# An azine-containing bispillar[5]arene-based multi-stimuli responsive supramolecular pseudopolyrotaxane gels for effective adsorption of rhodamine B

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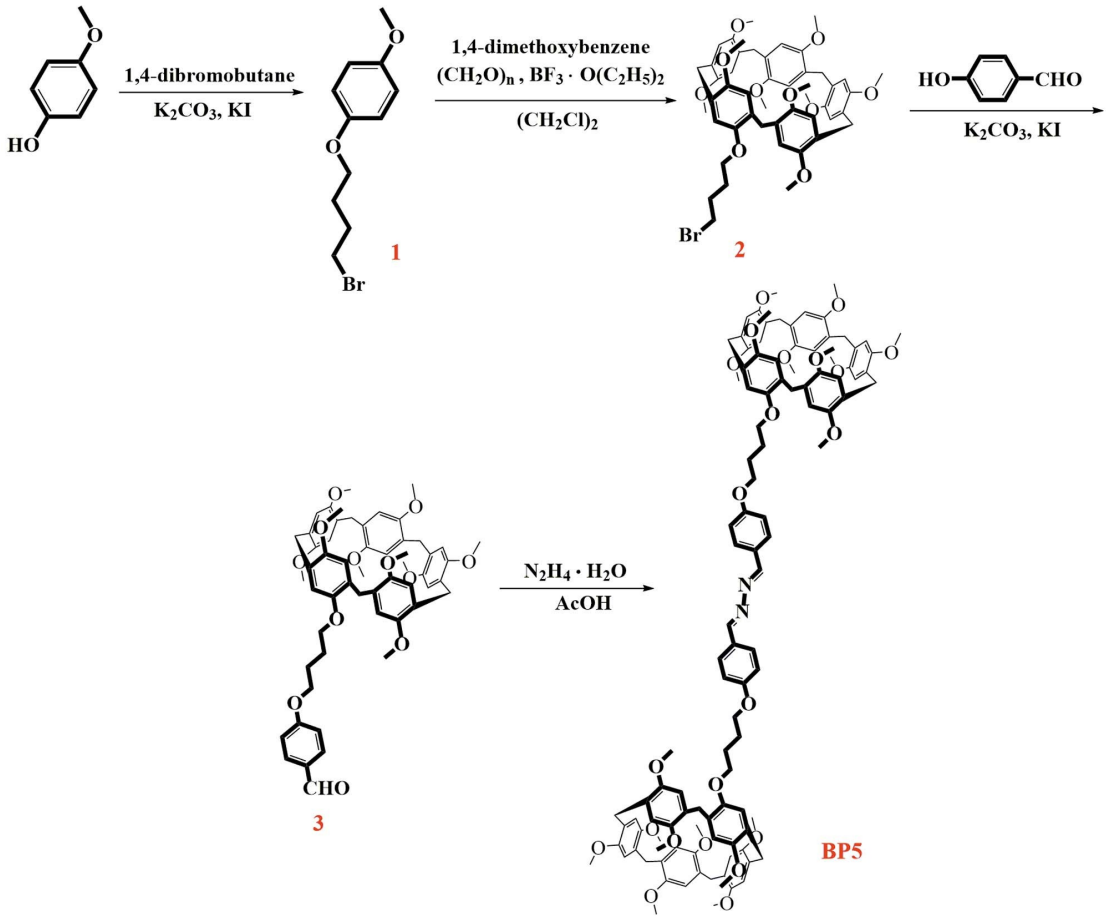
## 1. Materials and methods

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, $\delta$ 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 ($\lambda$ = 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 bispillar[5]arene P5S




**Scheme S1** Synthesis of bispillar[5]arene **BP5.**

**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-$d_6$) $\delta$ 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-$d_6$) $\delta$ 153.76, 152.99, 115.73, 114.98, 67.47, 55.76, 35.19, 29.61, 27.98.

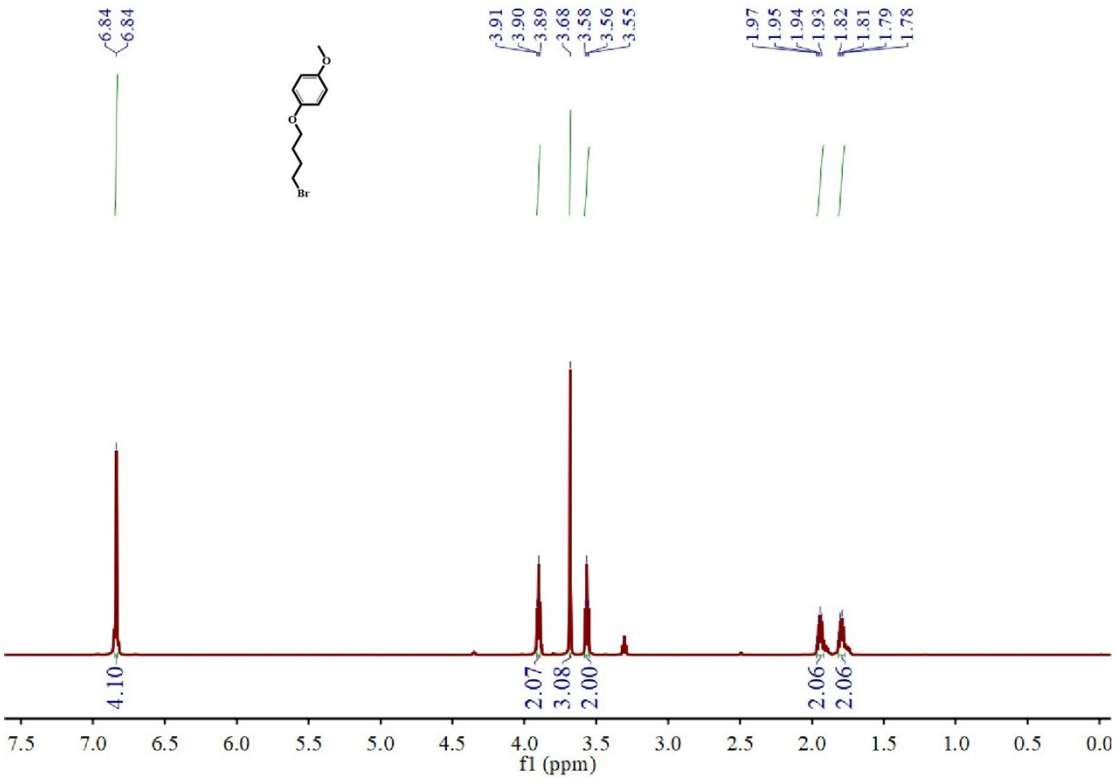



**Figure S1** $^{1}$H NMR spectrum (600 MHz, DMSO-$d_6$) of compound **1**.

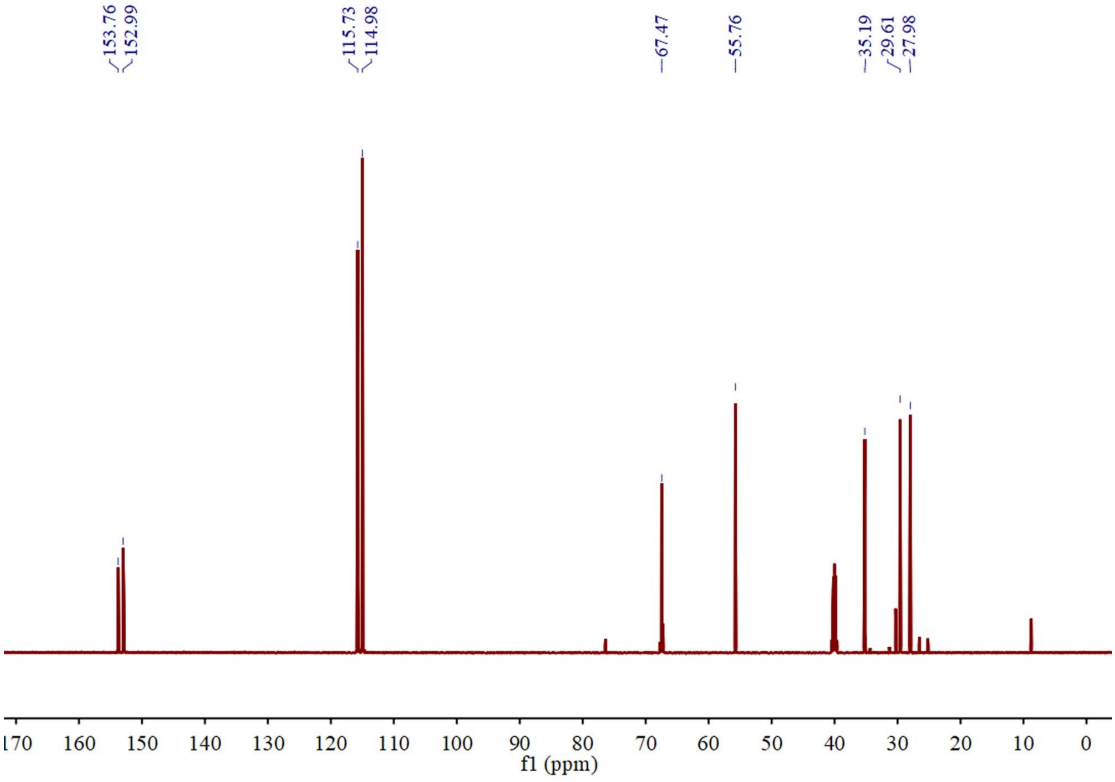



**Figure S2** $^{13}$C NMR spectrum (151 MHz, DMSO-$d_6$) of compound **1**.

**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℃. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 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-$d_6$) $\delta$ 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.

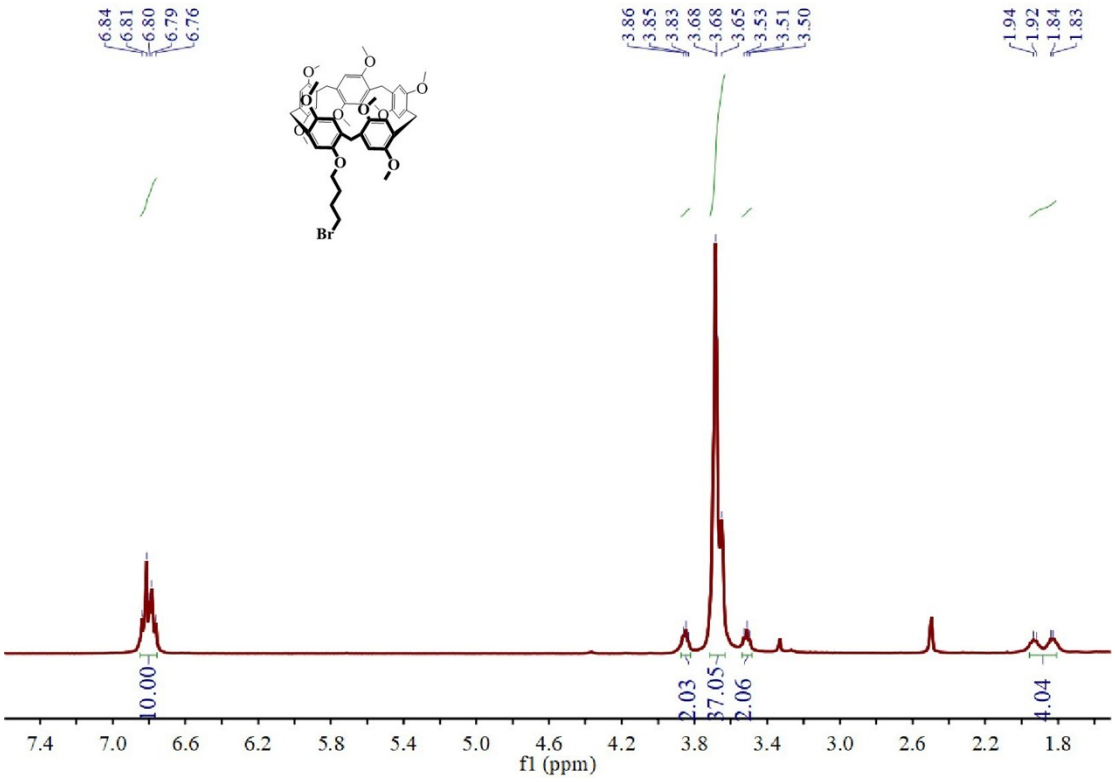



**Figure S3** $^1$H NMR spectrum (600 MHz, DMSO-$d_6$) of copillar[5]arene **2**.

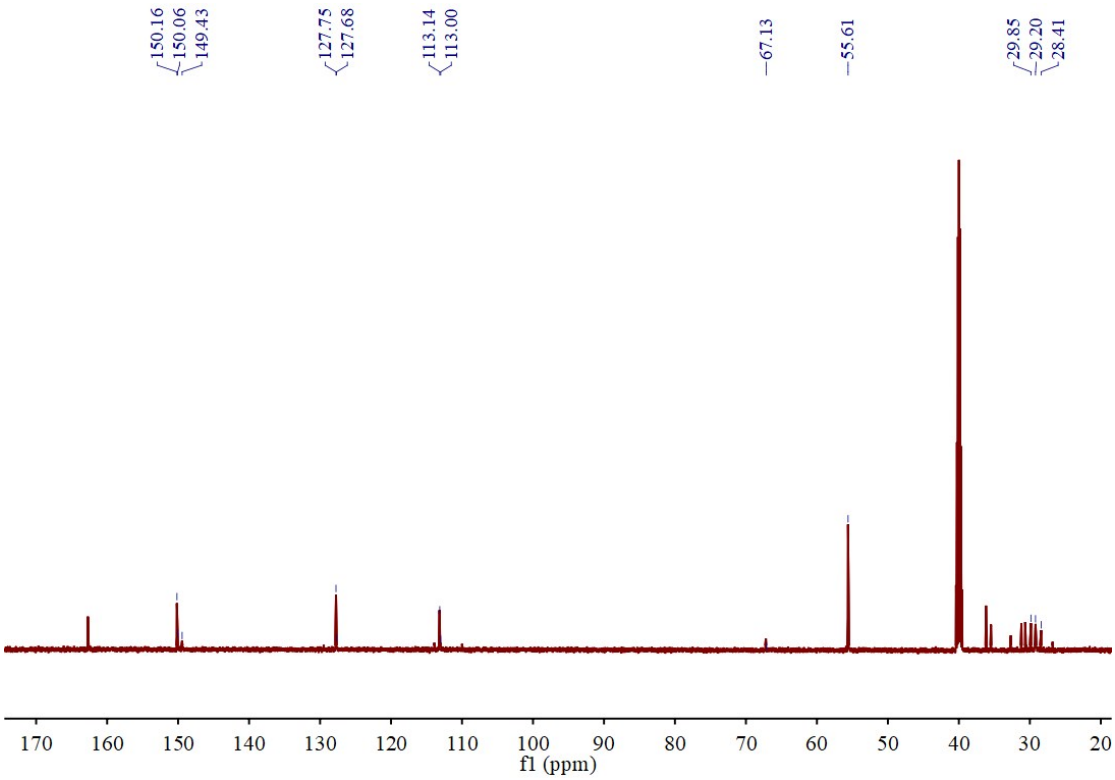



**Figure S4** $^{13}$C NMR spectrum (151 MHz, DMSO-$d_6$) of copillar[5]arene **2**.

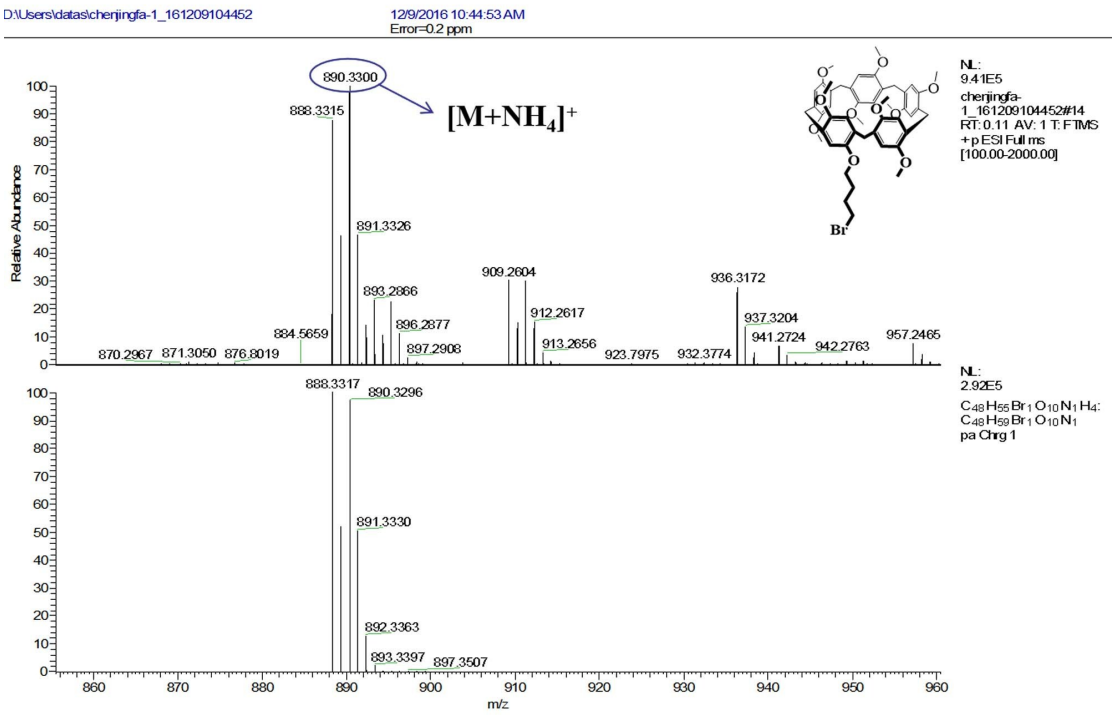



**Figure S5** Mass data of a copillar[5]arene **2**

**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-$d_6$) $\delta$ 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-$d_6$) $\delta$ 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.

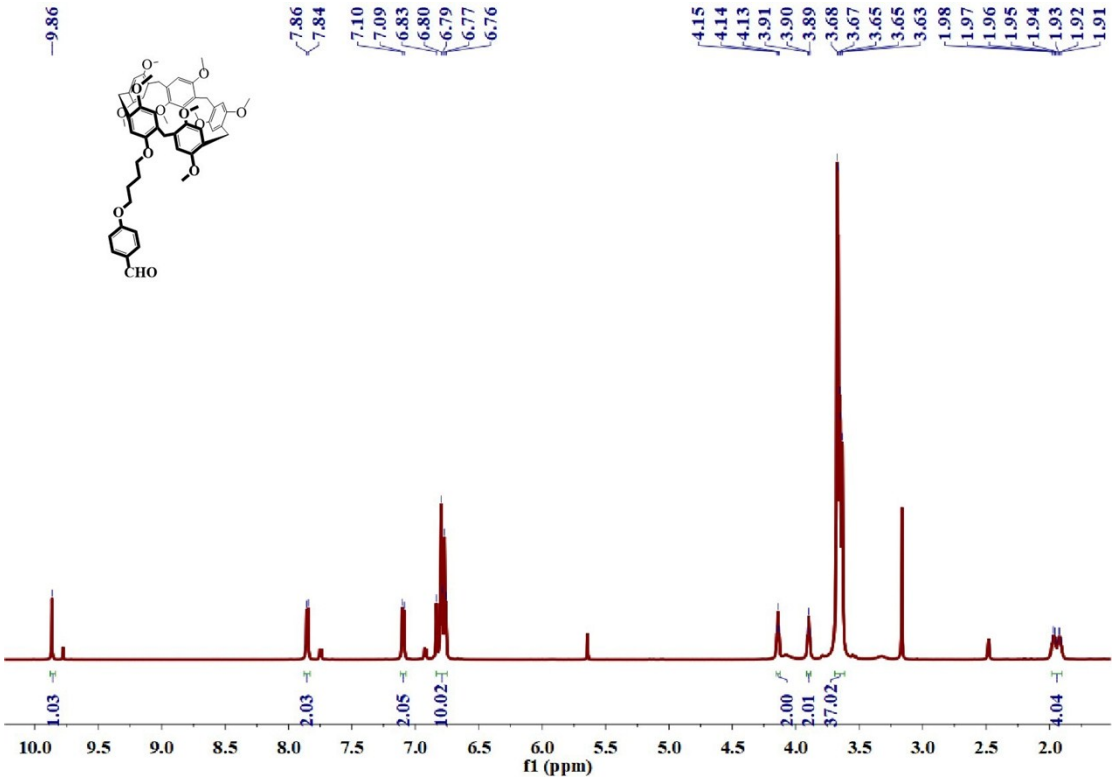



**Figure S6** $^1$H NMR spectrum (600 MHz, DMSO-$d_6$) of compound intermediate **3**.

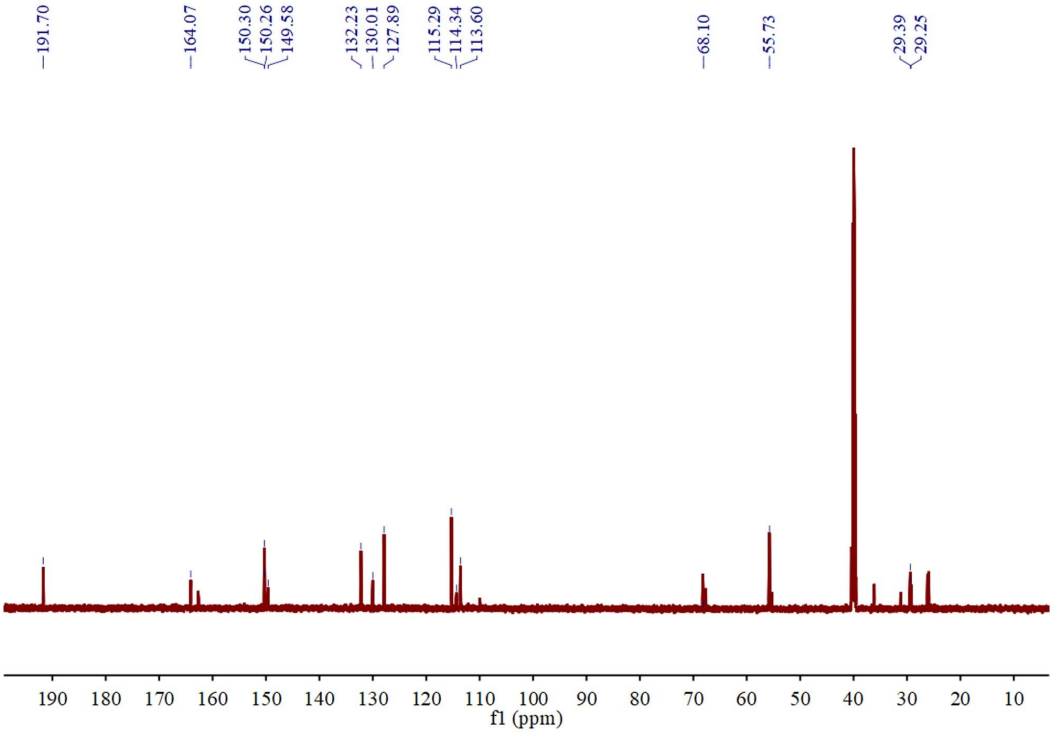



**Figure S7** $^{13}$C NMR spectrum (151 MHz, DMSO-$d_6$) of compound intermediate **3**.

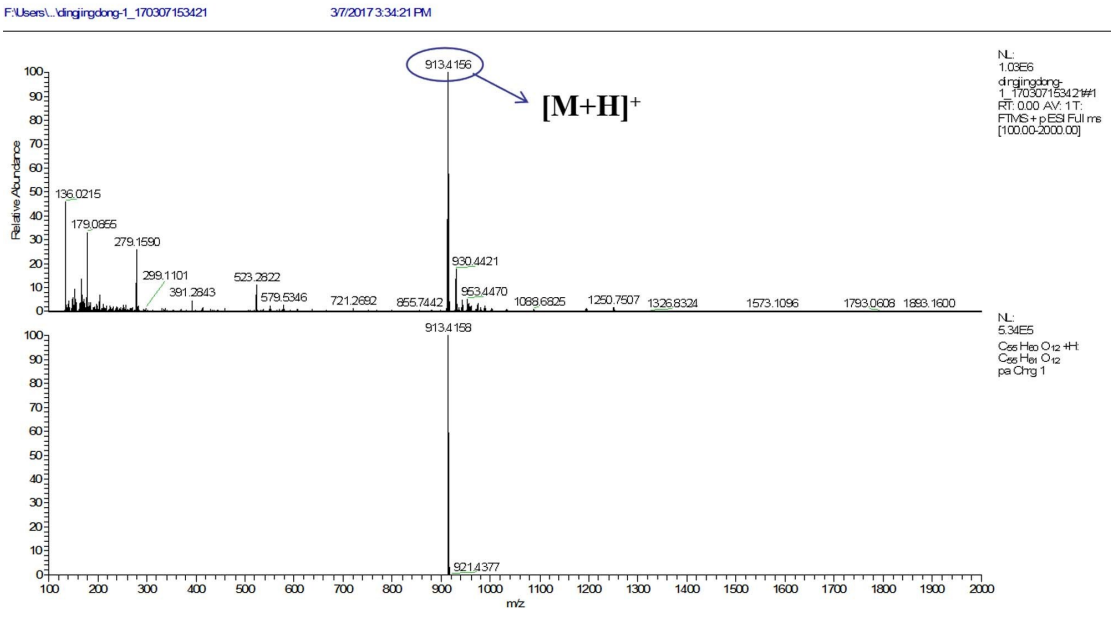



**Figure S8** High resolution mass data of compound intermediate **3**.

**Synthesis of bispillar[5]arene BP5:** Compound intermediate **3** (0.912 g, 1.0 mmol), hydrazine hydrate (4 mL, 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 = 1:1) afforded a white solid (0.86 g, 95%). Mp 125-128℃. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.62 (s, 2H), 7.77 (d, $J$ = 8.6 Hz, 4H), 6.93 (d, $J$ = 8.6 Hz, 4H), 6.80 - 6.74 (m, 20H), 4.03 (t, $J$ = 6.0 Hz, 4H), 3.91 (t, $J$ = 5.9 Hz, 4H), 3.77 (m, 20H), 3.66 - 3.62 (m, 54H), 2.00 - 1.93 (m, 8H). $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 161.52, 160.89, 150.36, 150.32, 149.62, 130.40, 127.89, 126.95, 115.23, 114.39, 113.67, 109.99, 67.89, 55.84, 55.77, 31.11, 29.42, 29.28. ESI-MS m/z: $[M+H]^+$ calcd for $C_{110}H_{120}O_{22}N_2$ 1822.1620; Found 1822.8418.

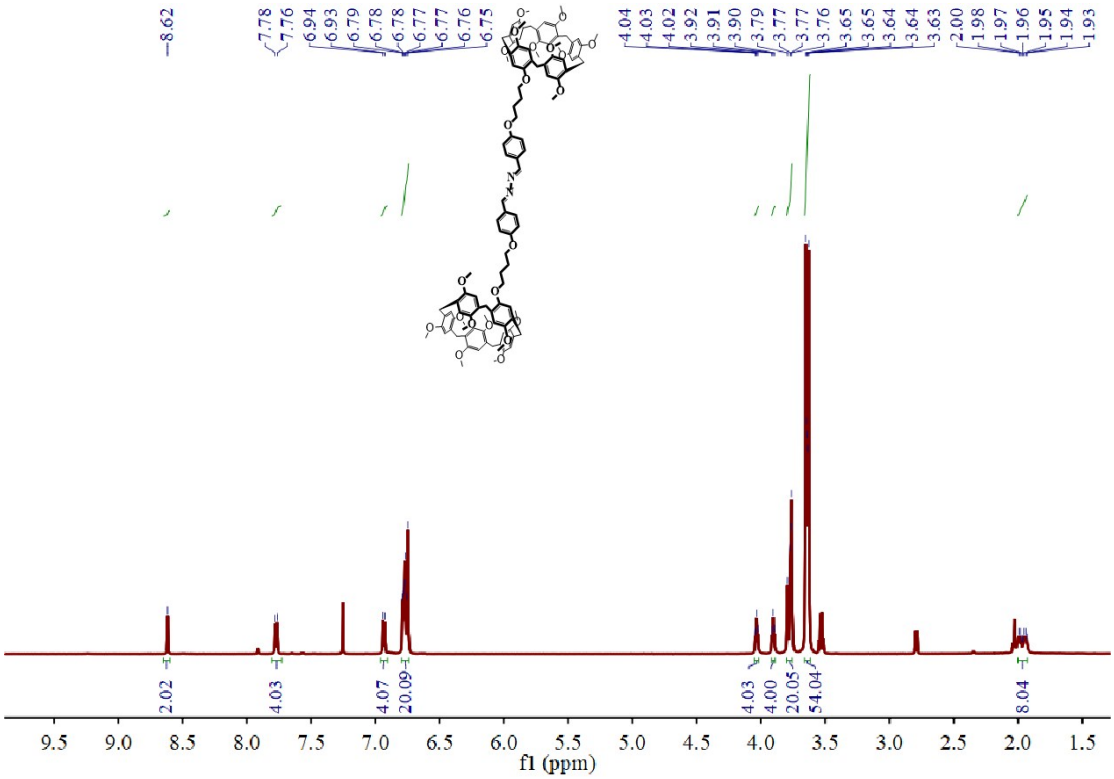



**Figure S9** $^1$H NMR spectrum (600 MHz, $CDCl_3$) of bispillar[5]arene **BP5**.

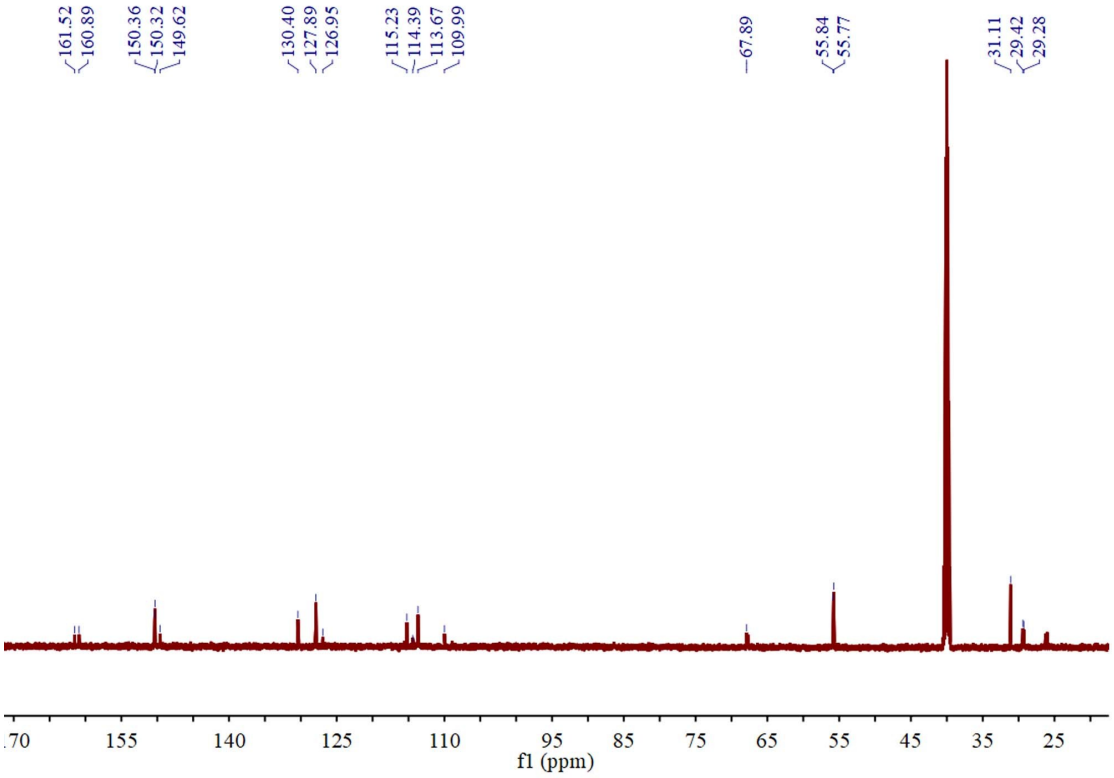



**Figure S10** $^{13}$C NMR spectrum (151 MHz, DMSO-$d_6$) of bispillar[5]arene **BP5**.

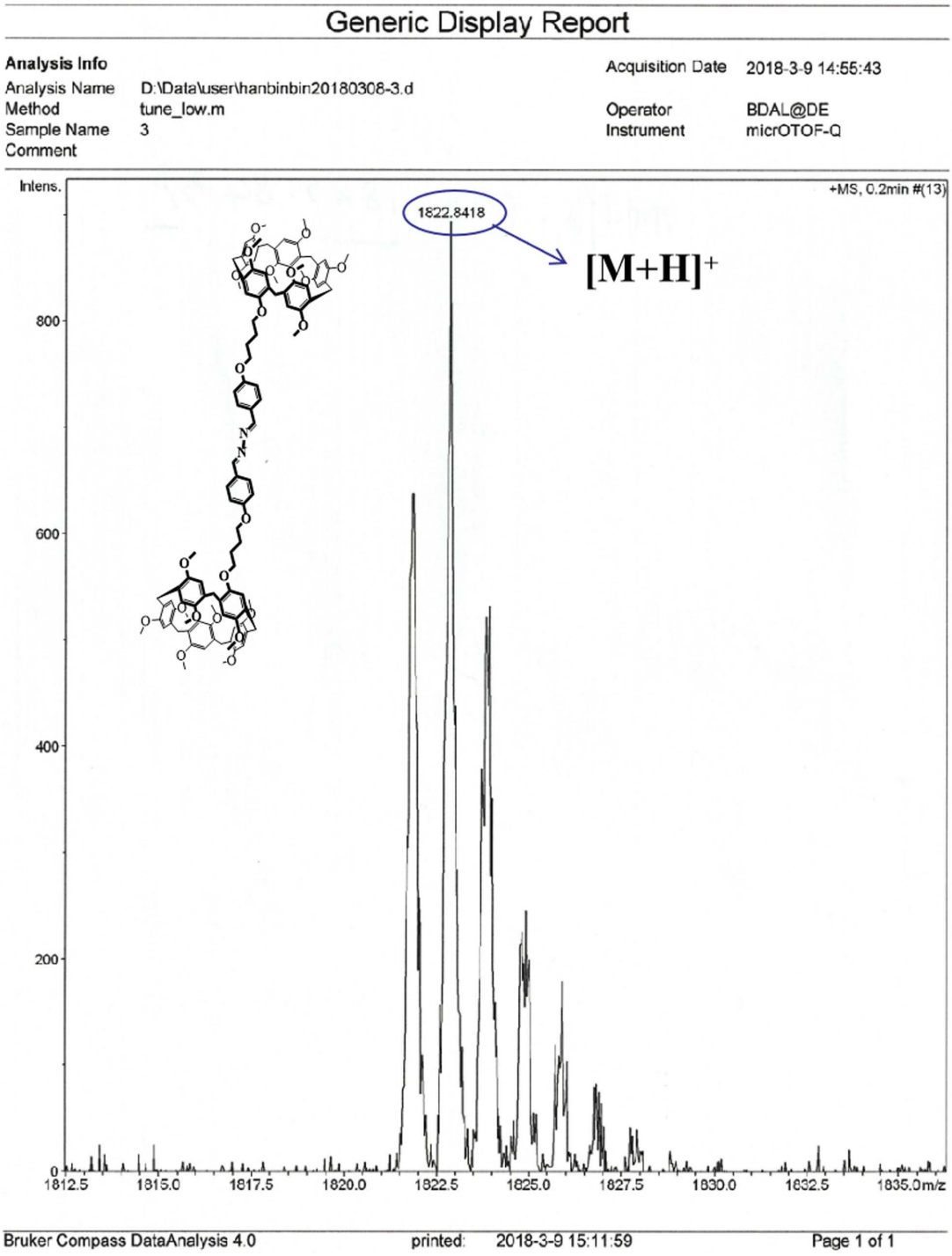
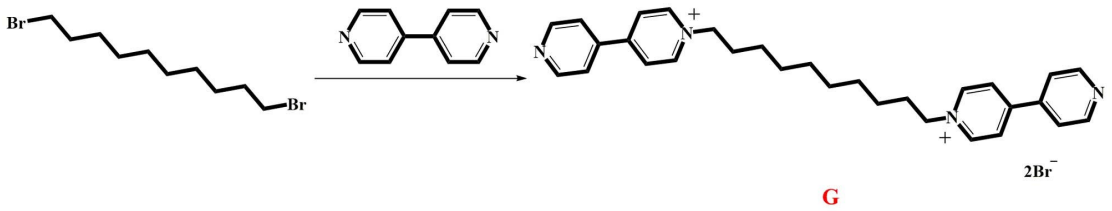



**Figure S11** High resolution mass data of bispillar[5]arene **BP5**.

## 3. Synthesis of G




G

**Scheme S2** Synthesis of guest **G**.

**Synthesis of compound G:** A solution of 1,10-dibromodecane (1.89 g, 6.3 mmol) in $CH_3CN$ (30 mL) was added dropwise into a stirred solution of 4,4'- bipyridine (5.56 g, 35.7 mmol) in $CH_3CN$ (50 mL) and refluxed overnight. 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 **G** (3.3 g, 86%). $^1$H NMR (600 MHz, $D_2O$) $\delta$ 8.82 (d, $J$ = 6.7 Hz, 4H), 8.60 (d, $J$ = 6.2 Hz, 4H), 8.25 (d, $J$ = 6.8 Hz, 4H), 7.75 (d, $J$ = 6.3 Hz, 4H), 4.51 (t, $J$ = 7.3 Hz, 4H), 1.92 - 1.89 (m, 4H), 1.22 - 1.13 (m, 12H).

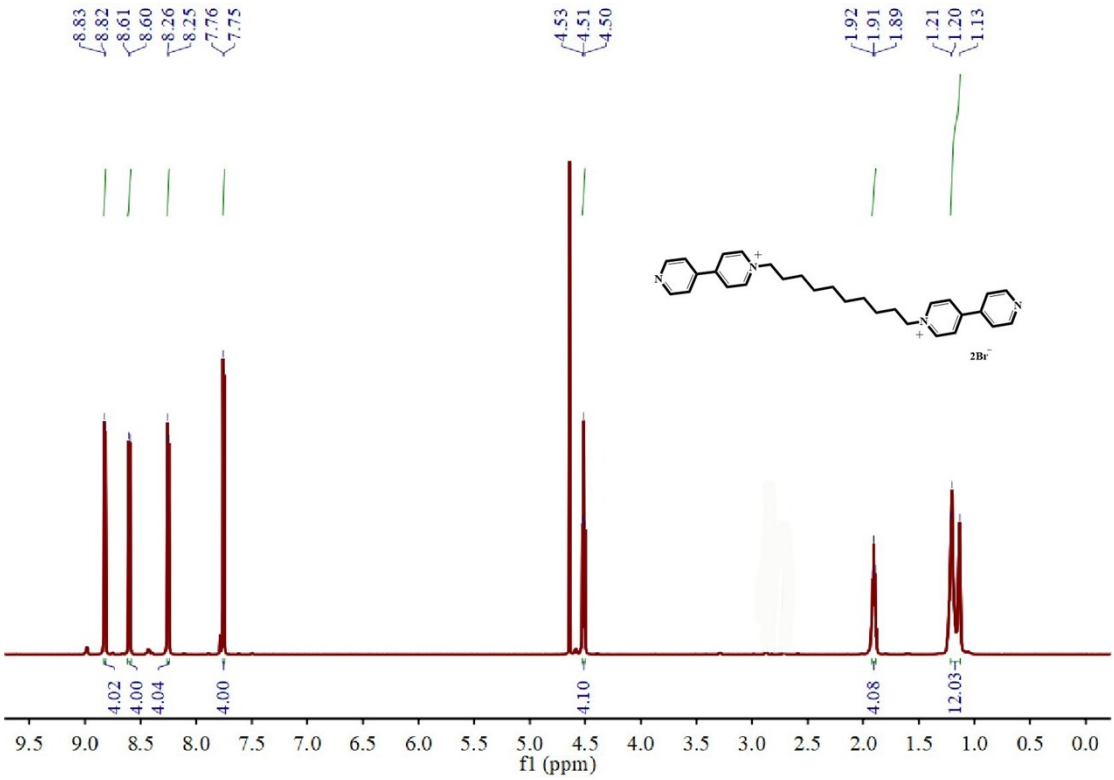



**Figure S12** $^1$H NMR spectrum (600 MHz, $D_2O$) of **G**.

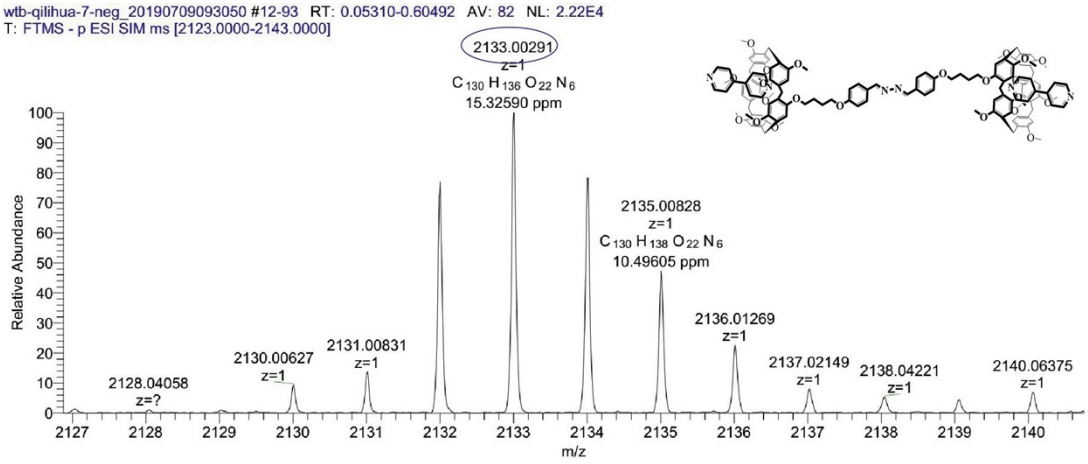



**Figure S13** High resolution mass data of bispillar[5]arene **BP5** and 4, 4'-Bipyridine.

**Table S1.** Gelation Properties of organogelator **BP5·G**

| 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 | 10% | 40-43℃ (10%) |
| 10 | $CH_2Cl_2$ | S | / | / |
| 11 | $CHCl_3$ | S | / | / |
| 12 | Petroleum ether | P | / | / |

| | | | | |
|---|---|---|---|---|
| 13 | Ethyl acetate | P | / | / |
| 14 | Cyclohexanol | G | 7% | 45-48℃ (7%) |
| 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 S14** Stability of supramolecular polypseudorotaxane gels.

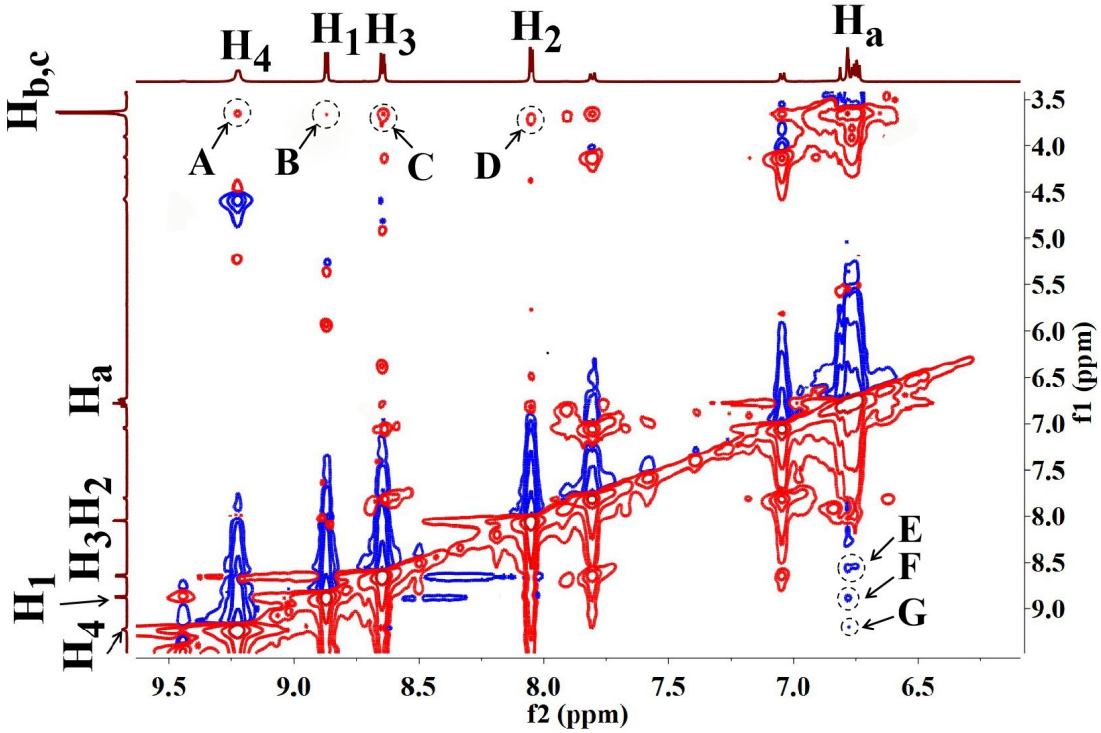



**Figure S15** 2D NOESY NMR spectrum (600 MHz, 298 K) of 10.0 mM **BP5** and **G** in DMSO-$d_6$ solution.

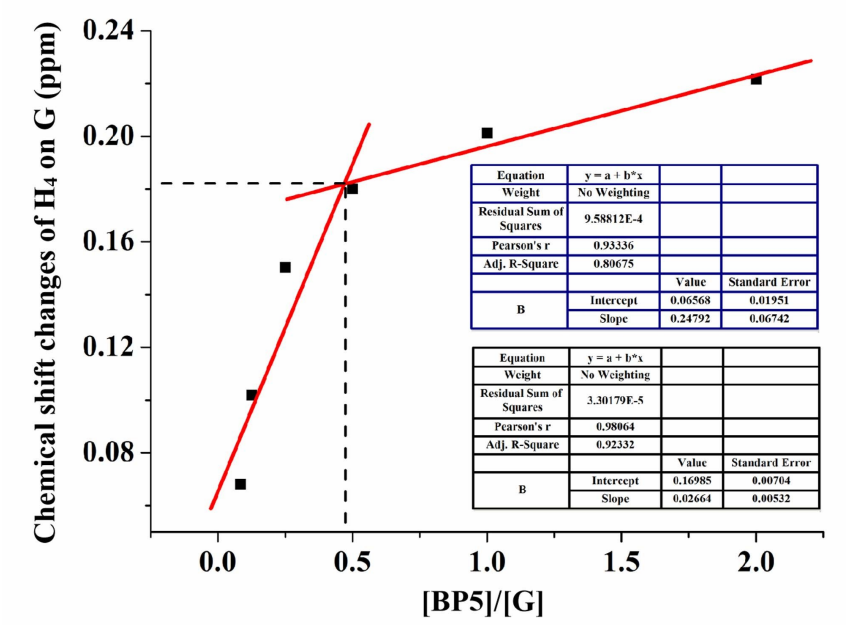



**Figure S16** A mole ratio plot for the complexation between **BP5** and **G**, indicating a 1:2 stoichiometry.

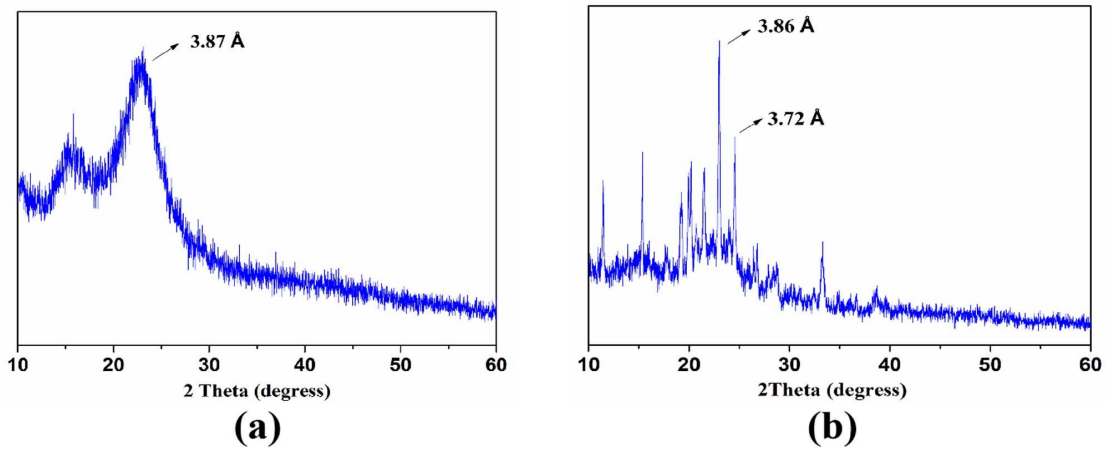



**Figure S17** XRD diagrams of xerogels powder formed by the gel of **BP5·G** (a) in cyclohexanol; (b) in DMSO-$H_2O$ (v:v, 8:2).

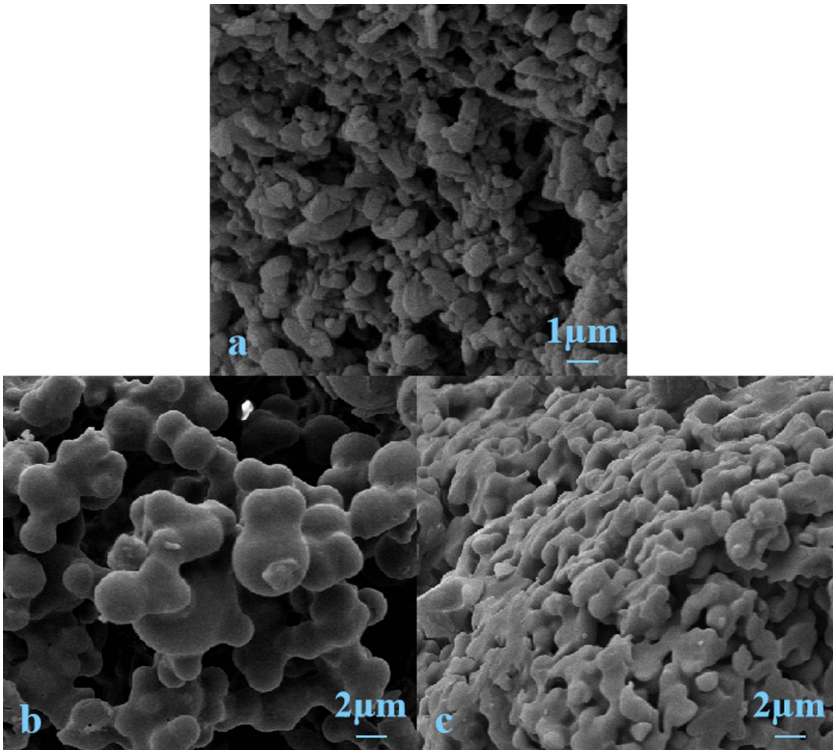



**Figure S18** Representative SEM images showing the morphology of (a) powder **BP5**; (b) xerogel **BP5·G·D**; (c) xerogel **BP5·G·C**.

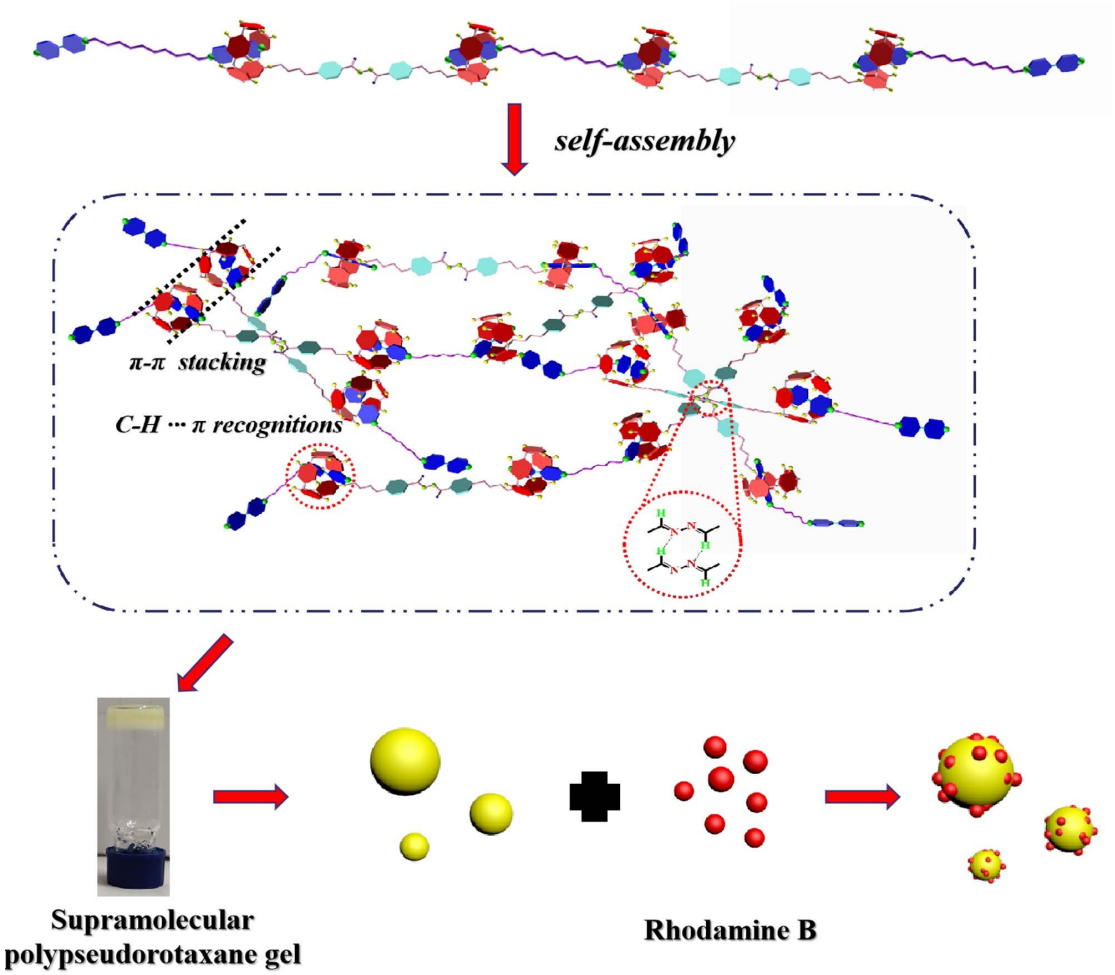



**Figure S19** Cartoon representation of the assembly process of supramolecular polypseudorotaxane gels **BP5·G·D**.

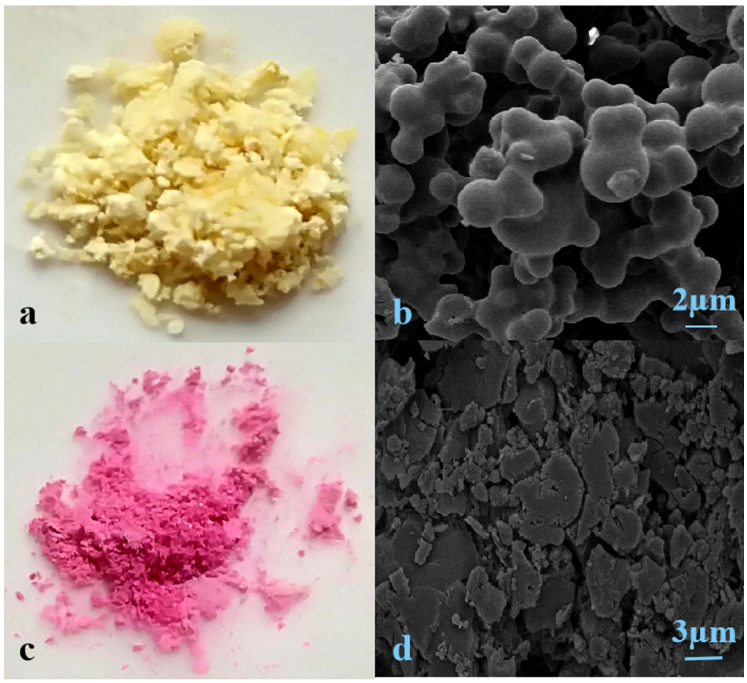



**Figure S20** a) xerogel **BP5·G·D** under visible light; c) xerogel **BP5·G·D** under visible light after adsorption rhodamine B; SEM images showing the morphology of b) xerogel **BP5·G·D**; d) xerogel **BP5·G·D** after adsorption rhodamine B.

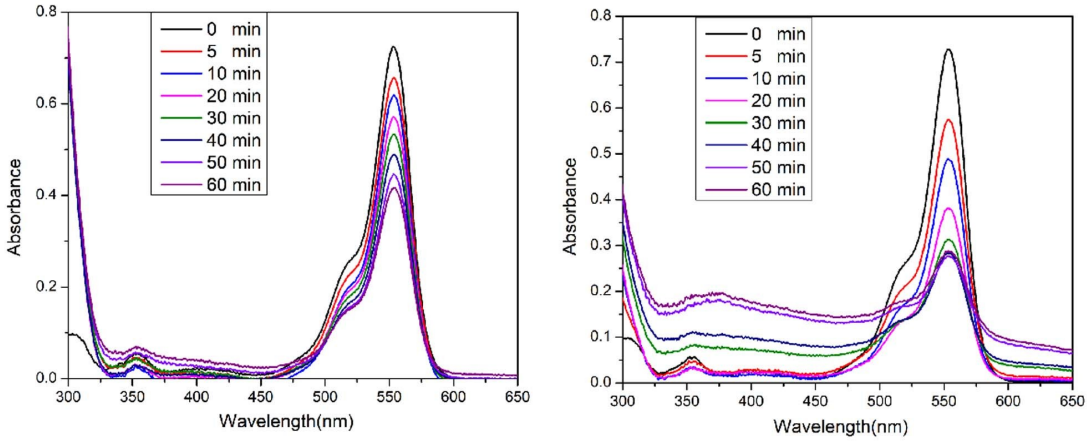



**Figure S21** Uv-vis spectra of rhodamine B in aqueous solution (black), a) rhodamine B in aqueous solution 1 h after the xerogel **BP5·G·C** was added; b) rhodamine B in aqueous solution 1 h after the xerogel **BP5·G·D** was added.

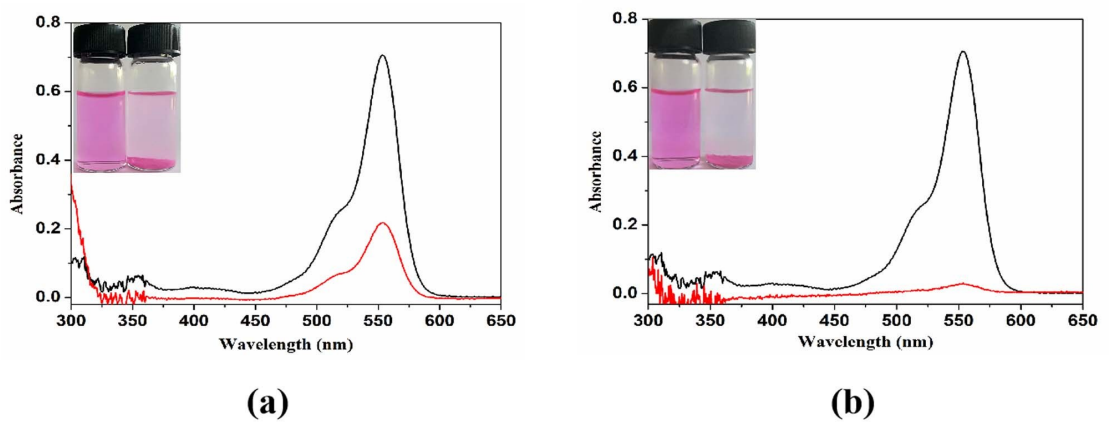



**Figure S22** Uv-vis spectrum of rhodamine B in aqueous solution (black), a) after addition of the xerogel **BP5·G·D** to rhodamine B in aqueous solution for 6 h (red), b) after addition of xerogel **BP5·G·C** to rhodamine B in aqueous solution for 6 h (red).

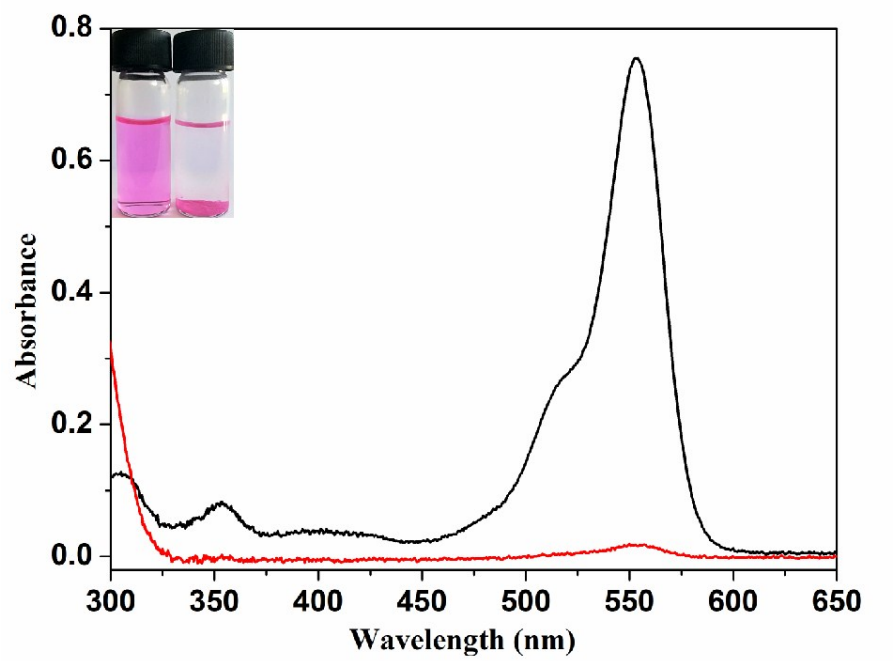



**Figure S23** Uv-vis spectra of rhodamine B in aqueous solution (black), after addition of the xerogel **BP5·G·D** to rhodamine B in aqueousr solution for 12 h (red).

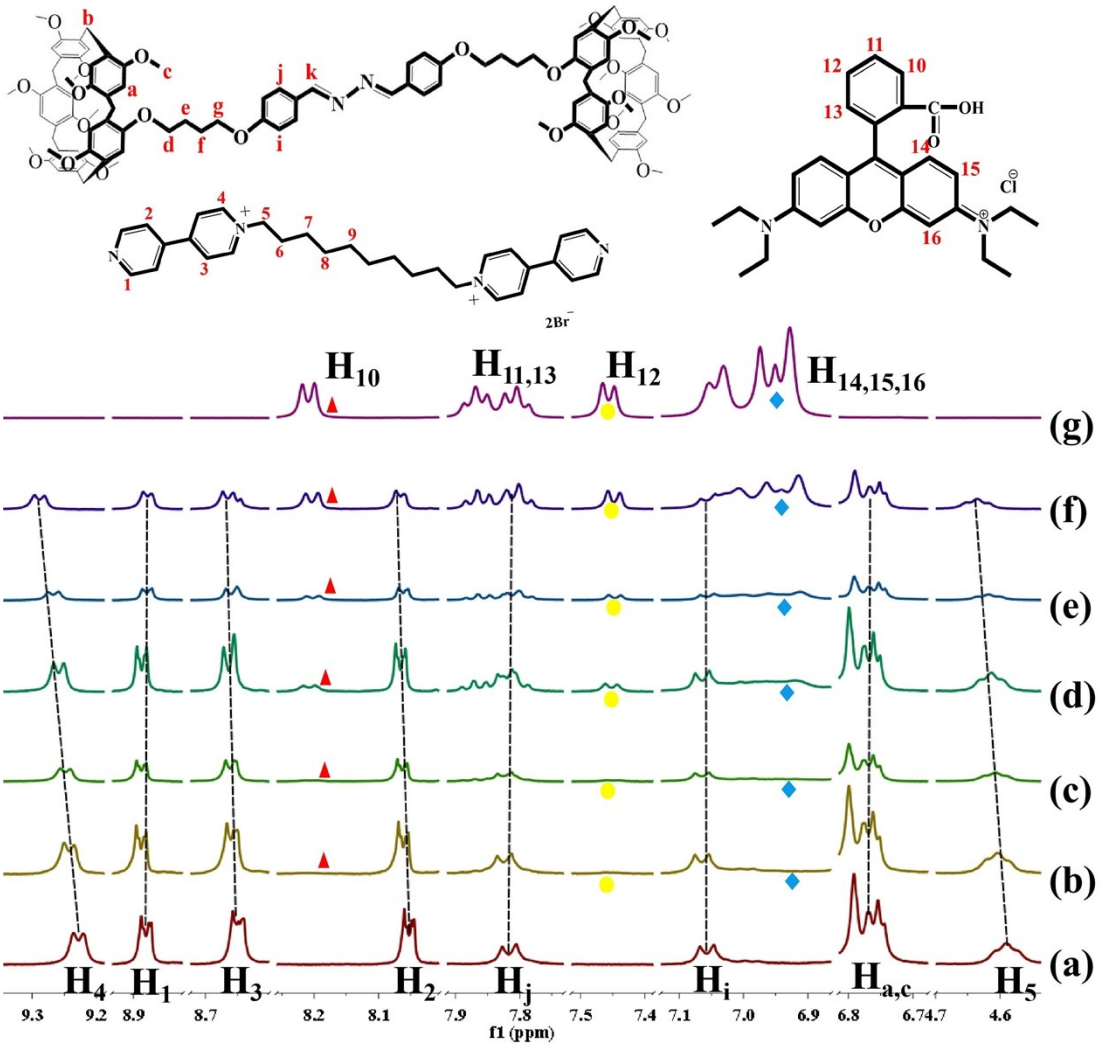



**Figure S24** $^{1}$H NMR titration spectrum (600 MHz, 298K) of 10.0 mM **BP5**·G with various equivalents of rhodamine B in DMSO-$d_6$ solution: (a) 0 equiv.; (b) 0.5 equiv.; (c) 1.0 equiv.; (d) 2.0 equiv.; (e) 4.0 equiv.; (f) 8.0 equiv.; (g) Rhodamine B.

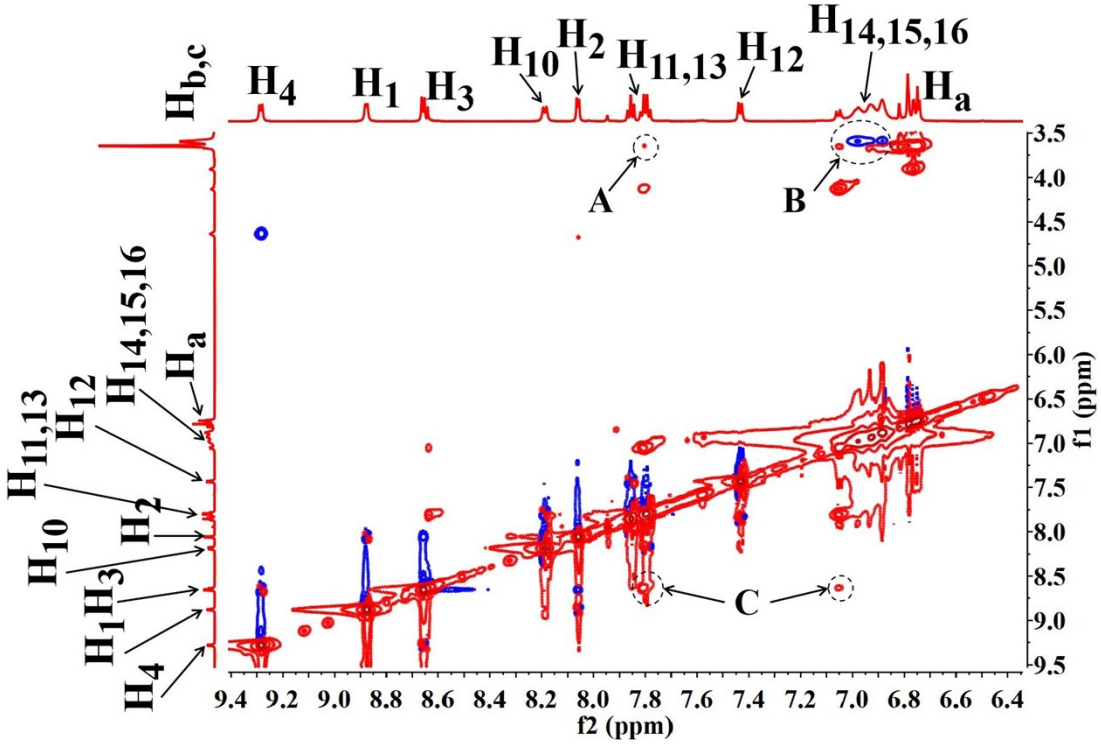



**Figure S25** 2D NOESY NMR spectrum (600 MHz, 298 K) of **BP5·G** (10.0 mM) and rhodamine B in DMSO-$d_6$ solution.

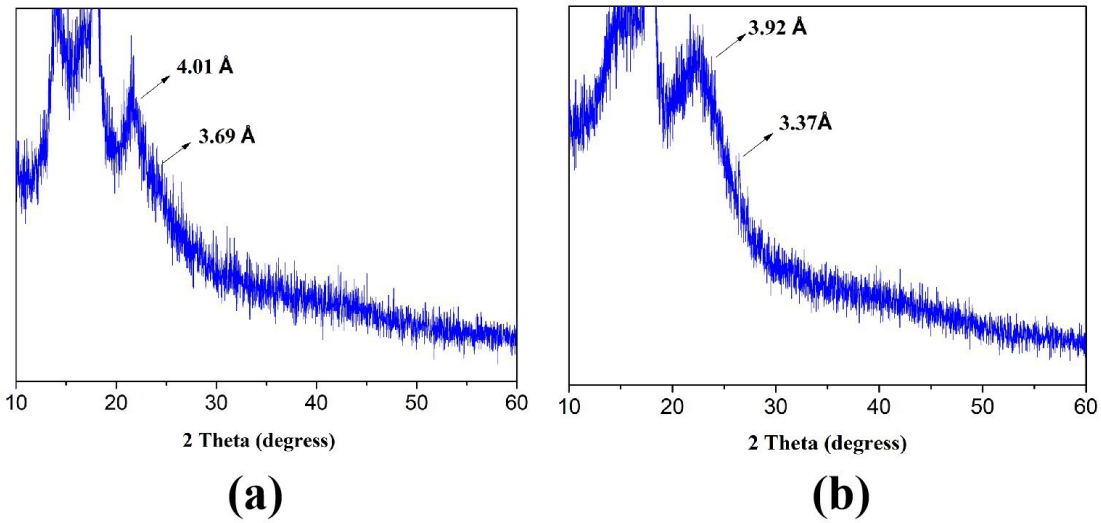



**Figure S26** Powder XRD patterns xerogel of (a) (**BP5·G·C**) + rhodamine B; (b) (**BP5·G·D**) + rhodamine B

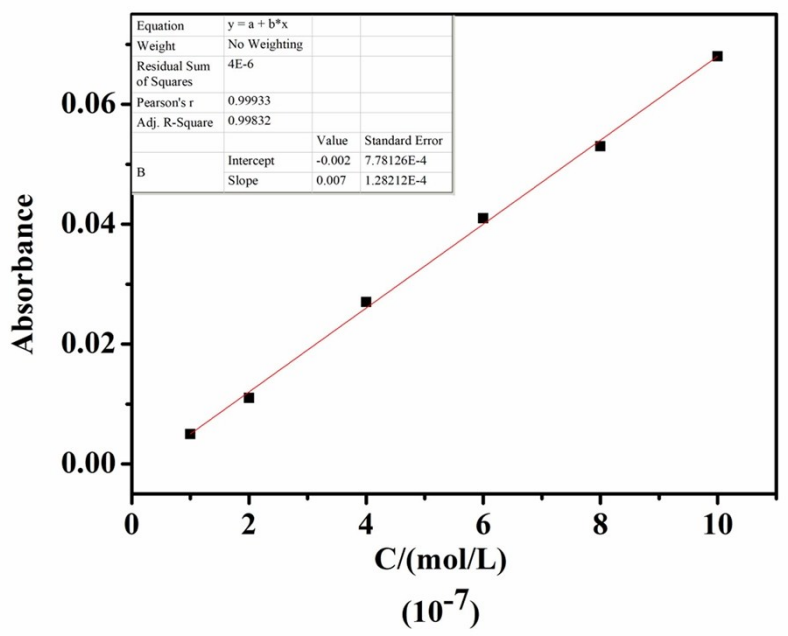



**Figure S27** The Absorption spectrum linear range for rhodamine B.

**The efficiency of rhodamine B adsorption：**

The efficiency of rhodamine B adsorption (%) by the **BP5·G** was determined by the following equation:

$$\%\ \text{Rhodamine B adsorption efficienc}\ \mathrm{Y} = \frac{(C_0\text{-}\mathrm{C_v})}{C_0} \times 100\%$$

where $C_0$ (mM) and $C_v$ (mM) are the initial and residual concentrations of the rhodamine B in the stock solutions and filtrates, respectively. Meanwhile, the linear relationship between concentration and absorbance inaqueous solution of rhodamine B.

**Table S2** The equilibrium uptake percentage and amount of bound dyes of **BP5·G**

| |
|---|
| % Rhodamine B adsorption efficienc： $\mathrm{Y} = \frac{(C_0\text{-}\mathrm{C_v})}{C_0} \times 100\%$ |
| Lambert-Beer law： $A = \lg(\frac{1}{T}) = Kbc$ |
| The linear relationship between concentration and absorbance inaqueous solution of |

| rhodamine B: A = 0.007c - 0.002 (Figure S27) | | |
|---|---|---|
| Absorbance of rhodamine B in aqueous solution: $A_0$=0.755 (Figure 5) | | |
| supramolecular pseudopolyrotaxane gels | **BP5·G·C** | **BP5·G·D** |
| Absorbance of rhodamine B after addition of the xerogel: $A_v$ | 0.01 (Figure 7) | 0.016 (Figure S23) |
| % Rhodamine B adsorption efficienc: Y | 98.4% | 97.6% |