Electronic Supplementary Information

Controllable aggregation-induced emission based on tetraphenylethylene-functionalized pillar[5]arene *via* host-guest recognition

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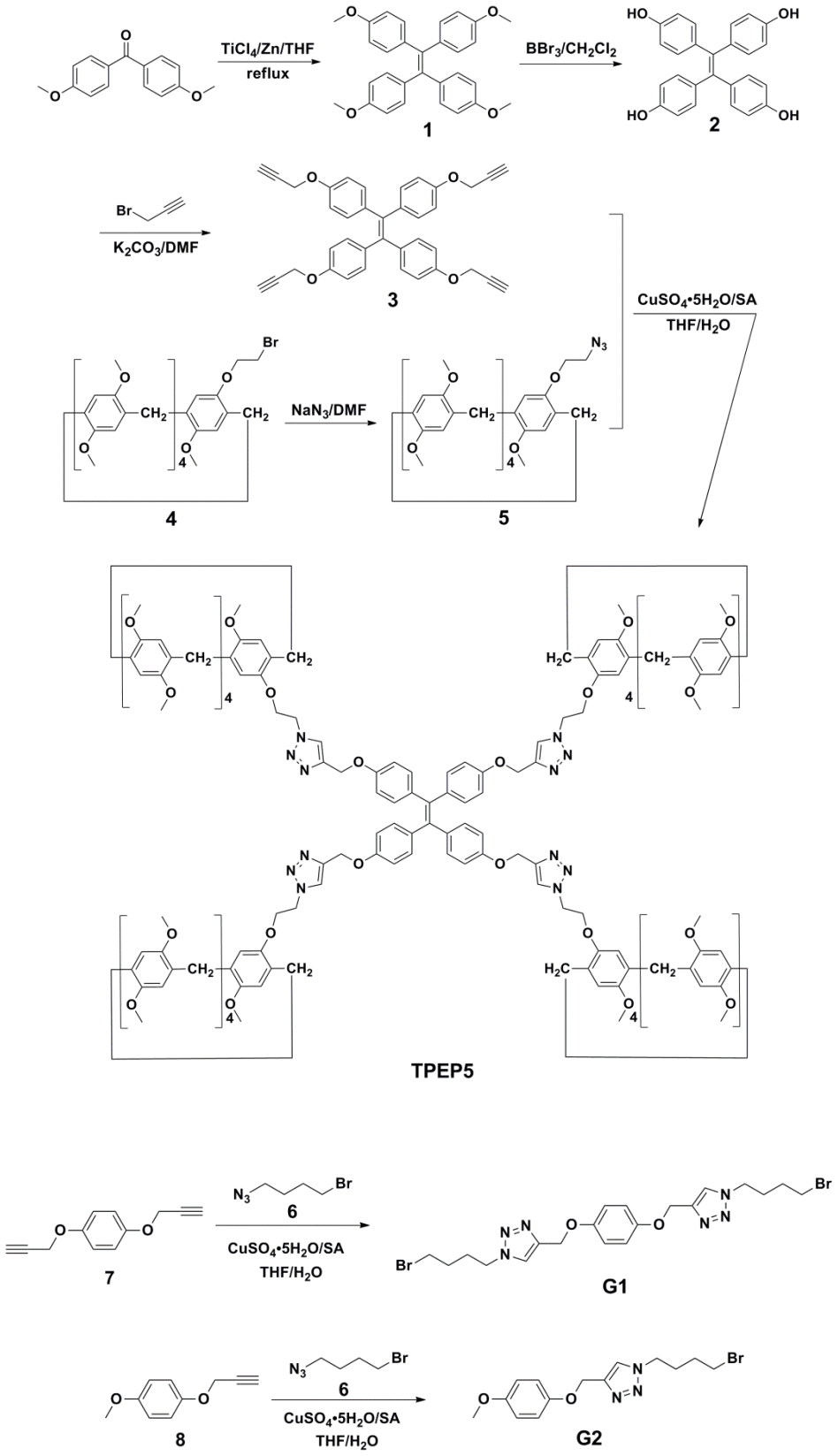
1. General information

All reactions were performed in atmosphere unless otherwise stated. The commercially available reagents were used as supplied without further purification. Chloroform and acetone were dried according to procedures described in the literature, and other solvents were used as received without further purification unless otherwise stated. Column chromatography was performed with silica gel (200-300 mesh) produced by Qingdao Marine Chemical Factory, Qingdao (China). 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, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. 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. Dynamic light scattering (DLS) measurements were carried out on a Brookhaven BI-9000AT system (Brookhaven Instruments Corporation, USA), using a 200-mW polarized laser source (λ = 514 nm). The UV-Vis absorption spectrum was measured on a Perkin Elmer Lambda 35 UV/Vis Spectrometer. The excitation and emission spectra were recorded on a Perkin Elmer LS55 Fluorescence Spectrometer. Transmission electron microscope (TEM) investigations were carried out on a JEM-2100 instrument.

2. Synthesis of TPEP5, G1, and G2

General procedure:



Scheme S1. Synthetic route for compounds **TPEP5**, **G1**, and **G2**.

Synthesis of compound **1**[S1]

To a solution of 4,4'-dimethoxybenzophenone (5 g, 20.64 mmol) and zinc powder (6.75 g, 103.2 mmol) in THF (100 mL) was added dropwise $TiCl_4$ (13.7 g, 72.23 mmol). After refluxing for 20 h, the reaction mixture was cooled to room temperature and filtered. The solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether (*v/v* = 1:2) as the eluent. Finally, compound **1** was obtained as a white solid (2.52 g, 54%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 6.93 (d, J = 8.7 Hz, 8H, phenyl protons), 6.64 (d, J = 8.8 Hz, 8H, phenyl protons), 3.74 (s, 12H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ (ppm): 157.79, 138.39, 136.91, 132.57, 113.04, 55.09. ESI-MS: *m/z* 491.10 $[M+K]^+$ (100%).

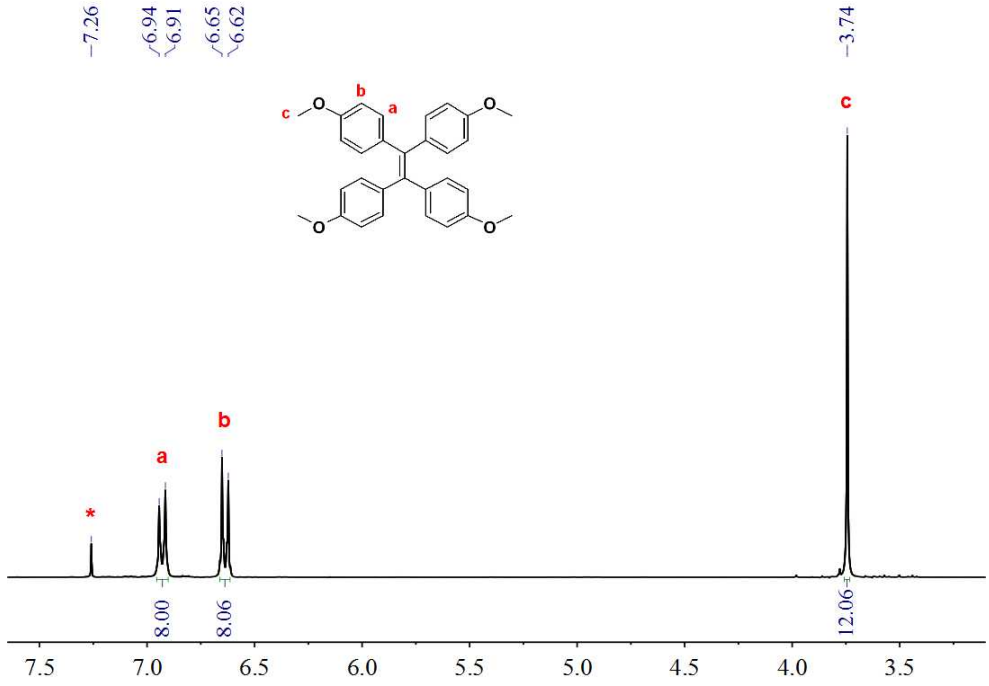


Fig. S1 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **1**. Asterisk indicates the solvent peak.

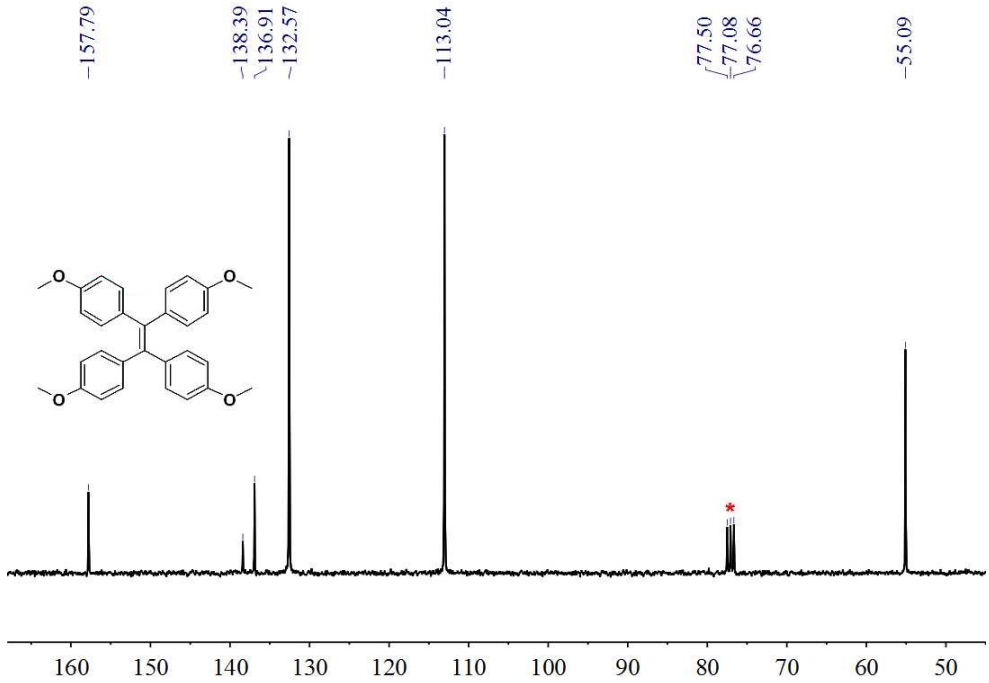


Fig. S2 ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of **1**. Asterisk indicates the solvent peak.

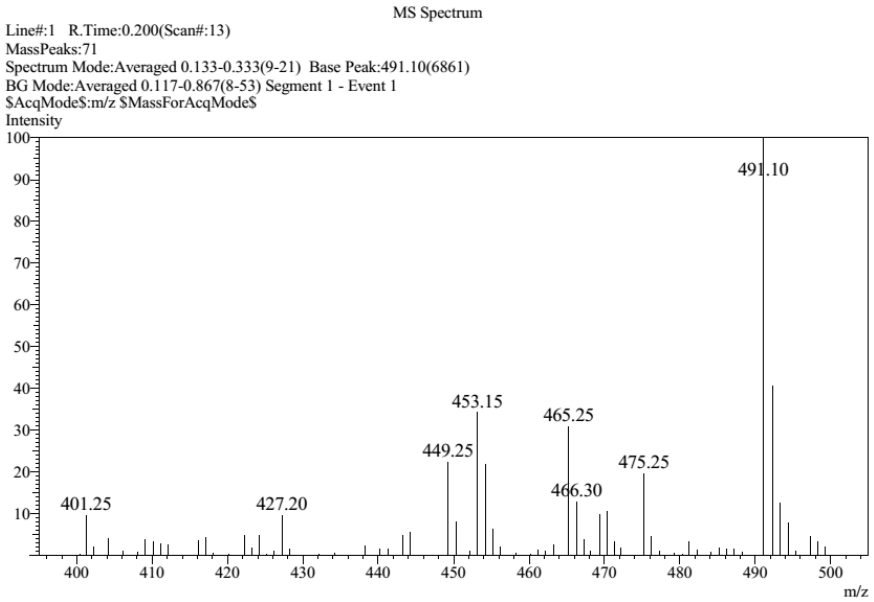


Fig. S3 Electrospray ionization mass spectrum of **1**.

Synthesis of compound **2**[S1]

To a cooled solution of compound **1** (1 g, 2.21 mmol) in dichloromethane (15 mL) was added dropwise BBr_3 (8.8 mL, 17.68 mmol, dissolved in 10 mL of CH_2Cl_2). After removal of the cooling bath, the resulting deep red solution was stirred at room temperature for 18 h and then hydrolyzed under ice-cooling by dropwise addition of

water (50 mL). The precipitate was collected by filtration and washed with water (200 mL), CH_2Cl_2 (200 mL), respectively. Then desired product **2** was obtained as a purple solid (0.79 g, 90%).

Synthesis of compound **3**[S2]

The mixture of compound **2** (0.79 g, 1.99 mmol), 3-bromo-1-propyme (2.37 g, 19.93 mmol), and KCO_3 (2.75 g, 19.93 mmol) in anhydrous DMF (20 mL) was vigorously stirred under nitrogen atmosphere at 70 °C for 24 h. The mixture was then cooled to room temperature and filtered. After removal of the solvent under reduced pressure, the crude product was subjected to silica gel chromatography using dichloromethane/petroleum ether (*v*/*v* = 1:1) as eluent. Compound **3** was obtained as a white solid (0.33 g, 30%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 6.93 (d, J = 8.8 Hz, 8H, Ar-H), 6.70 (d, J = 8.8 Hz, 8H, Ar-H), 4.62 (d, J = 2.3 Hz, 8H, O*CH*$_2$), 2.50 (t, J = 2.3 Hz, 4H, $CH_2C{\equiv}CH$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 156.09, 138.69, 137.56, 132.65, 114.12, 78.73, 75.56, 55.89. ESI-MS: *m/z* 587.10 $[M+K]^+$ (100%).

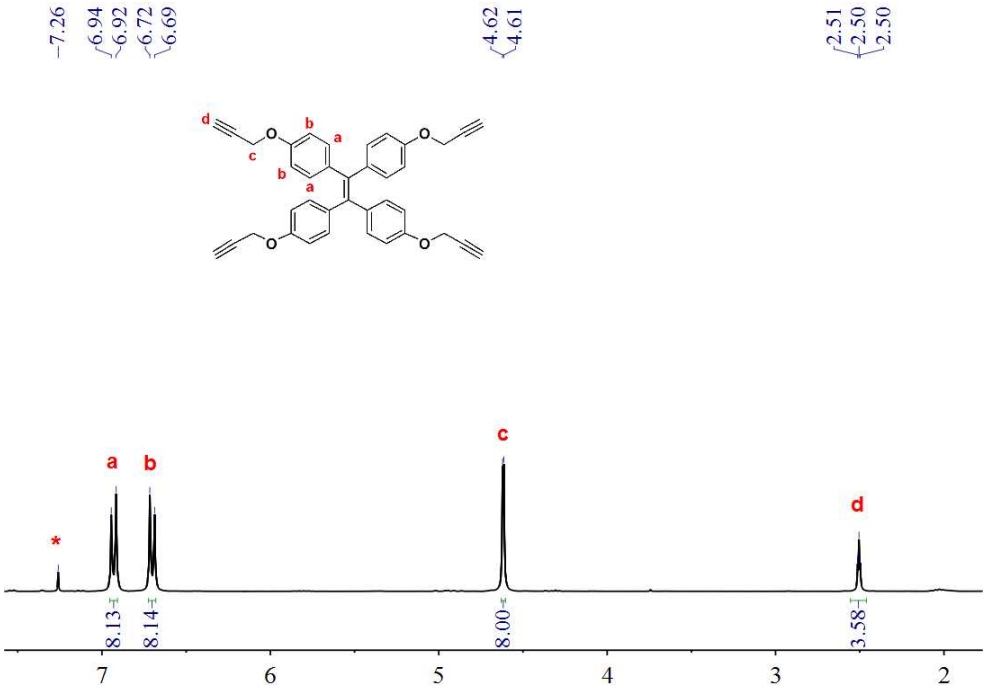


Fig. S4 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **3**. Asterisk indicates the solvent peak.

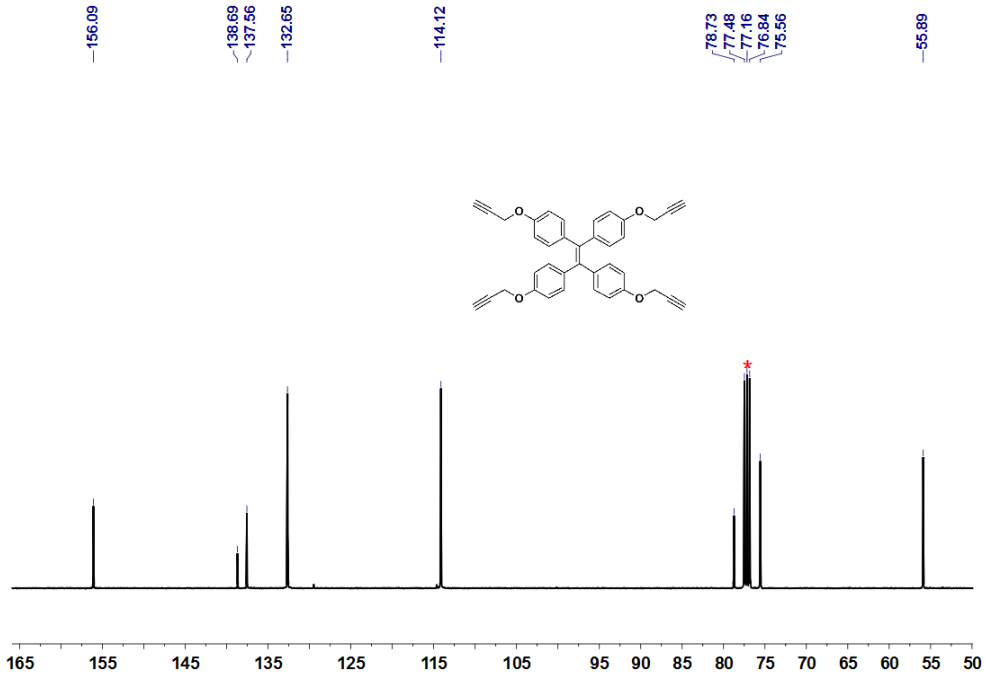


Fig. S5 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3**. Asterisk indicates the solvent peak.

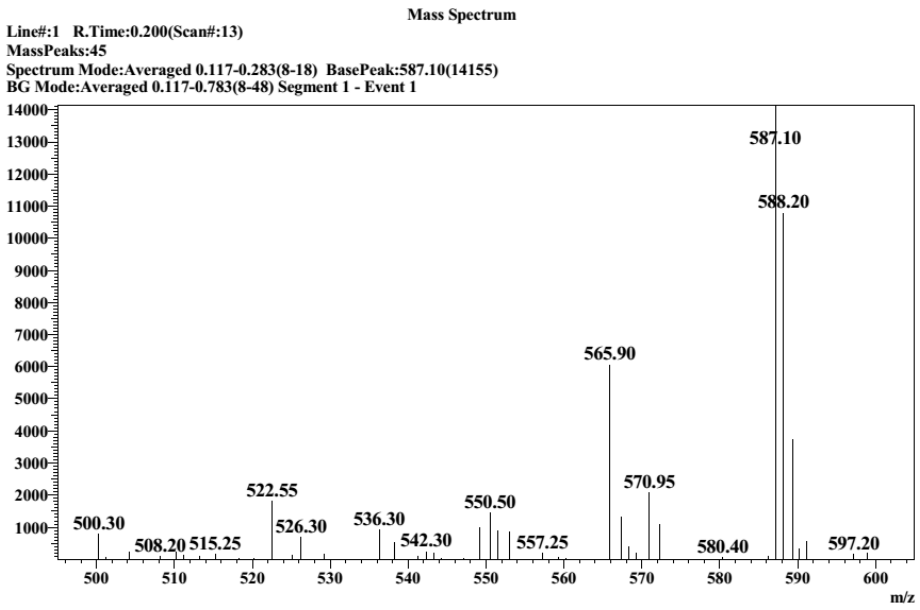


Fig. S6 Electrospray ionization mass spectrum of **3**.

Synthesis of compound **5**[S3]

Sodium azide (0.13 g, 2.0 mmol) was added to a solution of compound **4**[S4] (0.85 g, 1.0 mmol) in dry DMF (20 mL). The reaction mixture was stirred at 80 ^{o}C for 20 h, cooled to room temperature and poured into water (100 mL). The precipitate was collected by filtration and washed with water to yield compound **5** as a white solid

(0.76 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 6.78-6.72 (m, 9H, phenyl protons from pillar[5]arene), 6.66 (s, 1H, phenyl proton from pillar[5]arene), 3.86-3.76 (m, 12H, protons from $OCH_2CH_2N_3$ and methylene bridge protons of pillar[5]arene), 3.67-3.62 (m, 27H, methoxy protons of pillar[5]arene), 3.40-3.37 (m, 2H, protons from $OCH_2CH_2N_3$), which is in accordance with the results reported by Stoddart's group.[S3] ESI-MS: *m/z* 823.55 $[M+NH_4]^+$ (100%).

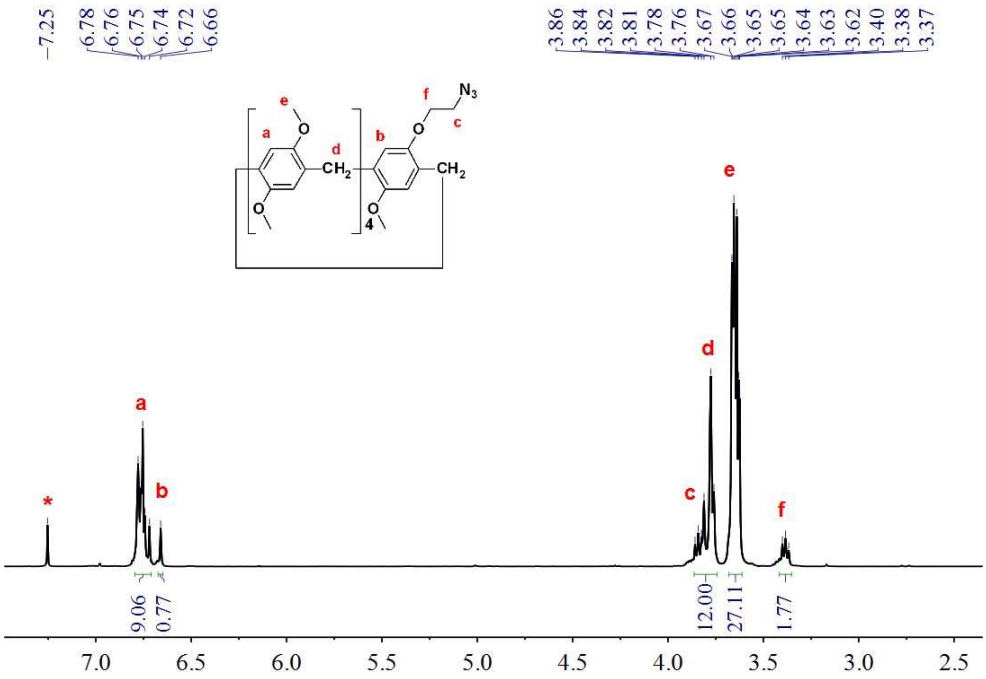


Fig. S7 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **5**. Asterisk indicates the solvent peak.

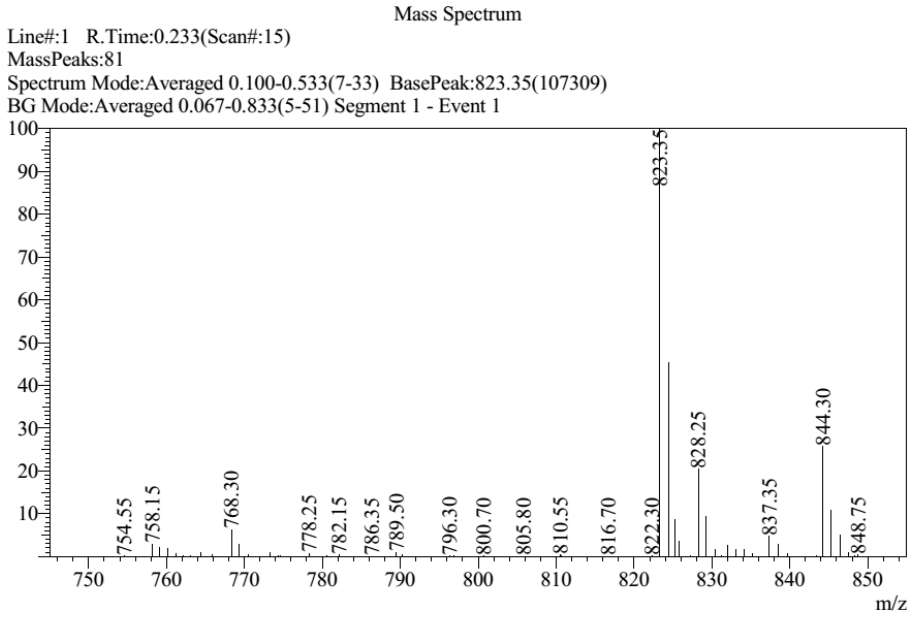
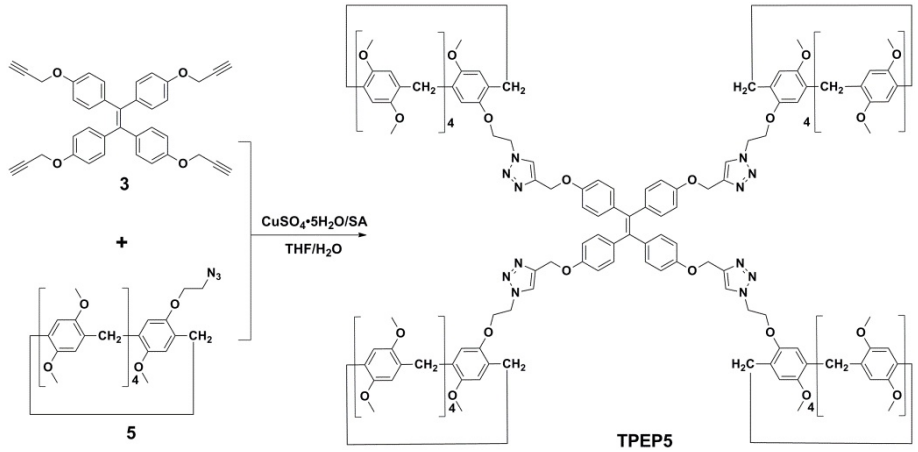


Fig. S8 Electrospray ionization mass spectrum of **5**.

Synthesis of compound **TPEP5**[S5]



To a 25 mL Schlenk tube were added **3** (54.8 mg, 0.1 mmol), **5** (0.4835 g, 0.6 mmol), and THF (4 mL). After complete dissolution of the starting materials, 0.8 mL of water and freshly prepared aqueous solutions of sodium ascorbate (4.0 mg, 0.02 mmol, 20 mol%) and $CuSO_4·5H_2O$ (5.0 mg, 0.02 mmol, 20 mol%) were added into the tube under vigorous stirring. The color of the solution turned to brown, orange and then yellow. The reaction mixture was stirred at 25 ^oC overnight. After the precipitate was filtered and THF was evaporated, the residue was extracted by dichloromethane three times, washed with saturated ammonium chloride solution, brine and water, repectively and dried over Na_2SO_4. After filtration and solvent evaporation, the crude product was purified by a silica gel solumn using a dichloromethane/methanol mixture (*v/v* = 50:1) as the eluent. Compound **TPEP5** was obtained as a white solid (0.17 g, 45%). ^1H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 7.73 (s, 4H, protons of triazole), 6.92 (d, J = 8.6 Hz, 8H, phenyl protons from tetraphenylethene), 6.81 (d, J = 7.1 Hz, 8H, phenyl protons from tetraphenylethene), 6.75-6.68 (m, 32H, phenyl protons from pillar[5]arene), 6.52 (s, 4H, phenyl protons from pillar[5]arene), 6.45 (s, 4H, phenyl protons from pillar[5]arene), 5.03 (s, 8H, protons from OCH_2C), 4.41 (s, 8H, protons from O$CH_2$$CH_2$N), 3.93 (s, 8H, protons from O$CH_2$$CH_2$N), 3.78-3.59 (m, 136H, methylene bridge protons and methoxy protons of pillar[5]arene), 3.48 (s, 12H, methoxy protons of pillar[5]arene). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 156.51, 151.53, 151.10, 150.99, 150.92, 150.77, 150.73, 150.68, 149.11, 143.51, 138.51, 137.27, 132.58, 128.85, 128.80, 128.59, 128.50, 128.44, 128.42, 128.33,

127.88, 127.67, 124.52, 115.05, 114.40, 114.36, 114.23, 114.13, 114.08, 113.87, 66.89, 61.24, 56.24, 55.99, 55.85, 55.65, 30.40, 30.16, 29.95, 29.72, 29.49, 29.23.

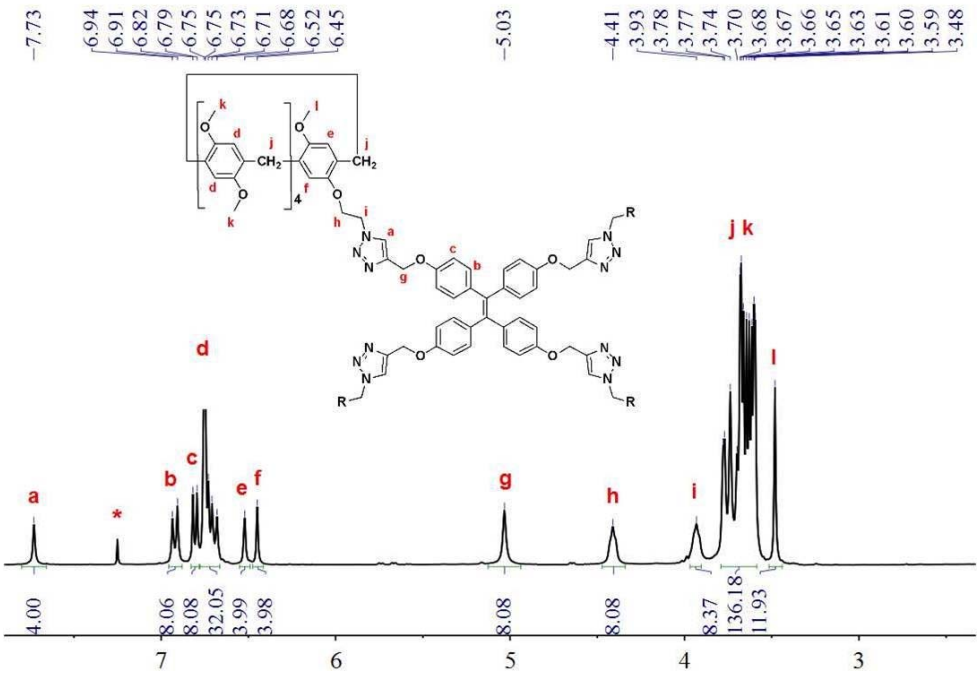


Fig. S9 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **TPEP5**. Asterisk indicates the solvent peak.

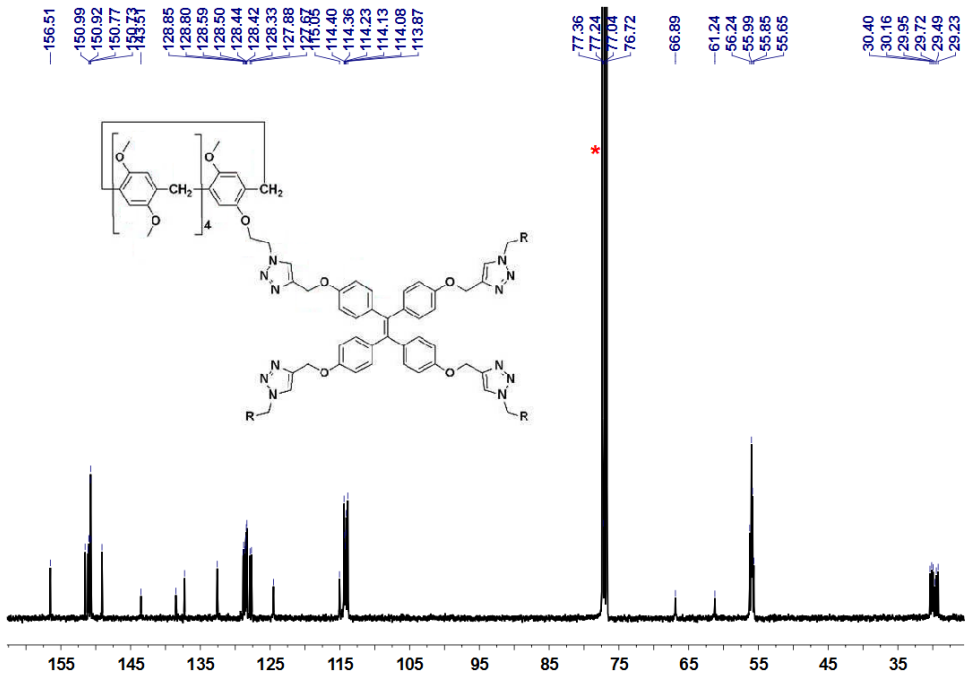
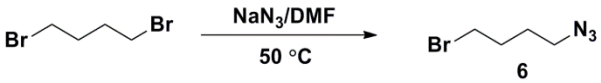


Fig. S10 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3**. Asterisk indicates the solvent peak.

Synthesis of compound **6**[S6]



To a solution of 1,4-dibromobutane (6.48 g, 30 mmol), sodium azide (0.98 g, 15 mmol) was added and the above mixture was stirred overnight in N,N'-dimethylformamide (25 mL) at 50 ^{o}C. The reaction was diluted with ethyl acetate, and the organic layer was washed with water and brine, and then dried over Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel using hexanes as the eluent to give the product **6** as colorless oil (1.07g, 20%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 3.44 (t, J = 6.5 Hz, 2H, BrCH_2CH$_2$), 3.34 (t, J = 6.6 Hz, 2H, CH$_2$$CH_2N_3$), 2.01-1.91 (m, 2H, BrCH$_2$$CH_2$), 1.81-1.72 (m, 2H, CH_2CH$_2$N$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ (ppm): 50.58, 32.95, 29.77, 27.47.

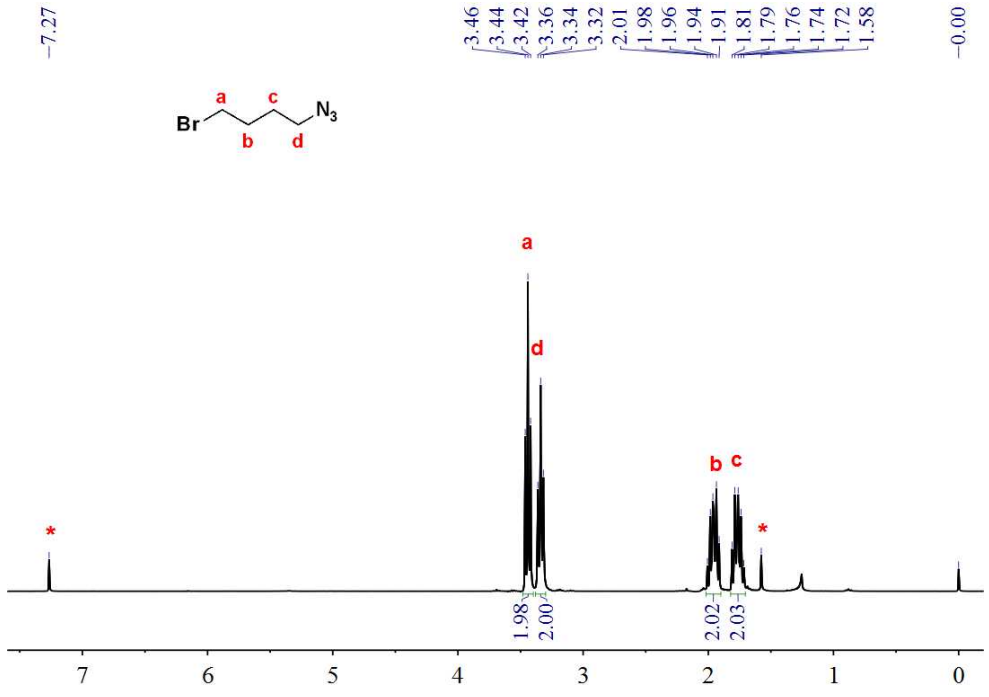


Fig. S11 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **6**. Asterisk indicates the solvent peak.

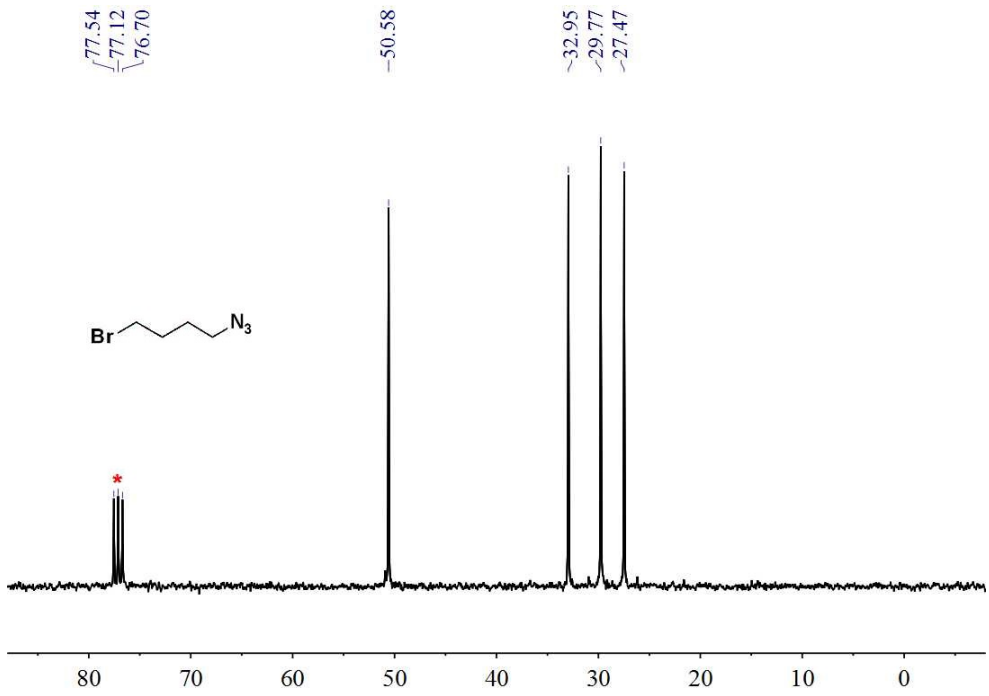


Fig. S12 ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of **6**. Asterisk indicates the solvent peak.

Synthesis of compound **G1**[S5]

To a 50 mL three-necked bottle were added **6** (801.0 mg, 4.5 mmol), **7** (279.0 mg, 1.5 mmol), and THF (20 mL). After complete dissolution of the starting materials, 5 mL of water and freshly prepared aqueous solutions of sodium ascorbate (29.7 mg, 0.15 mmol) and $CuSO_4{\cdot}5H_2O$ (37.5 mg, 0.15 mmol) were added into the tube under vigorous stirring. The color of the solution turned to brown, orange and then yellow. The reaction mixture was stirred at 25 ^{o}C overnight. After the precipitate was filtered and THF was evaporated, the residue was extracted by dichloromethane three times, washed with saturated ammonium chloride solution, brine and water, repectively and dried over $NaSO_4$. After filtration and solvent evaporation, the crude product was purified by a silica gel solumn using a dichloromethane/methanol mixture (*v*/*v* = 150:1) as the eluent. Compound **G1** was obtained as a white solid (0.544 g, 67%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 7.61 (s, 2H, triazole protons), 6.92 (s, 4H, Ar-H), 5.17 (s, 4H, OCH_2), 4.41 (t, J = 6.9 Hz, 4H, NCH_2), 3.42 (t, J = 6.4 Hz, 4H, BrCH_2), 2.10 (m, 4H, $BrCH_2CH_2$), 1.88 (dt, J = 13 Hz, 6.5 Hz, 4H, NCH_2CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 152.82, 144.50, 122.67, 115.93, 62.68,

49.53, 32.56, 29.33, 28.79. ESI-MS: *m/z* 542.90 $[M+H]^+$ (100%), 564.90 $[M+Na]^+$ (90%). HR-ESI-MS: *m/z* calcd for $[M + Na]^+$ $C_{20}H_{26}Br_2N_6NaO_2$, 565.0361, Found 565.0360.

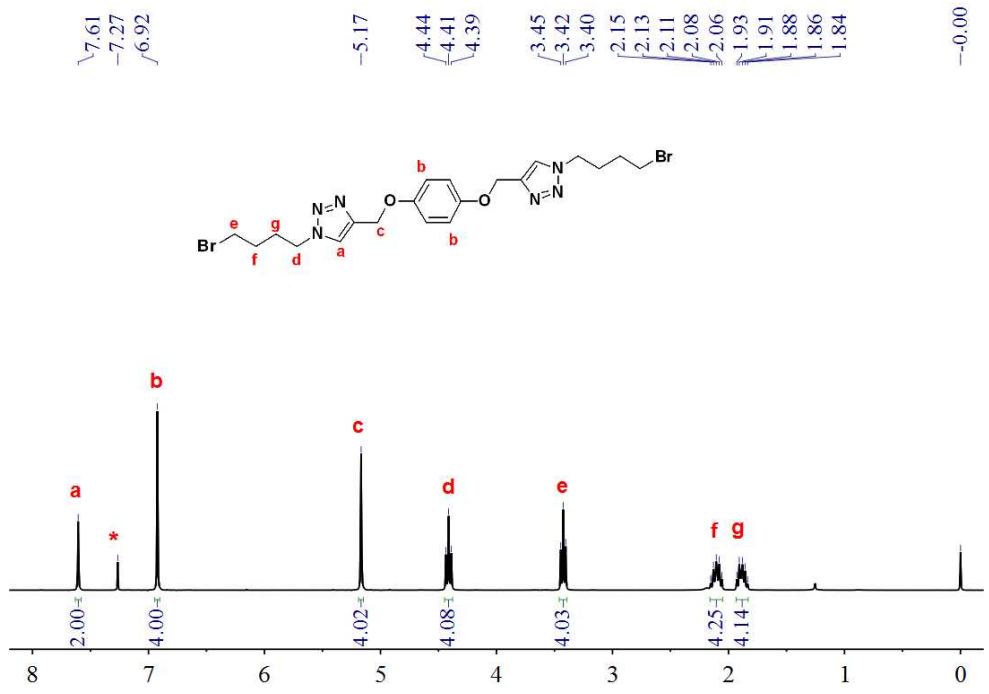


Fig. S13 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **G1**. Asterisk indicates the solvent peak.

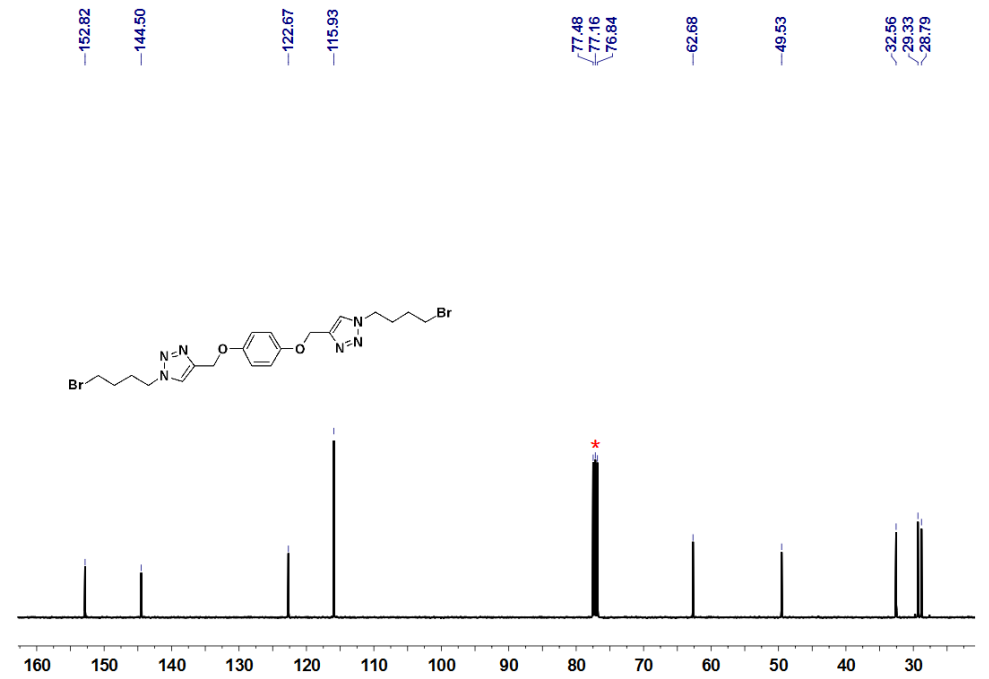


Fig.S14 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **G1**. Asterisk indicates the solvent peak.

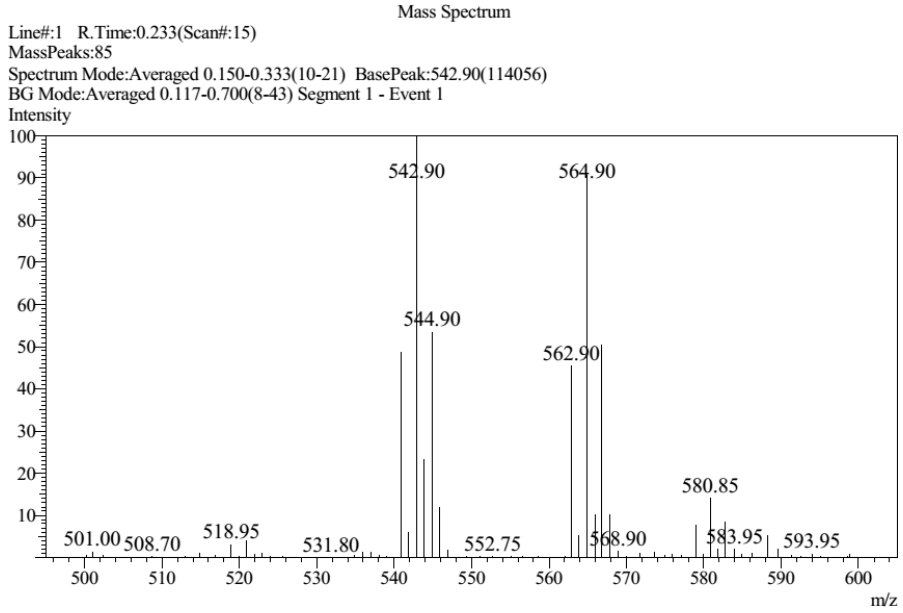


Fig. S15 Electrospray ionization mass spectrum of **G1**.

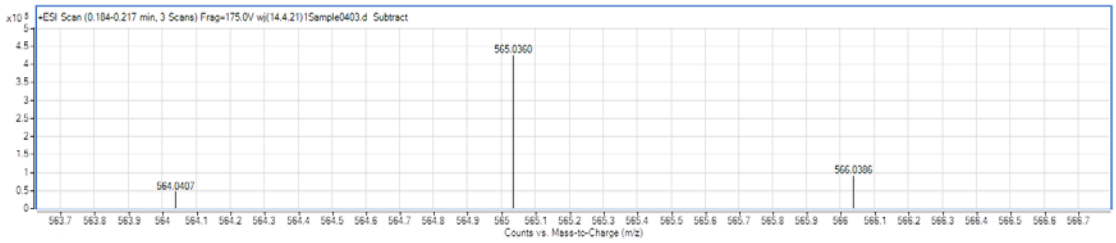


Fig. S16 High-resolution electrospray ionization mass spectrum of **G1**.

Synthesis of compound **G2**[S5]

To a 50 mL three-necked bottle were added **6** (534.0 mg, 3.0 mmol), **8** (729.0 mg, 4.5 mmol), and THF (20 mL). After complete dissolution of the starting materials, 5 mL of water and freshly prepared aqueous solutions of sodium ascorbate (59.3 mg, 0.3 mmol) and $CuSO_4 \cdot 5H_2O$ (75 mg, 0.3 mmol) were added into the tube under vigorous stirring. The color of the solution turned to brown, orange and then yellow. The reaction mixture was stirred at 25 ^oC overnight. After the precipitate was filtered and THF was evaporated, the residue was extracted by dichloromethane three times, washed with saturated ammonium chloride solution, brine and water, repectively and dried over $NaSO_4$. After filtration and solvent evaporation, the crude product was purified by a silica gel solumn using a dichloromethane/methanol mixture (*v*/*v* = 200:1) as the eluent. Compound **G2** was obtained as a white solid (0.734g, 72%). ^1H

NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 7.60 (s, 1H, triazole proton), 6.93 (d, J = 9.1 Hz, 2H, Ar-H), 6.83 (d, J = 9.1 Hz, 2H, Ar-H), 5.17 (s, 2H, OCH_2), 4.41 (t, J = 6.9 Hz, 2H, NCH_2), 3.77 (s, 3H, OCH_3), 3.42 (t, J = 6.4 Hz, 2H, $BrCH_2$), 2.10 (m, 2H, $BrCH_2CH_2$), 1.88 (dt, J = 12.8 Hz, 6.4 Hz, 2H, NCH_2CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 154.03, 152.16, 144.24, 122.63, 115.72, 114.53, 62.50, 55.56, 49.25, 32.50, 29.24, 28.59. ESI-MS: m/z 339.90 $[M+H]^+$ (100%), 361.90 $[M+Na]^+$ (20%). HR-ESI-MS: m/z calcd for $[M + Na]^+$ $C_{14}H_{18}BrN_3NaO_2$, 362.0480, Found 362.0476.

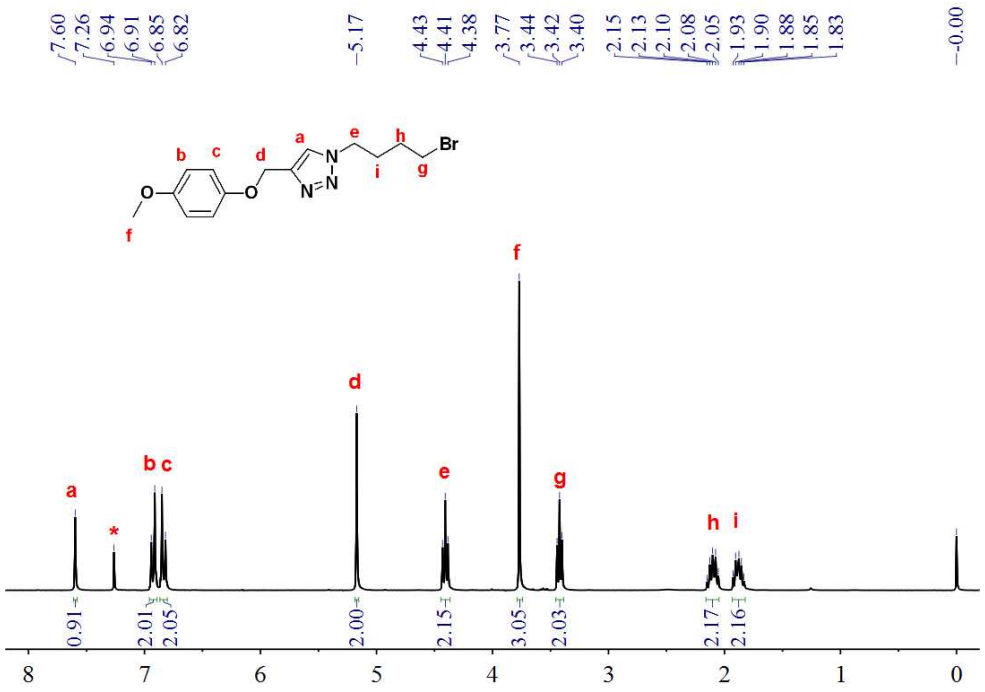


Fig. S17 ^1H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of **G2**. Asterisk indicates the solvent peak.

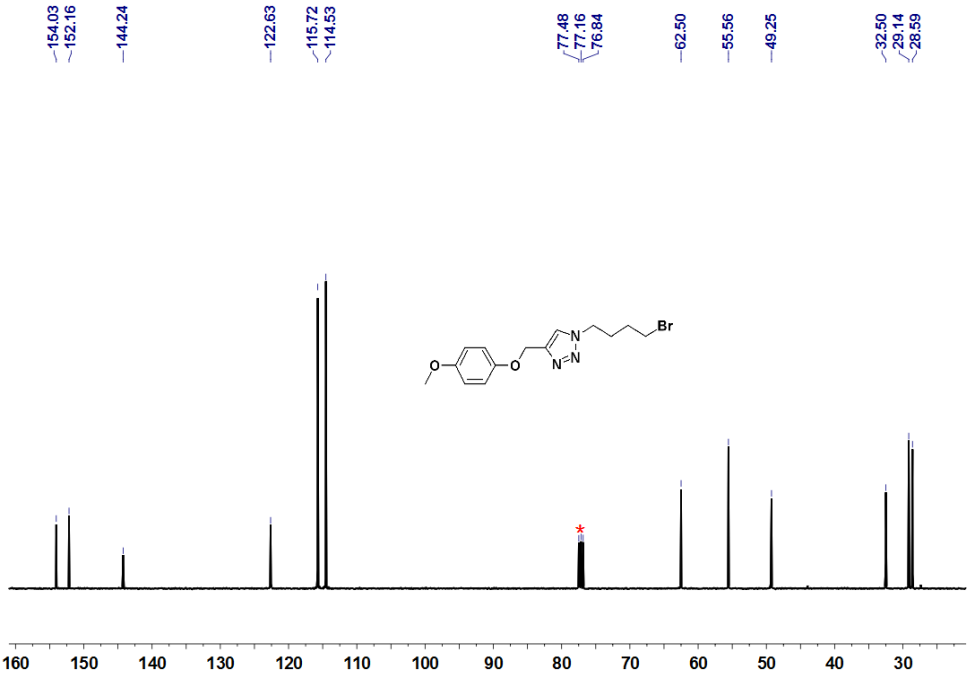


Fig. S18 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **G2**. Asterisk indicates the solvent peak.

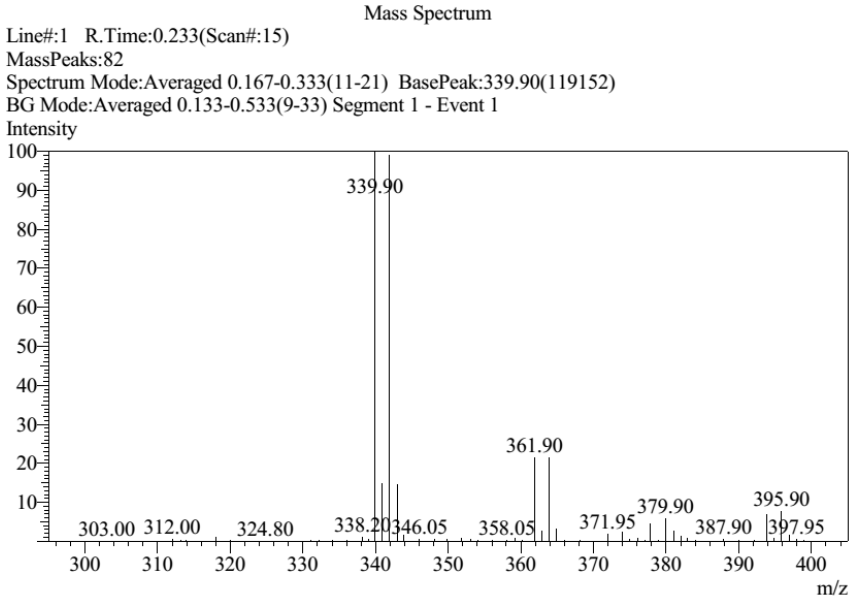


Fig. S19 Electrospray ionization mass spectrum of **G2**.

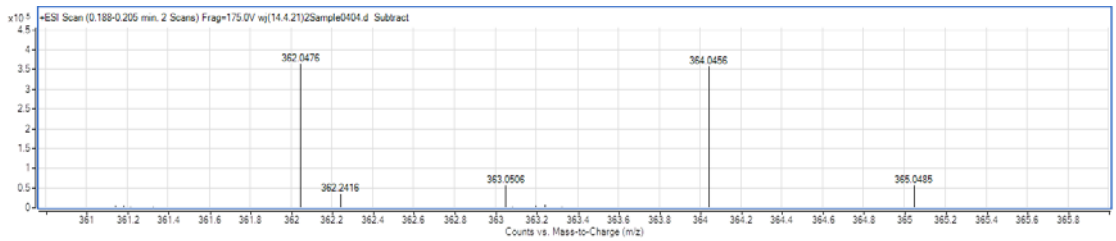


Fig. S20 High-resolution electrospray ionization mass spectrum of **G2**.

3. Complexation between DMP5 and G1

The ^{1}H NMR spectrum of a mixture of model compound DMpillar[5]arene (**DMP5**) and 0.5 equiv. of **G1** was investigated, As shown in Fig. S21b, after complexation remarkable broadening effects were observed for the guest **G1** protons H_d, H_e, H_f, H_g, which as well as the triazole protons H_a on **G1** showed obvious upfield shifts due to the shielding effect of the electron-rich cavities of **DMP5**. The proton signals derived from $H_{1'}$ and $H_{2'}$ on **DMP5** shifted downfield slightly. While, no obvious change was observed for the protons H_b and H_c on **G1**. The above results revealed that the guest **G1** was fully encapsulated by **DMP5** with the protons H_d, H_e, H_f, H_g and H_a in the **DMP5** cavity.

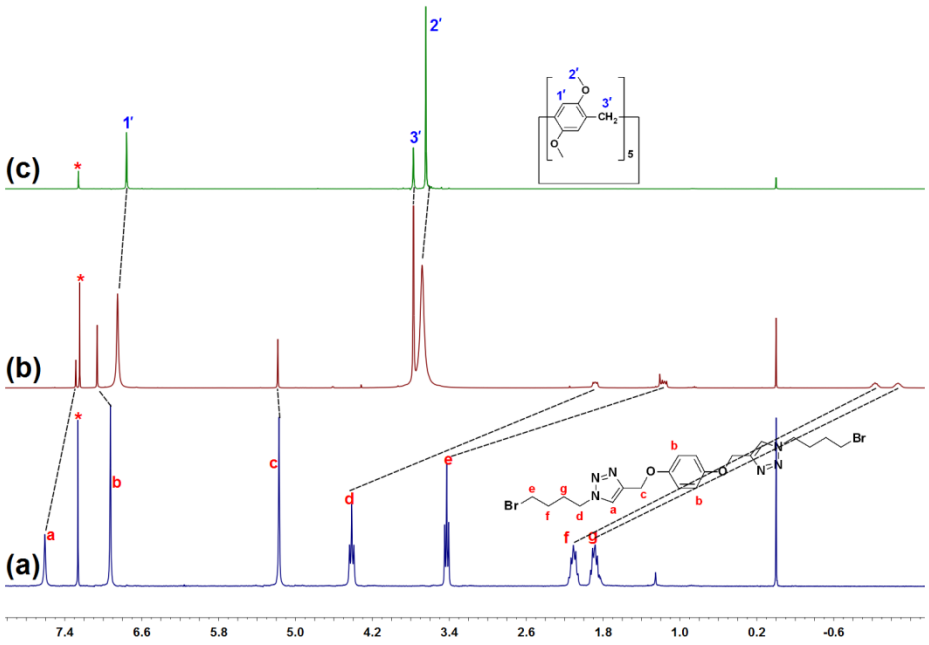


Fig. S21 Partial ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectra: (a) guest compound **G1** (5.0 mM); (b) **G1** (5.0 mM) and **DMP5** (10.0 mM); (c) **DMP5** (5.0 mM). Asterisk indicates the solvent peak.

Further investigation of the complex stoichiometry between **TPEP5** and **G1** was carried out by Job's plot method using model compound **DMP5**, one of the pillararene motif on **TPEP5**. The Job's Plot experiment based on the chemical shift change of $H_{1'}$ on **DMP5** demonstrated that a 2:1 stoichiometry complex was formed between **DMP5** and **G1**, which was shown in Figure S22.

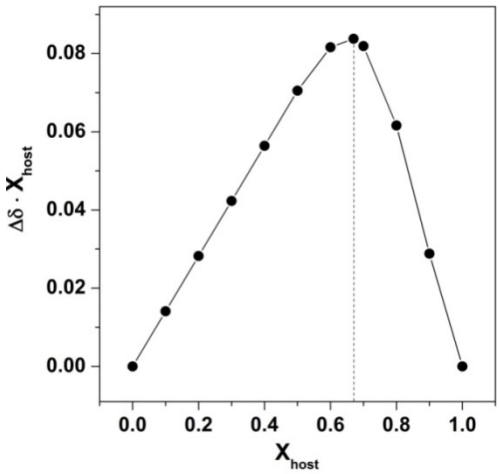


Fig. S22 Job plot showing the 2:1 stoichiometry of the complexation between **DMP5** and **G1** in $CDCl_3$/acetone-d_6 (1:8, *v/v*), ([Host] + [Guest] = 10 mM).

4. 2D NOESY spectra of the complexation between DMP5 and G1

The 2D-NOESY NMR spectrum of the solution of **DMP5-G1** (the concentration of **DMP5** and **G1** are 60.0 and 15.0 mM, respectively) showed the NOE peaks between protons $H_{1'}$ on **DMP5** and H_d, H_e, H_f, H_g on **G1**, as well as $H_{2'}$/$H_{3'}$ on **DMP5** and H_d, H_e, H_f, H_g on **G1**, which clearly confirmed the complexation between **DMP5** and **G1**.

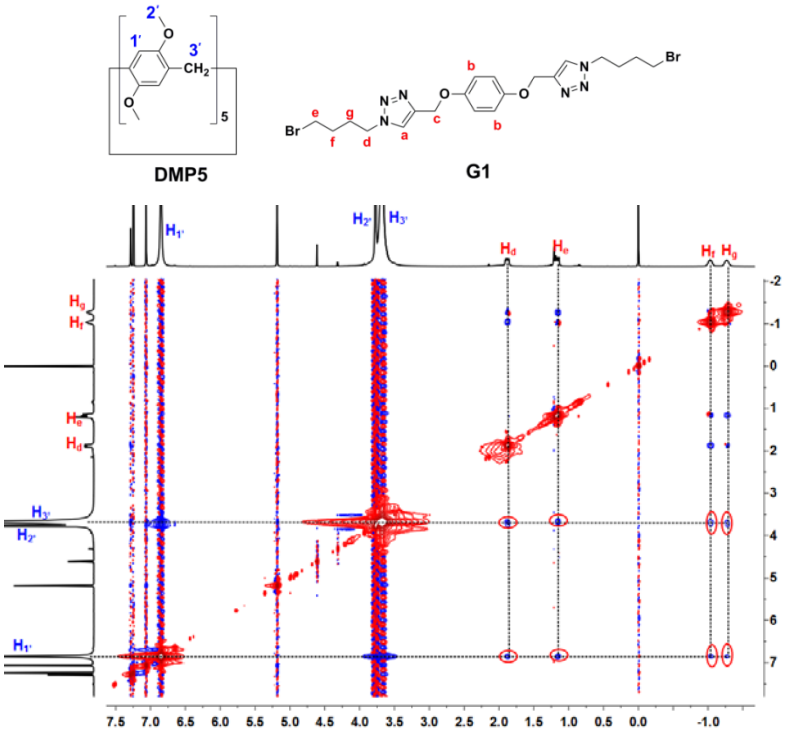


Fig. S23 2D-NOESY analysis of **DMP5** with **G1** in $CDCl_3$ solution with a mixing time of 300 ms (400 MHz, 298 K, the concentrations of **DMP5** and **G1** are 60.0 mM and 15.0 mM, respectively)

5. UV-Vis spectroscopy and solvent effect on the fluorescence intensity

Fig. S24 shows the UV-Vis absorption spectra of **TPEP5** and **TPEP5** upon gradual addition of **G1** in $CHCl_3$/acetone (1/8, *v*/*v*). It was found that the UV/vis absorption spectrum of **TPEP5** solution showed an absorption band at 329 nm, which was gradual enhanced upon addition of **G1**, and almost no wavelength shift was observed.

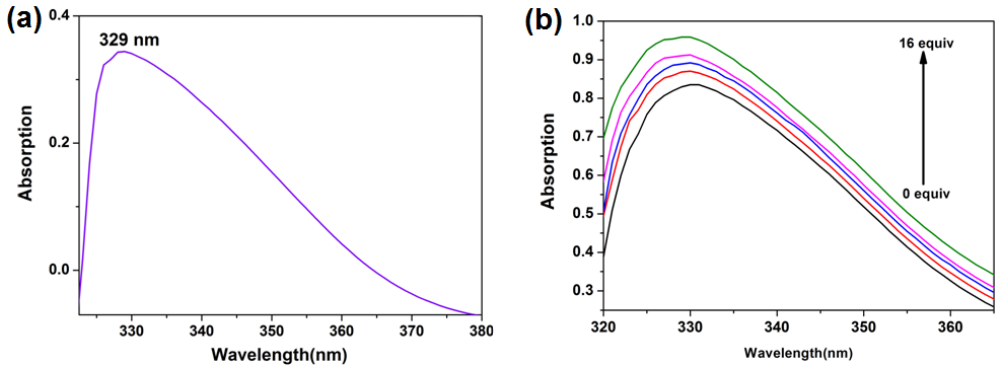


Fig. S24 (a) UV-Vis absorption spectra of **TPEP5** (1×10^{-5} M) in $CHCl_3$/acetone (1/8, *v*/*v*). (b) UV-Vis absorption spectra of **TPEP5** (4×10^{-5} M) upon gradual addition of **G1** (0-16 equiv.) in $CHCl_3$/acetone (1/8, *v*/*v*).

Then, we investigated the solvent effect on the fluorescence intensity of **TPEP5** upon addition of guest molecule **G1** (**TPEP5**:**G1** = 1:4) and the results were shown in Fig. S25. Initial investigation suggested that the fluorescence enhancement of **TPEP5** with **G1** was remarkable in acetone. But the solubility of **TPEP5** with **G1** was not so good in acetone, so we mixed $CHCl_3$ with acetone to increase the solubility. It was found that the intensity of the emissions spectra at 490 nm upon excitation at 330 nm undergone a sharp increase and then an inverse decrease upon gradually increasing the amount of acetone added. The inflection was observed at the CH_3Cl/acetone volum ratio of 1:8, which means that $CHCl_3$/acetone (1/8, *v*/*v*) is the best solvent system to enhance the fluorescence intensity and the solubility of **TPEP5** with **G1**.

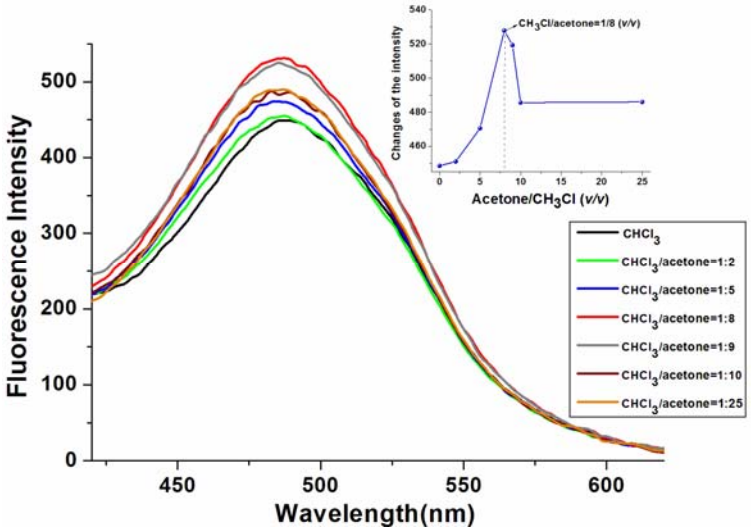
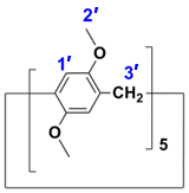


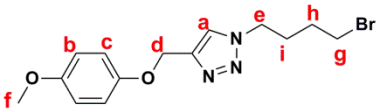
Fig. S25 Fluorescent spetra of **TPEP5** (1×10^{-5} M) with **G1** (4×10^{-5} M) in $CHCl_3$/acetone (*v/v*) solution with different volume ratio. (***Inset:*** Profile of the fluorescence intensity changes upon change the volume ratio of acetone/$CHCl_3$ (*v/v*). Changes in the fluorescence intensities at 490 nm upon change the volume ratio of acetone/$CHCl_3$ (*v/v*) were plotted.)

6. Determination of the K_a value

6.1 Determination of the K_a value for DMP5⊃G2



DMpillar[5]arene **(DMP5)**



G2

To investigate the binding affinity of pillar[5]arene-**G1** recognition motif, **DMP5** (host) and **G2** (guest) were chosen as the model compounds. The Job's plot experiment indicated the 1:1 stoichiometry of the complex between **DMP5** and **G2** in $CDCl_3$/acetone-d_6 (1/8, *v/v*) by plotting the $\Delta\delta$ in chemical shift of H_g on guest observed by ^{1}H NMR spectroscopy against the molefraction of guest (X_{guest}). (Fig. S26).

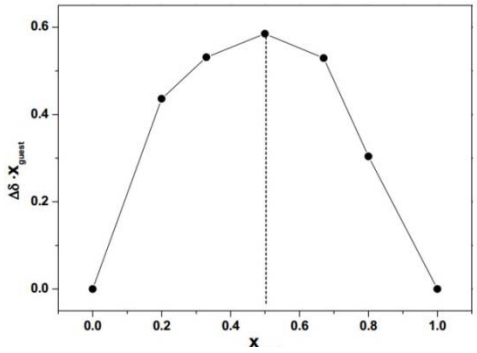


Fig. S26 Job Plot of the complex formed between **DMP5** (host) and **G2** (guest) showing a 1:1 stoichiometry. (The job Plot was conducted by varying the mole fractions of the guest and host. Concentration: [Host] + [Guest] = 10 mM.)

Then, ^{1}H NMR titrations were performed with a constant concentration of **DMP5** (4.00 mM) and varying concentrations of **G2** in the range of 2.0-80.0 mM (Fig. S27). By a non-linear curve-fitting method,[S7] the association constant (K_a) of **DMP5⊃G2** was estimated to be (7.30 ± 0.49) × 10^2 M^{-1} (Fig. S28).

The non-linear curve-fittings were based on the equation:

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

Where $\Delta\delta$ is the chemical shift change of $H_{1'}$ on **DMP5** at $[G]_0$, $\Delta\delta_\infty$ is the chemical shift change of $H_{1'}$ when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the varying concentrations of **G2**.

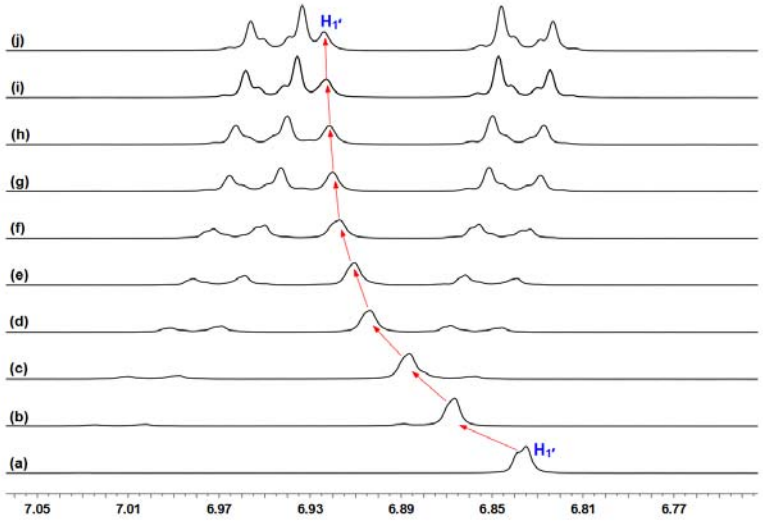


Fig. S27 Partial ^{1}H NMR titration spectra of 4.00 mM **DMP5** solution with (a) 0, (b) 0.5, (c) 1.0, (d) 2.0, (e) 3.0, (f) 5.0, (g) 8.0, (h) 10.0, (i) 15.0, and (j) 20.0 equiv of **G2**. Solvent system: $CDCl_3$/acetone-d_6 (1/8, *v*/*v*).

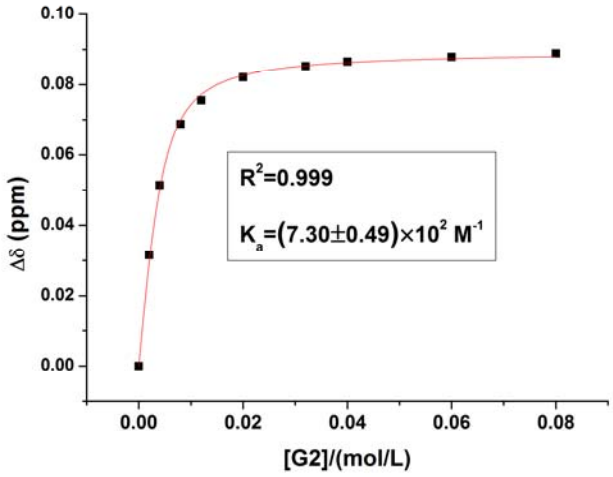
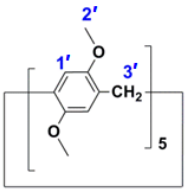
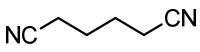


Fig. S28 The chemical shift changes of $H_{1'}$ on **DMP5** upon addition of **G2**. The red solid line was obtained from the non-linear curve-fitting using Eq.1.

6.2 K_a of DMP5 and G3



DMpillar[5]arene **(DMP5)**



G3

To investigate the binding constant of **TPEP5** with **G3**, ^{1}H NMR titrations were performed with a constant concentration of model compound **DMP5** (5.00 mM) and varying concentrations of **G3** in the range of 1.25-50.0 mM (Fig. S29). By a non-linear curve-fitting method,[S7] the association constant (K_a) of **DMP5⊃G3** was estimated to be (2.52 ± 0.46) × 10^3 M^{-1} (Fig. S30), which is much stronger than the binding affinity of **DMP5** with **G2**, indicating that the complexation between **TPEP5** and **G1** could be destroyed after the addition of competitive guest **G3**.

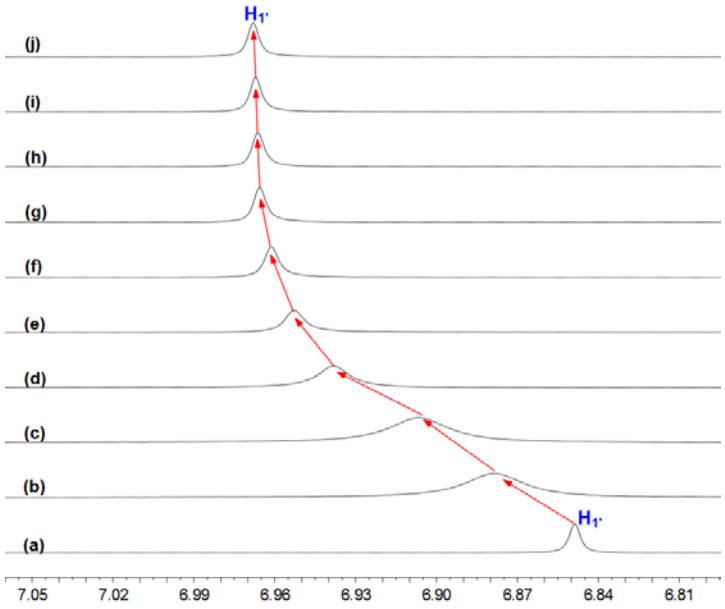


Fig. S29 Partial ^{1}H NMR titration spectra of 5.00 mM **DMP5** solution with (a) 0, (b) 0.25, (c) 0.5, (d) 1.0, (e) 1.5, (f) 2.5, (g) 4.0, (h) 5.0, (i) 7.5, and (j) 10.0 equiv. of **G3**. Solvent system: $CDCl_3$/acetone-d_6 (1/8, *v*/*v*).

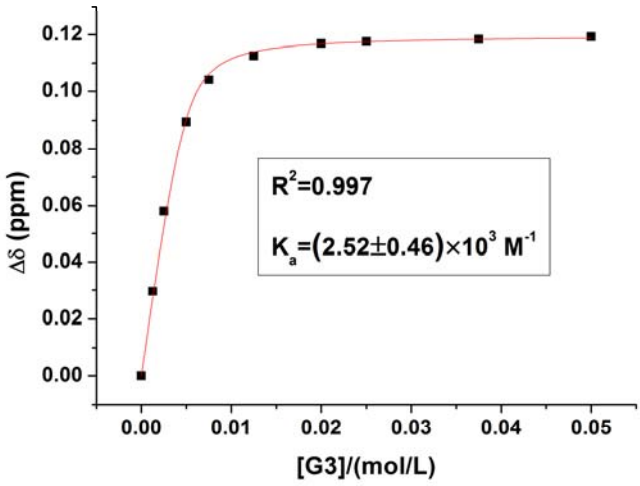


Fig. S30 The chemical shift changes of $H_{1'}$ on **DMP5** upon addition of **G3**. The red solid line was obtained from the non-linear curve-fitting using Eq.1.

7. Stoichiometry of TPEP5 with G1

To investigate the stoichiometry of the complex between **TPEP5** and **G1**, the Job's plot experiment was carried out and the result indicated the 1:2 stoichiometry of the complex between **TPEP5** and **G1** in $CDCl_3$/acetone-d_6 (1/8, *v*/*v*) by plotting the $\Delta\delta$ in chemical shift of H_b on guest observed by ^{1}H NMR spectroscopy against the

molefraction of guest (X_{guest}) (Fig. S31).

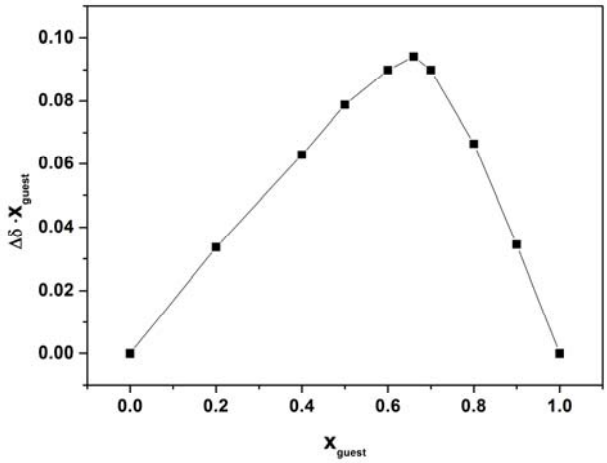


Fig. S31 Job Plot of the complex formed between **TPEP5** (host) and **G1** (guest) showing a 1:2 stoichiometry. (The job Plot was conducted by varying the mole fractions of the guest and host. Concentration: [Host] + [Guest] = 5 mM.)

8. 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 330 nm) as standard.[S8] The absorbance of the solutions was kept around 0.02 to avoid internal filter effect. The quantum yield of **TPEP5** with 8.0 equiv. **G1** was determined to be 12.3% according to the following equation:[S9]

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

Where Φ_{std} 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.

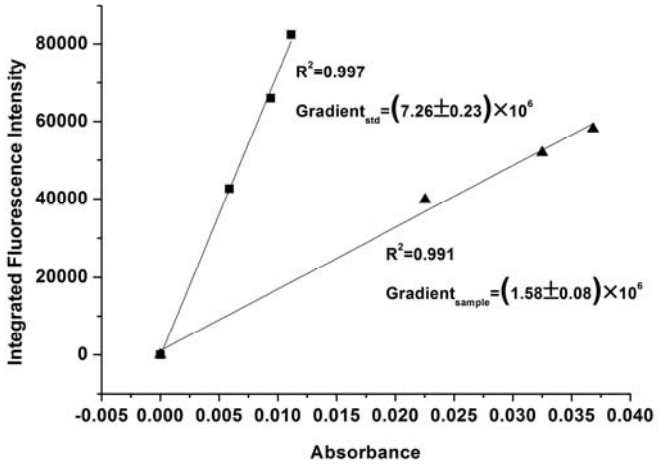
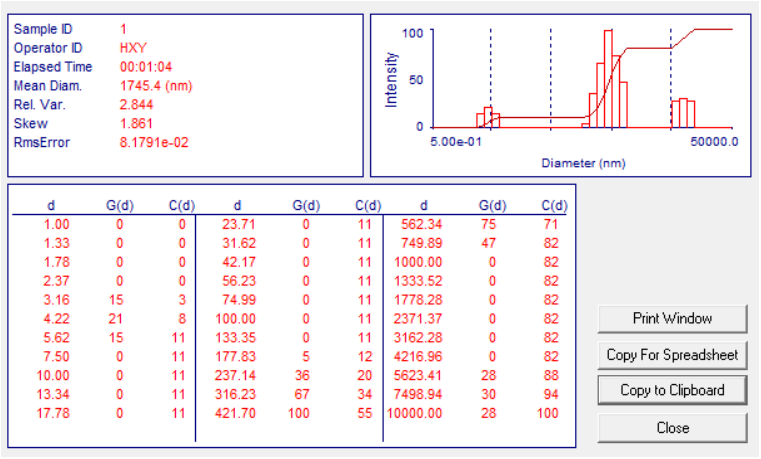


Fig. S32 Fluorescence quantum yield measurements of **TPEP5** with 8.0 equiv. **G1** (The Φ_F value was determined to be 12.3%)

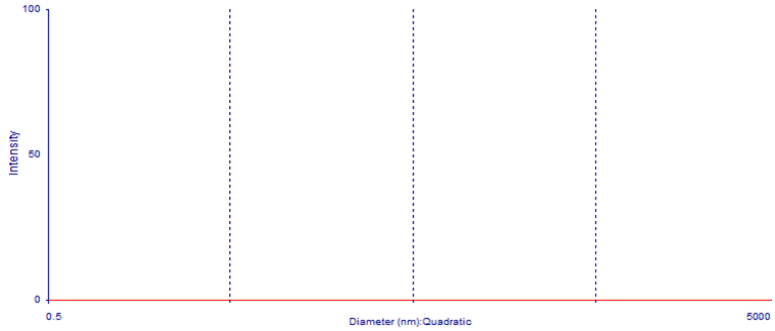
9. DLS of the supramolecular aggregates

We also conducted the DLS measurements of **TPEP5** with **G1** in 1:16 ratio in $CHCl_3$/acetone solution (1:8, *v/v*) to investigate the size of the aggregates, and the result shows that different size distributions were observed and the average hydrodynamic radius (R_h) values was 1745 nm, indicating the formation of large sized supramolecular aggregates. However, without addition of **G1**, no aggregates signals could be detected from the $CHCl_3$/acetone solution (1:8, *v/v*) of **TPEP5**, indicating that no aggregation was exist. Moreover, when 128 equiv. of competitive guest **G3** was added into the **TPEP5-G1** solution, only small sized aggregates with an average diameter of 55 nm could be observed, indicating that the complexation between **TPEP5** and **G1** was almost destroyed, and accompanied by the disassembly of the large sized supramolecular aggregates.

(a) TPEP5 with **G1** solution:



(b) TPEP5 solution:



(c) When **G3** was added into the **TPEP5-G1** solution:

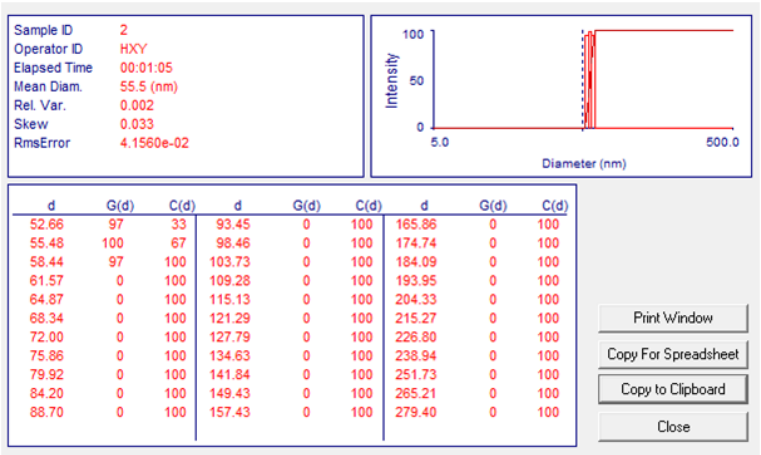


Fig. S33 Distribution of the hydrodynamic diameter of (a) **TPEP5** (2 mM) with **G1** (32 mM) in $CHCl_3$/acetone solution (1:8, *v/v*) at 298 K; (b) only **TPEP5**, no aggregates signals could be observed; (c) when **G3** (128 equiv.) was added into the above **TPEP5-G1** solution, only small sized aggregates (~ 50 nm) could be observed.

10. DOSY experiments

Since diffusion ordered ^{1}H NMR spectroscopy (DOSY) is a sensitive technique to investigate the self-assembly behavior of supramolecular polymers, because

different size of aggregates exhibit different diffusion coefficient. To further make sure whether the intramolecular encapsulation of **G1** in **TPEP5** is possible or not, we performed additional DOSY experiment of **TPEP5** (2 mM) and **TPEP5** (2 mM) with **G1** (16 mM) to confirm their self-assembly property in $CHCl_3$/acetone solution. As shown in Fig. S34, the DOSY signals for **TPEP5⊃G1** in dilute solution displayed a broad distribution, reflecting the broad molecular weight distribution of different aggregates, which was in good agreement with the DLS results, further indicating the formation of different and larged sized supramolecular polymers. On the contrary, the peaks for **TPEP5** in dilute solution showed a very well-defined distribution, corresponding to a single type of aggregate in solution. If intramolecular encapsulation of **G1** in **TPEP5** is the dominated self-assembly process, which will not lead to the formation of supramolecular polymers, on the contrary, a single type of aggregate will be formed in solution, and the DOSY peaks for such aggregate will show a very well-defined distribution. Therefore, we think that intermolecular cross-linking mediated aggregation is the dominated self-assembly process in our system, but we don't exclude the possibility of intramolecular encapsulation of **G1** in **TPEP5** in dilute solution.

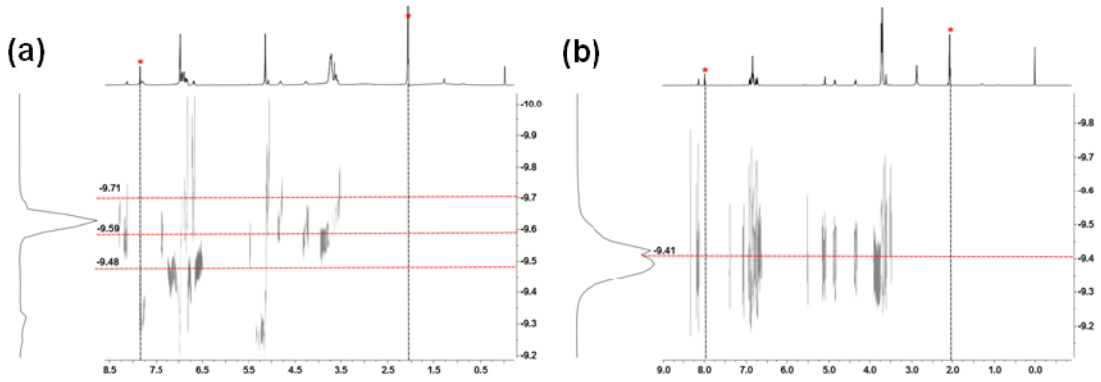


Fig. 34 (a) DOSY spectra (400 MHz, 298 K) of **TPEP5** (2 mM) and **G1** (16 mM) in $CDCl_3$/acetone-d_6 (1/8, *v*/*v*). (b) DOSY spectra (400 MHz, 298 K) of **TPEP5** (2 mM) in $CDCl_3$/acetone-d_6 (1/8, *v*/*v*)

11. References

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