Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Pertosylated Pillar[5]Arene: Self-Template Assisted Synthesis and Supramolecular Polymer Formation

Araya Ruengsuk,[a] Korawit Khamphaijan,[a] Puttipong Pananusorn,[a] Andrew Docker,[b]
Jonggol Tantirungrotechai,[a] Mongkol Sukwattanasinit,[c] David J. Harding,[d] and Thanthapatra Bunchuay[a*]

[a] Department of Chemistry and Center of Excellence for Innovation in Chemistry (PERCH-CIC), Faculty of Science, Mahidol University, Bangkok, 10400, Thailand
[b] Chemistry Research Laboratory Mansfield Road, Department of Chemistry, University of Oxford, Oxford, OX1 3TA, UK
[c] Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand.
[d] Functional Materials and Nanotechnology Center of Excellence, Walailak University, Thasala, Nakhon Si Thammarat, 80160, Thailand.

*E-mail: thanthapatra.bun@mahidol.edu and thanthapatra.bunchuay@gmail.com

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1. Materials and Experimental Methods

All reagents were purchased from Tokyo Chemical Industry (TCI Chemicals) and used without further purifications. Solvents in synthesis were purchased from RCI Labscan and deuterated solvents for NMR analysis were bought from Cambridge Isotope Laboratories.

The samples for NMR analysis were prepared as a $CDCl_3$ solution. Their ^1H NMR spectra were recorded by Bruker AVANCE 400 spectrometer (400 MHz), while ^{13}C NMR spectra were recorded on the same machine (100 MHz) at 298K. The peak assignments were obtained by NMR experiments including ^1H-^1H correlation spectroscopy (COSY) and 2D Nuclear Over Hauser Enhancement Spectroscopy (NOESY). The obtained spectral data were processed using Mnova software (Mestrelab Research, S.L.). High-Resolution Mass Spectra (HRMS) were collected data with a Bruker micro TOF spectrometer in the ESI mode. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were recorded in transmittance (% T) mode using a Bruker Alpha-P FTIR spectrometer in the ATR geometry with a diamond ATR unit.

X-ray crystallographic data were collected on a Rigaku SuperNova diffractometer with a HyPix3000 detector and CuK_α radiation (λ = 1.54184 Å) at 200 or 150 K for **1** and **1@dcb**, respectively. The data were reduced, scaled and integrated using CrysAlisPro (Rigaku, V1.171.40.58a, 2019). In both cases an analytical absorption correction was applied as implemented in SCALE3 ABSPACK (Rigaku, V1.171.40.58a, 2019). The structures were solved, and the space group determined by ShelXT using intrinsic phasing and refined by full matrix least squares minimisation on F^2 using ShelXL (version 2018/3) using OLEX^2 as a graphical interface.[1] All non-hydrogen atoms were refined anisotropically with the exception of the disordered dcb molecules in **1@dcb**. Hydrogen atom positions were calculated geometrically and refined using a riding model. In both cases, disorder was present in some of the tosyl groups which was modelled over two positions with appropriate SADI and RIGU restraints. The structures also contained diffuse solvent peaks which were removed using the solvent mask procedure in OLEX^2 and reported to be 0.85 and 1 molecule of THF for **1** and **1@dcb**, respectively. All pictures were created using OLEX^2. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 2008505 for **1** and 2008506 for **1@dcb**.

To study characteristics of **1** assembled into supramolecular polymer, ^1H NMR spectroscopic experiments including concentration-dependent studies, variable temperature NMR and the 2D diffusion-ordered (2D-DOSY) NMR were employed as a main tool. Concentration-dependent studies were carried out by recording ^1H-NMR spectra of **1** in $CDCl_3$ at concentrations of 0.5, 2.0, 5.0, 7.5, 10, 25, 50, 100, and 200 mM. The obtained ^1H NMR spectra was set a reference using $CHCl_3$ residue peak. Variable Temperature ^1H NMR (VT-NMR) experiments were performed on a Bruker AVANCE

(400 MHz) in the temperature range of 298K to 333K with 5 minutes of thermostatic time before each acquisition. The solution of **1** was prepared in the concentration of 10 mM in $CDCl_3$ and approximately 0.5 mL solution was transferred to a NMR tube equipped with a sealed cap. 2D-DOSY NMR spectra were recorded on a Bruker AVANCE 400 spectrometer at 298K without sample spinning. All samples were prepared at different concentration in $CDCl_3$. Dynamic light scattering (DLS) technique and scanning electron microscopy were also used to further confirm an aggregation of **1** in solution. The DLS experiment was recorded by a commercial laser light scattering spectrometer (Nano ZS zetasizer, Malvern Instruments Corporation) at 298K. Viscosity measurements of a solution of **1** in dichloromethane with different concentrations were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 298 K. The Scanning electron microscopy (SEM) analysis was collected data on a HITACHI SU-8010 instrument.

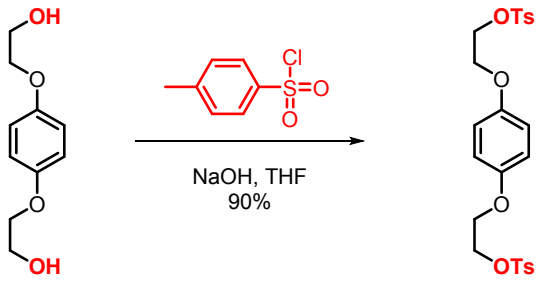
The utility of the tosylate group as a useful synthetic handle, a means to access a wide range of derivatives and its role as a templating agent is exemplified by the following;

1. **Tosylate as a leaving group in macrocyclic synthesis**
    a. Synthesis of Polyazamacrocyclic Compounds via Modified Richman-Atkins Cyclization of β-Trimethylsilylethanesulfonamides[2]
    b. Multi-gram syntheses of four crown ethers using K+ as templating agent[3]
    c. A Practical Synthesis of Benzocrown Ethers under Phase-Transfer Catalysis Conditions[4]
    d. Organic macrocyclic polyamine-based receptors for anions[5]

2. **Tosylate complexes**
    a. Surprising solvent-induced structural rearrangements in large [N···I^+···N] halogen bonded supramolecular capsules: an ion mobility-mass spectrometry study[6]
    b. Acid/base- and base/acid-switchable complexation between anionic-/cationic-pillar[6]arenes and a viologen ditosylate salt[7]

2. Synthesis and Characterisation

2.1 Synthesis of Ditosylate (Monomer 2)



Monomer 2

The synthetic method to prepare monomer **2** was modified from the literature procedure.[8] NaOH (14.0 g, 350 mmol) was dissolved in H_2O (20 ml) and added to a solution of 1,4-bis(2-hydroxyethoxy)benzene (11.5 g, 58 mmol) in THF (100 ml) and cooled down to 0 °C. A solution of *p*-toluenesulfonyl chloride (25g, 130 mmol) in THF (50 ml) was added dropwise, the reaction was stirred at room temperature for a further 2 hours, then THF removed to a minimum amount under reduced pressure. The mixture was poured into ice-water and extracted with DCM. The organic layer was washed with water three times, brine, and dried over anhydrous Na_2SO_4. Solvent was removed *in vacuo* on a rotary evaporator to afford a crude product which was further purified by trituration with EtOH at 0 °C to afford a white solid of monomer **2** (26.5 g, 90% yield).

^{1}H-NMR [400 MHz, $CDCl_3$] δ 7.82 (d, *J* = 8.0 Hz, 4H), 7.34 (d, *J* = 8.0 Hz, 4H), 6.69 (s, 4H), 4.34 (t, 4H), 4.10 (t, 4H), 2.45 (s, 6H).

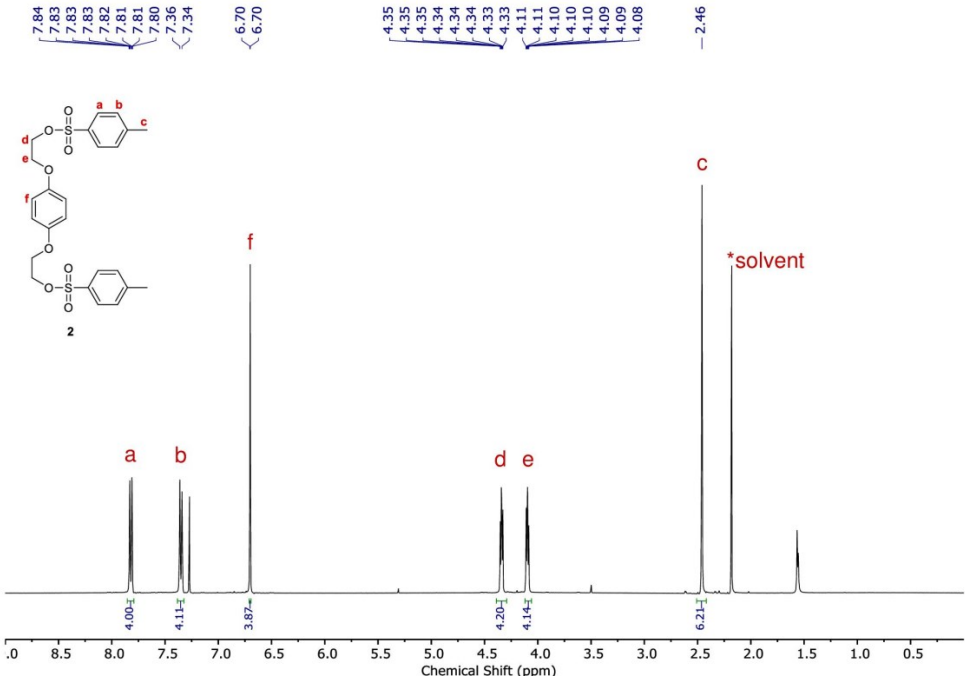
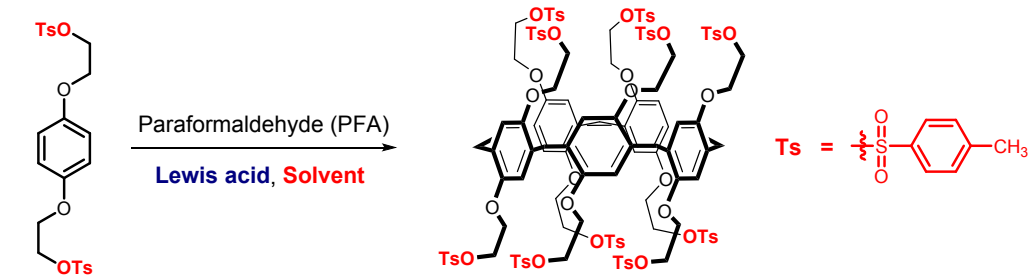


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of monomer **2**.

2.2 Synthesis of Pertosylated Pillar[5]arene 1



Monomer 2 **1**

Suitable reaction conditions for the synthesis of the target pillar[5]arene **1** were initially screened based on the literature procedures to synthesise peralkoxylated pillarenes (**Table S1**).[9]

Table S1: Reaction conditions for the synthesis of pertosylated pillar[5]arene **1**.

Condition	Starting Materials (equiv.)			Solvent[1]	Time(h)	Yield (%)
	Monomer2	PFA	Lewis acid			
1	1.00	3.00	$BF_3{\cdot}Et_2O$ (1.00)	DCE	4	70
2	1.00	3.00	$BF_3{\cdot}Et_2O$ (1.00)	DCM	4	20
3	1.00	3.22	$FeCl_3$ (0.21)	DCM	3	6
4	1.00	3.22	$FeCl_3$ (0.21)	DCE	24[2]	9
5	1.00	1.00	TFA (6.40)	DCE	72	0
6	1.00	1.50	$TsOH{\cdot}H_2O$ (0.15)	DCM	24	0

[1] DCE = 1,2-Dichloroethane and DCM = Dichloromethane
[2] After 3 hours, only trace amount of **1** was observed.

a) General Synthetic Procedure Using $BF_3{\cdot}Et_2O$

Monomer **2** (1.00 equiv.) was dissolved in DCE, followed by addition of finely ground PFA (3.00 equiv.) to a solution. The suspension was stirred for a further 10 minutes at room temperature. $BF_3{\cdot}Et_2O$ (1.00 equiv.) was subsequently added slowly to produce a greenish solution. The reaction was covered loosely with a stopper and stirred at 20°C for a further 4 hours. The reaction mixture was poured into methanol (50 ml) and diluted with DCM (150 ml). The organic layer was washed with water (3x50 ml) and brine (50 ml), then dried over Na_2SO_4 and the solvent removed in vacuo. The dark crude product was purified via silica gel column chromatography using MeOH/DCM (1:99 v/v) to afford the target product **1** as a white powder.

Note: Occasionally, purification of the crude material by silica gel chromatography gave a **1** as a brownish product. ^1H NMR spectroscopic analysis of this material showed high purity, however white samples of **1** can be obtained from re-subjecting the material to silica gel chromatography.

Condition 1 (Table S1)
Reagents:
Monomer **2** (2.00 g, 3.95 mmol), PFA (0.36 g, 11.84 mmol), $BF_3{\cdot}Et_2O$ (0.50 ml, 4.05 mmol), and DCE (10.00 ml). **Yield:** 1.43 g, 70% yield (an average yield of 10 experiments)

Condition 2 (Table S1)
Reagents:
Momomer **2**(1.00 g, 1.97 mmol), PFA (0.18 g, 5.92 mmol), $BF_3{\cdot}Et_2O$ (0.25 ml, 2.03 mmol), and DCM (5.00 ml). **Yield:** 202 mg, 20% yield (an average yield of 3 experiments)

The attempts to synthesise permethoxylated pillar[5]arene and perethoxylated pillar[5]arene using condition 2 were carried out by replacing monomer **2** with 1,4-dimethoxybenzene and 1,4-diethoxybenzene, respectively. However, no pillararene product was observed by TLC after 4 and 24 hours. Only black polymeric products were observed.

b) General Synthetic Procedure Using $FeCl_3$ (Condition 3 and 4, Table S1)

A mixture of monomer **2** (1.00 g, 2 mmol) and PFA (193 mg, 6.44 mmol) were dissolved in DCM (50 ml) and stirred under N_2 for 10 minutes at room temperature. Anhydrous iron(lll) chloride, $FeCl_3$ (68 mg, 0.42 mmol) was subsequently added and the solution was stirred for further 3 hours. The reaction was quenched with water (50 ml), the organic layer was washed with water (3x50 ml) and brine (50 ml), then dried over Na_2SO_4 and solvent removed in vacuo. The crude product was purified by column chromatography using MeOH/DCM (1:99 v/v) to afford the target product **1** as a white powder (56 mg, 6% yield). In condition 4, the reaction was carried out using all starting materials as the condition 3, but DCM solvent was replaced by the same volume of DCE. The target product **1** was isolated in 93 mg or 9 % yield.

c) General Synthetic Procedure Using TFA (Condition 5, Table S1)

A mixture of monomer **2** (1.00 g, 2 mmol) and PFA (60 mg, 2 mmol) in DCE (70 ml) was stirred at room temperature, TFA (1.00 ml, 6.40 mmol) was then added in one portion and heated to reflux at 85 °C. Reaction progress was monitored after 2, 4, 6, 8, 24 ,48, and 72 hours. However, no product **1** was observed by TLC. Starting materials still remained in the reaction mixture with no evidence for the formation of product **1**.

d) General Synthetic Procedure Using $TsOH{\cdot}H_2O$ (Condition 6, Table S1)

A mixture of monomer **2** (1.00 g, 2 mmol) and PFA (90 mg, 3 mmol) in DCM (60 ml) was mixed with *p*-toluenesulfonic acid monohydrate, $TsOH{\cdot}H_2O$ (57 mg, 0.3 mmol). The solution was refluxed at 40 °C for 24 hours. Only starting materials were observed with no residue of product **1**.

2.3 Spectroscopic Data for Pillararene S1

^{1}H NMR [400 MHz, $CDCl_3$] δ 7.72 (d, *J* = 8.0 Hz, 20H), 7.05 (d, *J* = 8.0 Hz, 20H), 6.80 (s, 10H), 4.49 – 4.45 (m, 10H), 4.37 – 4.32 (m, 10H), 4.29 – 4.24 (m, 10H), 4.10 – 4.05 (m, 10H), 3.61 (s, 10H), 2.28 (s, 30H).

^{13}C NMR [101 MHz, $CDCl_3$) δ 149.59, 144.95, 132.32, 130.00, 128.53, 127.98, 114.64, 69.86, 66.04, 31.07, 21.61.

HRMS (ESI) m/z: 2614.5271 ($[M+Na]^+$ = $[C_{125}H_{130}O_{40}S_{10}+Na]^+$ requires 2614.5271).

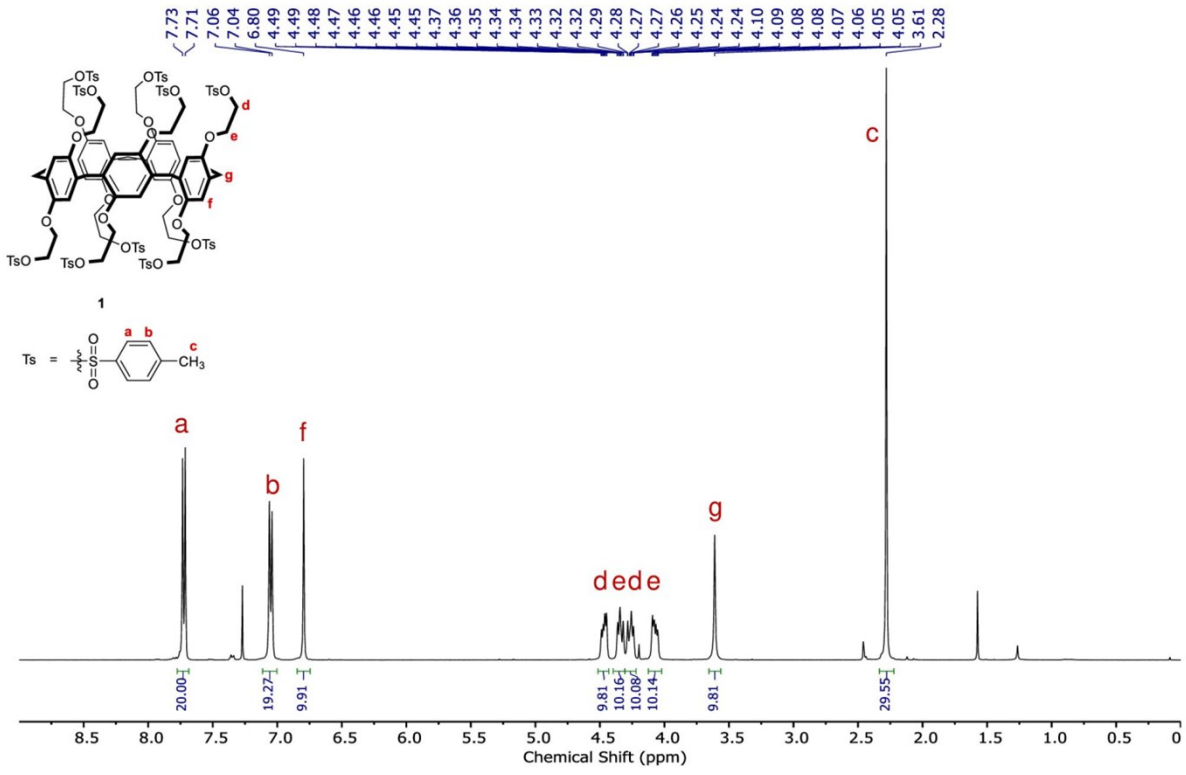


Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of pillar[5]arene **1**.

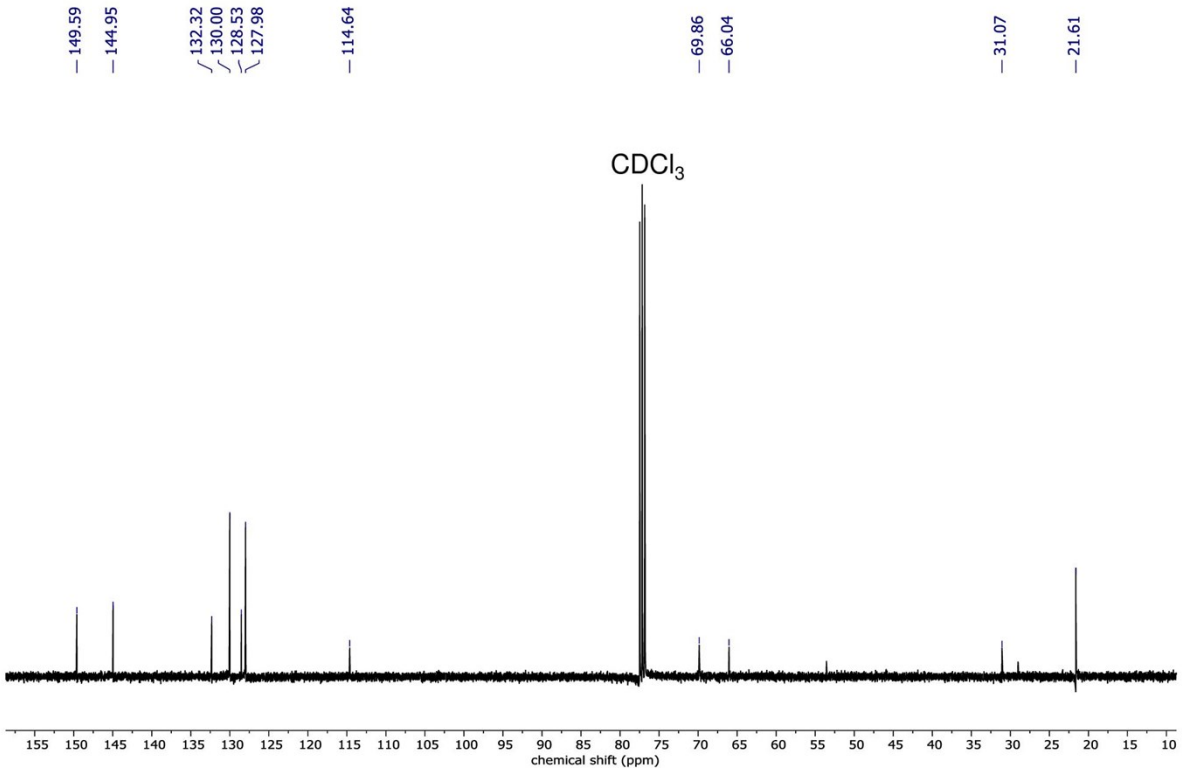


Figure S3. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of pillar[5]arene **1**.

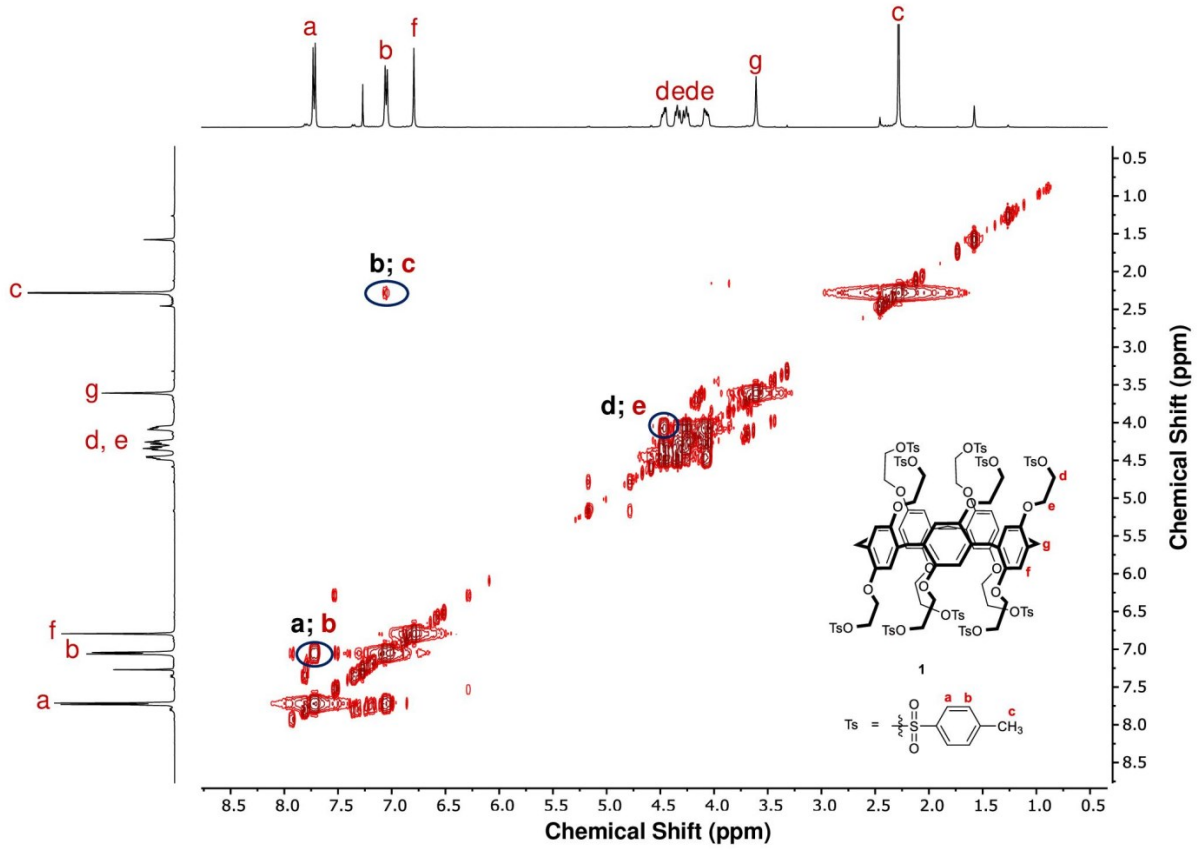


Figure S4. ^{1}H-^{1}H COSY ($CDCl_3$) of pillar[5]arene **1**.

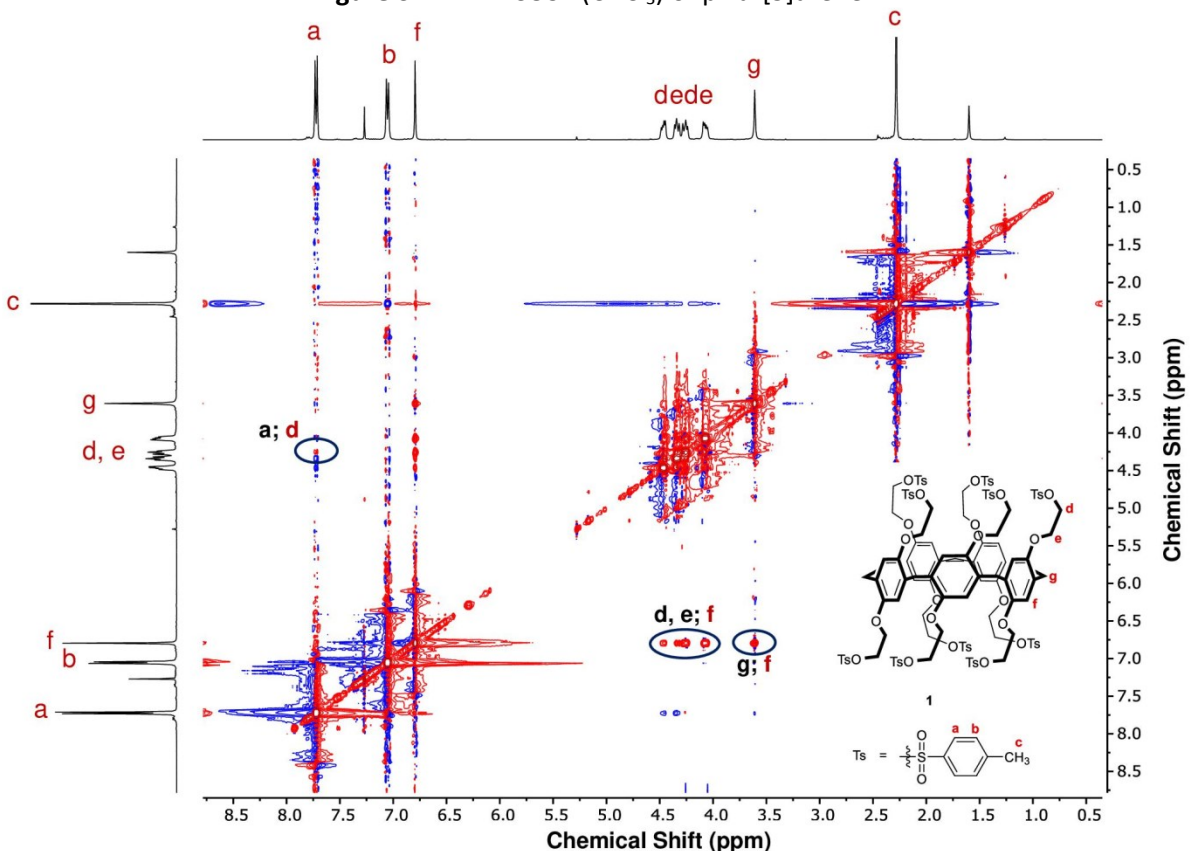


Figure S5. Truncated 2D-NOESY spectrum ($CDCl_3$) of pillar[5]arene **1**.

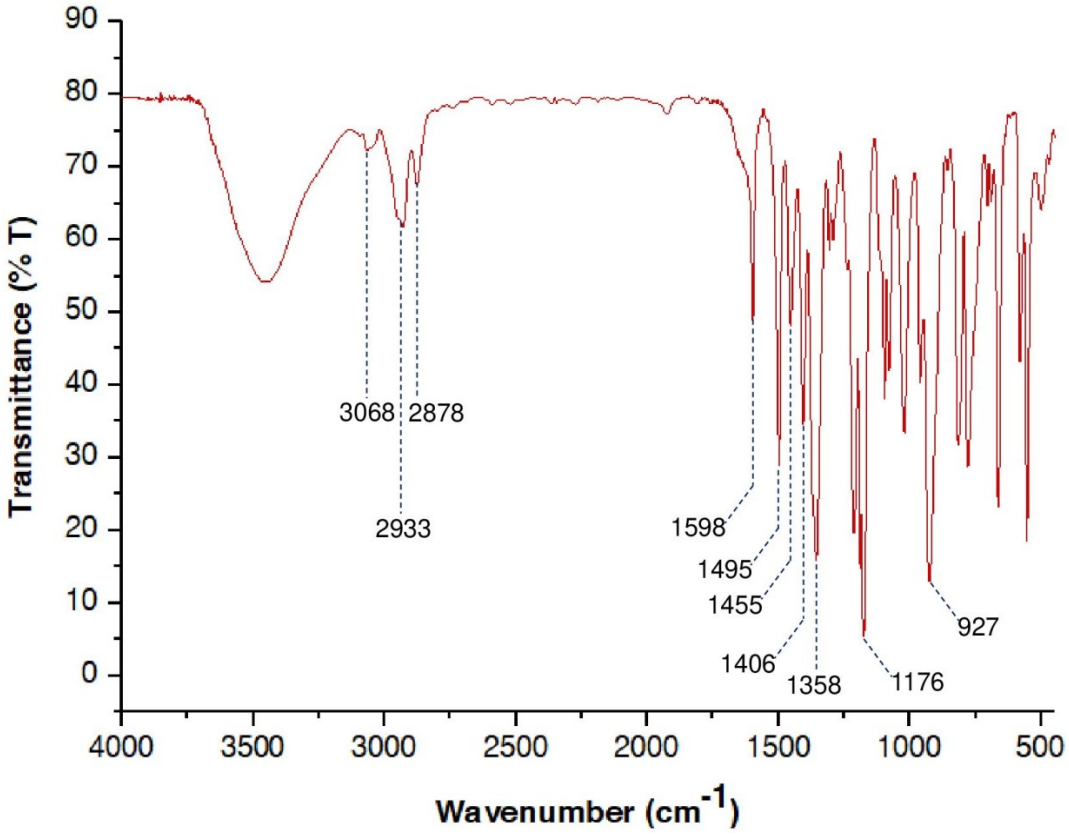


Figure S6. FTIR spectrum of pillar[5]arene **1**.

Table S2. FTIR peak assignments of pillar[5]arene **1**.

ῡ(cm^{-1})	Vibrational Mode
3068	Aromatic C–H stretching
2933, 2878	CH_2, CH_3 stretching
1598, 1495	Aromatic C=C stretching
1455	CH_2 bending
1406	CH_3 bending
1358, 1176	S=O stretching of sulfonate
927	S–O stretching of sulfonate

3. Supramolecular Polymer Characterisation

3.1 Temperature-dependent ^{1}H NMR studies

^{1}H NMR spectra of pillar[5]arene **1** in $CDCl_3$ (10 mM) were recorded at the temperature of 298, 303, 308, 313, 318, 323, and 328K. The temperature was elevated and hold for 5 minutes to equilibrate solution temperature, then the spectra of **1** were recorded.

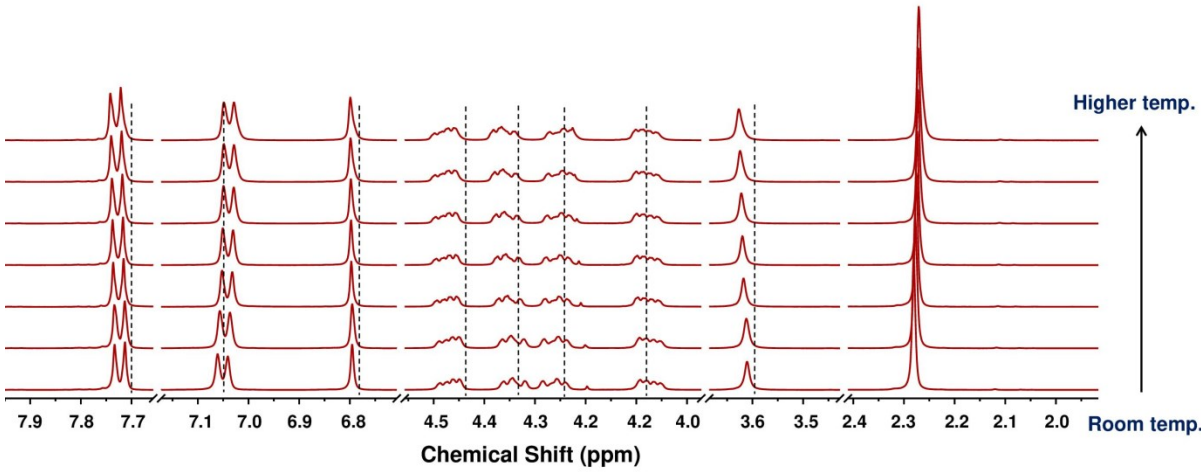


Figure S7. Variable temperature ^{1}H NMR spectra of 10 mM of pillar[5]arene **1** ($CDCl_3$, 400 MHz).

3.2 Dynamic Light Scattering (DLS) Experiments

DLS experiments provide further evidence for a formation of a supramolecular polymeric network of **1** in DCM solution. At concentrations of 1.00 and 5.00 mM, pillar[5]arene **1** exhibits an average hydrodynamic diameter (d) of approximately 0.7 and 0.8 nm, respectively (Figure S8a and S8b). Increasing the concentration of **1** to 20 mM significantly enhances the d value to around 221 nm (Figure S8c), indicating a concentration dependence of supramolecular polymer formation for **1**. The same experiments were conducted with permethoxylated pillar[5]arene, serving as control experiments; in contrast, no significant changes in the average hydrodynamic diameter were observed in DCM solution at between 1.00 – 20.0 mM (Figure S8d-f).

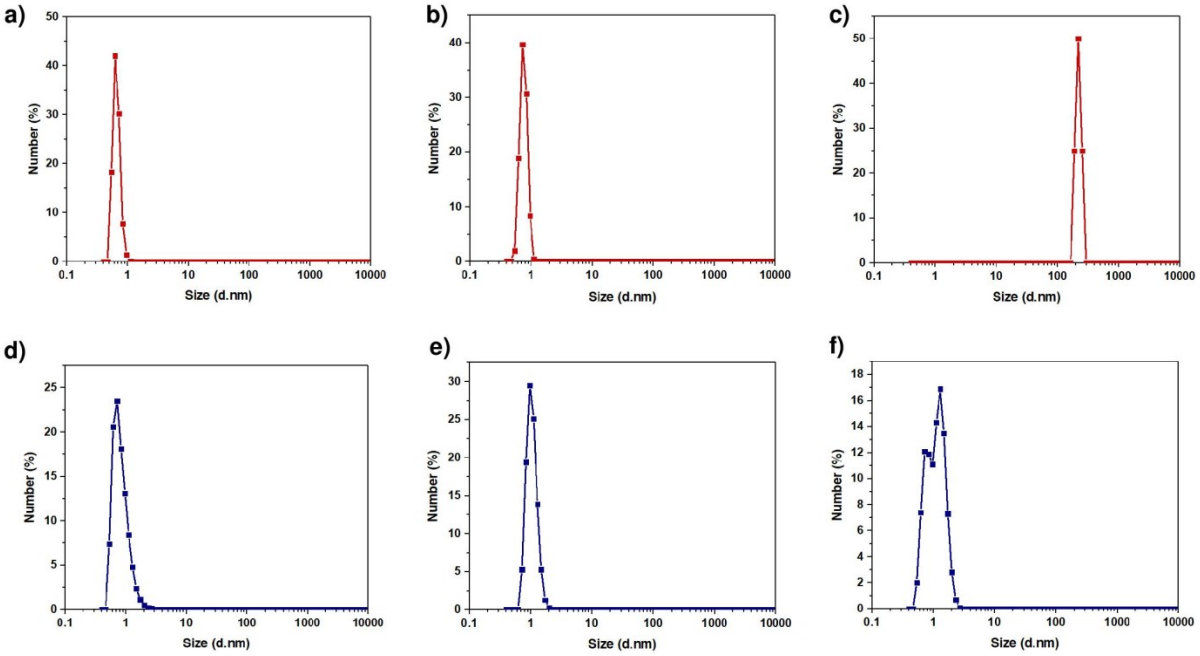


Figure S8. Dynamic light scattering profiles (DLS) reporting size distributions of pillar[5]arene **1** at different concentrations; (a) 1.00 mM, (b) 5.00 mM, and (c) 20.0 mM and size distributions of permethoxylated pillar[5]arene at concentration of (d) 1.00 mM, (e) 5.00 mM, and (f) 20.0 mM.

3.3 Scanning electron microscopy (SEM)

The morphology of the microfibril structure drawn from a solution of **1** (50 mM) in $CHCl_3$ was further investigated by SEM. Rod-shaped microfibres with a regular diameter between 200-250 nm were observed (Figure S9a and S9b), providing direct evidence of self-assembly of pillar[5]arene **1** into a unique microstructure in solution.

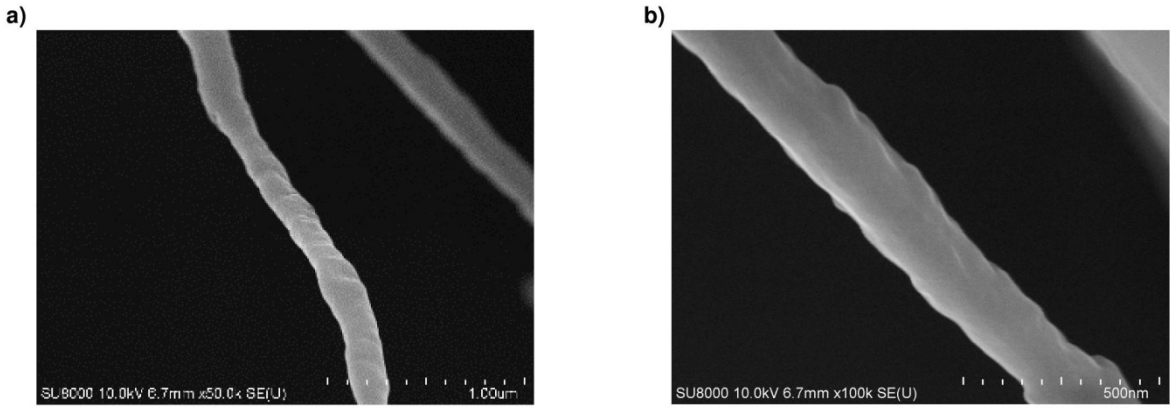


Figure S9. SEM images of pillar[5]arene **1** at a resolution of (a) 1.00 μm and (b) 500 nm.

3.4 Specific Viscosity

The specific viscosity measurements of **1** in DCM solutions were carried out at 298K using Cannon-Ubbelohde viscometer (Figure S10). In the low concentration range, the specific viscosity of **1** increased linearly with concentration, which indicated the formation of linear oligomers in solution. At the concentration above 65 mM, the specific viscosity of the solution increased significantly which strongly supported the formation of large supramolecular polymers *via* host-guest intermolecular interactions.

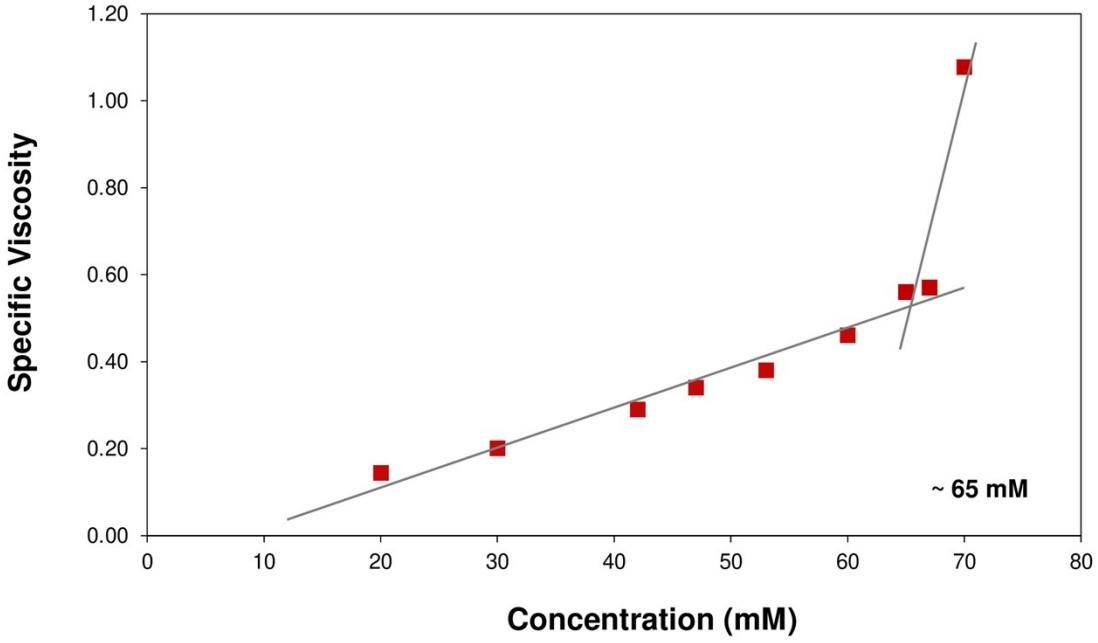


Figure S10. Specific viscosity of **1** in DCM at 298K versus concentrations of **1**

4. X-Ray Crystallographic Data

4.1 X-ray crystallography studies

Table S3 Crystal data and structure refinement for **1** and **1@dcb**.

	1	**1@dcb**
Empirical formula	$C_{125}H_{130}O_{40}S_{10}$	$C_{131}H_{138}N_2O_{40}S_{10}$
Formula weight	2592.88	2701.03
Temperature/K	200.0(1)	150(2)
Crystal system	monoclinic	triclinic
Space group	C2/c	$P\bar{1}$
a/Å	21.5402(2)	14.98554(16)
b/Å	22.7876(2)	18.2946(2)
c/Å	28.6846(2)	28.2056(2)
α/°	90	103.6550(9)
β/°	97.9790(10)	90.0967(8)
γ/°	90	113.6128(11)
Volume/Å^3	13943.5(2)	6844.64(14)
Z	4	2
ρ_{calc}g/cm^3	1.235	1.311
μ/mm^{-1}	2.099	2.164
F(000)	5440.0	2836.0
Crystal size/mm^3	0.61 × 0.466 × 0.317	0.245 × 0.213 × 0.106
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.674 to 136.902	5.458 to 137.784
Index ranges	-25 ≤ h ≤ 25, -25 ≤ k ≤ 27, -30 ≤ l ≤ 34	-15 ≤ h ≤ 18, -22 ≤ k ≤ 22, -33 ≤ l ≤ 33
Reflections collected	55553	72103
Independent reflections	12743 [R_{int} = 0.0369, R_{sigma} = 0.0219]	24930 [R_{int} = 0.0347, R_{sigma} = 0.0322]
Data/restraints/parameters	12743/203/898	24930/2148/2335
Goodness-of-fit on F^2	1.057	1.011
Final R indexes [I ≥ 2σ (I)]	R_1 = 0.0744, wR_2 = 0.2371	R_1 = 0.0700, wR_2 = 0.2062
Final R indexes [all data]	R_1 = 0.0789, wR_2 = 0.2434	R_1 = 0.0754, wR_2 = 0.2118
Largest diff. peak/hole / e Å^{-3}	1.01/-0.61	1.21/-0.76
CCDC no.	2008505	2008506

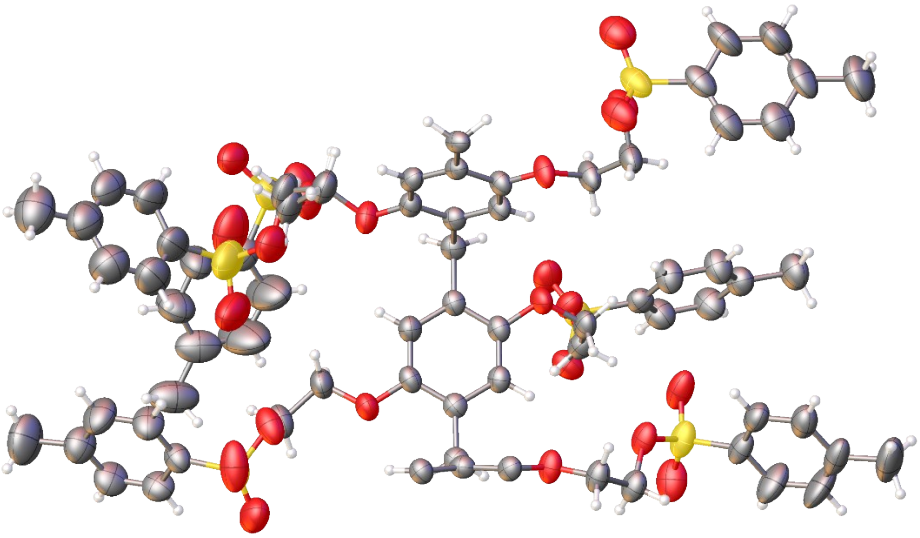


Figure S11. View of the asymmetric unit in **1** at 200 K with ellipsoids drawn at 50%.

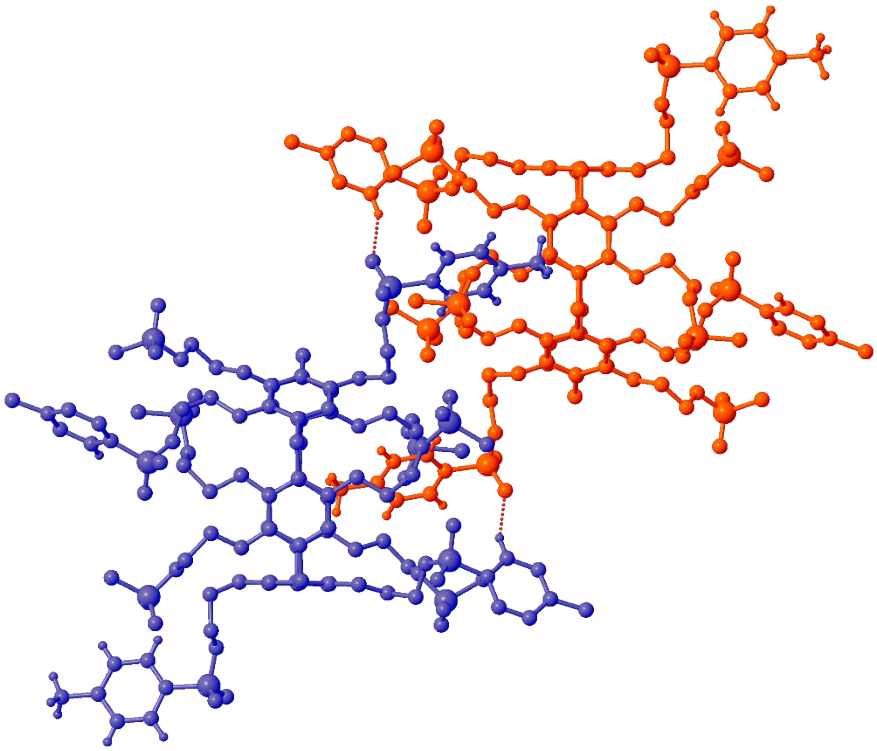


Figure S12. View of the C-H···O interactions that support the self-inclusion of the tosyl groups into neighbouring pillar[5]arenes.

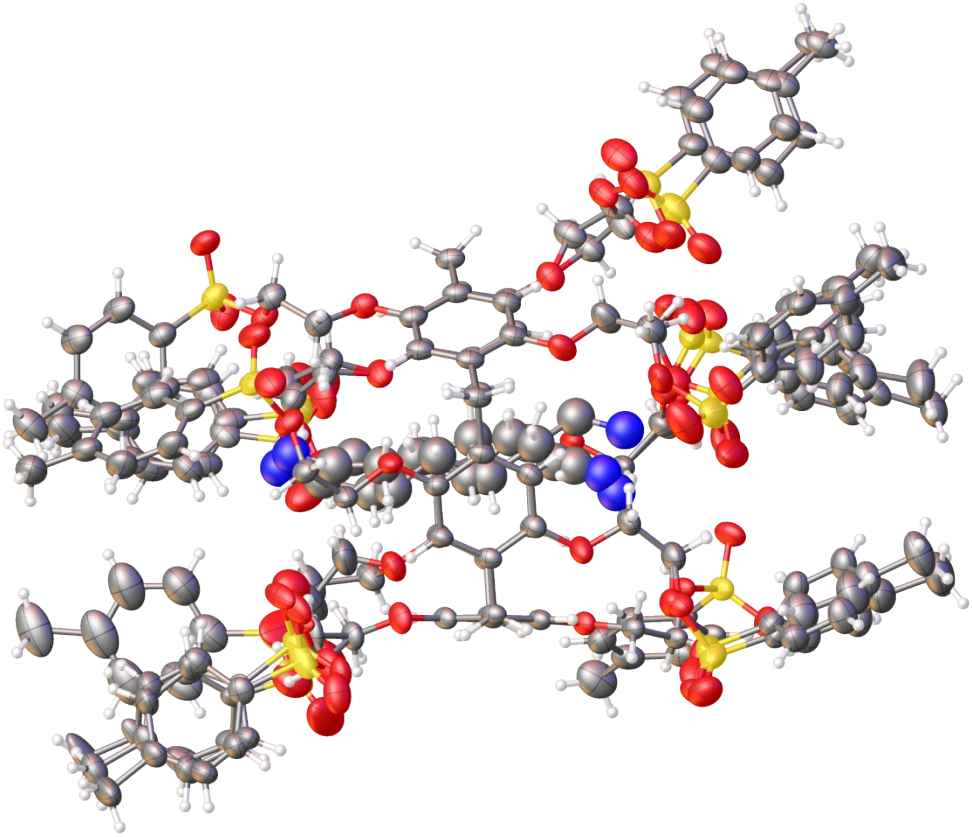


Figure S13. View of the asymmetric unit in **1@dcb**.

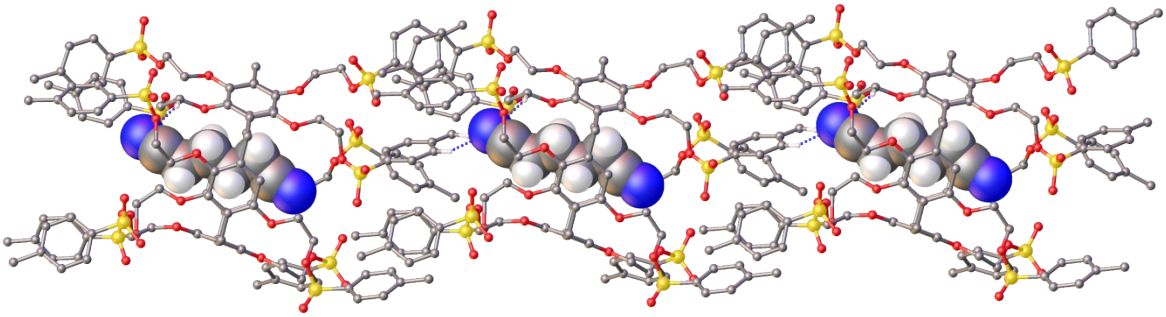
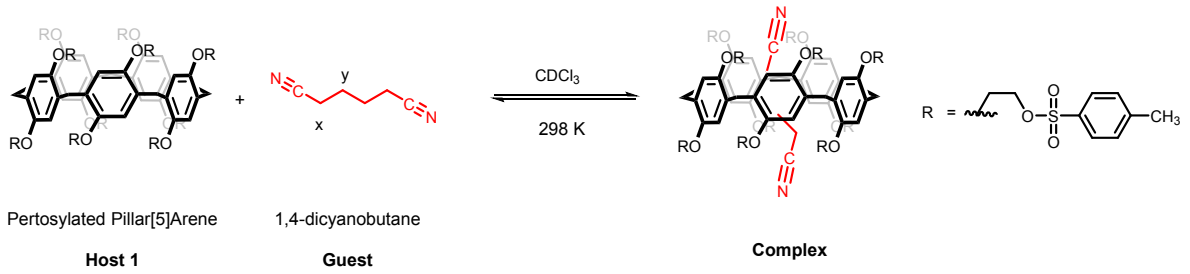


Figure S14. View of the C-H···N interactions in **1@dcb** with dcb shown as a spacefill model. Only part 1 and the interacting hydrogens are shown for clarity.

5. Preliminary Host-Guest Binding Studies

The association constant (K_a) for the inclusion complex of pertosylated pillar[5]arene **1** and 1,4-dicynaobutane (**dcb**) guest was determined by ^{1}H NMR spectroscopic titrations in $CDCl_3$ (Scheme S1). The concentration of **dcb** was kept constant at 10.0 mM with varying concentration of **1**. The spectra of the guest in the presence of **1** show two sets of signals corresponding to the free guest ($\mathbf{H_x}$ and $\mathbf{H_y}$) and complexed guest ($\mathbf{H_{x'}}$ and $\mathbf{H_{y'}}$), indicating that complexation is slow on the NMR timescale (Figure S15). Therefore, the actual concentration of host, guest, and complex can be directly calculated by single point method based on their ^{1}H-NMR integration.[10]



Scheme S1. Host-guest complexation between pertosylated pillar[5]arene **1** (**Host**) and **dcb** (**Guest**) in $CDCl_3$ at 298K.

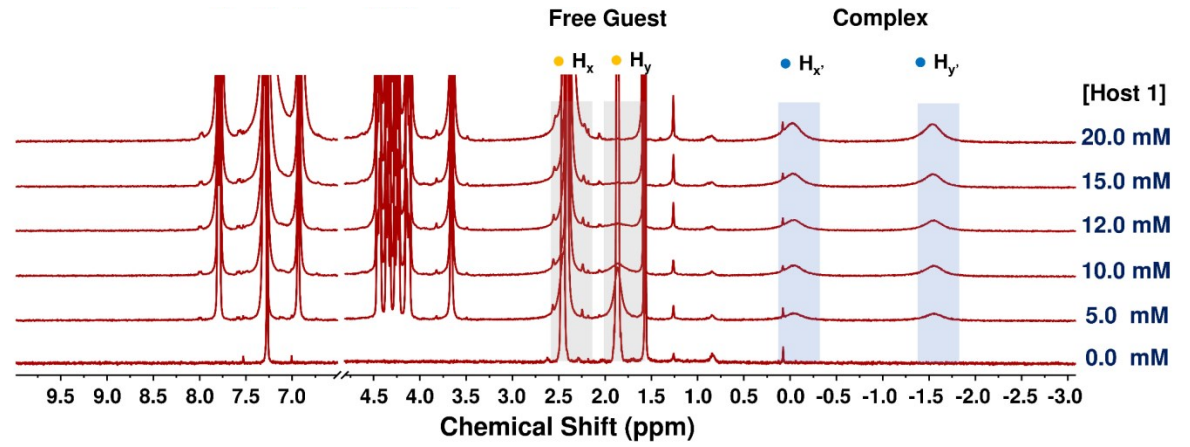


Figure S15. Truncated ^{1}H-NMR spectra of **dcb** ($\mathbf{[Guest]_{tot}}$ = 10mM) in the presence of pillar[5]arene **1** at different concentrations ($\mathbf{[Host\ 1]_{tot}}$ = 5.0, 10.0, 12.0, 15.0, and 20.0 mM), (400 MHz, $CDCl_3$, 298K). The signal of $\mathbf{H_x}$ coalesces into a $\mathbf{H_c}$ signal of **1**.

Table S4. ^{1}H-NMR integration of complexed and free **dcb** under different conditions.

Total Concentration (mM)		^{1}H-NMR Integration		
[Host 1]$_{tot}$	**[Guest]$_{tot}$**	**Complex**	**Free Guest**	**Total**
10.0	10.0	1.00	1.21	2.21
5.00	10.0	1.00	2.74	3.74
12.0	10.0	1.00	0.90	1.90

a) Percentage of Complexation

At an equimolar mixture of host **1** and **dcb** (**[Host 1]$_{tot}$** = **[Guest]$_{tot}$**= 10 mM),

$$\%\textbf{Complexation} = \frac{\text{integration of complex}}{\text{integration of complex + free guest}} \times 100$$

$$\%\text{complex} = \frac{1.00}{1.00 + 1.21} \times 100$$

$$\%\text{complex} = 45.2\%$$

The concentration of the complex formed under these conditions, **[Complex]**, can be calculated by;

$$\textbf{[Complex]} = \frac{\%\text{Complex} \times [\textbf{Guest}]_{\textbf{tot}}}{\frac{100}{1}} = \frac{45.2 \times 10.0}{\frac{100}{1}} = 4.52 \text{ mM}$$

b) Calculation of Association Constant (K_a)

$$K_a = \frac{\textbf{[Complex]}}{[\textbf{Host}]_{\textbf{free}} \times [\textbf{Guest}]_{\textbf{free}}}$$

Table S5. ^{1}H-NMR integration determined concentrations of host-guest complex, and free **1** and **dcb** at different initial concentrations.

Total Concentration (mM)		Concentration at Equilibrium (mM)			K_a (M^{-1})
[Host 1]$_{tot}$	**[Guest]$_{tot}$**	**[Host 1]$_{free}$**[1]	**[Guest]$_{free}$**[2]	**[Complex]**	
10.0	10.0	5.48	5.48	4.52	151
5.00	10.0	2.33	7.33	2.67	156
12.0	10.0	6.74	4.74	5.26	165

[1] **[Host 1]$_{free}$** = [Host 1]$_{tot}$ – [Complex]
[2] **[Guest]$_{free}$** = [Guest]$_{tot}$ – [Complex]

Association constants (K_a) were calculated under three different conditions (Table S5), providing K_a values of 151, 156, and 165 M^{-1}. These K_a values are of the same order of magnitude, giving an average K_a value of 157 $\pm$ 7 M^{-1}.

6. References

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