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Stimuli-responsive supramolecular polymer network based on bi-pillar[5]arene for efficient multiple organic dye contaminants adsorption

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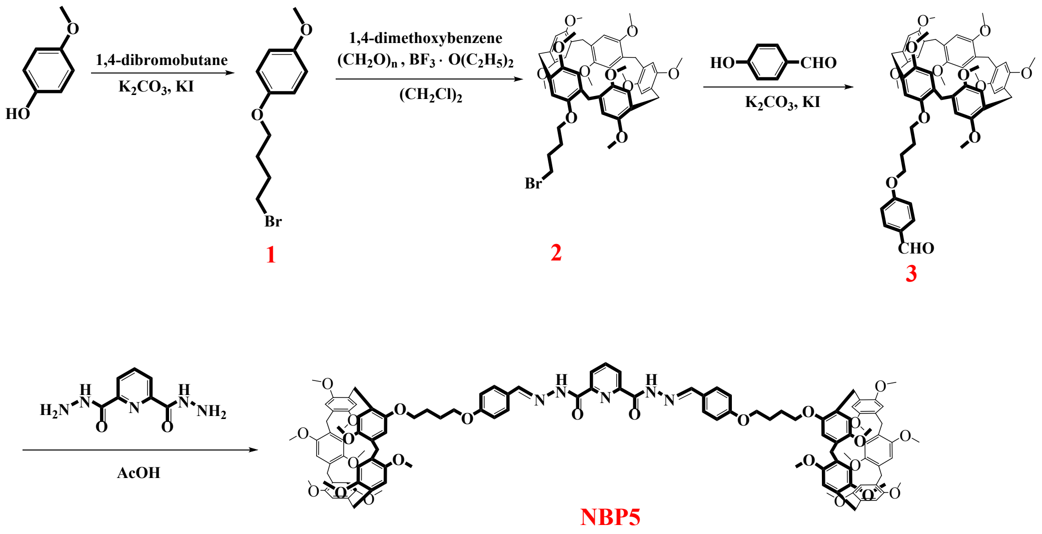
1. Materials and methods

1,4-dimethoxybenzene, boron trifluoride ethyl ether complex, 1,4-dibromobutane, and 1,10-dibromodecane were reagent grade and used as received. Solvents were either employed as purchased or dried by $CaCl_2$. ^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 151 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with 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 in a transmission mode with a Rigaku RINT2000 diffractometer equipped with graphite monochromated CuKa radiation (λ = 1.54073 Å). The morphologies and sizes of the xerogels were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 5 kV. Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer.

2. Synthesis of bi-pillar[5]arene NBP5



Scheme S1 Synthesis of bi-pillar[5]arene **NBP5**.

Synthesis of compound 1 : In a 500 mL round-bottom flask, 4-methoxyphenol (2.48 g, 20.0 mmol), K_2CO_3 (8.40 g, 60 mmol), KI (3.30 g, 20mmol), 1,4-dibromobutane (17.20g, 80 mmol) and acetone (400.0 mL) were added. The reaction mixture was stirred at reflux for 2 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 : ethyl acetate = 20:1) afforded a white solid (4.96 g, 95 %). Mp 45-47℃. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.84 (d, J = 1.3 Hz, 4H), 3.90 (t, J = 6.2 Hz, 2H), 3.68 (s, 3H), 3.56 (t, J = 6.7 Hz, 2H), 1.95 (dd, J = 14.3, 7.2 Hz, 2H), 1.80 (dd, J = 14.5, 6.5 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 153.76, 152.99, 115.73, 114.98, 67.47, 55.76, 35.19, 29.61, 27.98.

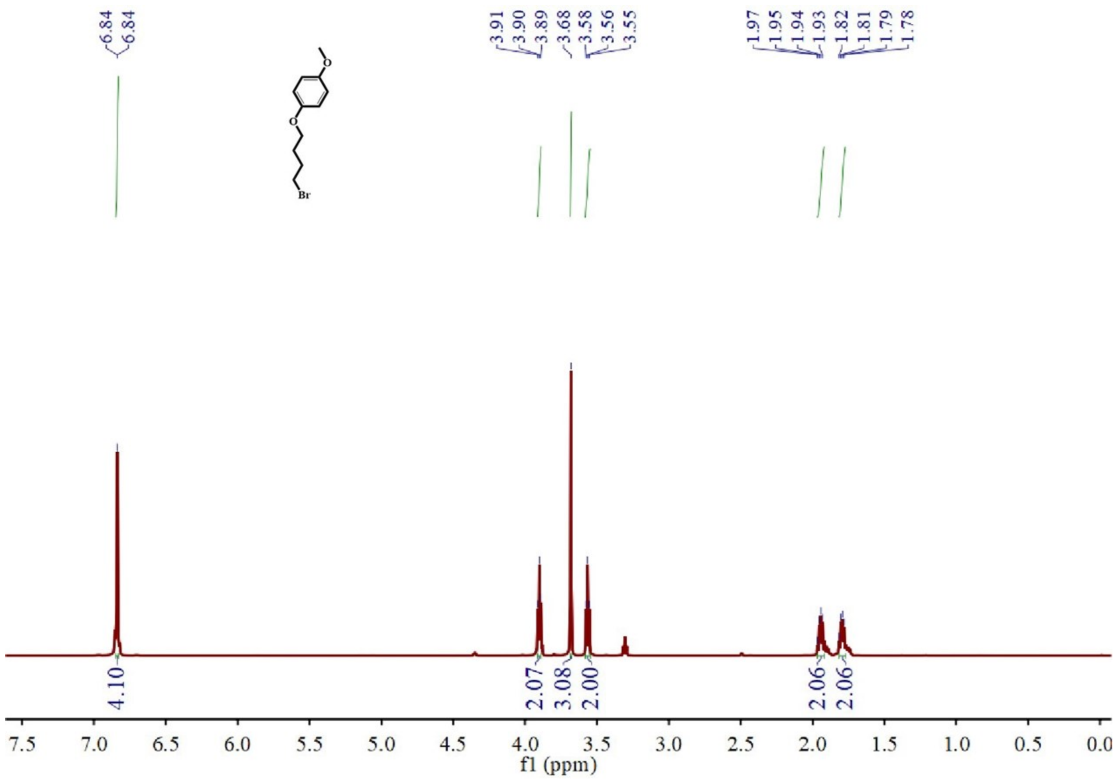


Figure S1 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound **1**.

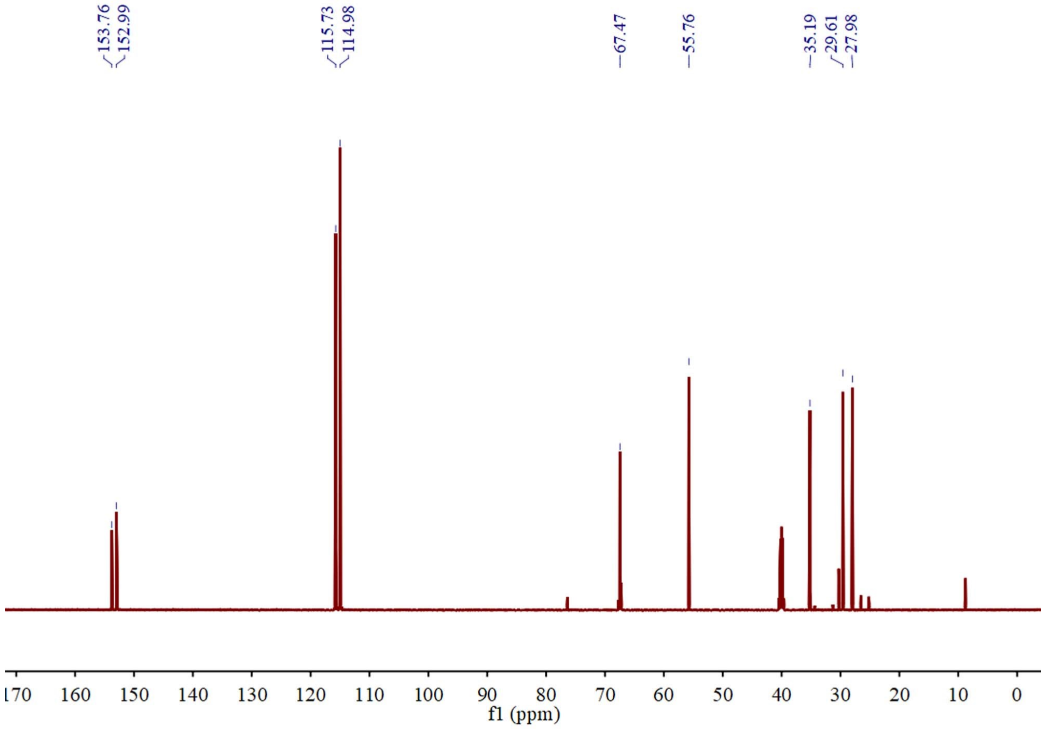


Figure S2 ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of compound **1**.

Synthesis of a copillar[5]arene 2 : To a solution of compound **1** (1.29 g, 5.0 mmol) and 1,4-dimethoxybenzene (2.76 g, 20.0 mmol) in 1,2-dichloroethane (80 mL), paraformaldehyde (0.75 g, 25.0 mmol) was added. Then boron trifluoride diethyl etherate (6.75 mL, 25 mmol) was added to the solution and the mixture was stirred at 30℃ for 1 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 **2** (1.3 g, 30%) as a white solid. Mp 74-77℃. ^1H NMR (600 MHz, DMSO-d_6) δ 6.85 - 6.76 (m, 10H), 3.85 (t, J = 5.9 Hz, 2H), 3.71 - 3.63 (m, 37H), 3.51 (t, J = 6.3 Hz, 2H), 1.88 (dd, J = 37.2, 6.2 Hz, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 150.16, 150.06, 149.43, 127.75, 127.68, 113.14, 113.00, 67.13, 55.61, 29.85, 29.20, 28.41. ESI-MS m/z: $(M+NH_4)^+$ Calcd for $C_{48}H_{59}O_{10}BrN$ 890.3302; Found 890.3300.

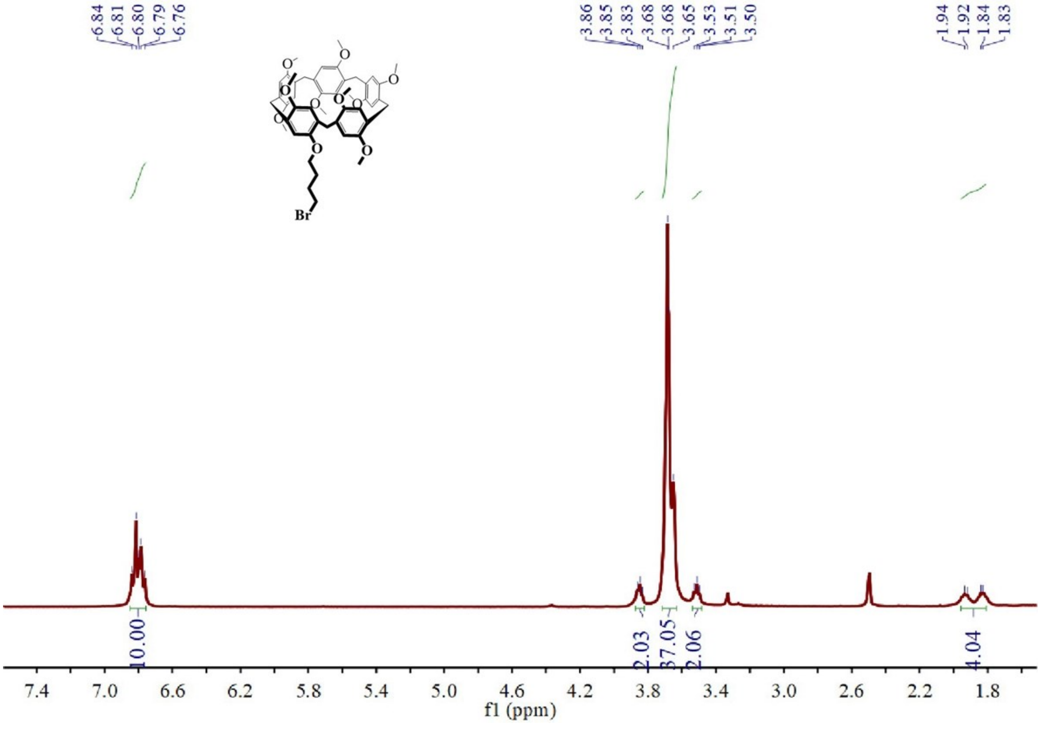


Figure S3 ^1H NMR spectrum (600 MHz, DMSO-d_6) of copillar[5]arene **2**.

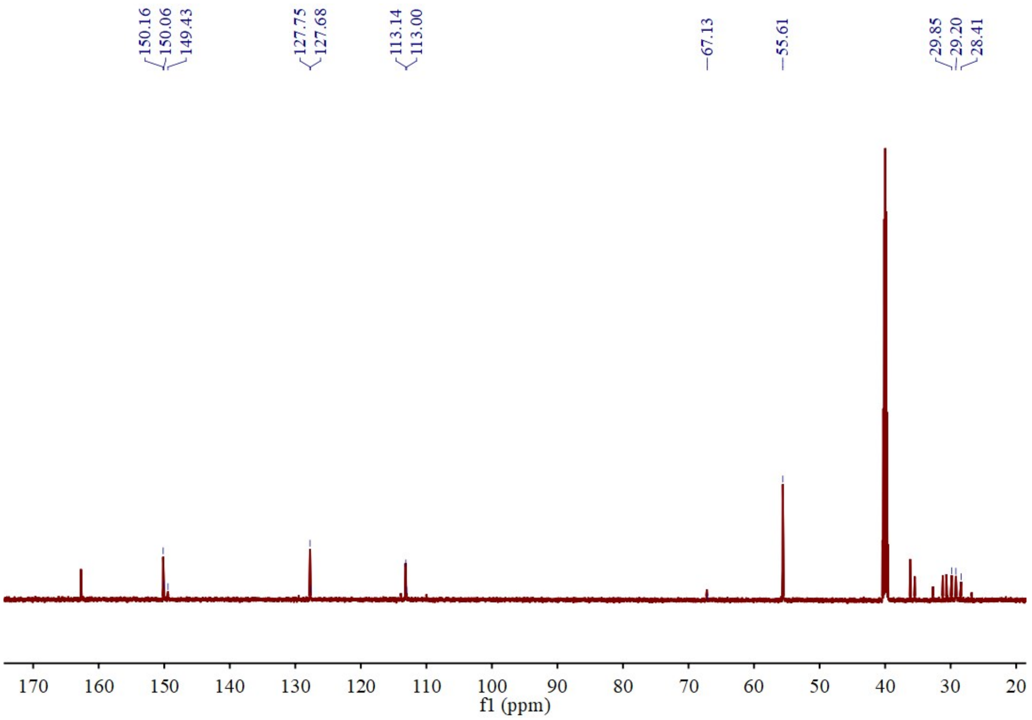


Figure S4 ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of copillar[5]arene **2**.

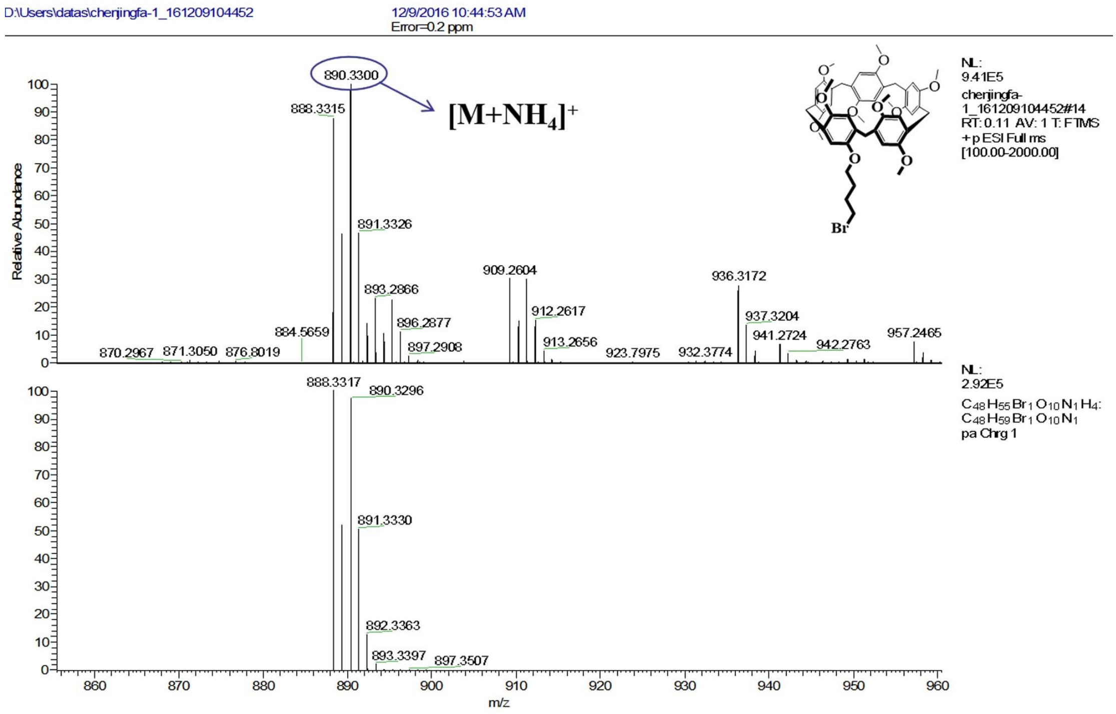


Figure S5 Mass data of a copillar[5]arene **2**.

Synthesis of compound intermediate 3 : Copillar[5]arene **2** (1.20 g, 1.38 mmol), and 4-hydroxybenzaldehyde (0.41 g, 3.36 mmol) was dissolved in acetone (80 mL).

K_2CO_3 (1.55 g, 11.23 mmol) was added and the reaction mixture was stirred at reflux for 24 h. After solvent was evaporated and the residue was dissolved in CH_2Cl_2. Column chromatography (silica gel; petroleum ether : ethyl acetate = 20 : 1) afforded a white solid (0.37 g, 30%). Mp 76-78℃. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.86 (s, 1H), 7.85 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.7 Hz, 2H), 6.83 - 6.75 (m, 10H), 4.14 (t, J = 6.1 Hz, 2H), 3.90 (t, J = 6.0 Hz, 2H), 3.69 - 3.61 (m, 37H), 1.94 (ddd, J = 19.0, 13.5, 6.8 Hz, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 191.70, 164.07, 150.30, 150.26, 149.58, 132.23, 130.01, 127.89, 115.29, 114.34, 113.60, 68.10, 55.73, 29.39, 29.25. ESI-MS m/z: $(M+H)^+$ Calcd for $C_{55}H_{61}O_{12}$ 913.4163; Found 913.4156.

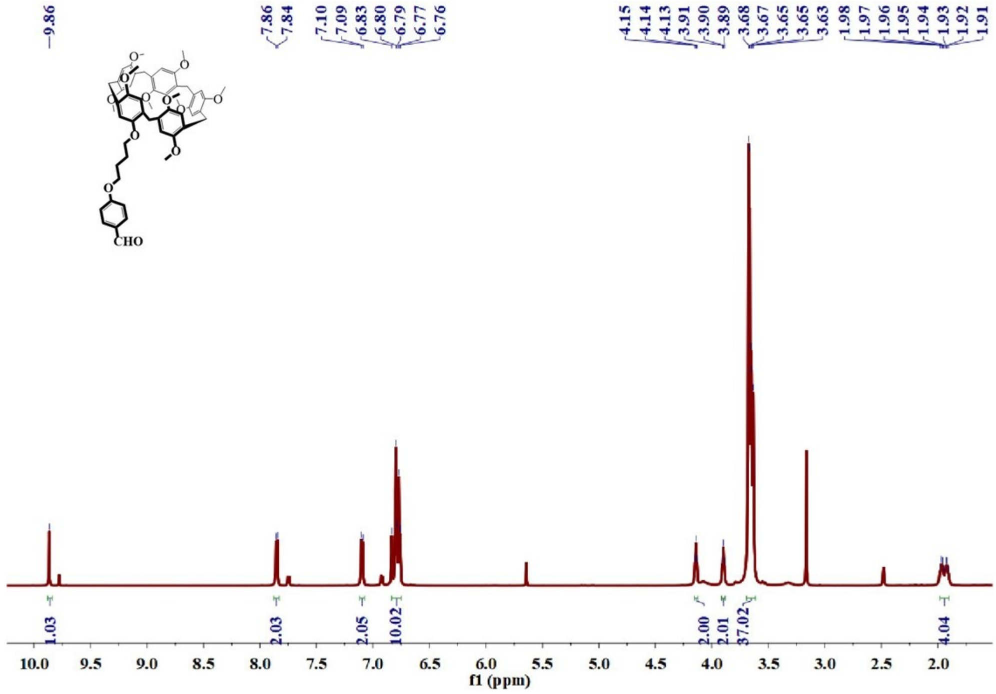


Figure S6 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of compound intermediate **3**.

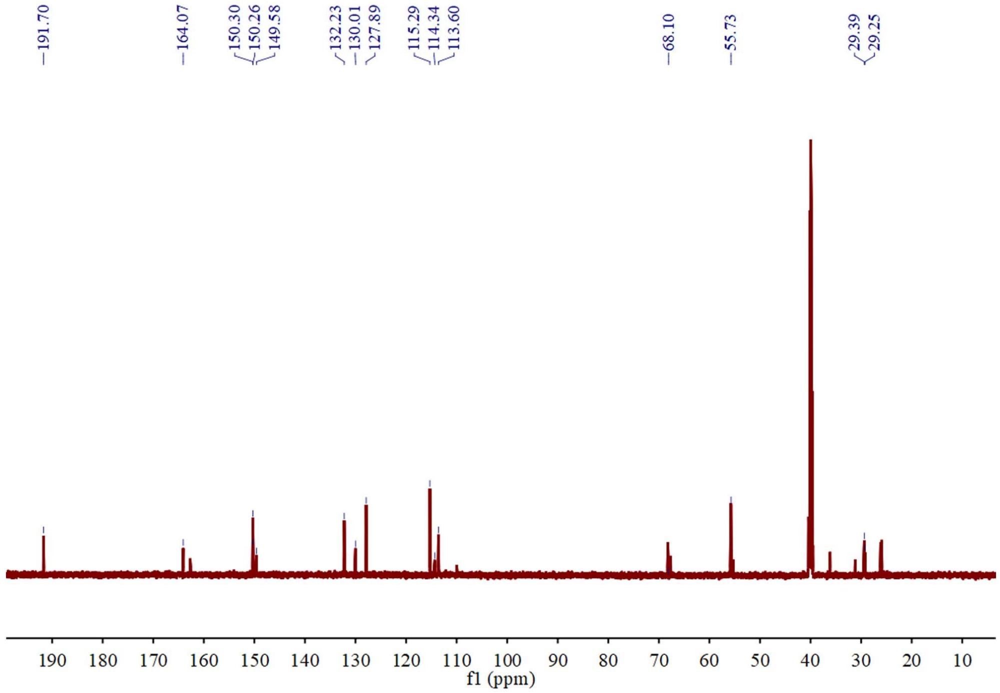


Figure S7 ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of compound intermediate **3**.

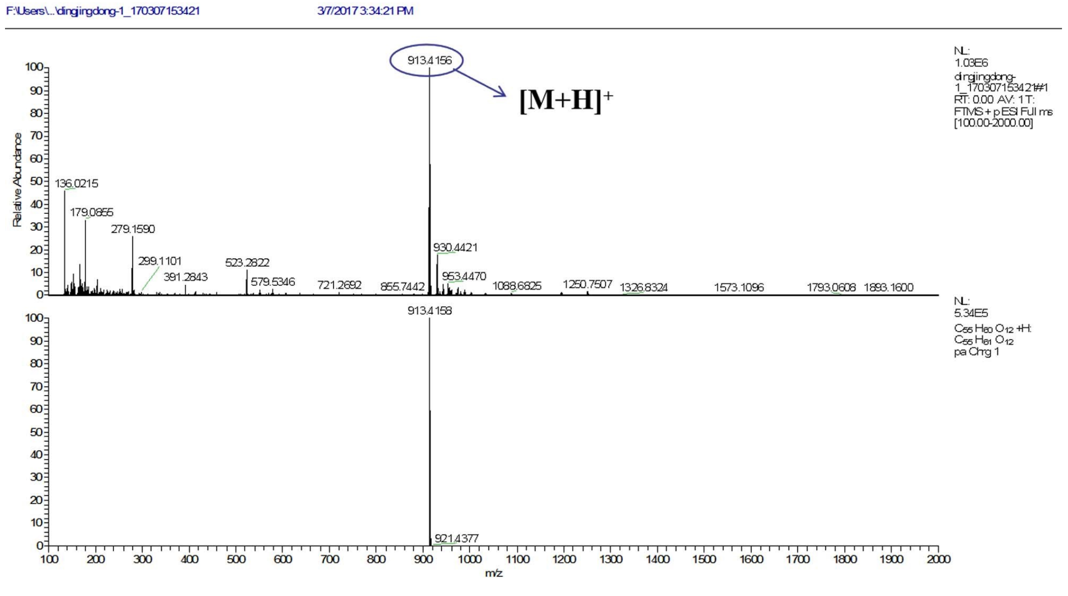


Figure S8 High resolution mass data of compound intermediate **3**.

Synthesis of bi-pillar[5]arene NBP5: Compound intermediate 3 (0.22 g, 1.2 mmol), Pyridyl di-hydrazide (0.02, 0.5 mmol) and two drops of glacial acetic acid were added to ethanol (50 mL). Then the reaction mixture was stirred under refluxed conditions for 24 hours, after the solvent was evaporated and the residue was dissolved in CH_2Cl_2. Column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) afforded a white solid (0.18 g, 81%). Mp 128-130℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ

11.28 (s, 2H), 8.69 (s, 2H), 8.32 (d, J = 7.8 Hz, 2H), 7.94 (t, J = 7.8 Hz, 1H), 7.66 (d, J = 8.6 Hz, 4H), 6.89 (d, J = 8.7 Hz, 4H), 6.78 - 6.74 (m, 20H), 4.03 (t, J = 6.0 Hz, 4H), 3.90 (t, J = 5.9 Hz, 4H), 3.77 (d, J = 3.1 Hz, 20H), 3.64 (dd, J = 7.3, 3.7 Hz, 54H), 2.00-1.93 (m, 8H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 161.41, 160.14, 150.92, 150.85, 150.51, 150.01, 148.91, 129.59, 128.37, 128.31, 126.23, 125.91, 114.99, 114.82, 114.14, 68.02, 67.85, 55.86, 29.77, 26.50. ESI-MS m/z: $[M]^+$ calcd for $C_{117}H_{125}O_{24}N_5$ 1983.8714; Found 1983.8679.

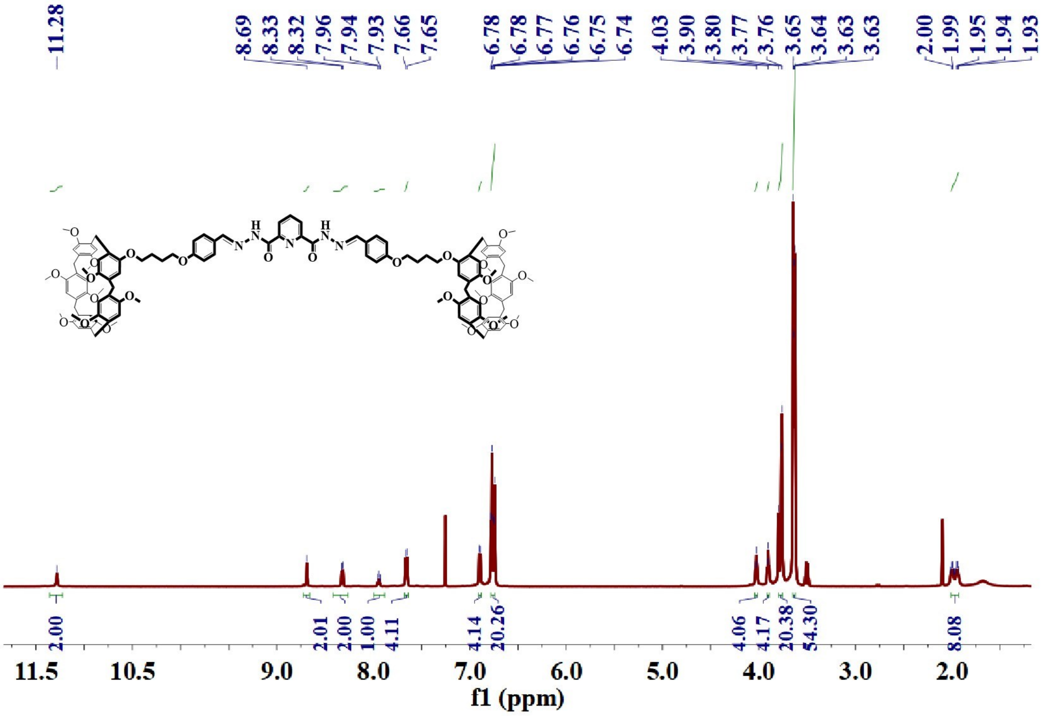


Figure S9 ^{1}H NMR spectrum (600 MHz, CDCl$_3$) of bi-pillar[5]arene **NBP5**.

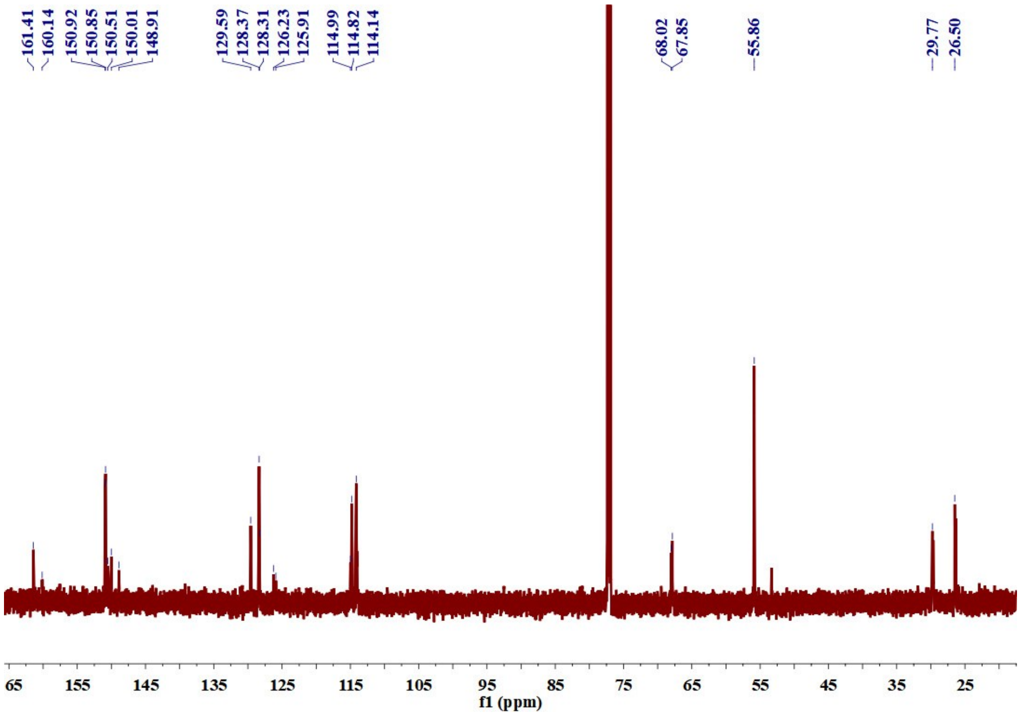


Figure S10 ^{13}C NMR spectrum (151 MHz, $CDCl_3$) of bi-pillar[5]arene **NBP5**.

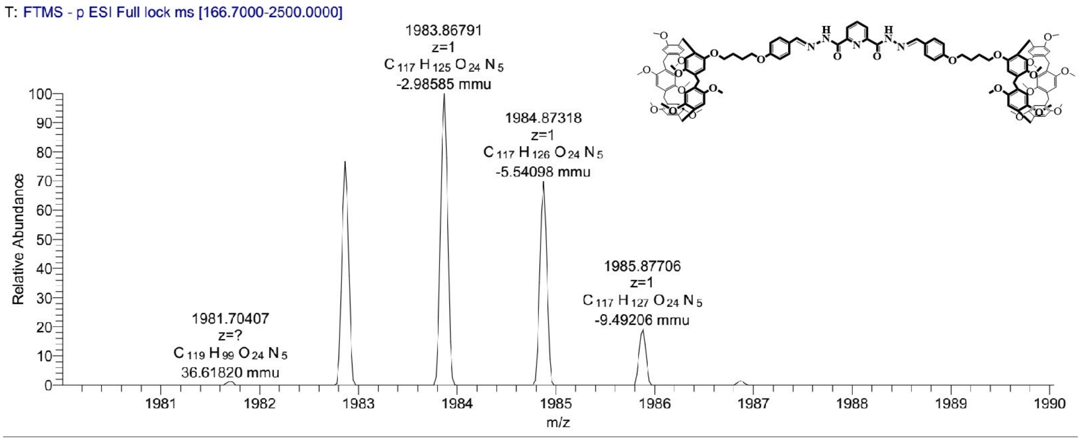
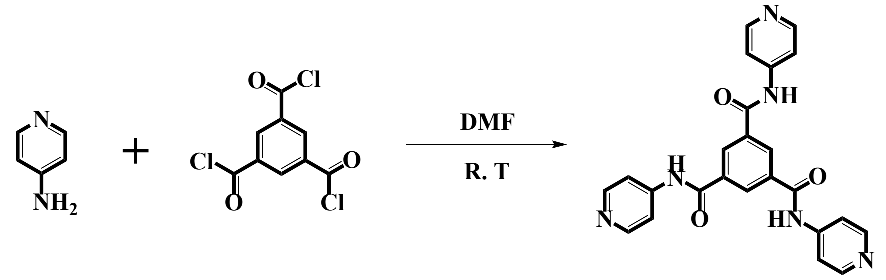


Figure S11 High resolution mass data of bi-pillar[5]arene **NBP5**.

3. Synthesis of G



Scheme S2 Synthesis of guest **TG**.

To a solution of 1,3,5-benzenetricarbonyl trichloride (0.1 mmol, 0.025g) was dropwise added into the mixture of 4-aminopyridine (0.33 mmol, 0.031g) and TEA (1 mL) in dichloromethane. The mixture was stirred at room temperature for 20 h. The product **TG** was collected by filtration, washed by water, and dried under vacuum (0.0421 g, 96%). M.p. 167-169 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.04 (s, 3H), 8.80 (s, 3H), 8.54 (d, J = 6.3 Hz, 6H), 7.87 (d, J = 6.3 Hz, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 165.62, 150.78, 146.20, 135.29, 131.06, 114.57. ESI-MS m/z: [**TG**]$^+$ calcd for $C_{24}H_{18}N_6O_3$: 439.1474, found 439.1509.

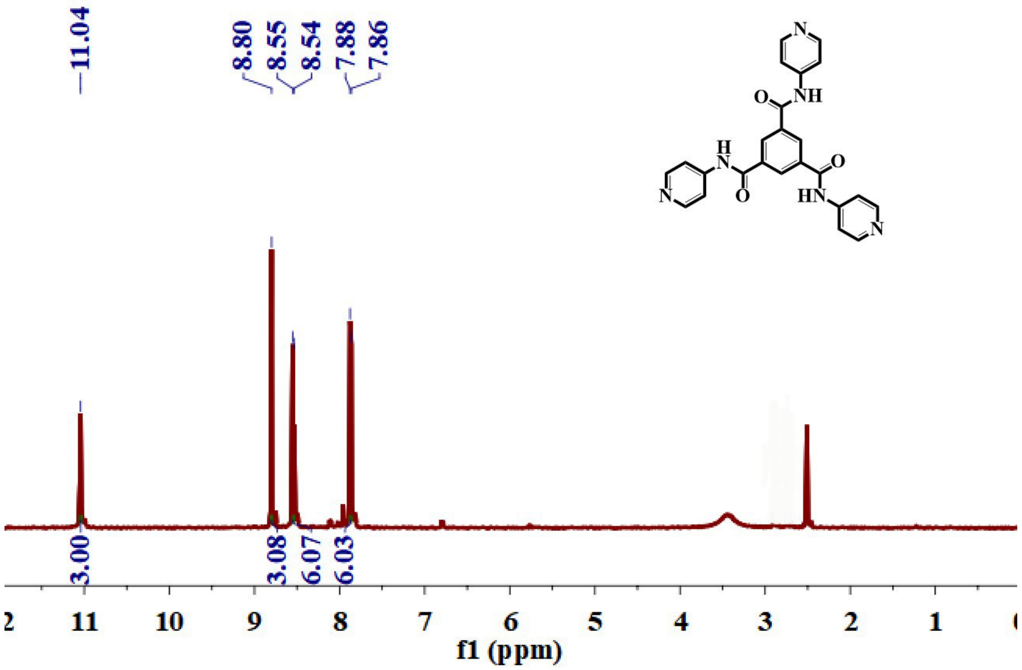


Figure S12 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **TG**.

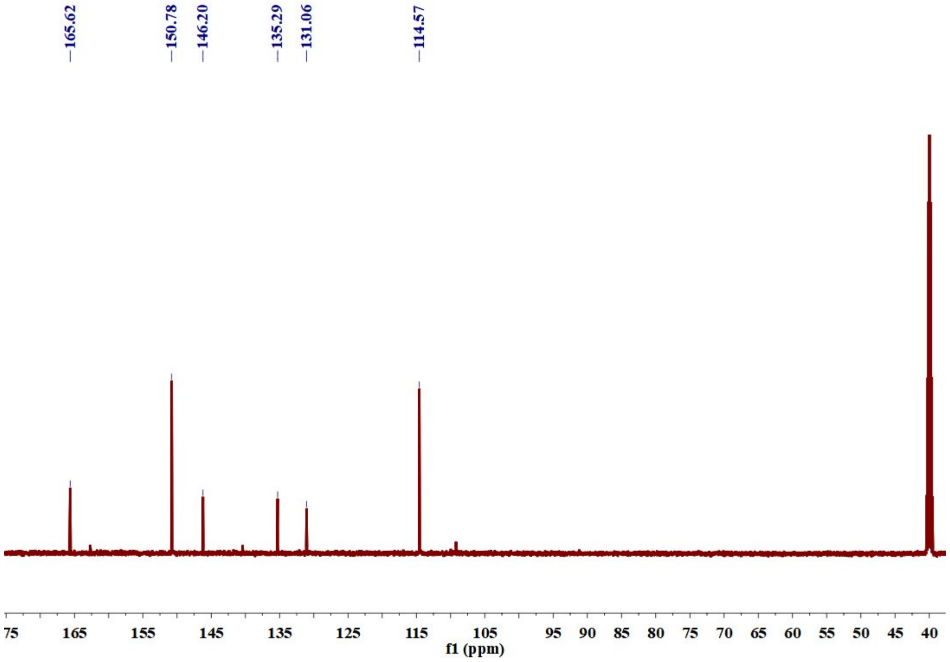


Figure S13 ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **TG**.

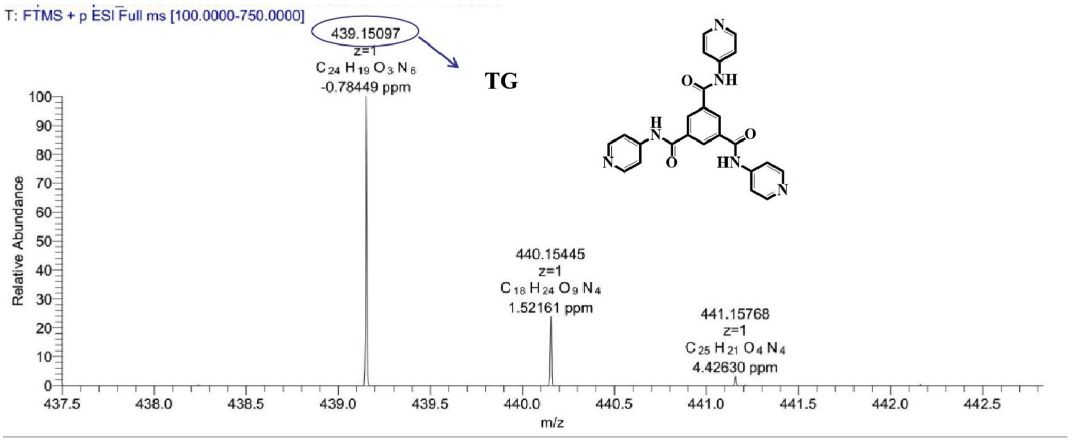


Figure S14 High resolution mass data of **TG**.

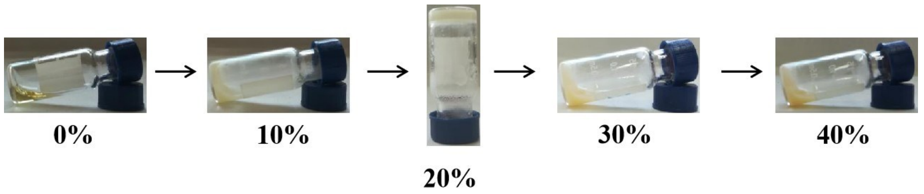


Figure S15 Stability of **NT**.

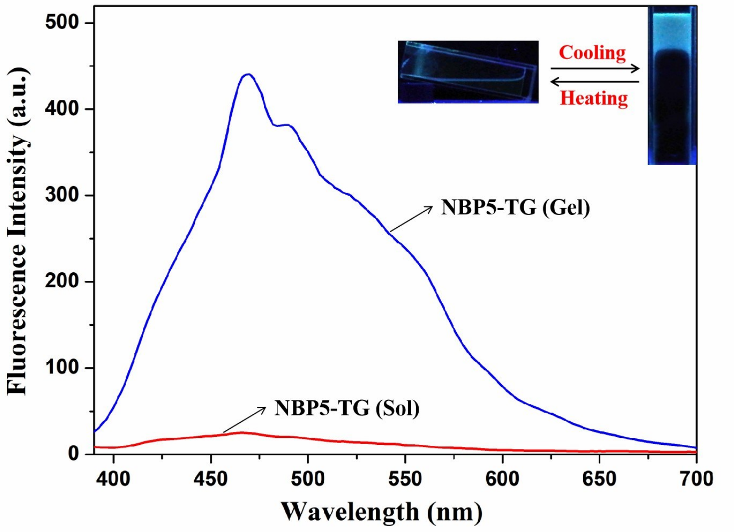


Figure S16 Fluorescence spectra of **NT** in DMSO/H_2O solution (v : v = 8 : 2).

Table S1. Gelation Properties of organogelator **NT**

Entry	Solvent	State[a]	CGC[b]	Tgel[c](℃,wt%)
1	Acetone	P	/	/
2	Methanol	P	/	/
3	Ethanol	P	/	/
4	Isopropanol	P	/	/

5	Isopentanol	P	/	/
6	Acetonitrile	P	/	/
7	DMF	S	/	/
8	DMSO	P	/	/
9	DMSO/H_2O (v:v, 8:2)	G	7%	40-43℃ (7%)
10	CH_2Cl_2	S	/	/
11	$CHCl_3$	S	/	/
12	Petroleum ether	P	/	/
13	Ethyl acetate	P	/	/
14	Cyclohexanol	G	/	/
15	N-Hexanoic acid	S	/	/
16	Tetrahydrofurane	S	/	/
17	Hexanol	P	/	/
18	Ethylene glycol	P	/	/
19	Acetic acid	P	/	/
20	Water	P	/	/
21	Tert-butanol	P	/	/
22	N-propanol	P	/	/
23	Butanol	p	/	/
24	Propionic acid	S	/	/
25	CCl_4	P	/	/
26	Cyclohexane	P	/	/

[a] G, P and S denote gelation, precipitation and solution, respectively.

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

[c] The gelation temperature (℃).

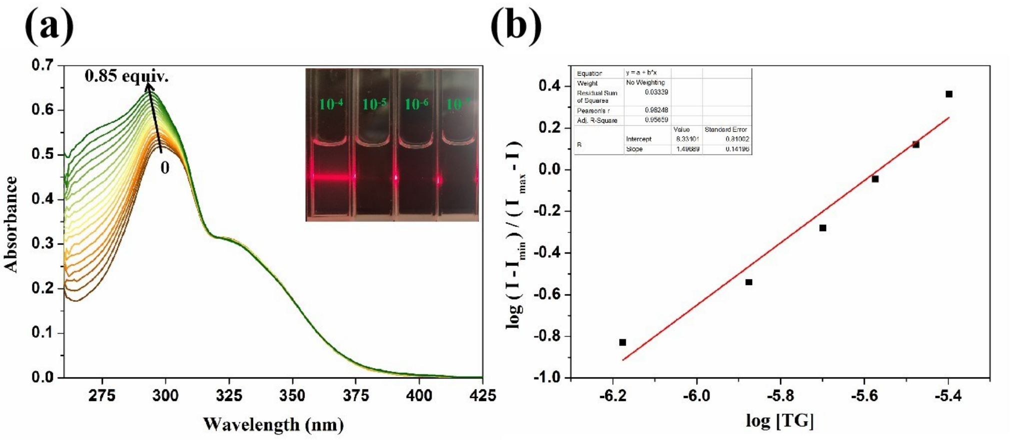


Figure S17 (a) Absorption spectrum of **NBP5** (10 μM) in the presence of different equiv of **TG** in DMSO solutions; (b) The photograph of the absorption spectrum linear range for **TG**. Tyndall effect photos of **NT** in DMSO/H_2O (f_w = 20%) solution with different concentration(10^{-4}-10^{-7}M).

The association constant (K_a) for the complexation of **NBP5** and **TG** was estimated by means of absorption titration experiments at room temperature in DMSO. The K_a for **NT** was obtained as 2.14×10^{8} M^{-1}.

$$log \frac{I - I_{min}}{I_{max} - I} = log\, K_a + log[C]$$

K = 2.14×10^{8} M^{-1}.

I is the observed the absorbance of **TG** at the fixed concentrations of **NBP5**. $\mathbf{I_{max}}$ and $\mathbf{I_{min}}$ are the corresponding maximum and minimum, respectively. **I** is the observed the absorbance of **TG** at the fixed concentrations of **NBP5**. [**C**] is the the concentration of **TG**.

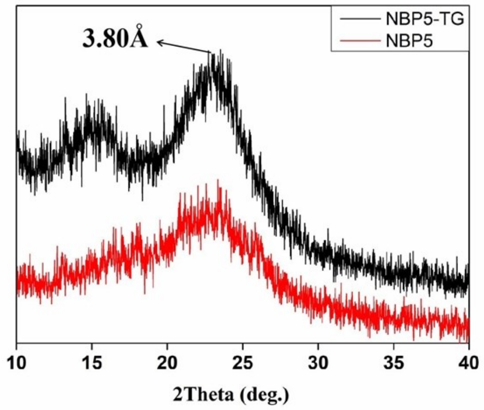


Figure S18 Powder XRD patterns of **NBP5** and xerogel of **NT.**

Figure S19 SEM images of xerogel (a) **NBP5**; (b) **TG**; (c) **NT**

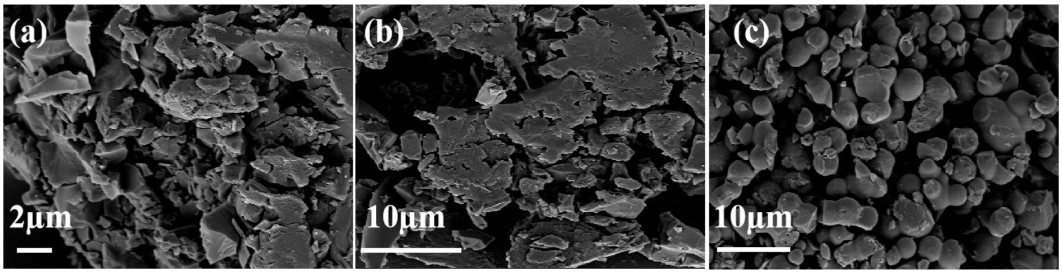
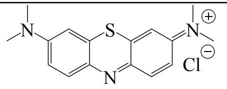
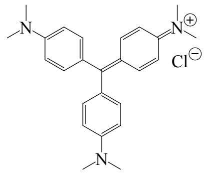
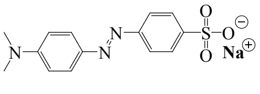
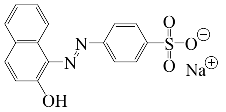
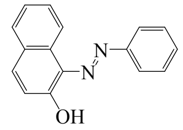
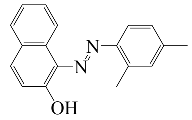


Figure S20 (a) **NT** treated with adiponitrile; (b) **NT** treated with triethylamine; (c) **NT-**triethylamine treated with CH_3COOH.

Table S2. Chemical name, chemical structures and exact weight of organic dye

Entry	Chemical name	Chemical structures	Molar mass (g/mol)
1	methylene blue (MB)		319.09
2	crystal violet (CV)		407.98
3	methyl orange (MO)		327.06
4	orange I (OI)		350.03
5	sudan I (SDI)		248.28
6	sudan Ⅱ (SDⅡ)		276.33

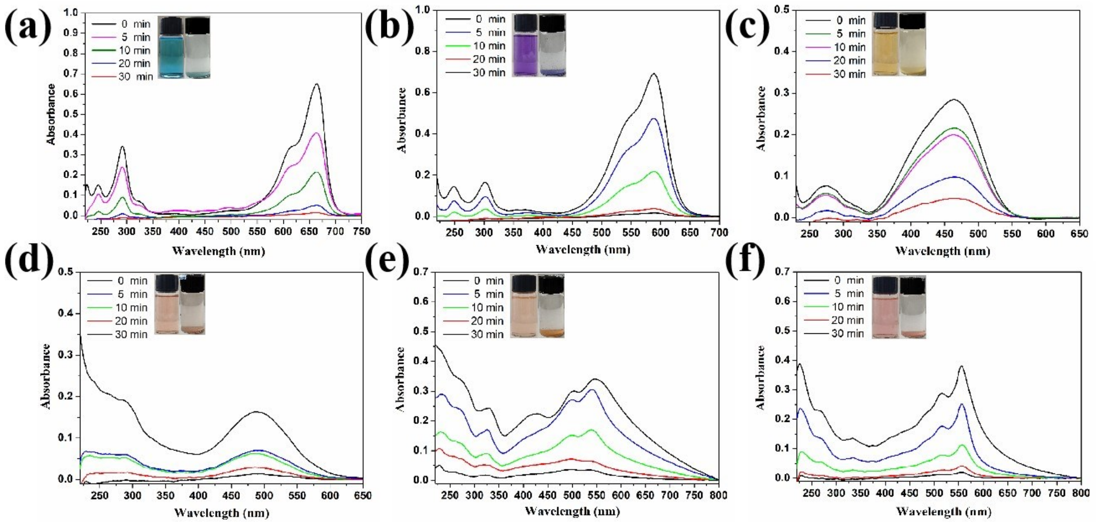


Figure S21 UV-vis spectra a recorded as a function of contact times with **NT**: (a) methylene blue; (b) crystal violet; (c) methyl orange; (d) orange I; (e) sudan I; (f) sudan Ⅱ.

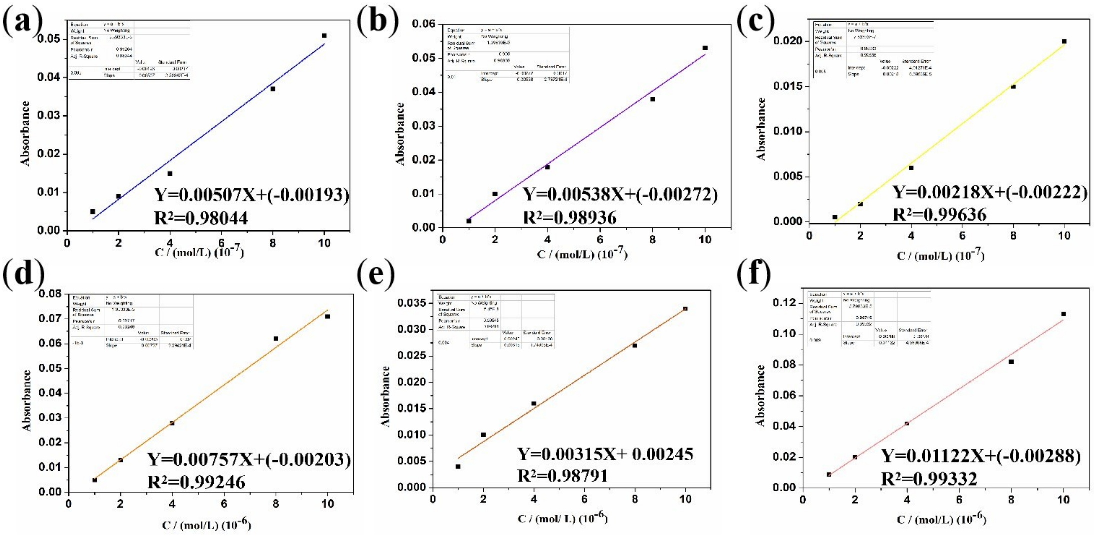


Figure S22 A plot of concentration of crystal violet vs. absorbance intensity.

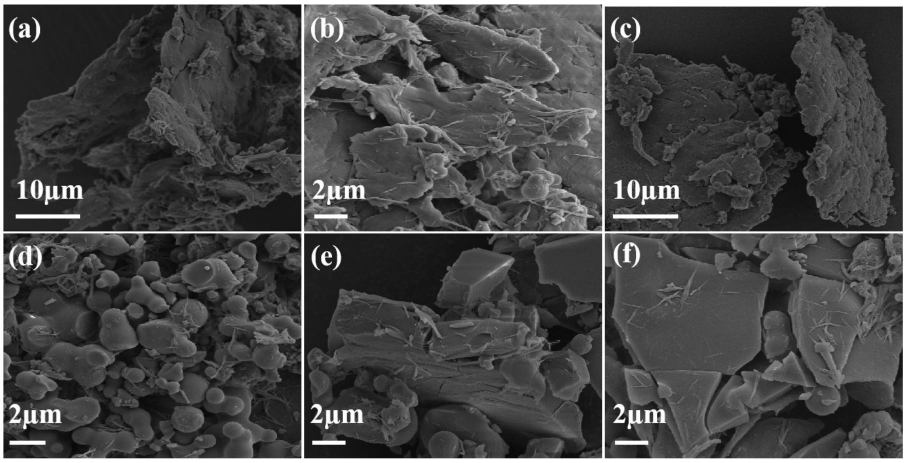


Figure S23 SEM images of xerogel (a) **NT** treated with methylene blue; (b) **NT** treated with crystal violet; (c) **NT** treated with methyl orange; (d) **NT** treated with orange I; (e) **NT** treated with sudan I; (f) **NT** treated with sudan Ⅱ.

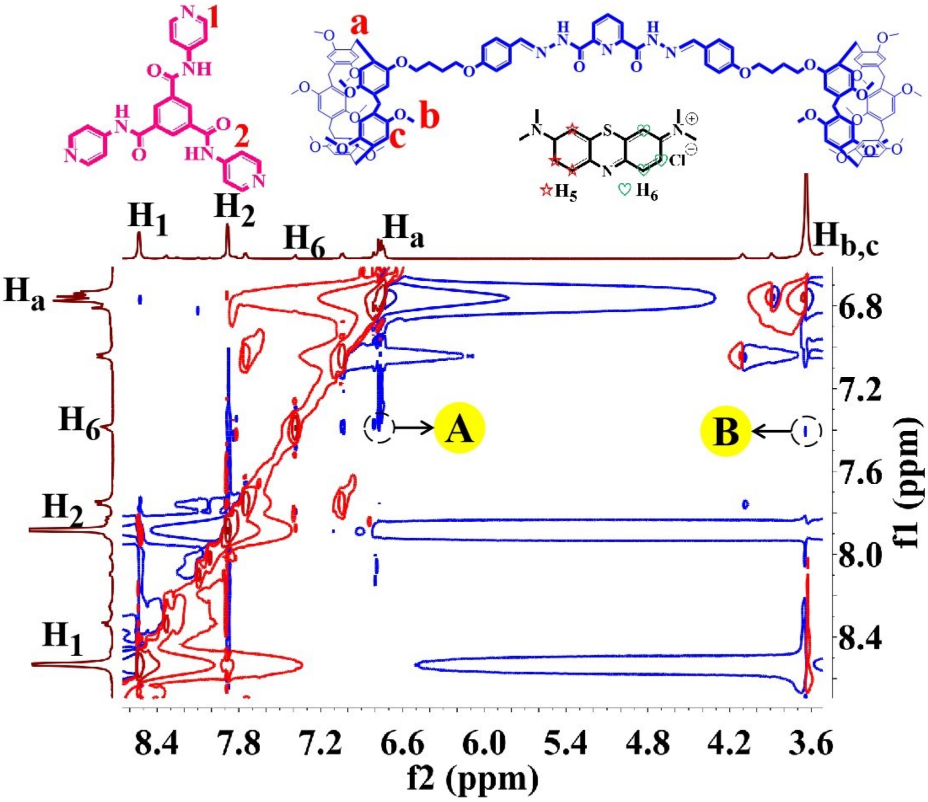


Figure S24 2D NOESY NMR spectrum (600 MHz, 298 K) of 10.0 mM **NT** and MB in DMSO-d_6 solution.

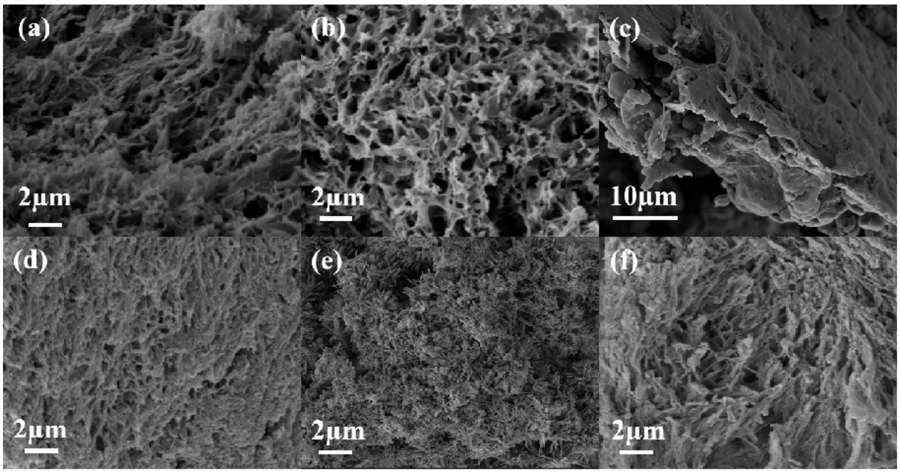


Figure S25 SEM images of xerogel desorption in ethanol (a) **NT-** MB; (b) **NT-**CV; (c) **NT-**MO ; (d) **NT**-OI; (e) **NT**-SDI; (f) **NT**-SDⅡ.

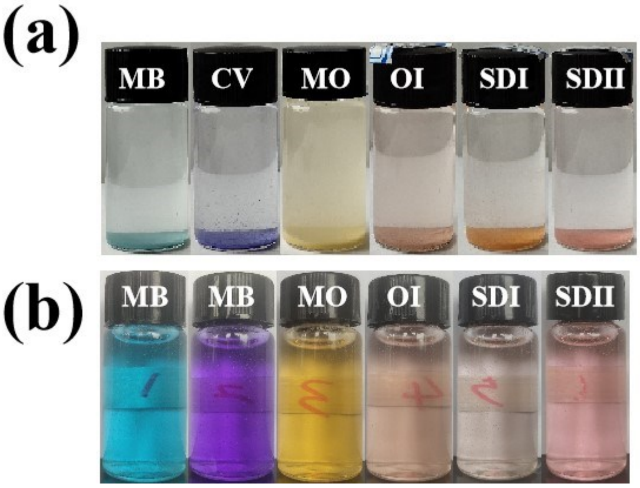


Figure S26 (a) The adsorption separation of various organic dyes by **NT**; (b) The adsorption separation of various organic dyes by **NBP5**.