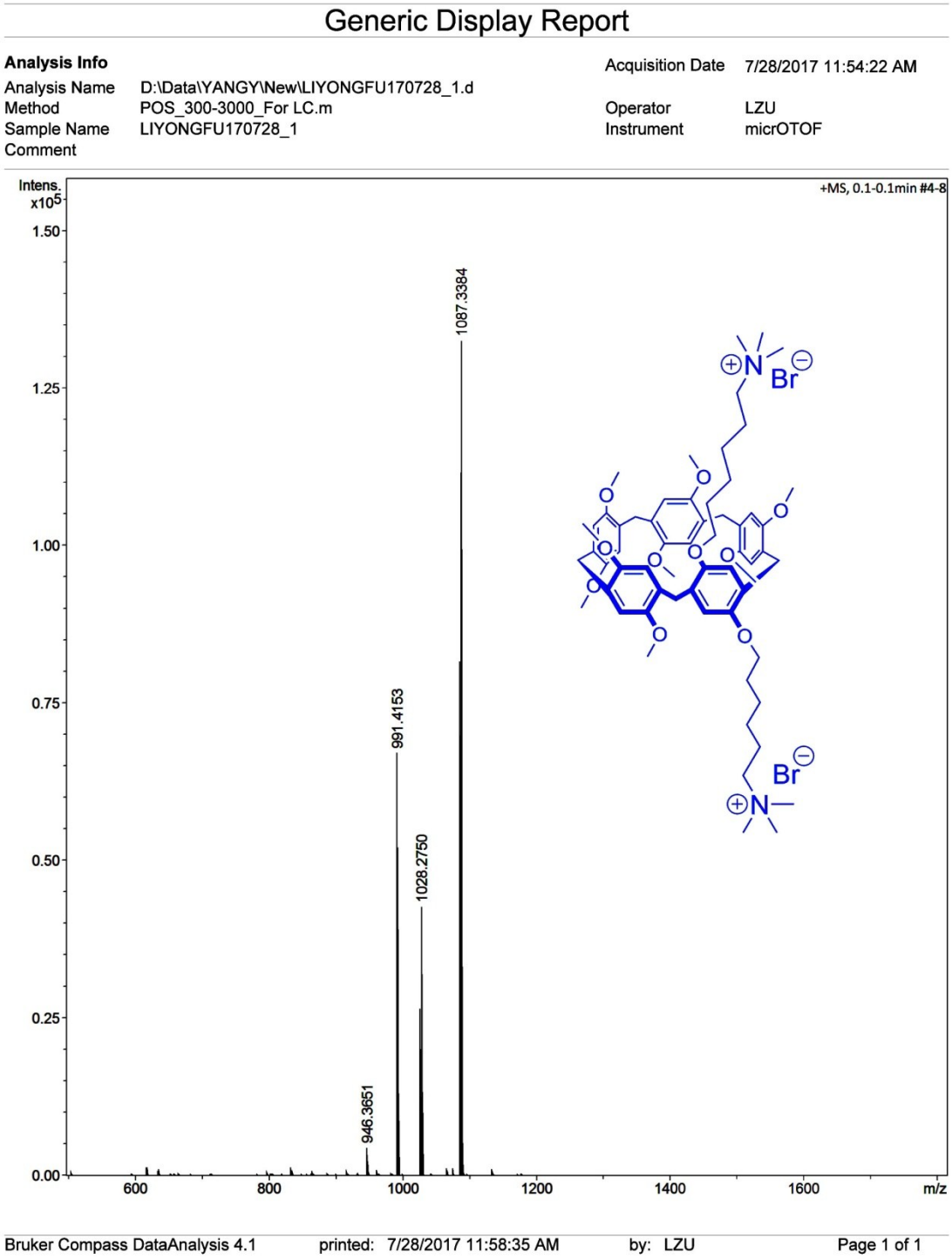


Fig. S11 ESI-MS spectrum of compound **MJP5**.

Synthesis of bisfunctionlized pillar[5]arene AP5: In a 100 mL round bottom flask, copillar[5]arene **CP5** (1.5844 g, 1.5 mmol), K_2CO_3 (2.55 g, 20 mmol), KI (0.63 g, 4 mmol), **NA** (3.06 g, 12 mmol) and acetonitrile (75 ml) was added and the reaction mixture was stirred for 48 h at 80 ^oC.

After removal of the inorganic salt by filtration, the solvent was evaporated and afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (10:1). The fractions containing the product were combined and concentrated under vacuum to give **AP5** (0.45 g, 21 %) as a light yellow solid. Mp: 120 - 125 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, *J* = 7.3 Hz, 4H), 8.24 (d, *J* = 8.2 Hz, 4H), 7.77 (t, *J* = 7.7 Hz, 4H), 6.87 (m, *J* = 12.3 Hz, 10H), 4.21 (t, *J* = 6.8 Hz, 4H), 3.77 (m, *J* = 13.4 Hz, 42H), 1.71 (m, *J* = 7.9, 7.2 Hz, 4H), 1.58 – 1.51 (m, 8H), 1.42 (m, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ/ppm：168.42, 163.44, 150.30 – 150.25 (m), 149.56, 135.30 , 131.76, 131.52, 128.00, 127.96, 127.88, 127.85, 127.74, 127.68, 121.74, 113.68, 68.06, 65.38, 55.78, 55.74, 55.70, 41.57, 30.09, 29.48, 29.35, 28.39, 25.75, 25.52. ESI-MS m/z: [$C_{83}H_{84}O_{18}N_2$ + NH_4^+] calcd for 1414.6057; Found 1414.6035.

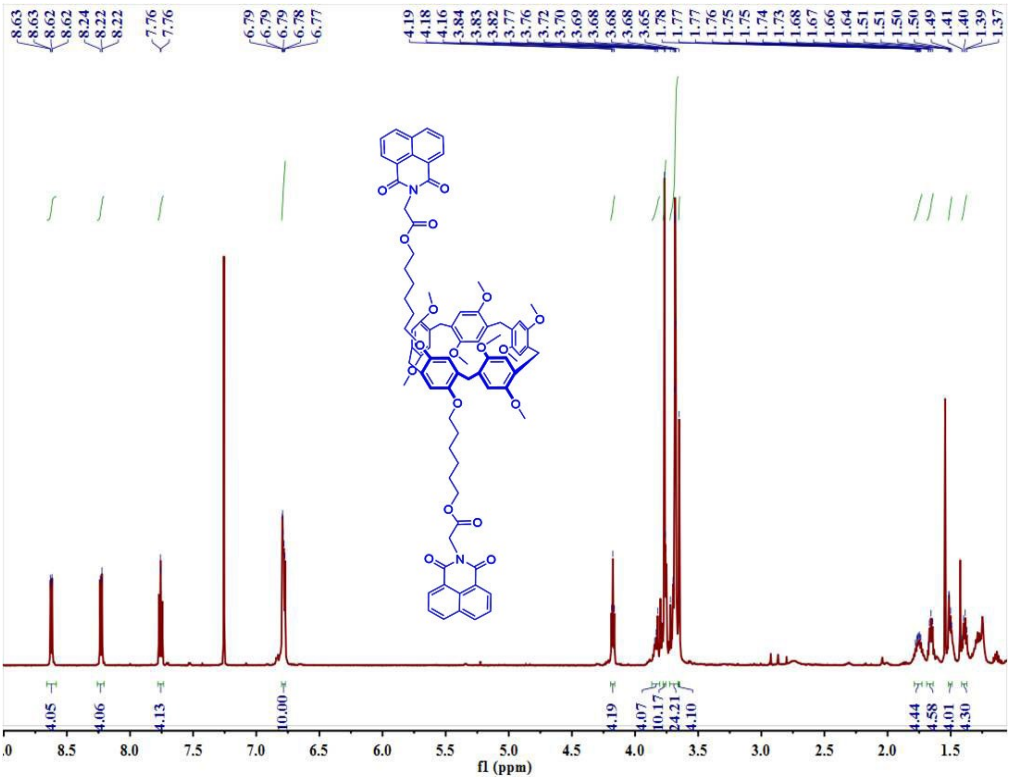


Fig. S12 ^{1}H NMR spectra (600 MHz, $CDCl_3$) of **AP5**.

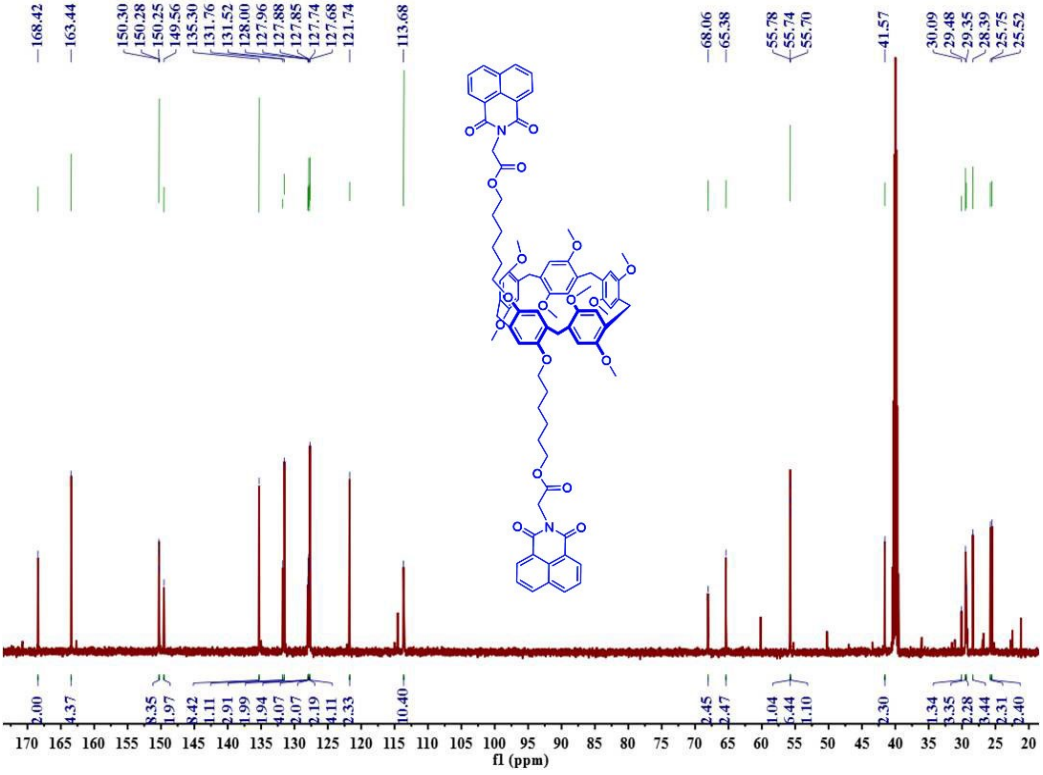


Fig. S13 ^{13}C NMR spectra (600 MHz, DMSO-d_6) of **AP5**.

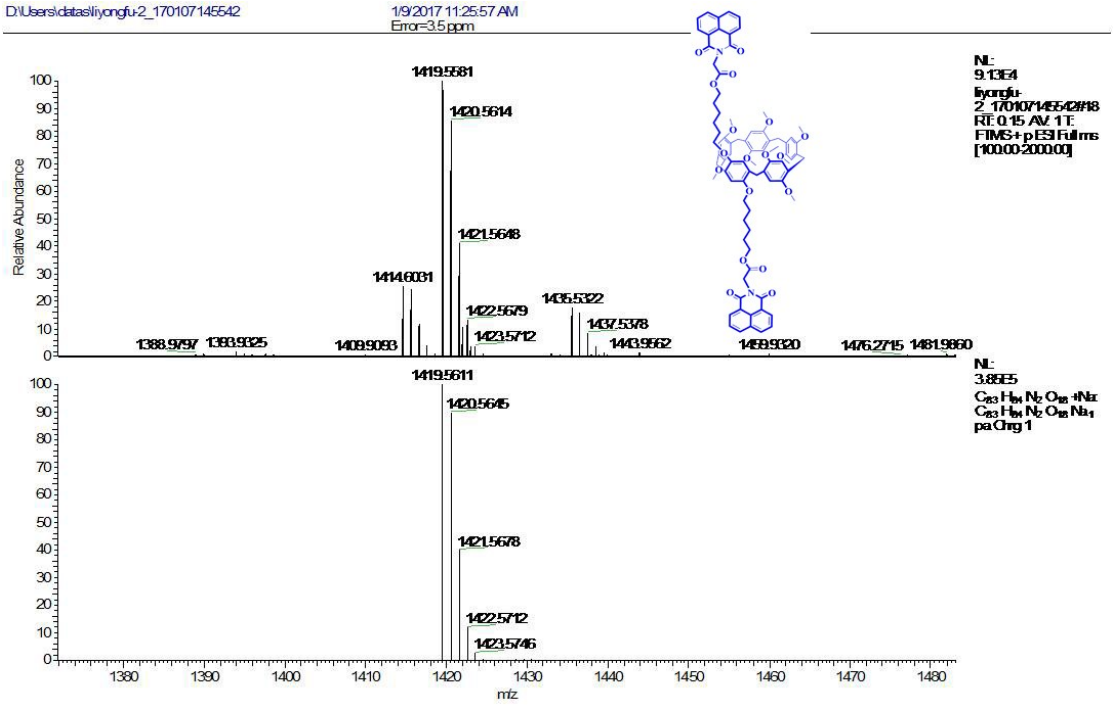


Fig. S14 High resolution mass data of **AP5**.

Table S1. Gelation Property of supramolecular organic framework **(SOF-AMP)**.

Entry	Solvent	State[a]	CGC[b](%)	Tgel[c] (^{o}C, wt%)
1	DMSO	S		\
2	DMF	S	\	\
3	acetonitrile	P	\	\
4	ethanol	P	\	\
5	methanol	P	\	\
6	isopentanol	P	\	\
7	CH_2Cl_2	S	\	\
8	$CHCl_3$	S	\	\
9	ethyl acetate	S	\	\
10	THF	S	\	\
11	acetone	P	\	\
12	CCl_4	S	\	\
13	CH_2ClCH_2Cl	S	\	\
14	n-hexane	P	\	\
15	cyclohexanol	G	3.8	43
16	isopropanol	P	\	\
17	petroleum ether	P	\	\
18	n-butyl alcohol	P	\	\
19	n-hexanol	P	\	\
20	n-propanol	P	\	\
21	ethanediol	P	\	\
22	Tertbutylalcohol	P	\	\
23	Glycerol	P	\	\

[a]G, P and S denote gelation, precipitation and solution, respectively, c = 0.8%.

[b]The critical gelation concentration (wt%, 10mg/ml = 1.0%).

[c]The gelation temperature (^{o}C).

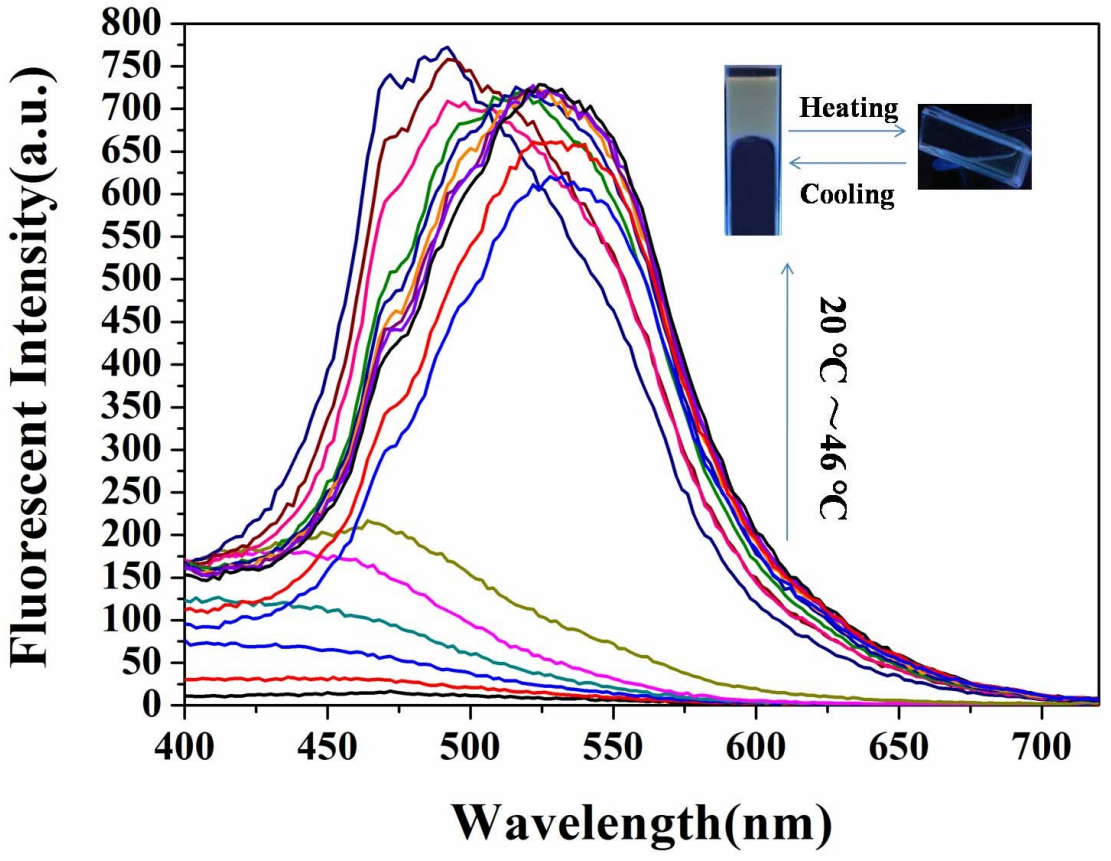


Fig. S15 Temperature-dependent fluorescent spectra of **SOF-AMP-G** (3.8% w/v in cyclohexanol solution) during gelation process (λ_{ex} =375 nm).

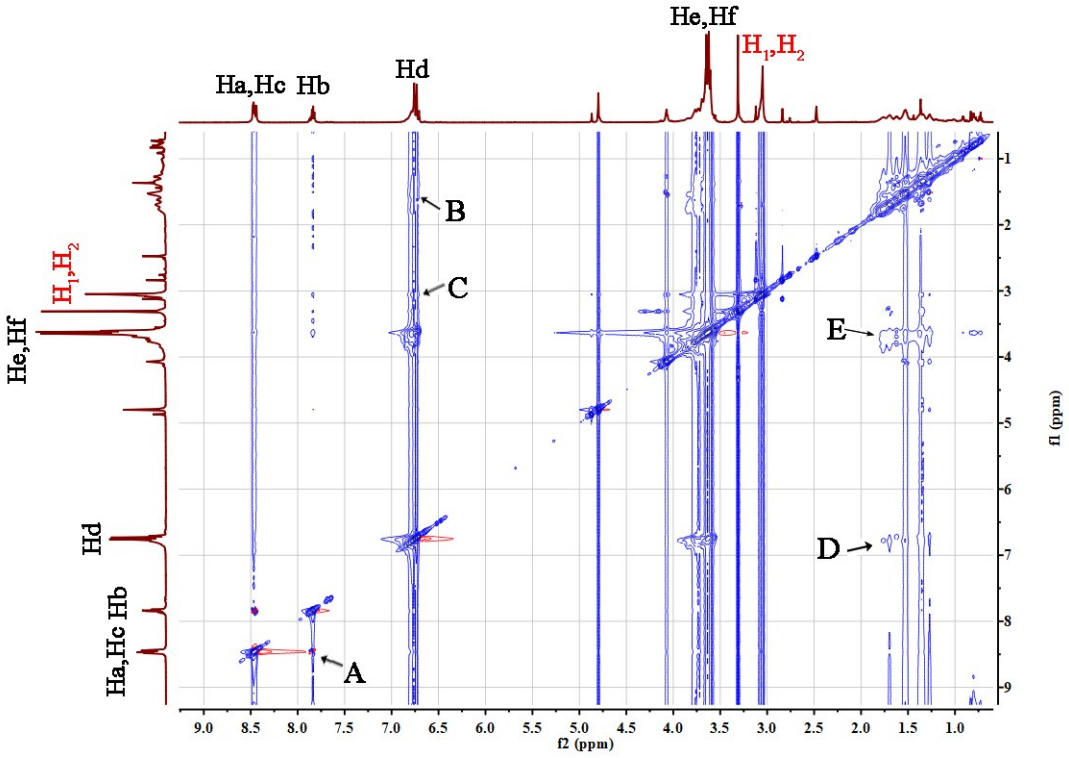


Fig. S16 2D NOESY NMR spectrum (600 MHz, 298 K) of 30.0 mM **AP5** and **MJP5** in DMSO-d_6 solution.

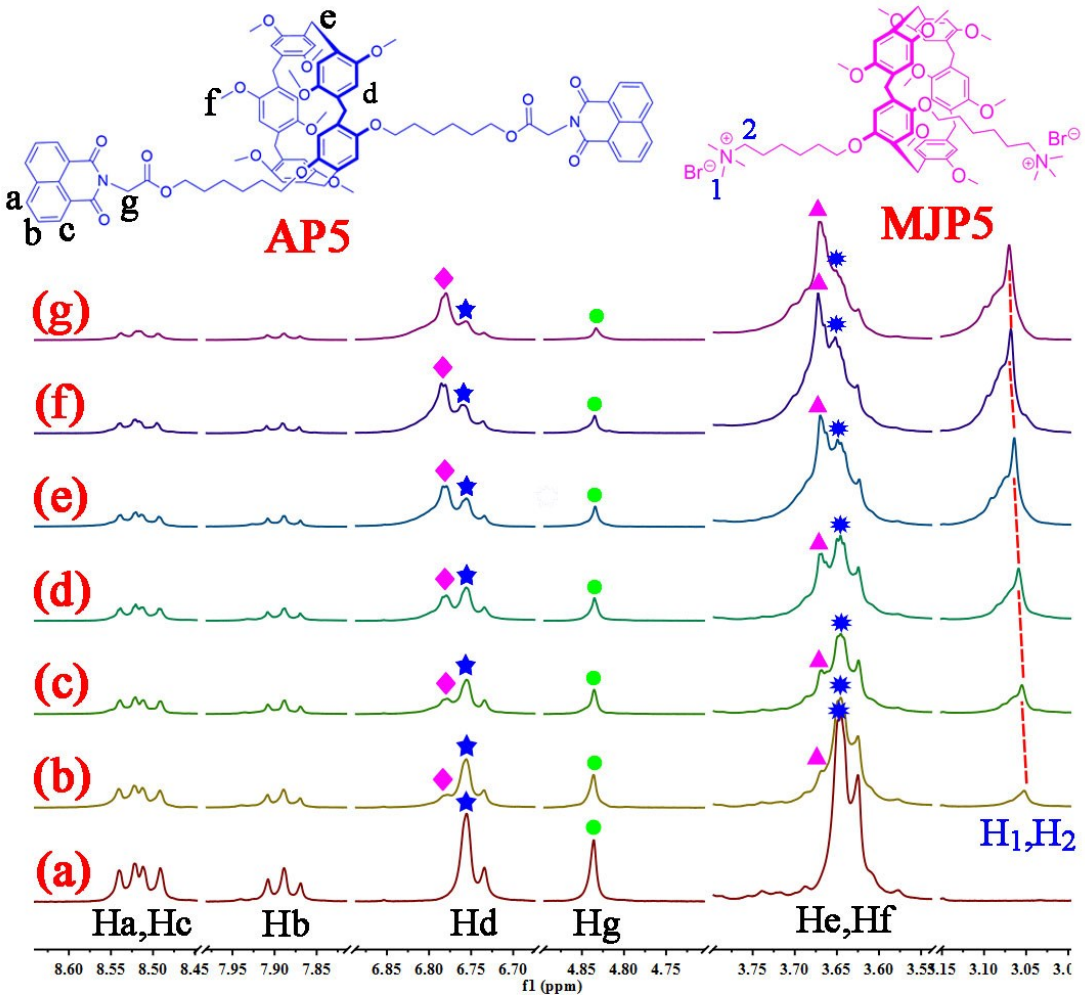


Fig. S17 Partial ^{1}H NMR spectra of **AP5** (0.01 mol/L) in DMSO-d_6 with increasing amounts of **MJP5**, (a) Free **AP5**; (b) 0.2 equiv. (c) 0.5 equiv. (d) 1.0 equiv. (e) 2.0 equiv. (f) 3.0 equiv. (g) 4.0 equiv.

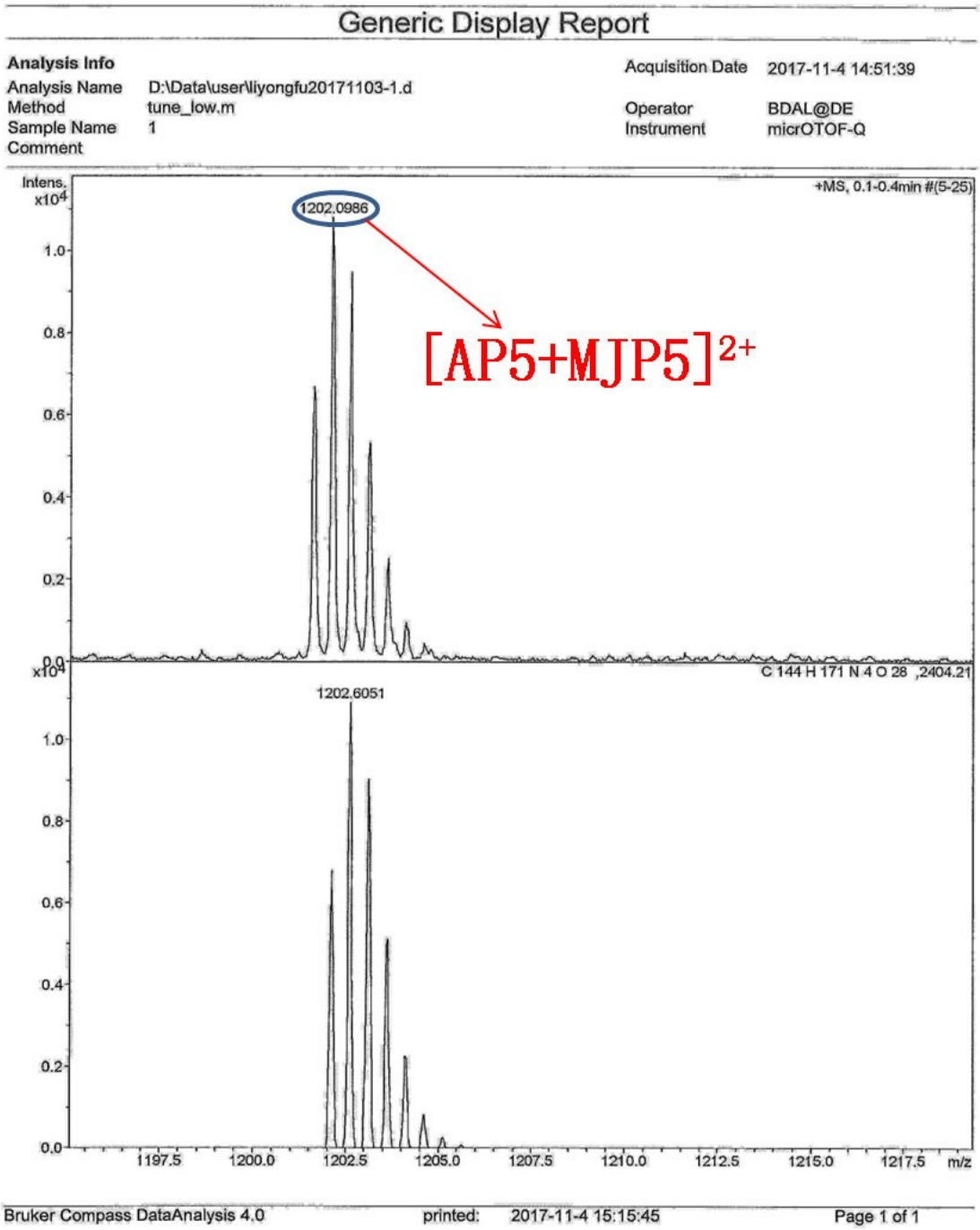


Fig. S18 ESI-MS spectrum of **SOF-AMP.**

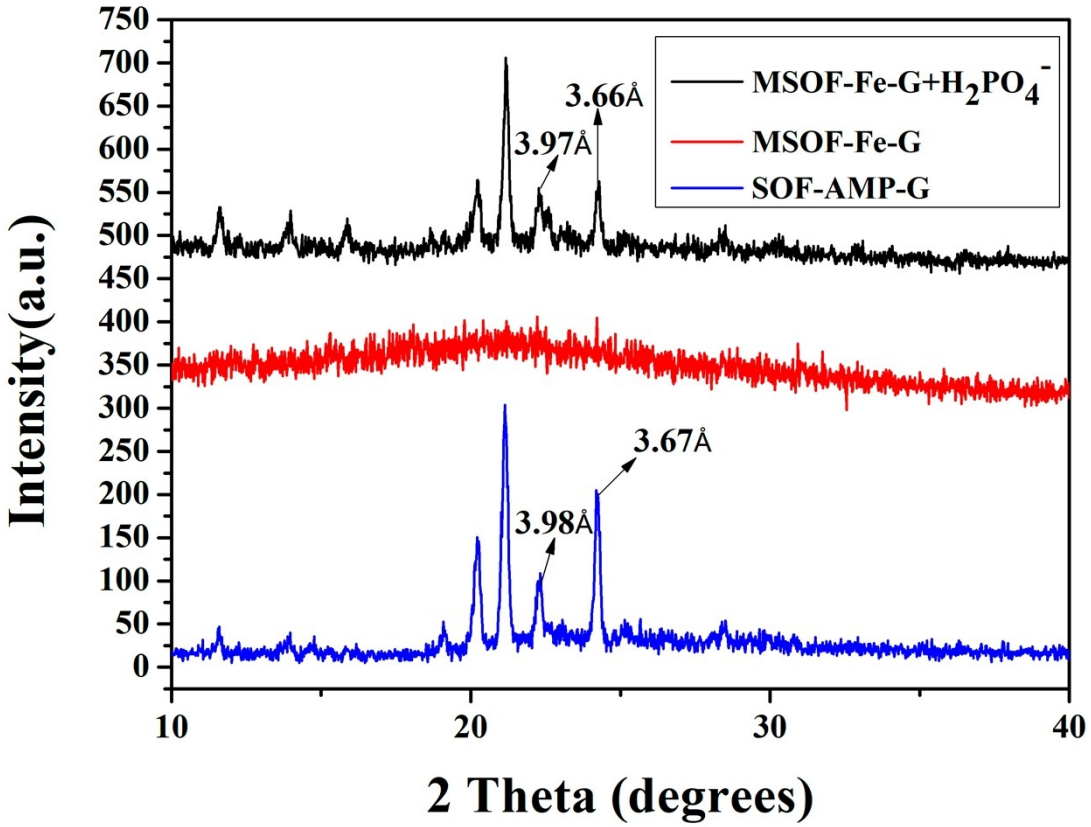


Fig. S19 Powder XRD patterns of xerogel **SOF-AMP-G**, metallogel **MSOF-Fe-G** and xerogel **MSOF-Fe-G + $H_2PO_4^-$.**

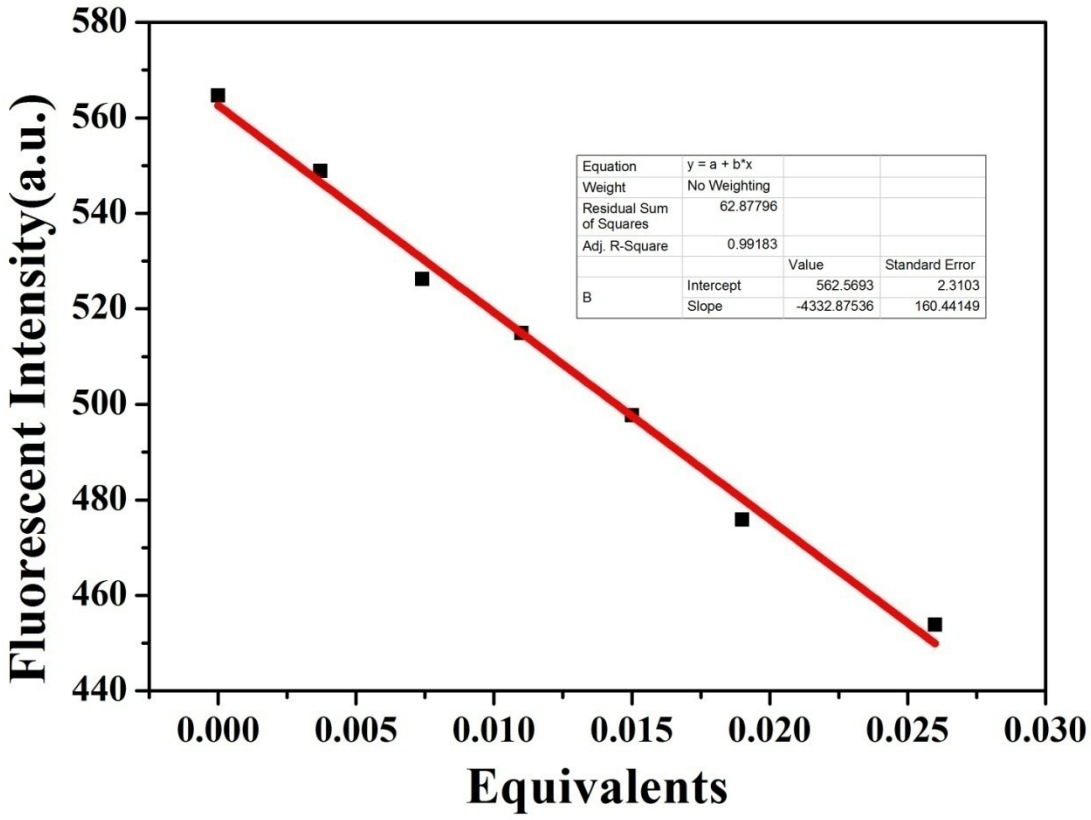


Fig. S20 Plot of the intensity at 538 nm for a mixture of **SOF-AMP-G** and Fe^{3+} (λ_{ex}= 375 nm).

Linear Equation: Y=−4332.875X+562.5693 R^2=0.99183

S=4332.875×10^6

$$\delta = \sqrt{\frac{\sum(Fi - F0)^2}{N - 1}}$$ =10.88619 (N=20)

K=3

LOD =K×δ/S= 7.54×10^{-9} M

Fi is the absorbance intensity of **SOF-AMP-G**; F0 is the average of the Fi.

Table S2. A part of the literatures about the uptake of cations (Fe^{3+}) and the LOD for Fe^{3+} were provided in the followed table.

	Author	Journal and Year. Volume. Page	Adsorption percentage for Fe^{3+}	Limit of Detection for Fe^{3+}
1	X. P. Yan. Etc.	*Anal. Chem.*, 2013, **85**, 7441.	98.2%	
2	Q. Lin. Etc.	*Chem. -Eur. J., 2018, **19**, 777.*	99.29%	1×10^{-7} M
3	T. B. Wei. Etc.	RSC Adv., 2016, **6**, 65898.	___	1.25×10^{-8} M
4	S. H. Li. Etc.	Anal. Chem., 2014, **86**, 10201.	___	0.42×10^{-8} M
5	B. X. Shen. Etc.	J. Mater. Chem. B., 2016, **4**, 7549.	___	5.15×10^{-7} M
6	T. B. Wei. Etc.	*RSC Adv.,* 2016, **6**, 20987.	___	9.0×10^{-7} M
7	C. X. Wang. Etc.	*Analyst.,* 2016, **141**, 4488.	___	1×10^{-8} M
8	L. V. Mulaudzi. Etc.	*Anal. Chim. Acta*., 2002, **467**, 35.	___	1.8×10^{-6} M
9	A. Ohashi. Etc.	*Talanta*, 2005, **65**, 525.	___	1×10^{-7} M
10	J. Zarębski. Etc.	*Anal. Bioanal. Chem*., 2005, **382**, 1691.	___	7.7×10^{-9} M
		This work	99.85%	7.54×10^{-9} M

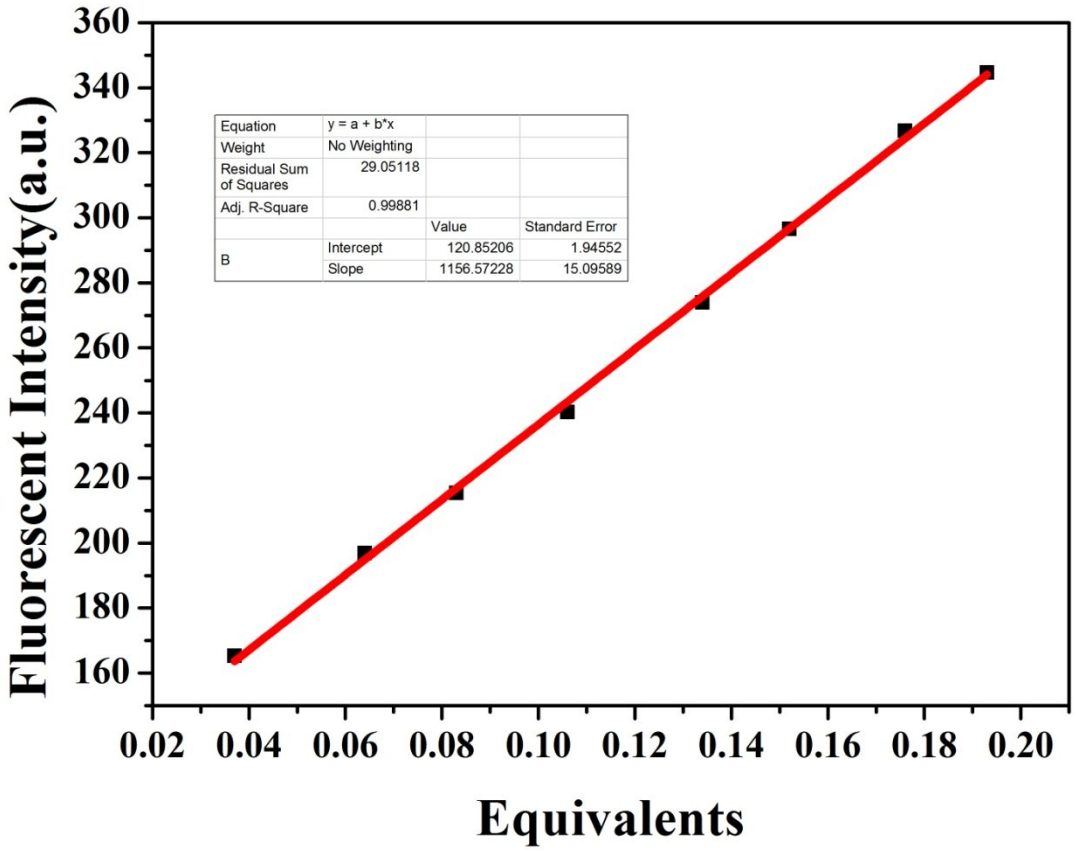


Fig. S21 The photograph of the linear range of **MSOF-Fe-G** for $H_2PO_4^-$.

Linear Equation: Y=1156.57228X+120.85206 R^2=0.99881

S=1156.57228×10^6

$$\delta = \sqrt{\frac{\sum(Fi - F0)^2}{N - 1}}$$ =1.62 (N=20)

K=3

LOD =K×δ/S= 4.21×10^{-9} M

Fi is the absorbance intensity of **MSOF-Fe-G**; F0 is the average of the Fi.

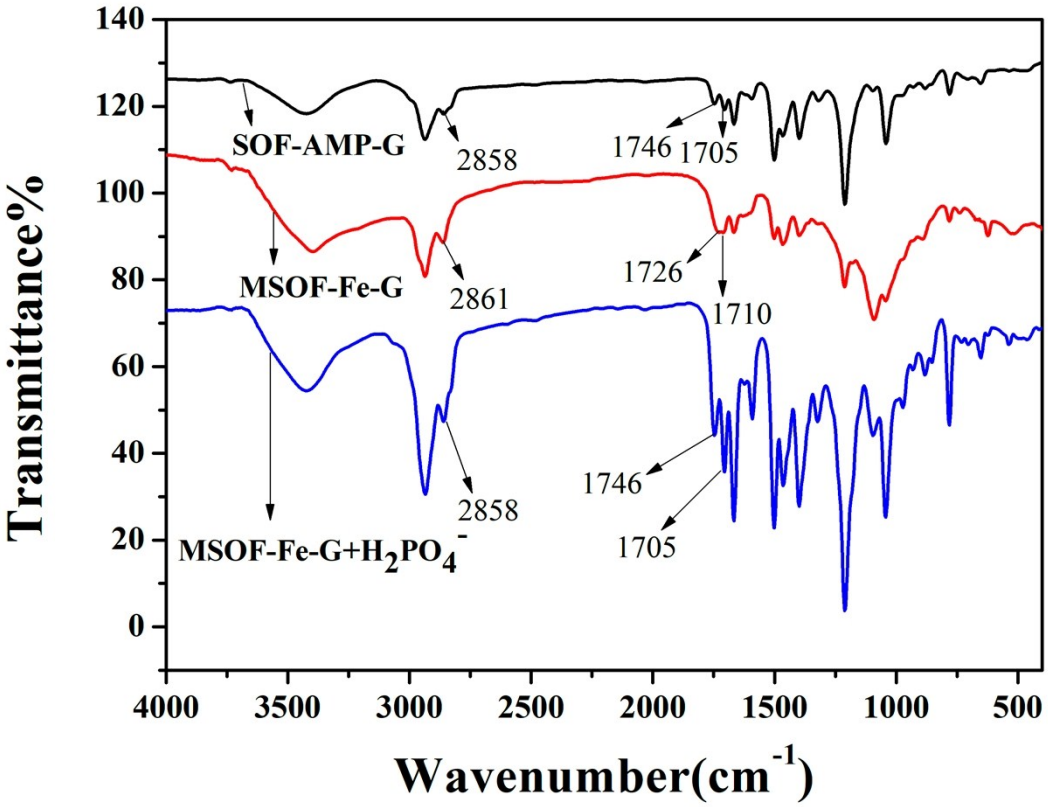


Fig. S22 FT-IR spectra of xerogel **SOF-AMP-G**, metallogel **MSOF-Fe-G**, and xerogel **MSOF-Fe-G + $H_2PO_4^-$**.

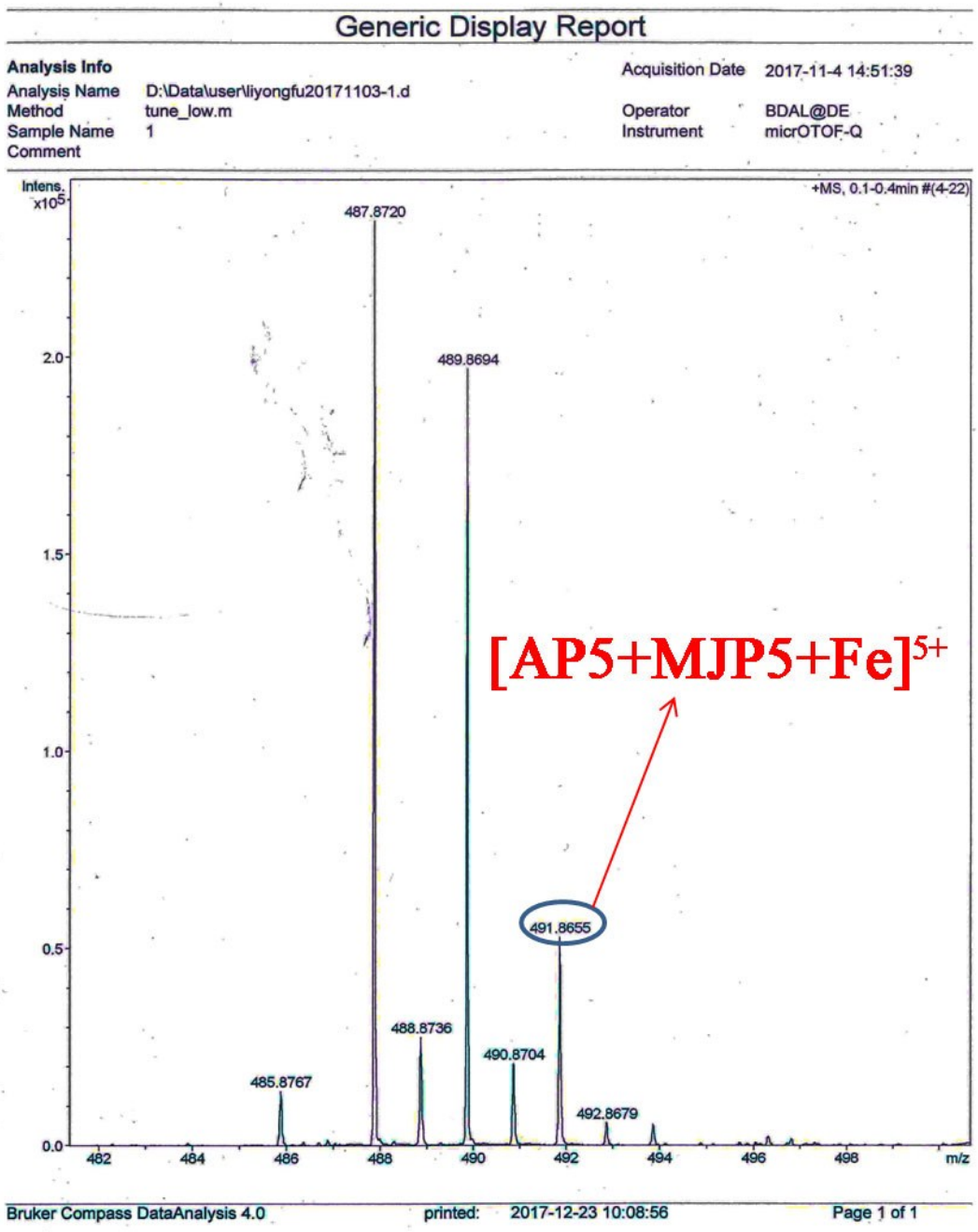


Fig. S23 ESI-MS spectrum of **MSOF-Fe.**

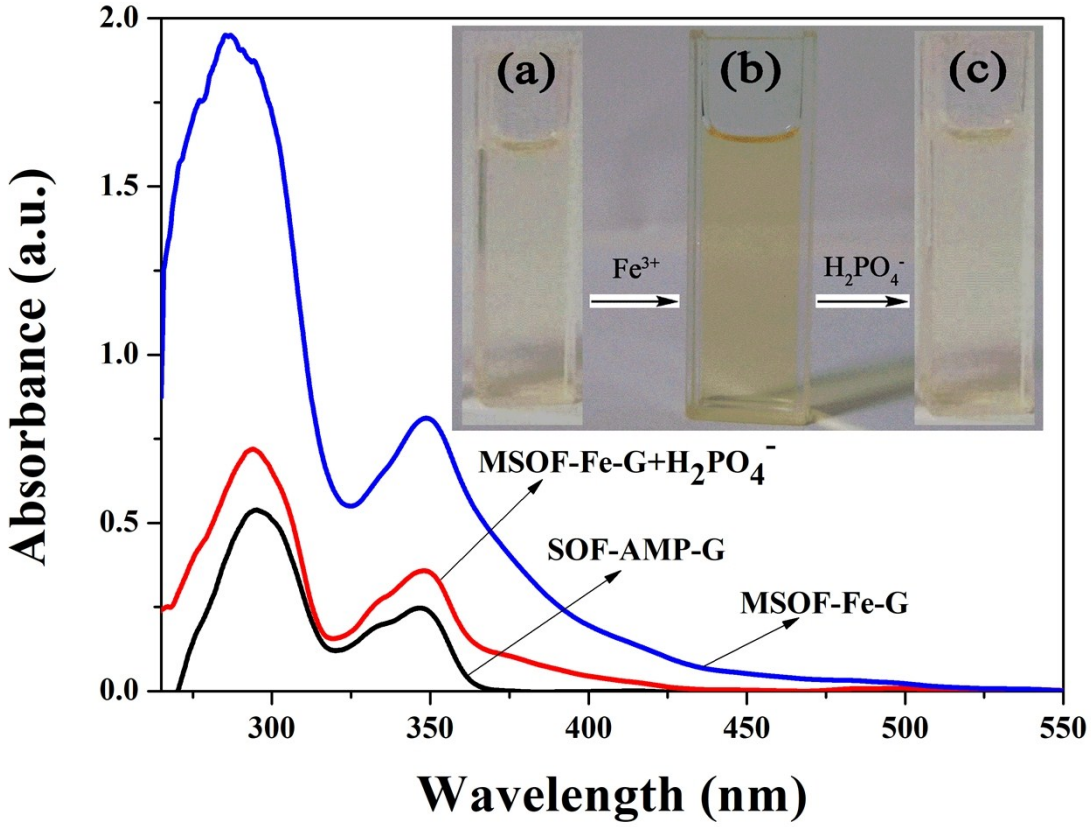


Fig. S24 Absorbance spectra of **SOF-AMP-G** (2.0×10^{-5} M) in cyclohexanol solution upon the addition of Fe^{3+} (5.0 equiv.) and $H_2PO_4^-$ (20.0 equiv.). Inset: photograph showing the change in color of the solution of **SOF-AMP-G** in cyclohexanol after addition of Fe^{3+} and $H_2PO_4^-$ at room temperature.

Table S3 Adsorption percentage of **SOF-AMP-G** for Fe^{3+}

.

Ions	Initial concentration (M)	Residual concentration(M)	Adsorption percentage %
Fe^{3+}	1×10^{-5}	1.5×10^{-8}	99.85

Calculation method of adsorption percentage:

$$\text{Adsorption percentage}(\%) = \left(1 - \frac{C_R \times V_R}{C_I \times V_I}\right) \times 100\%$$

(state: C_R is the residual concentration of Fe^{3+}, C_I is the initial concentration of Fe^{3+}, V_R=V_I)