Electronic Supplementary Information

Pillar[5]arene-based side-chain polypseudorotaxanes as an anion-responsive fluorescent sensor

Shu Sun,[a,b] Xiao-Yu Hu,*[b] Dongzhong Chen,[b] Jianbing Shi,[a] Yuping Dong,[a] Chen Lin, [b] Yi Pan[b] and Leyong Wang*[b]

[a] *College of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China*

[b] *Key Laboratory of Mesoscopic Chemistry of MOE, Center for Multimolecular Chemistry, Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*

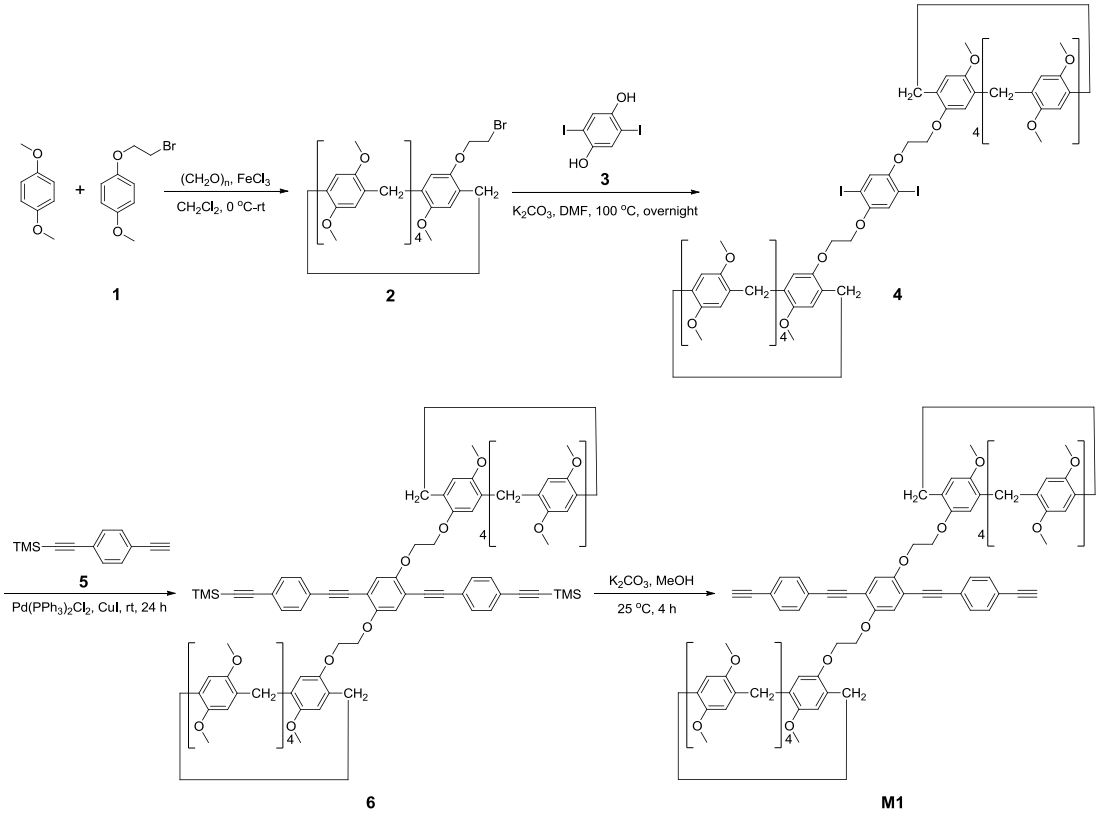
Table of Contents

1. Materials and methods

2,5-Diiodo-1,4-dihydroxybenzene **3**[S1] and *p*-(trimethylsilylethynyl)phenylacetylene **5**[S2] were prepared according to the previously reported method. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer (or Bruker DPX 400 MHz spectrometer) with internal standard tetramethylsilane (TMS) and solvent signals as internal references at room temperature. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan Mat TSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum was obtained with α-cyano-4-hydroxycinnamic acid as a matrix on a Bruker Autoflex Ⅲ spectrometer. Gel Permeation Chromatographic (GPC) measurements were carried out at 40 ^{o}C on a Waters 2410 instrument using THF as eluent at a flow rate of 0.3 mL/min. All the GPC data were calibrated by using polystyrene (PS) standards. The UV–vis absorption spectra were measured on a Perkin Elmer Lambda 35 UV–vis Spectrometer. Luminescence measurements were carried out using a Perkin Elmer LS55 Fluorescence Spectrometer.

2. Synthesis of pillar[5]arene-based monomer M1

General procedure:



Scheme S1. Synthetic route of monomer **M1**.

Synthesis of compound **2**[S3]

1,4-dimethoxybenzene (11.96 g, 86.56 mmol), **1** (1.25 g, 5.41 mmol), paraformaldehyde (7.80 g, 259.68 mmol) were dissolved in CH_2Cl_2 (350 mL). After cooling to 0 ^oC, $FeCl_3$ (2.19 g, 13.53 mmol) was added under argon atmosphere, then the mixture was stirred at 0 ^oC for 1 h and then it was raised to room temperature for 2 h. After the reaction was completed, water (50 mL) was added and the organic layer was washed with water (100 mL), saturated brine (100 mL) and dried over Na_2SO_4. Then, the solvent was removed under vacuum and the residue was purified by silica-gel flash column chromatography using petroleum ether/CH_2Cl_2/EtOAc (200:200:1) as the eluent. The desired product **2** was obtained as a white solid (2.3 g, 50.3%). ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 6.79-6.75 (m, 9H, phenyl protons from pillar[5]arene), 6.69 (s, 1H, phenyl proton from pillar[5]arene), 4.02 (t, *J*

= 6.1 Hz, 2H, protons from OCH_2CH_2Br), 3.80-3.76 (m, 10H, methylene bridge protons of pillar[5]arene), 3.67-3.63 (m, 27H, methoxy protons of pillar[5]arene), 3.43 (t, J = 6.1 Hz, 2H, protons from OCH_2CH_2Br), which is in accordance with the results reported by Stoddart's group[S4] [δ = 6.80-6.76 (m, 9H), 6.70 (s, 1H), 4.04 (t, J = 6 Hz, 2H), 3.80-3.75 (m, 10H), 3.68-3.64 (m, 27H), 3.44 (t, J = 6 Hz, 2H)].

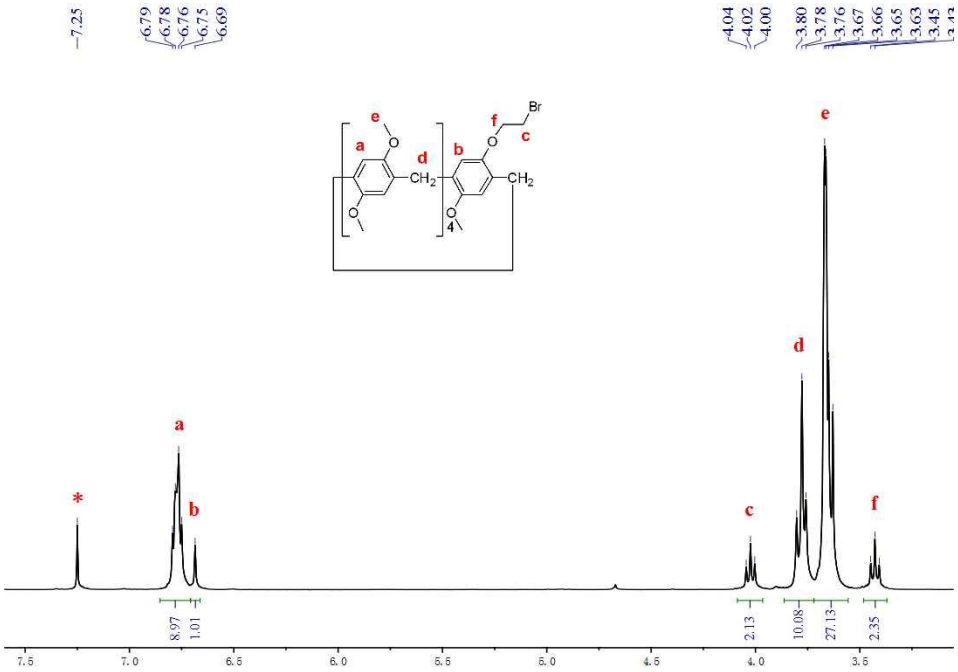


Fig. S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **2**. Asterisk indicates the solvent peak.

Synthesis of compound **4**

2 (2.10 g, 2.49 mmol), **3** (0.41 g, 1.13 mmol), and dry K_2CO_3 (3.47 g, 25.09 mmol) were placed in a round-bottom flask and dried at 80 ℃ in vacuo for 2 h. The mixture was dissolved in DMF (30 mL) and stirred at 100 ℃ overnight. Then, the mixture was diluted with $CHCl_3$ (50 mL) and washed with saturated aqueous $NaHCO_3$ (80 mL) and brine (80 mL), respectively. The organic layer was separated and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel using petroleum ether/CH_2Cl_2/EtOAc (50:100:2) as the eluent. The desired product **4** was obtained as a white solid (0.833 g, 39.2%). M. P. 99-101 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 7.33 (s, 2H, phenyl protons), 6.82-6.74 (m, 20H, phenyl protons from pillar[5]arene), 4.26-4.23 (m, 4H, protons from OCH_2 linked to phenyl), 4.17-4.14 (m, 4H, protons from OCH_2 linked to

pillar[5]arene), 3.85-3.76 (m, 20H, methylene bridge protons of pillar[5]arene), 3.65-3.56 (m, 54H, methoxy protons of pillar[5]arene). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ (ppm): 153.33, 151.45, 150.85, 149.58, 129.22, 128.41, 128.29, 128.23, 128.14, 123.78, 116.10, 114.42, 114.18, 114.10, 86.66, 69.64, 67.65, 55.99, 55.91, 55.86, 55.81, 55.70, 30.01, 29.78, 29.70. LRESIMS (*m/z*): 1910.45 $[M + Na]^+$, HRESIMS (*m/z*): calcd for $[M + Na]^+$ $C_{98}H_{104}I_2O_{22}Na$, 1910.5040, found 1910.5011.

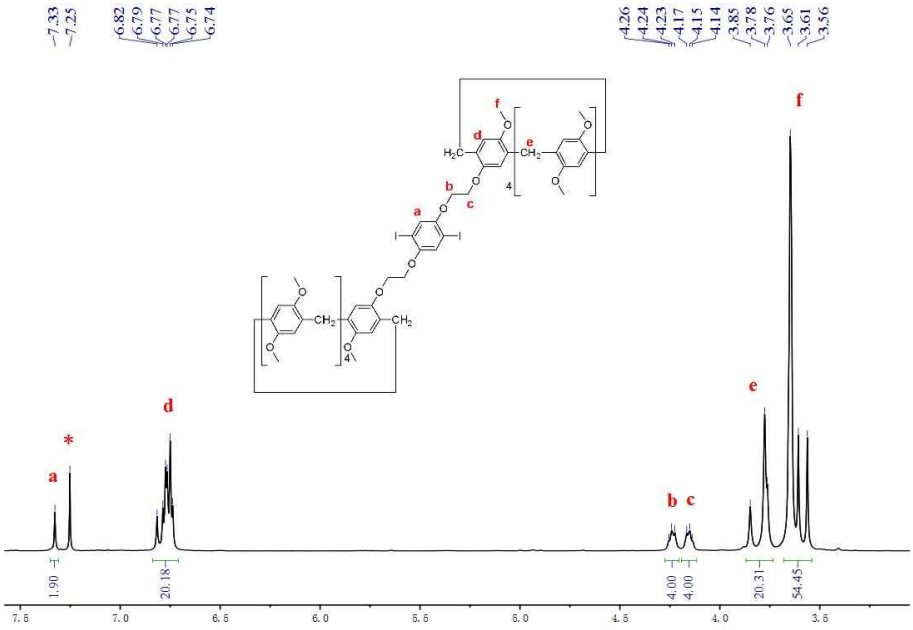


Fig. S2. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **4**. Asterisk indicates the solvent peak.

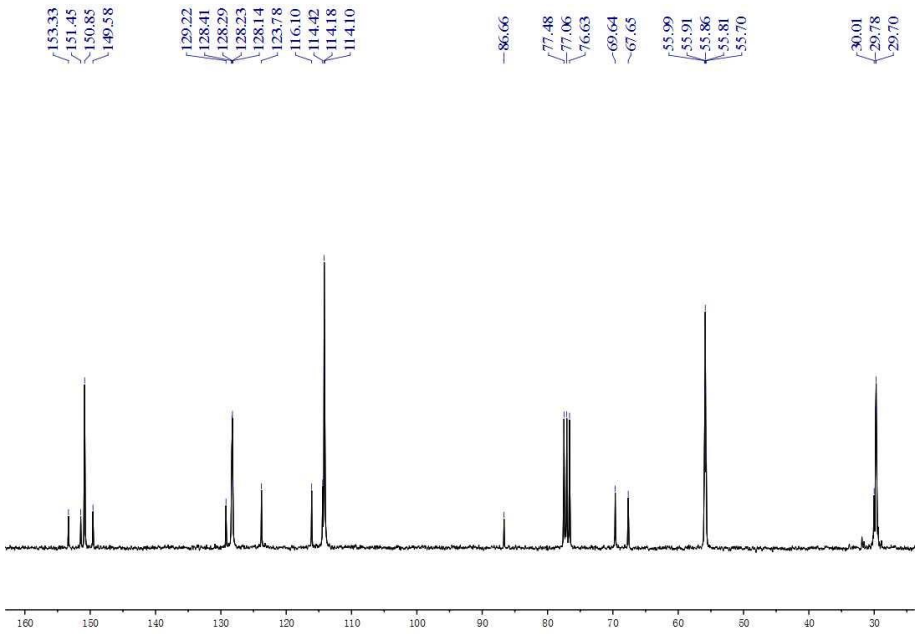


Fig. S3. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of **4**.

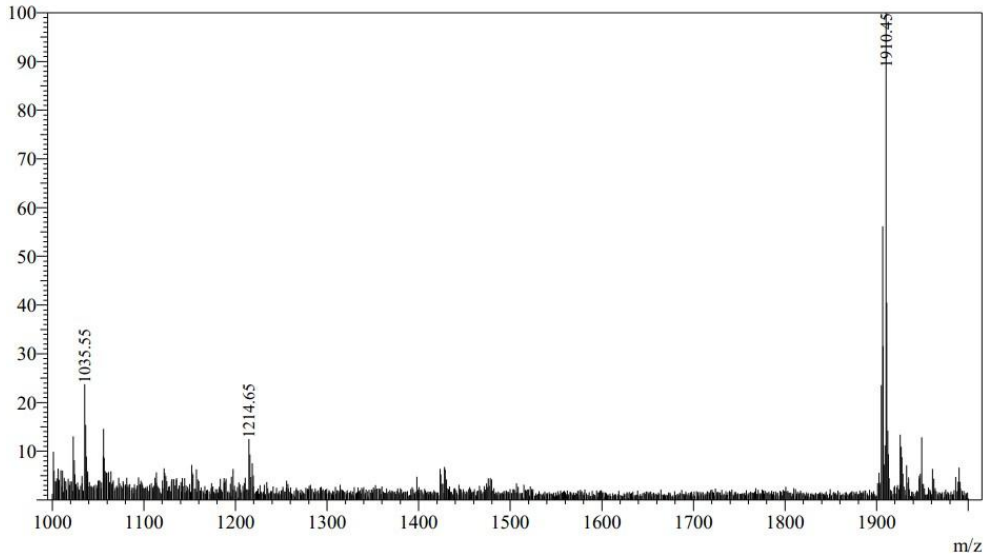


Fig. S4. Electrospray ionization mass spectrum of **4**.

Synthesis of compound **6**

To a solution of **4** (0.82 g, 0.434 mmol) in *i*Pr_2NH (15 mL, contain $CHCl_3$ 5 mL) was added $Pd(PPh_3)_2Cl_2$ (0.0152 g, 0.0217mmol), CuI (0.0041 g, 0.0217 mmol), and **5** (0.258 g, 1.302 mmol) under nitrogen. After stirring for 24 h at room temperature, the mixture was filtered and concentrated, followed by a chromatographic purification on silica gel with petroleum ether/CH_2Cl_2/EtOAc (100:100:5) as the eluent. The desired product **6** was obtained as a yellow solid (0.65 g, 74.1%). M. P. 102-104 ^oC. ^1H NMR (300 MHz, $CDCl_3$, 298K) δ (ppm): 7.37 (s, 8H, phenyl protons), 7.14 (s, 2H, central phenyl protons), 6.79-6.71 (m, 20H, phenyl protons from pillar[5]arene), 4.33 (t, J = 4.5 Hz, 4H, protons from OCH_2 linked to phenyl), 4.17 (t, J = 4.5 Hz, 4H, protons from OCH_2 linked to pillar[5]arene), 3.77-3.75 (m, 20H, methylene bridge protons of pillar[5]arene), 3.64-3.53 (m, 54H, methoxy protons of pillar[5]arene), 0.27 (s, 18H, Si$(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 298K) δ (ppm): 153.77, 151.45, 150.85, 149.74, 131.86, 131.41, 129.35, 128.41, 128.35, 128.23, 123.20, 123.07, 117.81, 116.29, 114.48, 114.29, 114.18, 114.08, 104.72, 96.46, 95.16, 87.47, 68.85, 68.07, 55.83, 55.69, 30.02, 29.67, -0.03. HRESIMS (*m/z*): calcd for $[M + H]^+$ $C_{124}H_{131}O_{22}Si_2$, 2027.8665, found 2027.8604; calcd for $[M + Na]^+$ $C_{124}H_{130}O_{22}Si_2Na$, 2050.8524, found 2050.8501.

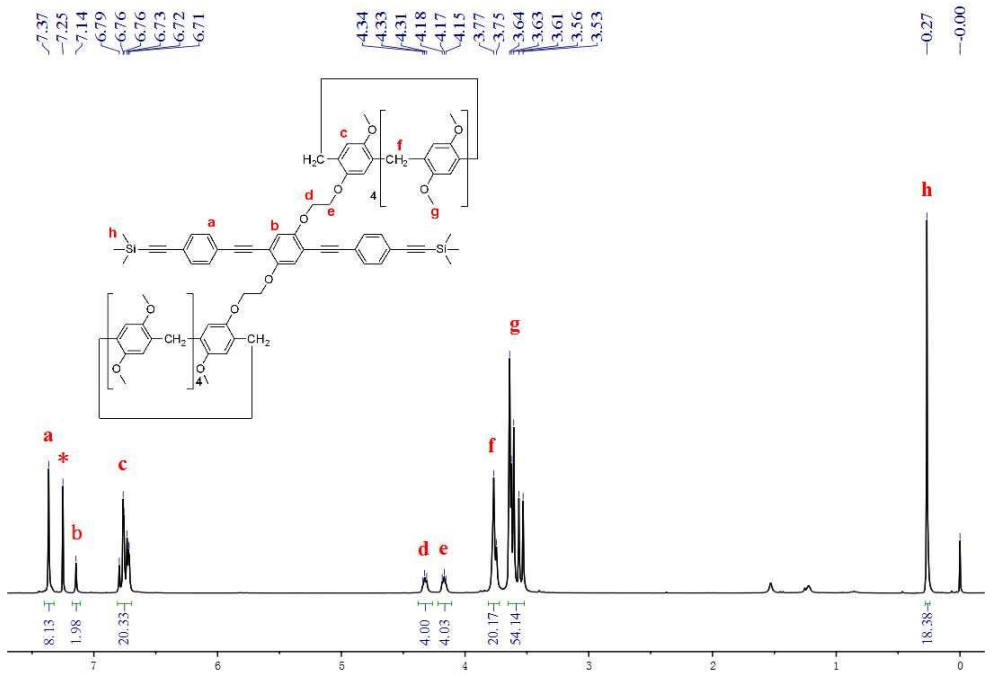


Fig. S5. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **6**. Asterisk indicates the solvent peak.

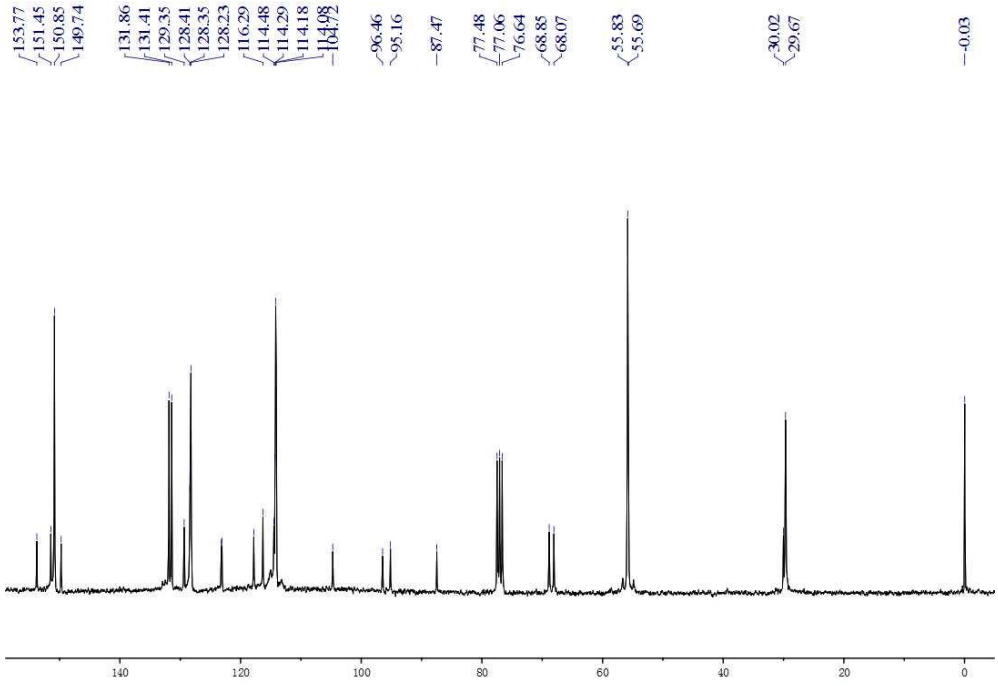


Fig. S6. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of **6**.

Synthesis of compound **M1**

To a solution of **6** (0.54 g, 0.266 mmol) in MeOH (10 mL, contain $CHCl_3$ 2.5 mL) was added K_2CO_3 (1.29 g, 9.31 mmol). After stirring for 4 h at 25 ℃, the mixture was diluted with $CHCl_3$ (30 mL) and washed with brine (50 mL). The organic layer was

separated and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2/EtOAc (100:200:3) as the eluent. The desired product **M1** was obtained as a yellow solid (0.43 g, 85.8%). M. P. 108-109 ^oC. ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 7.41-7.34 (m, 8H, phenyl protons), 7.15 (s, 2H, central phenyl protons), 6.80-6.72 (m, 20H, phenyl protons from pillar[5]arene), 4.33 (t, J = 4.6 Hz, 4H, protons from O*CH*$_2$ linked to phenyl), 4.17 (t, J = 4.5 Hz, 4H, protons from O*CH*$_2$ linked to pillar[5]arene), 3.78-3.74 (m, 20H, methylene bridge protons of pillar[5]arene), 3.64-3.53 (m, 54H, methoxy protons of pillar[5]arene), 3.18 (s, 2H, protons of alkyne). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ (ppm): 153.80, 151.49, 150.86, 149.74, 132.02, 131.49, 129.39, 128.40, 128.36, 128.25, 128.15, 123.60, 122.00, 117.81, 116.38, 114.47, 114.30, 114.20, 114.09, 94.80, 87.51, 83.36, 79.08, 68.87, 68.14, 55.85, 55.79, 55.76, 55.67, 30.00, 29.70. LRESIMS (*m/z*): 1906.75 $[M + Na]^+$, HRESIMS (*m/z*): calcd for $[M + Na]^+$ $C_{118}H_{114}I_2O_{22}Na$, 1906.7729, found 1906.7733.

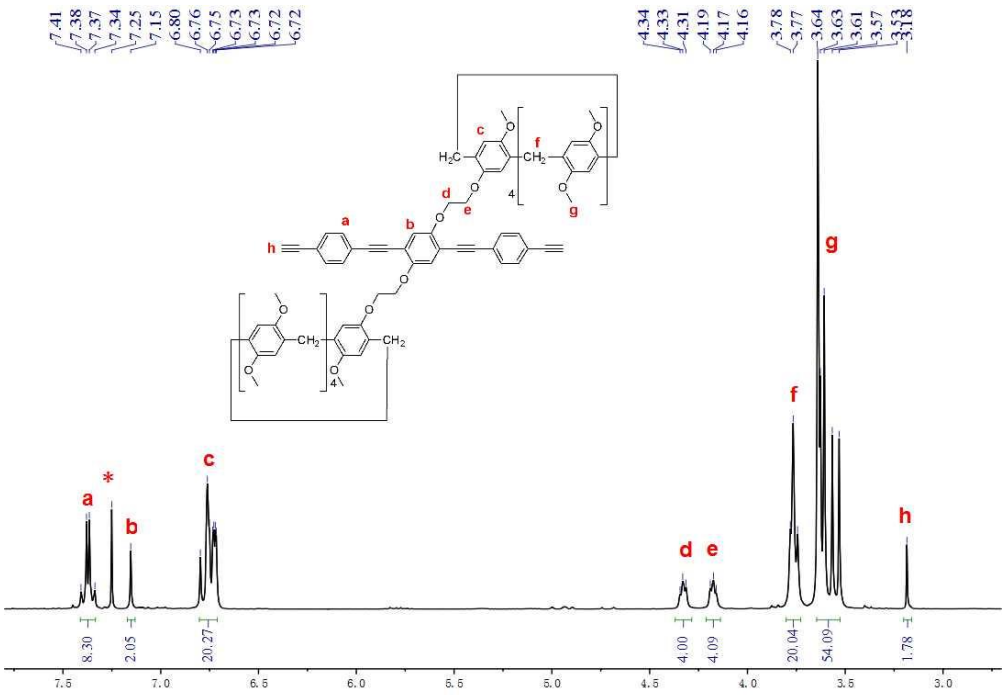


Fig. S7. ^1H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **M1**. Asterisk indicates the solvent peak.

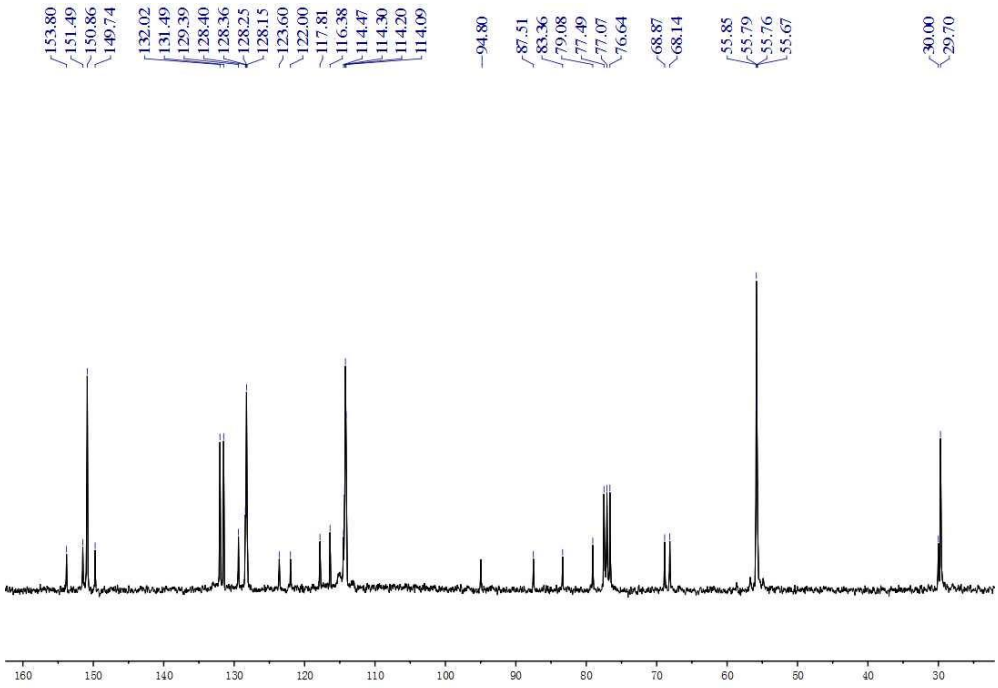


Fig. S8. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of **M1**.

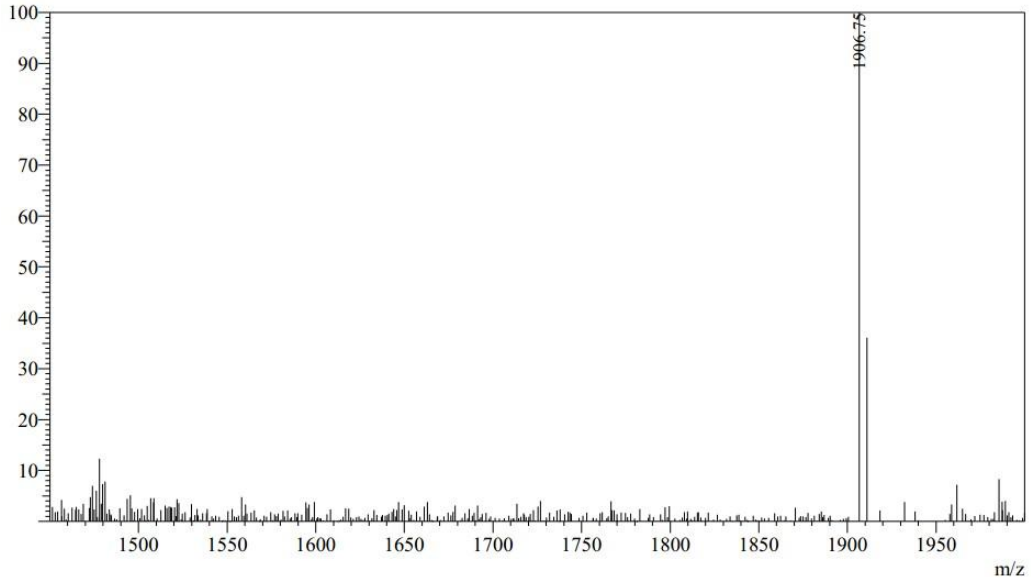
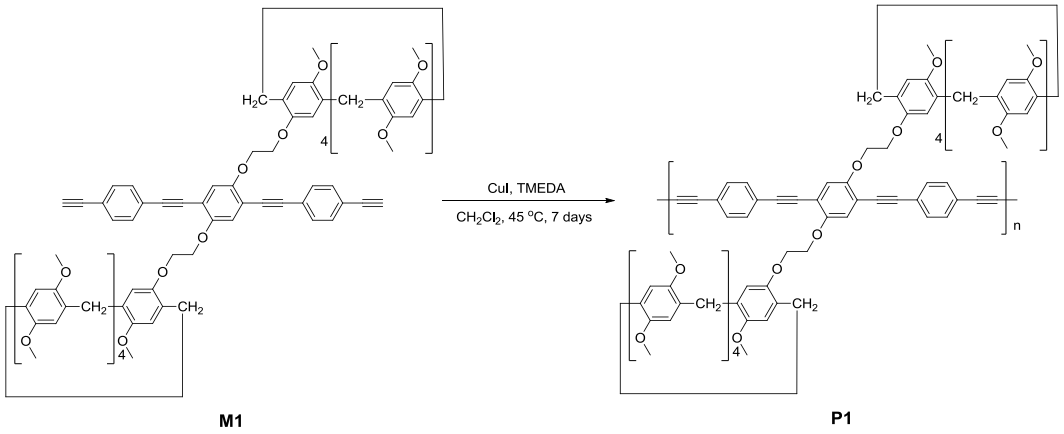


Fig. S9. Electrospray ionization mass spectrum of **M1**.

3. Synthesis of pillar[5]arene-based polymer P1



Scheme S2. Synthesis of polymer **P1** by polymerization of **M1** in CH_2Cl_2.

To a solution of **M1** (0.2 g, 0.106 mmol) in CH_2Cl_2 (20 mL) was added CuI (0.2022 g, 0.1062 mmol) and TMEDA (2 mL). The mixture was stirred at 45 ^oC for 7 days and quenched with 1 N HCl aq (20 mL). The organic layer was extracted with CH_2Cl_2 (40 mL) and washed with brine (60 mL). The organic phase was dried over Na_2SO_4 and evaporated to give a yellow solid **P1** (0.12 g, 60.0%). ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 7.46-7.37 (m, 8H, phenyl protons), 7.17 (s, 2H, central phenyl protons), 6.81-6.74 (m, 20H, phenyl protons from pillar[5]arene), 4.34 (brs, 4H, protons from O*CH*$_2$ linked to phenyl), 4.19 (brs, 4H, protons from O*CH*$_2$ linked to pillar[5]arene), 3.77 (s, 20H, methylene bridge protons of pillar[5]arene), 3.64-3.54 (m, 54H, methoxy protons of pillar[5]arene). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ (ppm): 153.85, 151.55, 150.91, 150.86, 149.73, 132.39, 131.65, 129.47, 128.45, 128.40, 128.31, 128.26, 128.17, 117.74, 116.50, 114.31, 114.21, 114.12, 68.90, 68.25, 55.93, 55.87, 55.81, 55.79, 55.77, 55.69, 29.80, 29.75. GPC (THF, 40 ^oC, Polystyrene standards as calibrant): Mw = 24900; Mn = 15800; PDI = 1.58 (degree of polymerization [DP] ≈ 8).

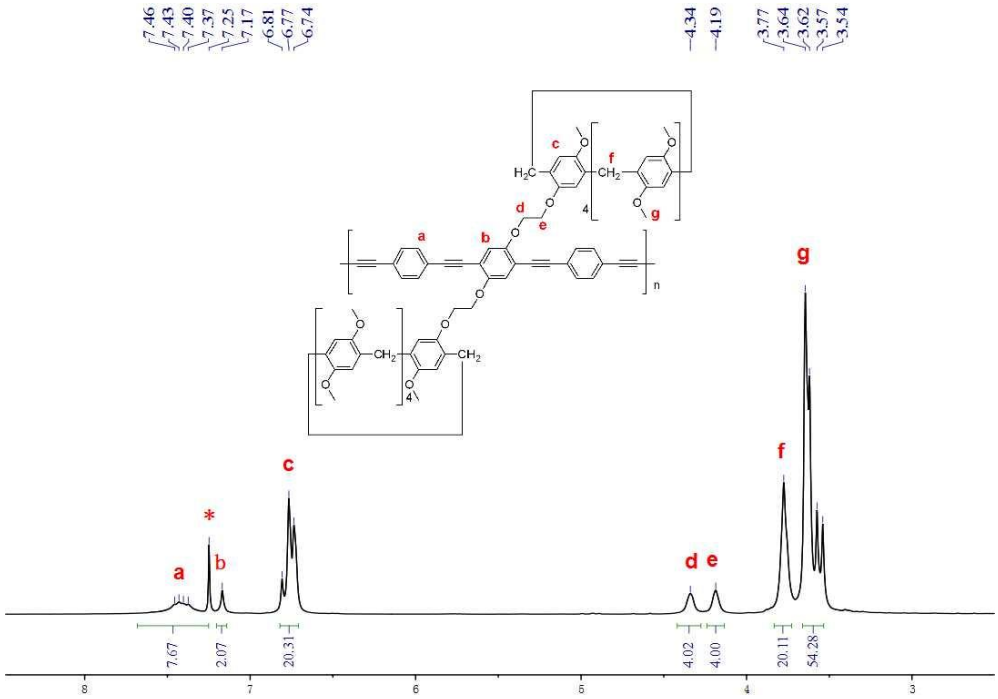


Fig. S10. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **P1**. Asterisk indicates the solvent peak.

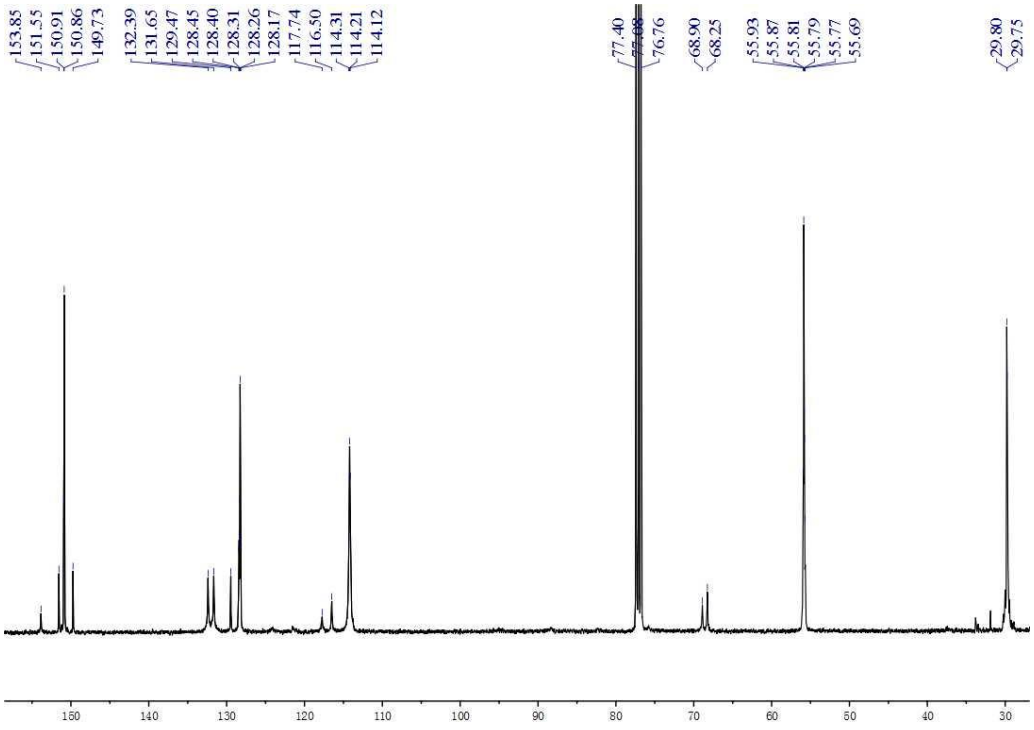


Fig. S11. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **P1**.

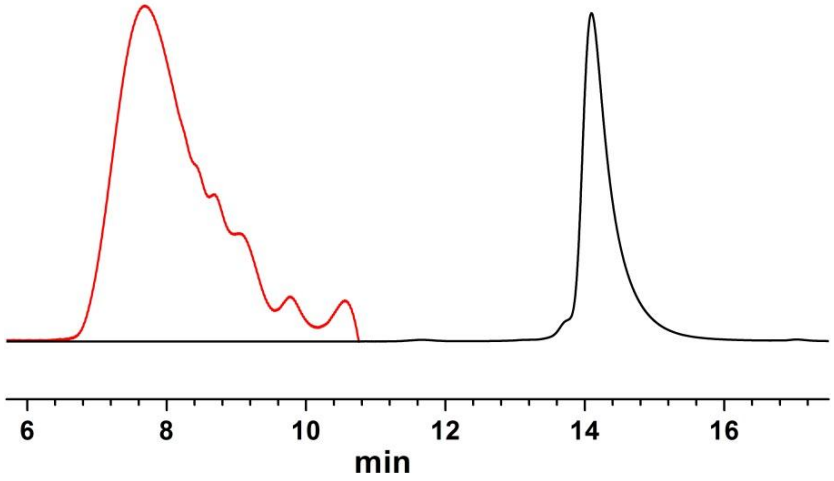


Fig. S12. GPC traces of monomer **M1** (before polymerization, black line) and polymer **P1** (after polymerization, red line).

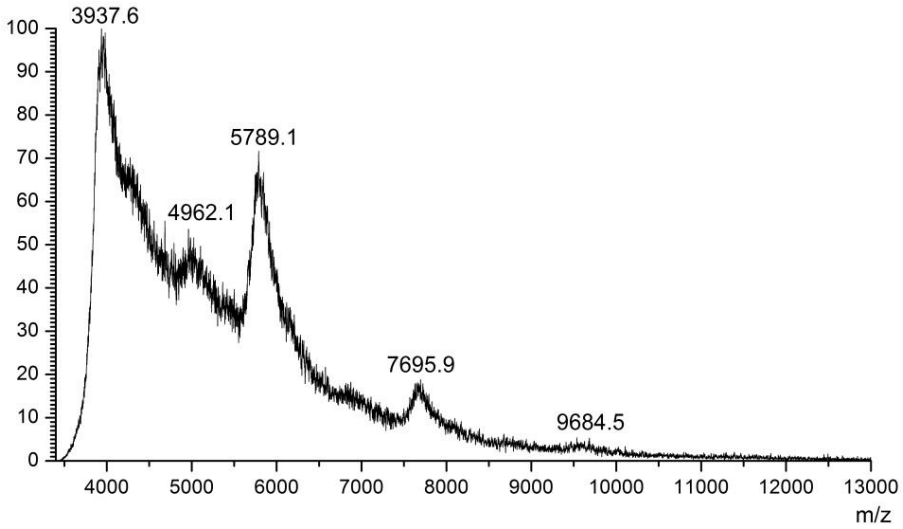
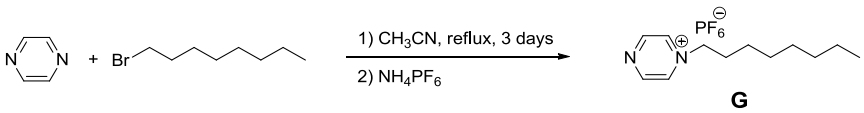


Fig. S13. MALDI-TOF mass spectrum of **P1**.

4. Synthesis of the guest molecule G



Scheme S3. Synthesis of the guest molecule **G**.

Compound **G** was synthesized using a modified method of literature[S5], which was previously used to prepare some quaternary salts of pyrazine.

A solution of 1-bromooctane (0.60 g, 3.12 mmol) in CH_3CN (15 mL) was added

dropwise into a stirred and refluxed solution of pyrazine (1 g, 12.49 mmol) in CH_3CN (10 mL) over 6 h. After addition, the mixture was further stirred and refluxed for 3 days. After it cooled, the solvent was removed under reduced pressure and the product was precipitated with diethyl ether. The suspension was filtered and then dried in an oven to afford a pink solid. It was dissolved in minimum deionized water and aqueous NH_4PF_6 (1.02 g, 6.24 mmol) was added to precipitate a white solid. The resulting solid was filtered and washed with water to afford the desired product **G** (0.22 g, 20.8%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 9.40 (s, 2H, pyrazine protons), 8.68 (s, 2H, pyrazine protons), 4.66 (m, 2H, $CH_2CH_2(CH_2)_5CH_3$), 2.03 (m, 2H, $CH_2CH_2(CH_2)_5CH_3$), 1.31 (m, 10H, $CH_2CH_2(CH_2)_5CH_3$), 0.88 (t, J = 5.8 Hz, 3H, $CH_2CH_2(CH_2)_5CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ (ppm): 150.93, 136.78, 62.71, 31.43, 30.74, 28.67, 28.60, 25.74, 22.23, 12.98. LRESIMS (m/z): 193.10 [M – PF_6]$^+$.

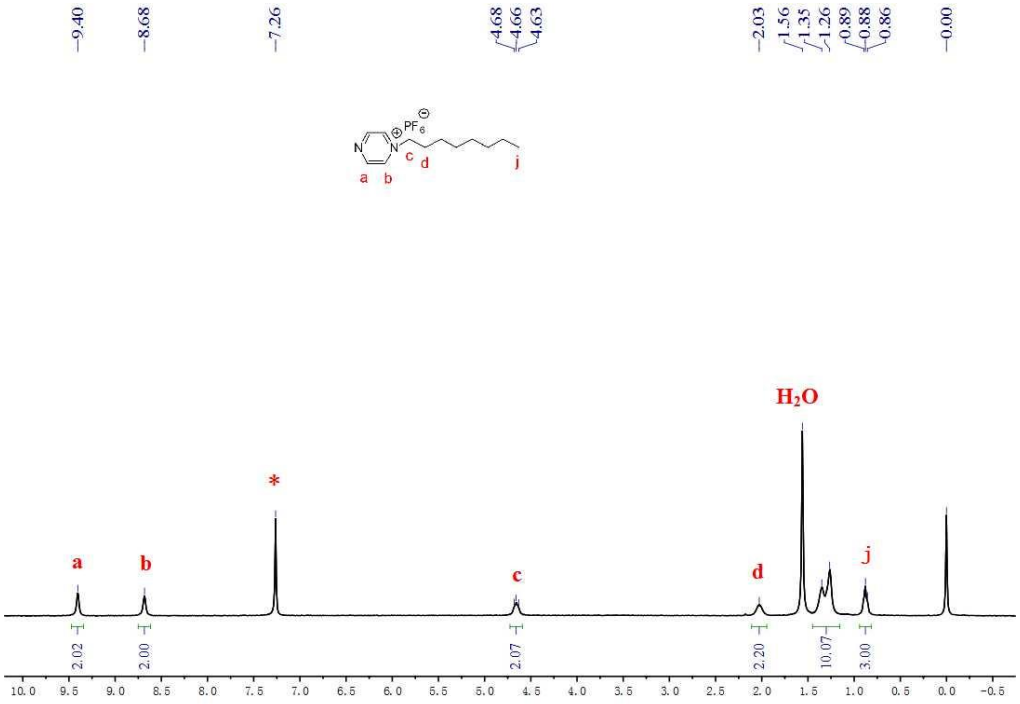


Fig. S14. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **G**. Asterisk indicates the solvent peak.

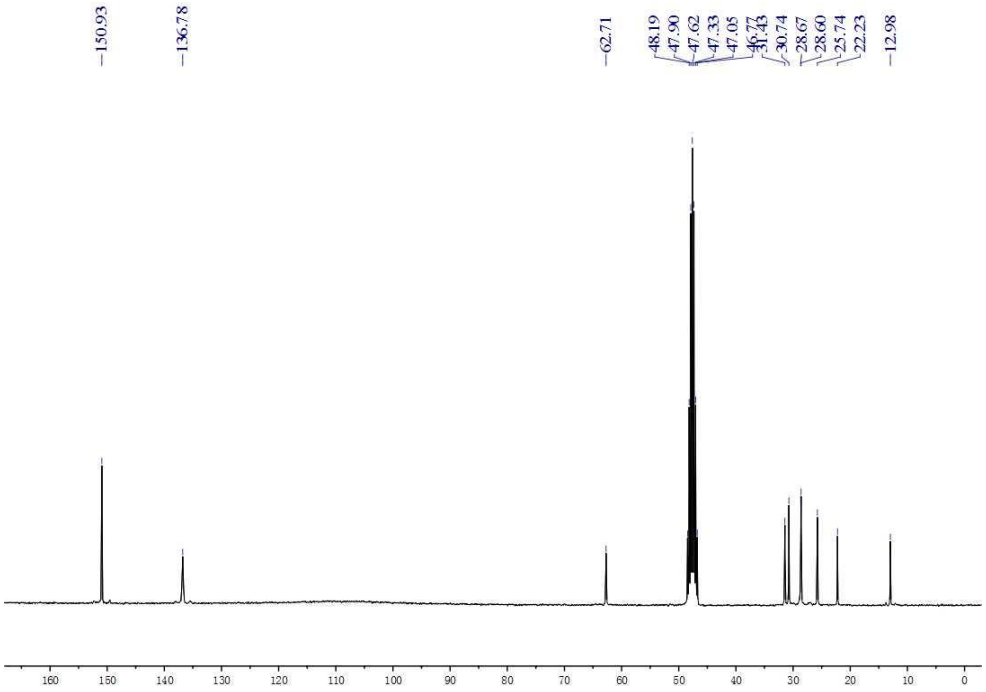


Fig. S15. ^{13}C NMR spectrum (75 MHz, CD_3OD, 298 K) of **G**.

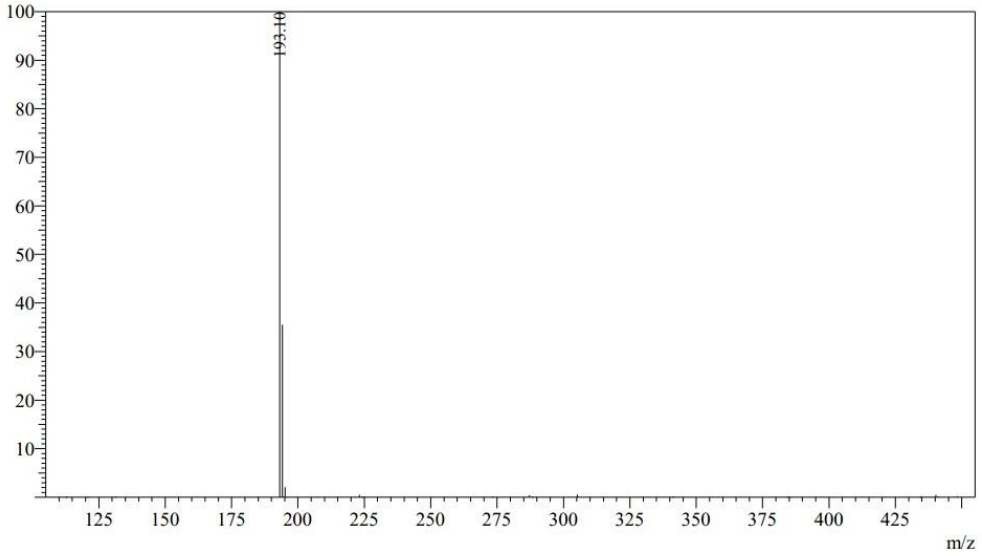


Fig. S16. Electrospray ionization mass spectrum of **G**.

5. 2D COSY and 2D ROESY spectrum of a mixture of monomer M1 and G

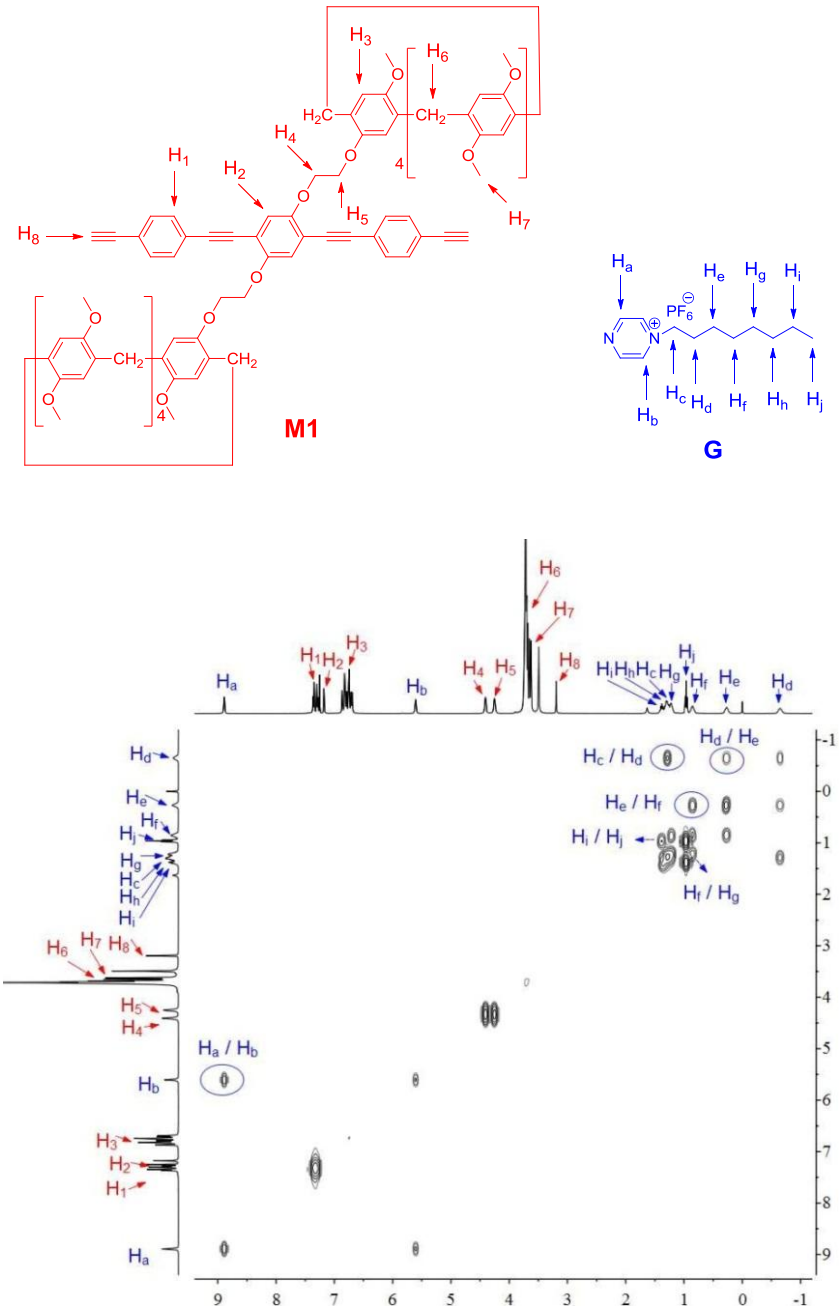


Fig. S17. 2D COSY NMR spectrum of monomer **M1** (40.0 mM) and **G** (64 mM) in $CDCl_3$.

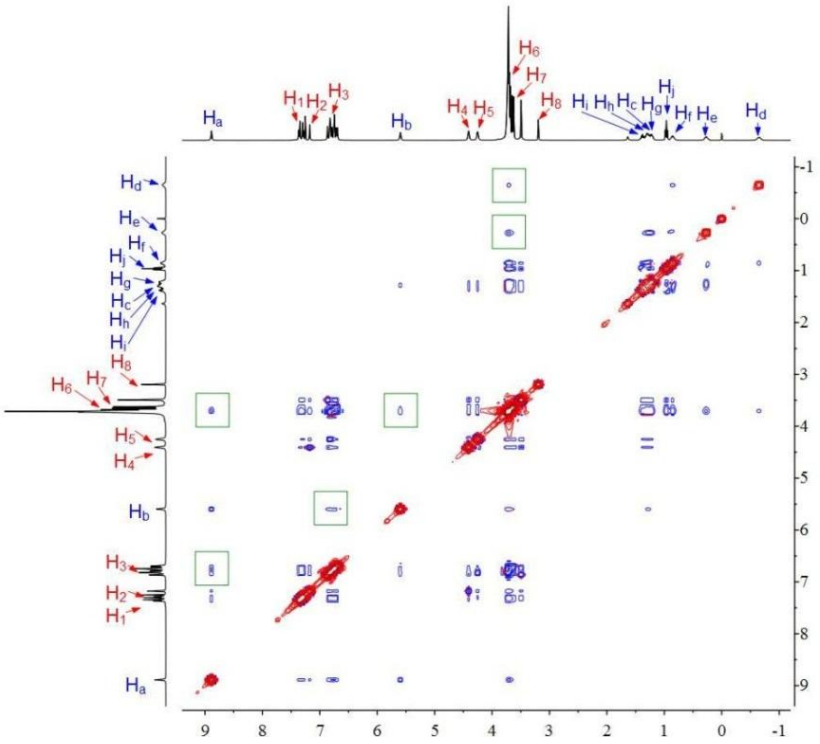


Fig. S18. 2D ROESY NMR spectrum of a mixture of monomer **M1** (40.0 mM) and **G** (64 mM) in $CDCl_3$. NOE correlations were observed between protons of methylene bridge, methoxy and benzene groups of monomer **M1** and protons of pyrazine and methylene groups of **G**, indicating that **G** was located in the pillar[5]arene cavities of monomer **M1**.

6. Electrospray ionization mass spectrum of the complexation between DMP5 and G

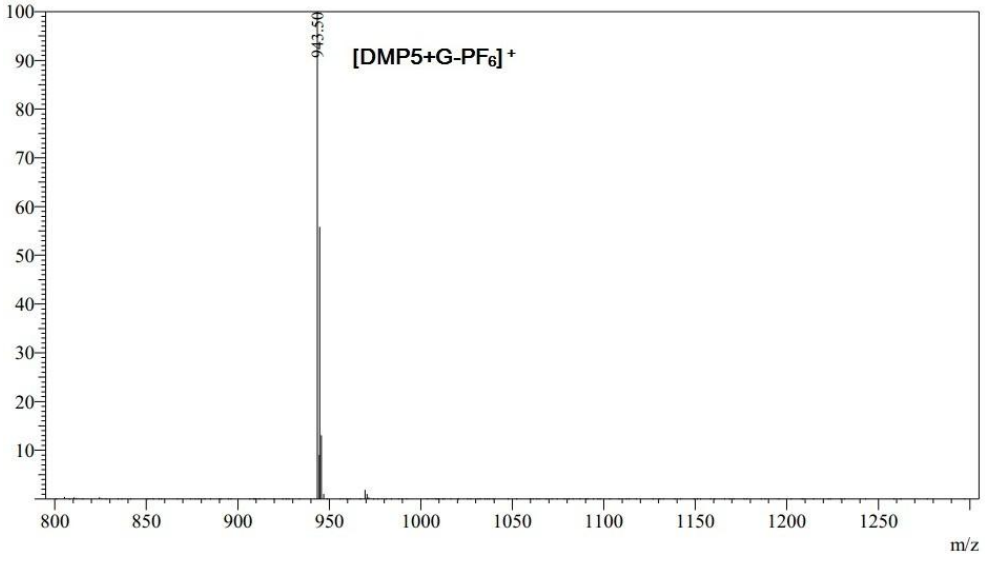
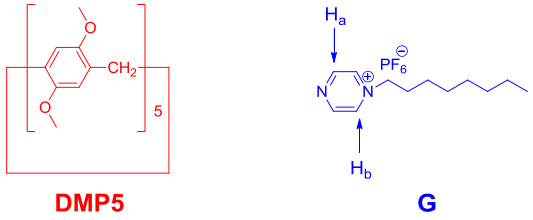


Fig. S19. Electrospray ionization mass spectrum of a mixture of **DMP5** with equimolar **G**.

7. Stoichiometry and association constant determination for the complexation between DMP5 and G



DMP5 **G**

The stoichiometry of complexation between **DMP5** and **G** were determined using the method of Job Plot. By this method, a 1:1 stoichiometry was obtained.

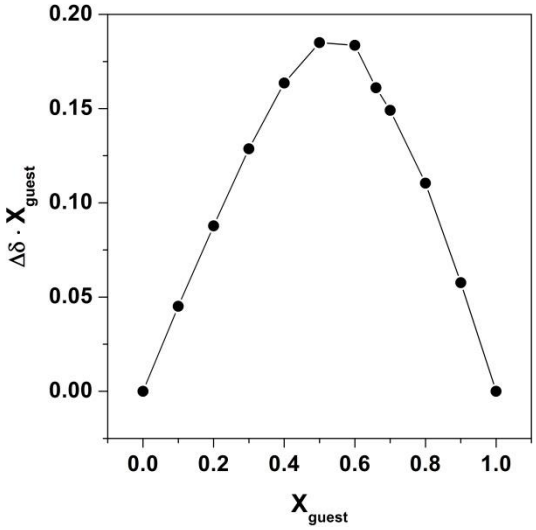


Fig. S20. Job Plot showing the 1:1 stoichiometry of the complexation between **DMP5** and **G** in $CDCl_3$ by plotting the $\Delta\delta$ in chemical shift of the guest's pyrazine proton H_a observed by ^1H NMR spectroscopy against the mole fraction of **G**. ([host] + [guest] = 6 mM)

To determine the association constant between **DMP5** and **G**, ^1H NMR titrations were done with solutions which had a constant concentration of **G** (5.4 mmol) and varying concentrations of **DMP5**. By a non-linear curve-fitting method, the association constant (K_a) of **DMP5**⊃**G** was estimated to be about 1267 ± 78 M^{-1}.

The non-linear curve-fitting was based on the following equation:[S6]

$$\Delta\delta = (\Delta\delta_\infty/[G]_0)\ (0.5[H]_0 + 0.5([G]_0 + 1/K_a) - (0.5\ ([H]_0^2 + (2[H]_0(1/K_a - [G]_0)) + (1/K_a + [G]_0)^2)^{0.5})) \quad \text{(Eq. S1)}$$

Where $\Delta\delta$ is the chemical shift change of H_a on **G** at $[H]_0$, $\Delta\delta_\infty$ is the chemical shift

change of H_a when the guest is completely complexed, $[G]_0$ is the fixed initial concentration of the guest, and $[H]_0$ is the varying concentrations of **DMP5**.

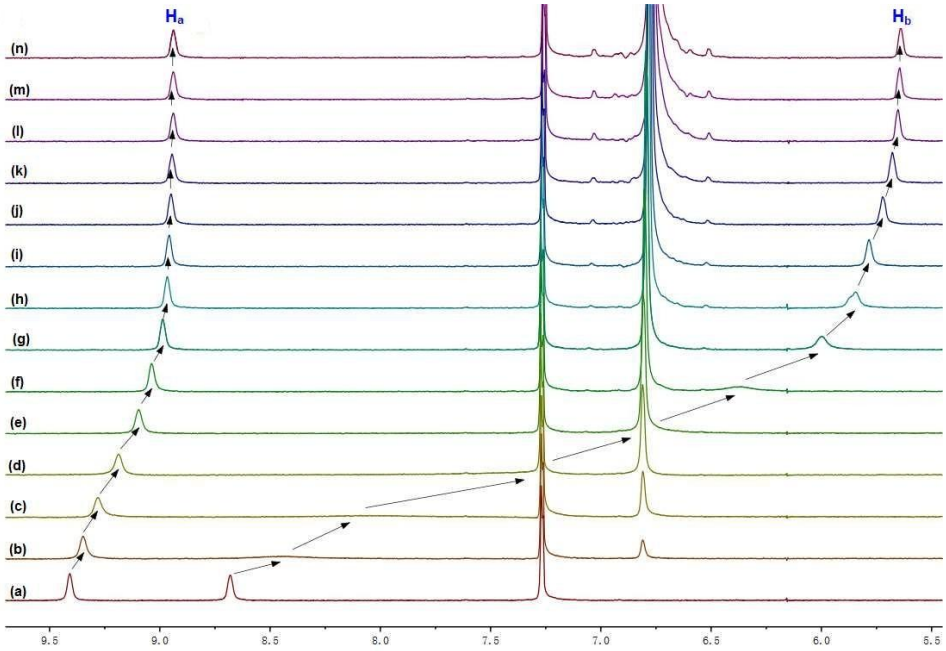


Fig. S21. Partial ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K) of **G** at a concentration of 5.4 mM upon addition of **DMP5**: (a) 0.00 mM, (b) 0.67 mM, (c) 1.67 mM, (d) 3.33 mM, (e) 5.00 mM, (f) 6.67 mM, (g) 10.00 mM, (h) 13.33 mM, (i) 16.67 mM, (j) 23.33 mM, (k) 33.33 mM, (l) 43.33 mM, (m) 50.00 mM, (n) 56.67 mM.

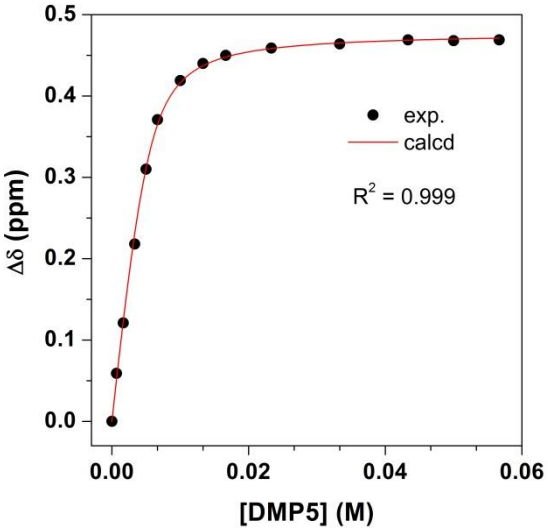


Fig. S22. The chemical shift changes of H_a on **G** upon addition of **DMP5**. The red solid line was obtained from the non-linear curve-fitting using Eq.S1. The association constant (K_a) of **DMP5** and **G** was estimated to be about 1267 ±78 M^{-1}.

8. Electrospray ionization mass spectrum of the complexation between monomer M1 and G

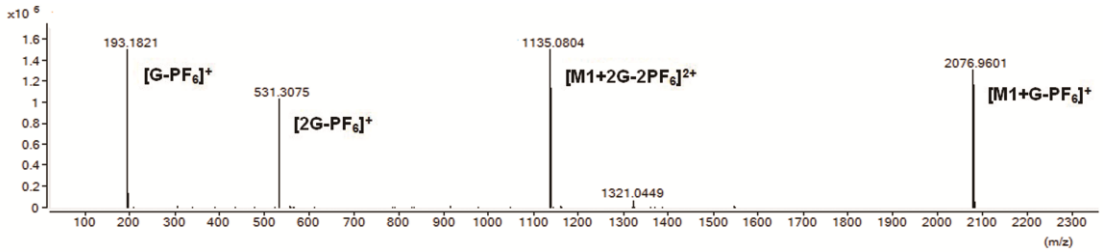
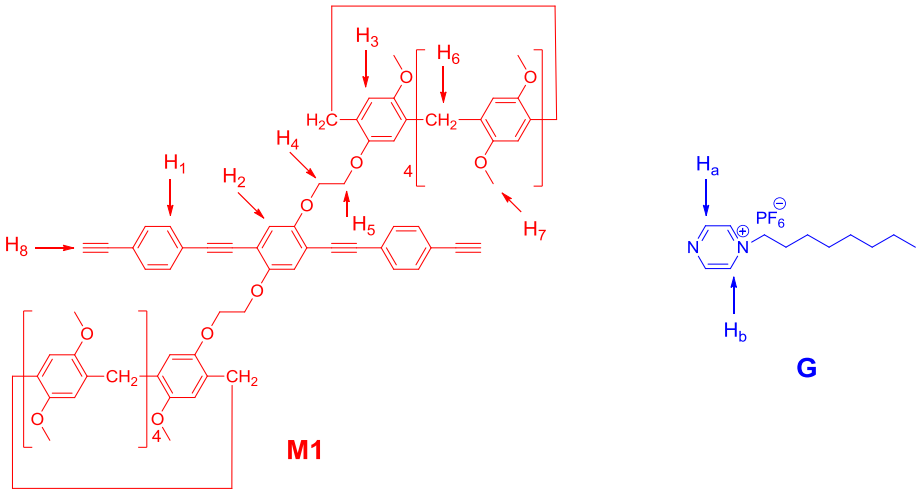


Fig. S23. Electrospray ionization mass spectrum of a mixture of **M1** with excess **G**.

9. Association constants determination for the complexation between M1 and G



To determine the association constant between **M1** and **G**, ^{1}H NMR titration experiments were done with solutions which had a constant concentration of **M1** (5.0 mmol) and varying concentrations of **G**. The chemical shift changes of H_3 on **M1** were monitored. By using the Benesi-Hildebrand methodand[S7] and Scatchard plot[S8] method, the association constants K_1 and K_2 of **M1**⊃2**G** were estimated to be about 4.4 (±0.26) × 10^2 M^{-1} and 2.6 (±0.07) × 10^2 M^{-1}, repectively.

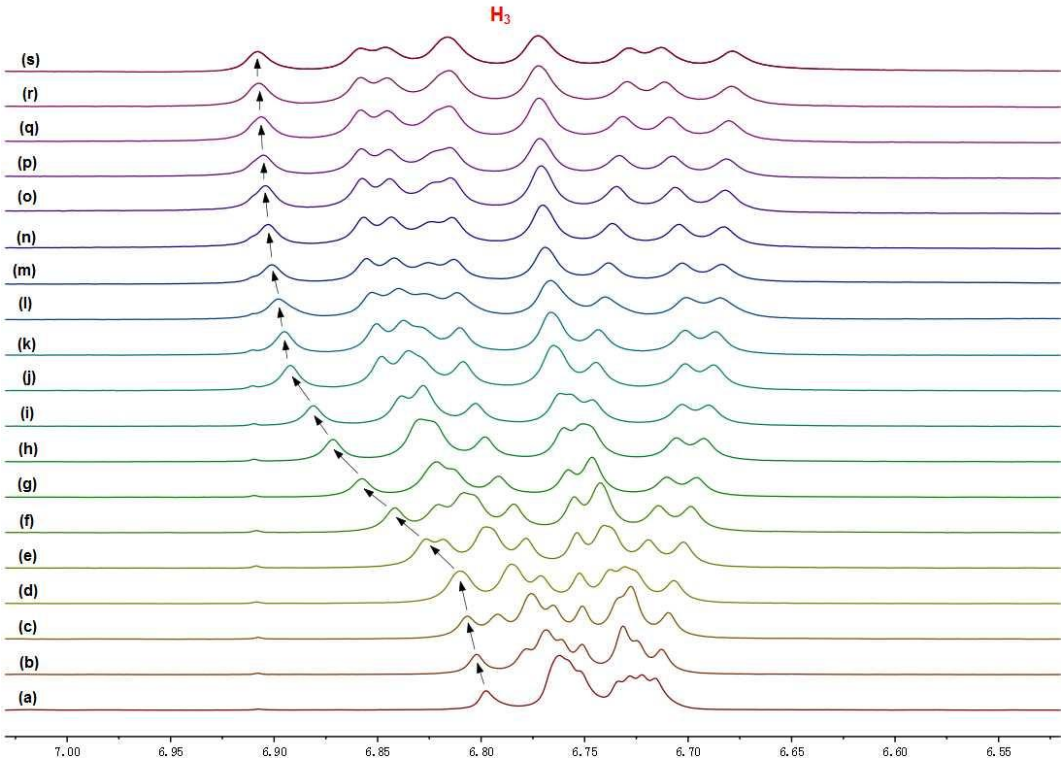


Fig. S24. Partial ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K) of **M1** at a concentration of 5.0 mM upon addition of **G**: (a) 0.00 mM, (b) 2.00 mM, (c) 4.00 mM, (d) 6.00 mM, (e) 8.00 mM, (f) 10.00 mM, (g) 12.00 mM, (h) 14.00 mM, (i) 16.00 mM, (j) 18.00 mM, (k) 20.00 mM, (l) 22.25 mM, (m) 24.50 mM, (n) 26.75 mM, (o) 29.00 mM, (p) 31.25 mM, (q) 36.00 mM, (r) 43.50 mM, (s) 56.00 mM.

On the basis of the ^{1}H NMR titration experiments with constant monomer **M1** and various values of **G**, the difference in δ values (Δ_0) for H_3 of **M1** in the uncomplexed and fully complexed species was determined by extrapolation of a plot of $\Delta = \delta - \delta_u$ versus 1/[**G**] in the high initial concentration range of **G**, where δ_u is the chemical shift for H_3 of **M1** in the uncomplexed state.

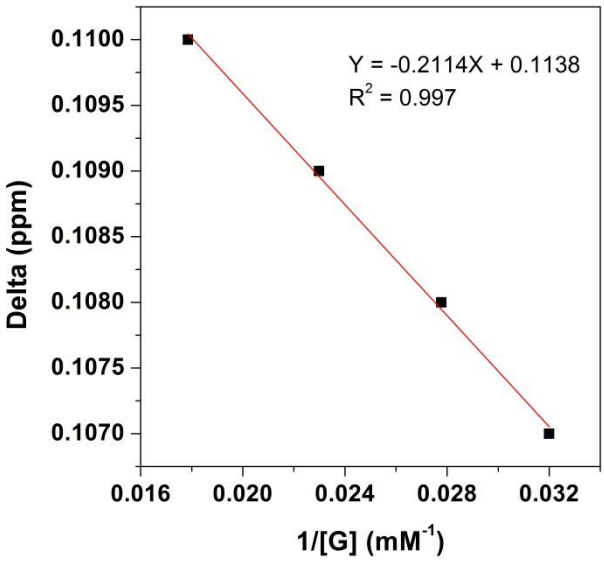


Fig. S25. Benesi-Hildebrand plot ($CDCl_3$, 298 K) for complexation between monomer **M1** ($[\mathbf{M1}]_0$ = 5 mM) and **G**. Δ_0 = 0.1138 ppm.

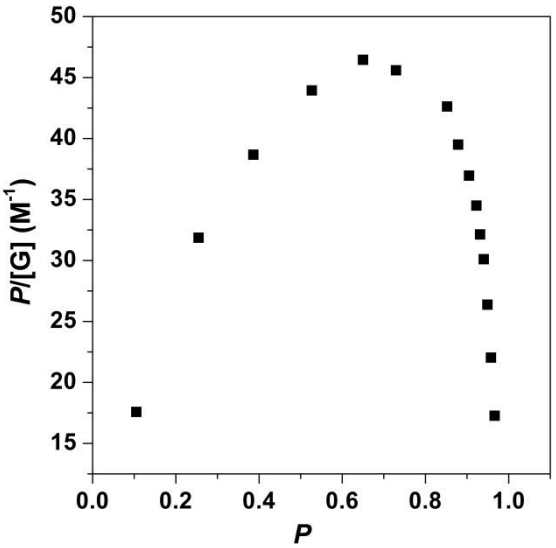


Fig. S26. Scatchard plot ($CDCl_3$, 298 K) for the complexation of **M1** ($[\mathbf{M1}]_0$ = 5 mM) with **G**. *p* defines the fraction of pillar[5]arene units bound. $p = \Delta/\Delta_0$, where Δ is the observed chemical shift change relative to the uncomplexed species. The Scatchard plot is nonlinear and has a maximum, which indicates that the two pillar[5]arene units of **M1** act cooperatively. The slope of the first three data points for low *p* gave the value of $2K_2 - K_1$, while the slope of the last four data points for high *p* gave the value of $-2K_2$.[S9] Errors of the two association constants were calculated on the basis of errors of the slope. Thus, the values for K_1 and K_2 of **M1**⊃2**G** was estimated to be about 4.4 (±0.26) × 10^2 M^{-1} and 2.6 (±0.07) × 10^2 M^{-1}, respectively.

10. UV–vis absorption and Fluorescence spectra of M1 and P1

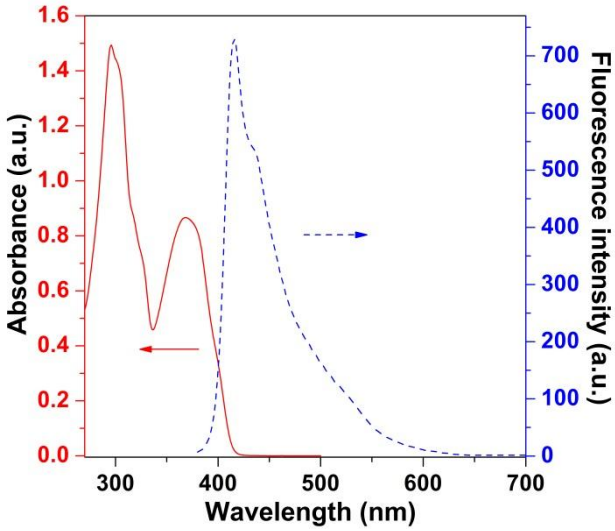


Fig. S27. UV–vis absorption (solid line, 20 μM) and fluorescence (dashed line, 10 μM, λ_{ex} = 369 nm) spectra of **M1** in $CHCl_3$.

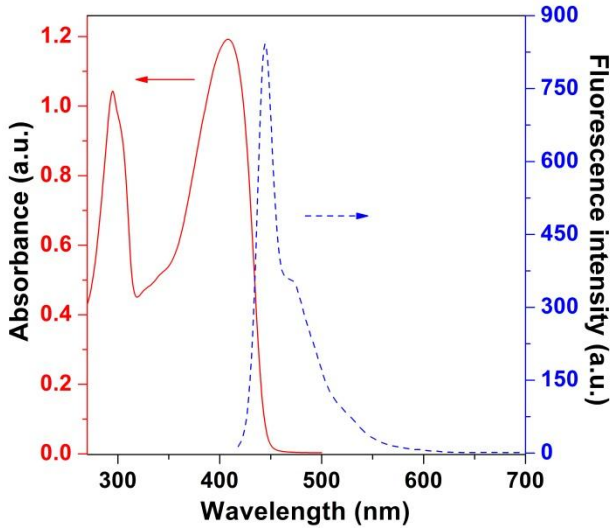


Fig. S28. UV–vis (solid line, [RU] = 20 μM) and fluorescence (dashed line, [RU] = 10 μM, λ_{ex} = 408 nm) spectra of polymer **P1** in $CHCl_3$.

11. Fluorescence quantum yield measurements

Fluorescence quantum yields (Φ_F) were estimated using quinine sulfate in 0.1 M sulfuric acid (Φ_F = 54.6%, excitation at 340 nm) as standard.[S10] The absorbance of the solutions was kept around 0.05 to avoid internal filter effect. The quantum yield of **M1** and **P1** is determined according to the following equation:[S11]

$$\Phi_F = \Phi'_F \left(\frac{Grad_{sample}}{Grad_{std}}\right)\left(\frac{\eta^2_{sample}}{\eta^2_{std}}\right)$$

where Φ'_F is the fluorescence quantum yield of the reference compound, Grad is the slope from the plot of integrated fluorescence intensity versus absorbance, η is the refractive index of the corresponding solution.

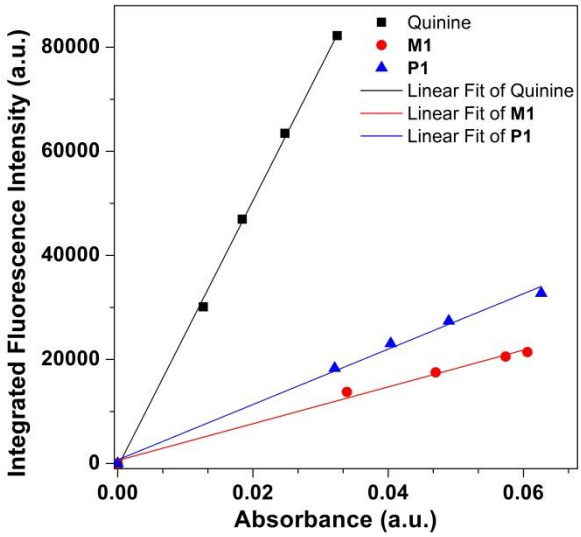
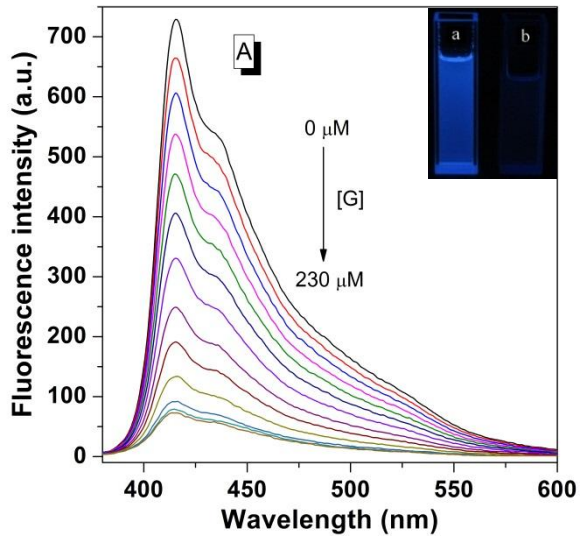


Fig. S29. Fluorescence quantum yield measurements of **M1** and **P1**. (The Φ_F values of **M1** and **P1** are 8.88% and 13.36%, respectively)

12. Fluorescence quenching experiment of monomer M1



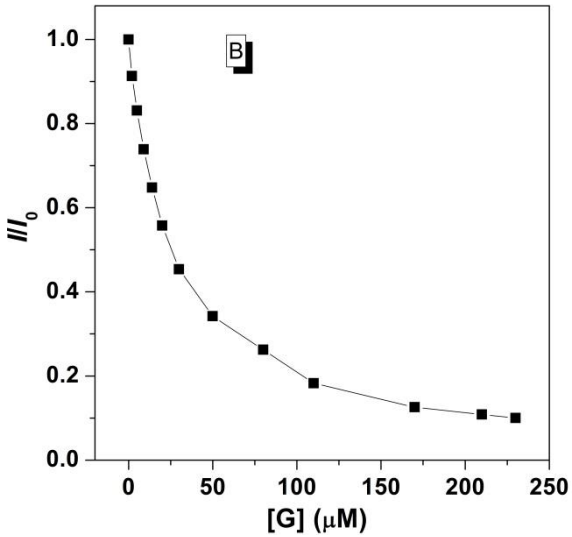


Fig. S30. (A) Fluorescence spectra of **M1** (10 μM in $CHCl_3$) in the presence of different amounts of **G** (from 0 to 230 μM), λ_{ex} = 369 nm. The inset shows the photographs of the solution of **M1** in the (a) absence and (b) presence of **G** (230 μM) under UV light (365 nm) illumination. (B) Plot of the relative fluorescence intensity (I/I_0) of **M1** (10 μM in $CHCl_3$) versus the concentration of **G**; the fluorescence intensity was monitored at 415 nm.

13. Fluorescence turn-on experiment of monomer M1

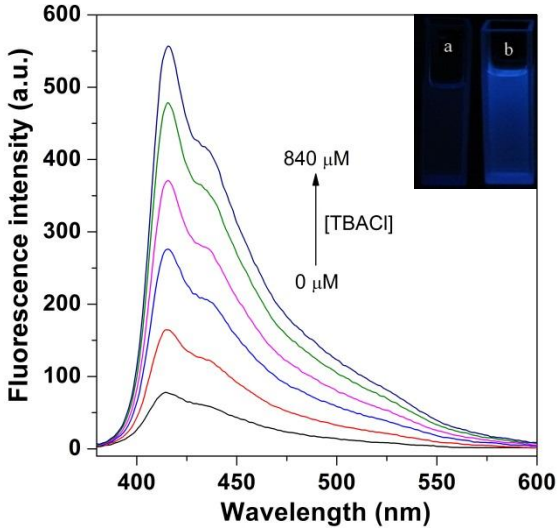


Fig. S31. Fluorescence spectra of **M1** (10 μM) and **G** (230 μM) in $CHCl_3$ in the presence of different concentrations of TBACl (0, 120, 210, 300, 480, 840 μM), λ_{ex} = 369 nm. Inset shows the photographs of the solution of **M1** and **G** in the (a) absence and (b) presence of TBACl (840 μM) under UV light (365 nm) illumination.

References:

S1. T. Shiraki, S. Haraguchi, Y. Tsuchiya and S. Shinkai, *Chem.-Asian J.*, 2009, **4**, 1434.

S2. J. G. Rodr ́guez, J. L. Tejedor, T. La Parra and C. D ́az, *Tetrahedron*, 2006, **62**, 3355.

S3. L. Liu, D. Cao, Y. Jin, H. Tao, Y. Kou and H. Meier, *Org. Biomol. Chem.*, 2011, **9**, 7007.

S4. N. L. Strutt, R. S. Forgan, J. M. Spruell, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 5668.

S5. C. T. Bahner and L. L. Norton, *J. Am. Chem. Soc.*, 1950, **72**, 2881.

S6. P. R. Ashton, R. Ballardini, V. Balzani, M. Bělohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 4931.

S7. H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.

S8. (a) A. G. Marshall, *Biophysical Chemistry*, J. Wiley and Sons: New York, 1978; (b) D. M. Freifelder, Physical Biochemistry, W. H. Freeman and Co.: New York, 1982; (c) K. A. Connors, *Binding Constants*, J. Wiley and Sons: New York, 1987.

S9. B. Perlmutter-Hayman, *Acc. Chem. Res.*, 1986, **19**, 90.

S10. J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

S11. A. T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067.