Electronic Supplementary Material (ESI) for Polymer Chemistry

Electronic supplementary information

Pillar[5]arene−Neutral Guest Recognition Based Supramolecular Alternating Copolymer Containing [c2]Daisy Chain and bisPillar[5]arene Units.

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Contents

Materials and methods.

Pillar[5]arene dimer **2** was prepared by our previously reported method.[S1] Solvents were either employed as purchased or dried according to procedures described in the literatures. Chemical yields referred to pure isolated products. Purification of products was accomplished by column chromatography with silica gel.

NMR measurements. ^{1}H NMR, ^{13}C NMR, 2D NOESY, and DOSY spectra were recorded on a Bruker AV500 instrument.

High-resolution mass spectra (HRMS). HRMS were recorded on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument.

Dynamic light scattering (DLS) measurements. Supramolecular polymer sizing was analyzed using dynamic light scattering (DLS) on a Malvern Zetasizer 3000HSA at 298 K.

Viscosity measurements. Viscosity measurements were carried out with Ubbelohde micro dilution viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 298 K in chloroform.

Synthesis and characterization of compounds.

Synthesis of copillar[5]arene 1.

1,4-bis(4-bromobutoxy)benzene.

1,4-bis(4-bromobutoxy)benzene was synthesized according to a literature procedure.[S2] ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm): 6.81 (s, 4H), 3.94 (t, *J* = 6.0 Hz, 4H), 3.49 (t, *J* = 6.5 Hz, 4H), 2.06 (m, 4H), 1.91 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm): 153.2, 115.5, 77.4, 77.2, 76.9, 67.6, 33.7, 29.6, 28.1.

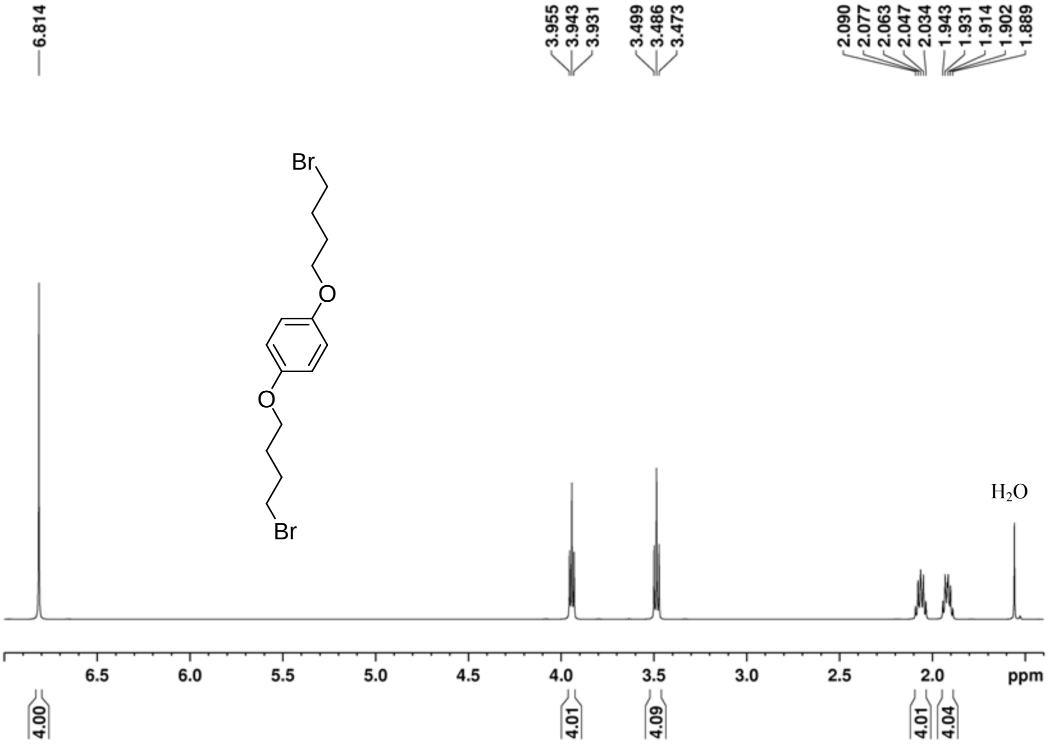


Figure S1. ^{1}H NMR spectrum (500 MHz) of 1,4-bis(4-bromobutoxy)benzene in $CDCl_3$

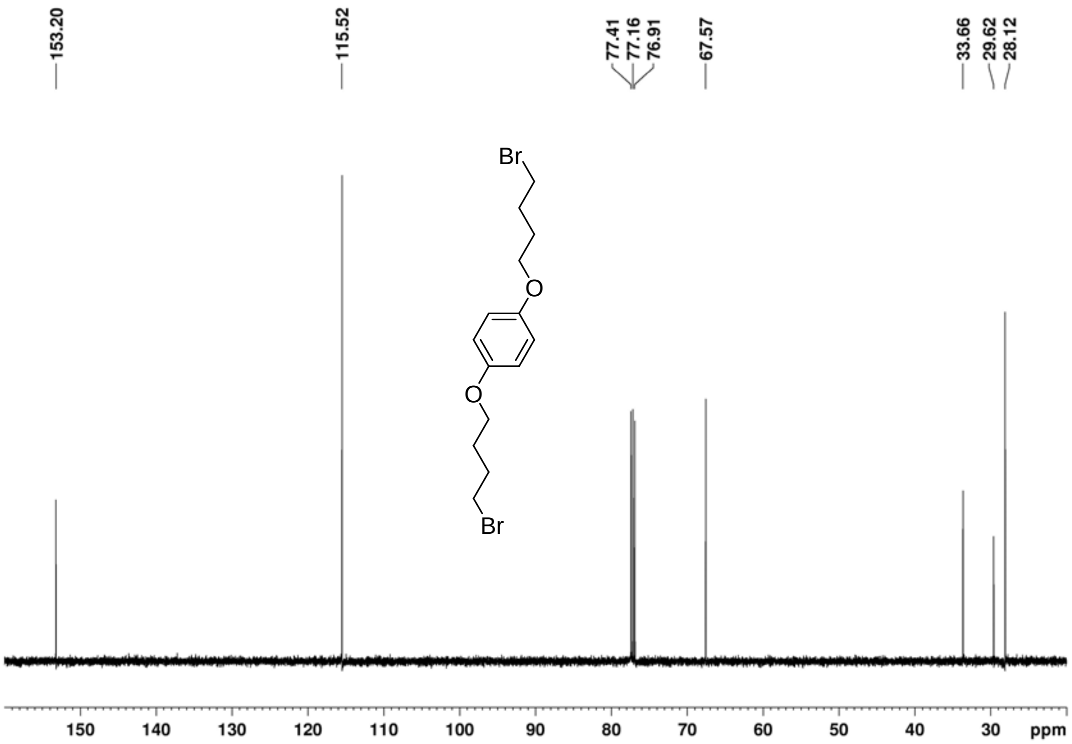
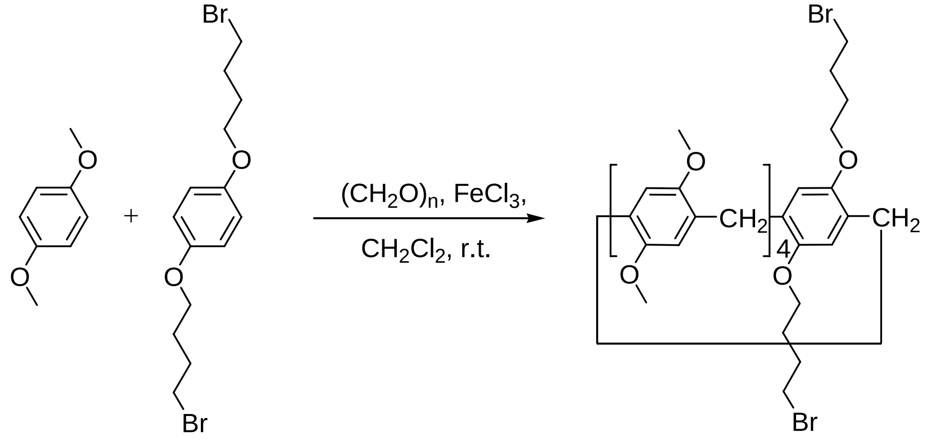


Figure S2. ^{13}C NMR spectrum (125 MHz) of 1,4-bis(4-bromobutoxy)benzene in $CDCl_3$.

Copillar[5]arene **1.**



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To a solution of 1,4-dimethoxybenzene (4.4 g, 32 mmol) and 1,4-bis(4-bromobutoxy)benzene (0.76 g, 2.0 mmol) in CH_2Cl_2 (150 mL), paraformaldehyde (2.9 g, 96 mmol) and anhydrous $FeCl_3$ (1.6 g, 10 mmol) were added under argon atmosphere. The mixture was then stirred at 25 °C for about 2 hours and the progress was monitored using TLC detection. After the completion of the reaction, water (80 mL) was added and the product was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phase was washed with saturated brine (80 mL) and dried over with anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 = 2: 1, v/v) to afford the desired product **1** as a yellow solid (0.62 g, 31 %). m.p. 191−193 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ (ppm): 6.77 (m, 8H), 6.71 (s, 2H), 3.84 (t, *J* = 6.0 Hz, 4H), 3.77 (m, 10H), 3.64 (m, 24H), 3.32 (t, *J* = 6.7 Hz, 4H), 1.93 (m, 4H), 1.81 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm): 150.9, 150.9, 150.8, 150.7, 150.0, 128.6, 128.4, 128.4, 128.3, 128.23, 115.0, 114.3, 114.2, 114.0, 113.8, 77.4, 77.2, 76.9, 67.4, 56.1, 56.1, 55.9, 55.8, 33.5, 29.9, 29.6, 29.3, 28.5. HRMS: Calcd for $C_{51}H_{60}Br_2O_{10}Na$ $[M+Na]^+$: 1013.2445 , Found 1013.2469

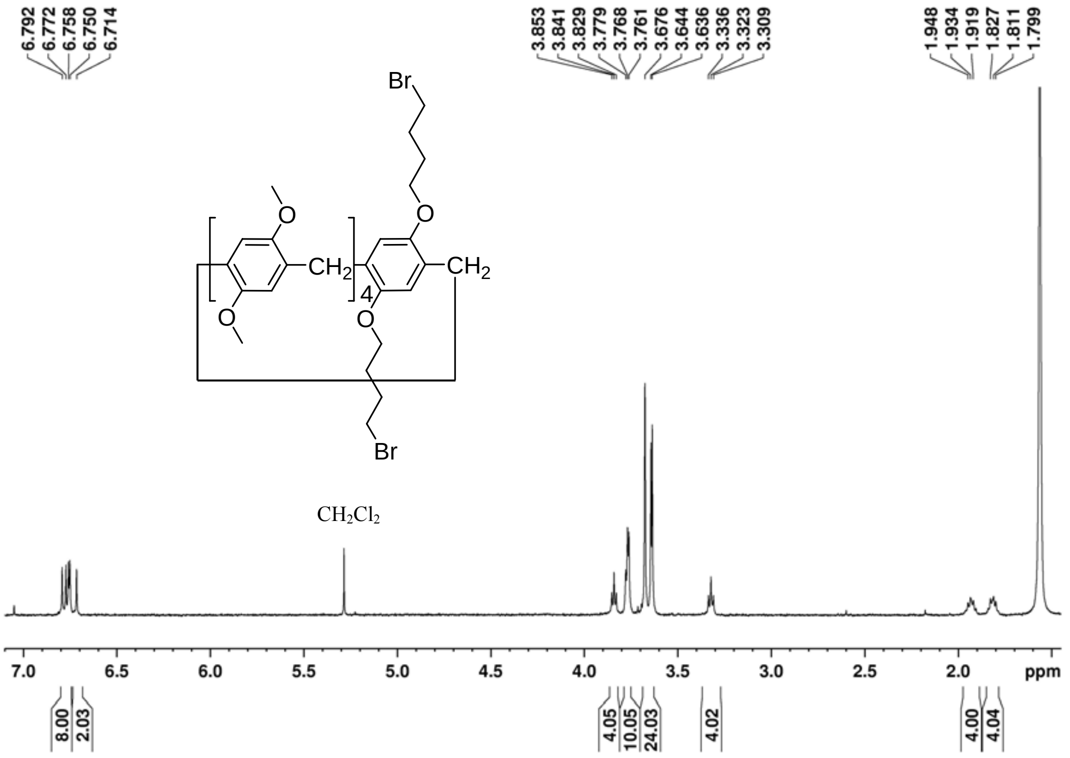

Figure S3. ^{1}H NMR spectrum (500 MHz) of **1** (at very low concentration) in $CDCl_3$.

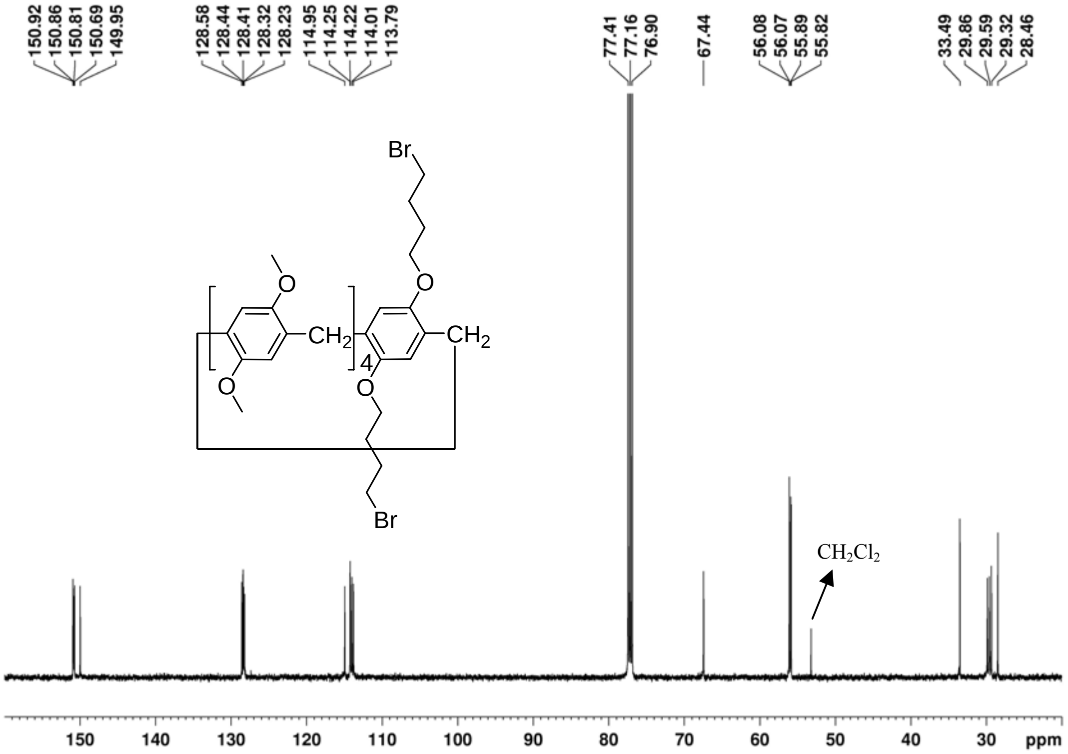

Figure S4. ^{13}C NMR spectrum (125 MHz) of **1** in CDCl$_3$.

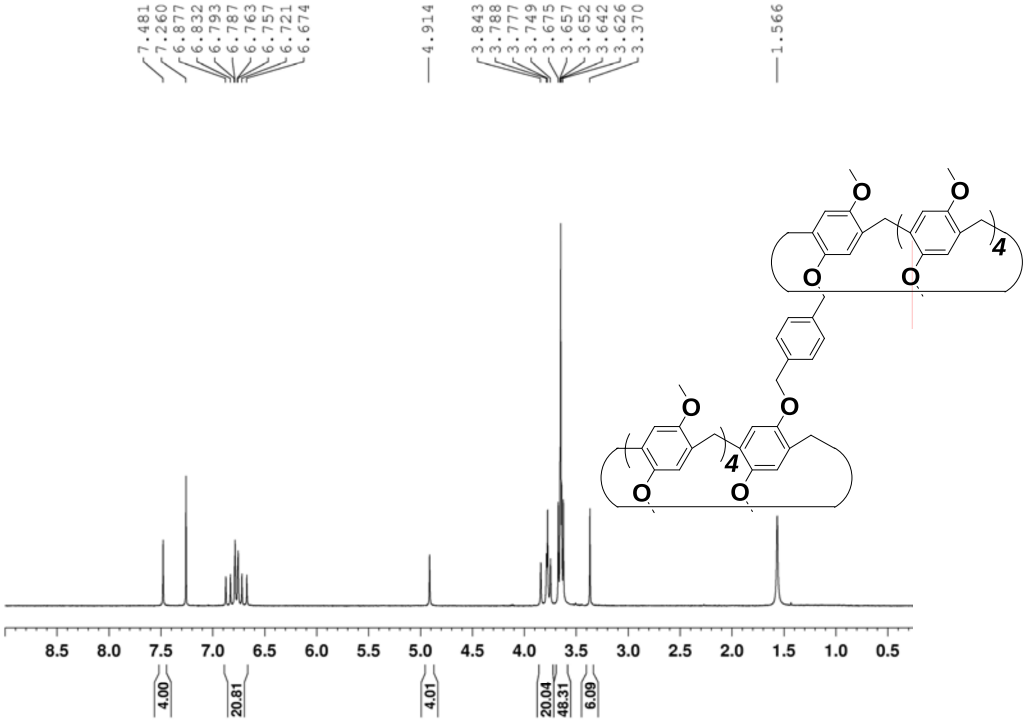

Figure S5. ^{1}H NMR spectrum (500 MHz) of **2** in CDCl$_3$.

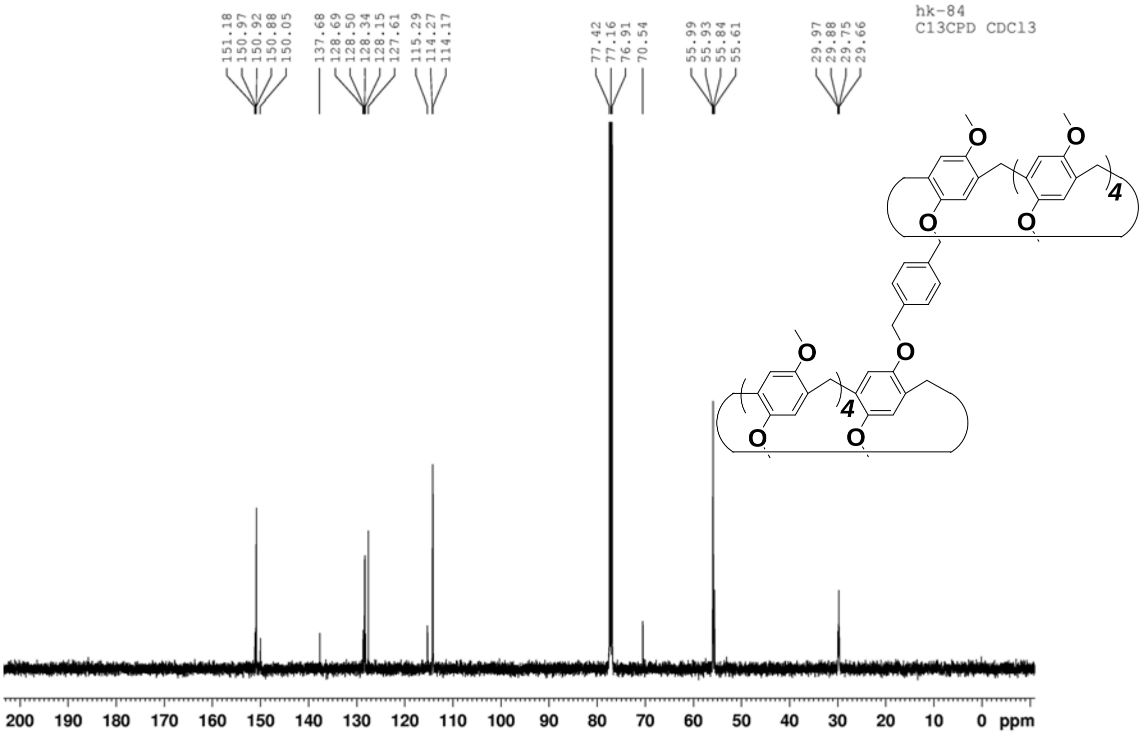

Figure S6. ^{13}C NMR spectrum (125 MHz) of **2** in $CDCl_3$.

^{1}H NMR spectra.

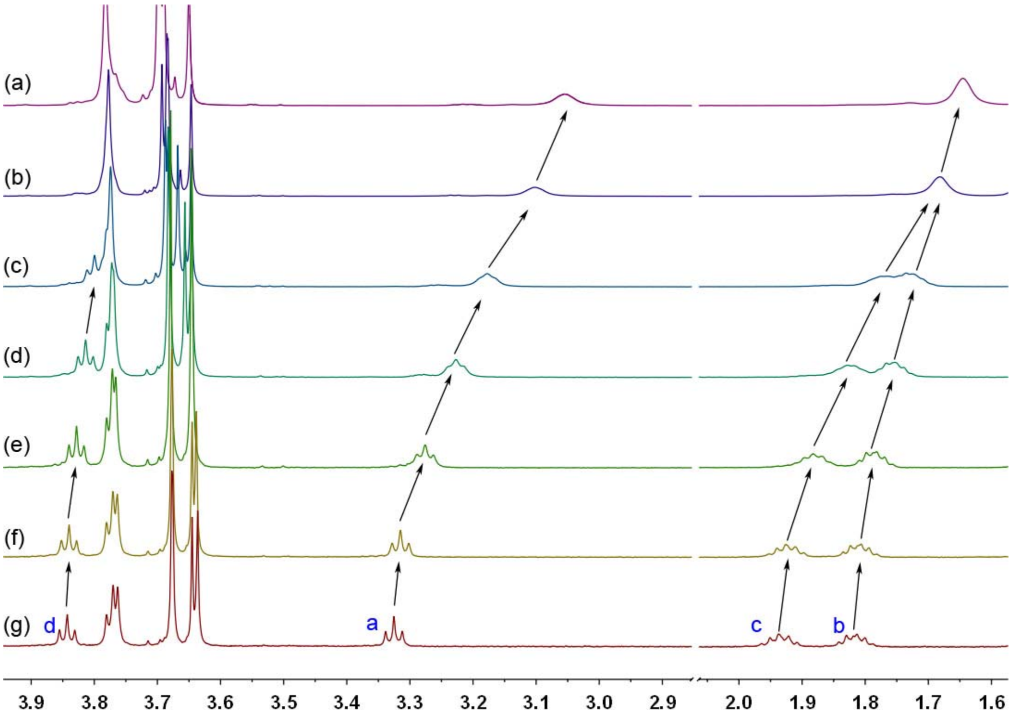

Figure S7. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of copillar[5]arene **1** at different concentrations: (a) 40, (b) 20, (c) 10, (d) 6.0, (e) 3.0, (f) 1.0, and (g) 0.5 mM.

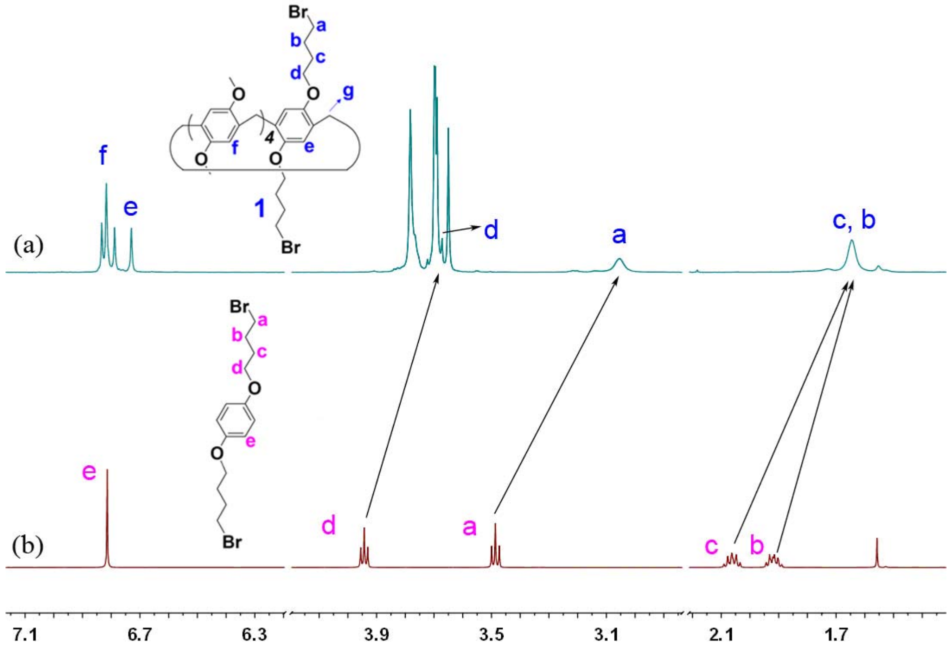

Figure S8. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of copillararene **1** (a), and 1,4-bis(4-bromobutoxy)benzene (b) at 30 mM.

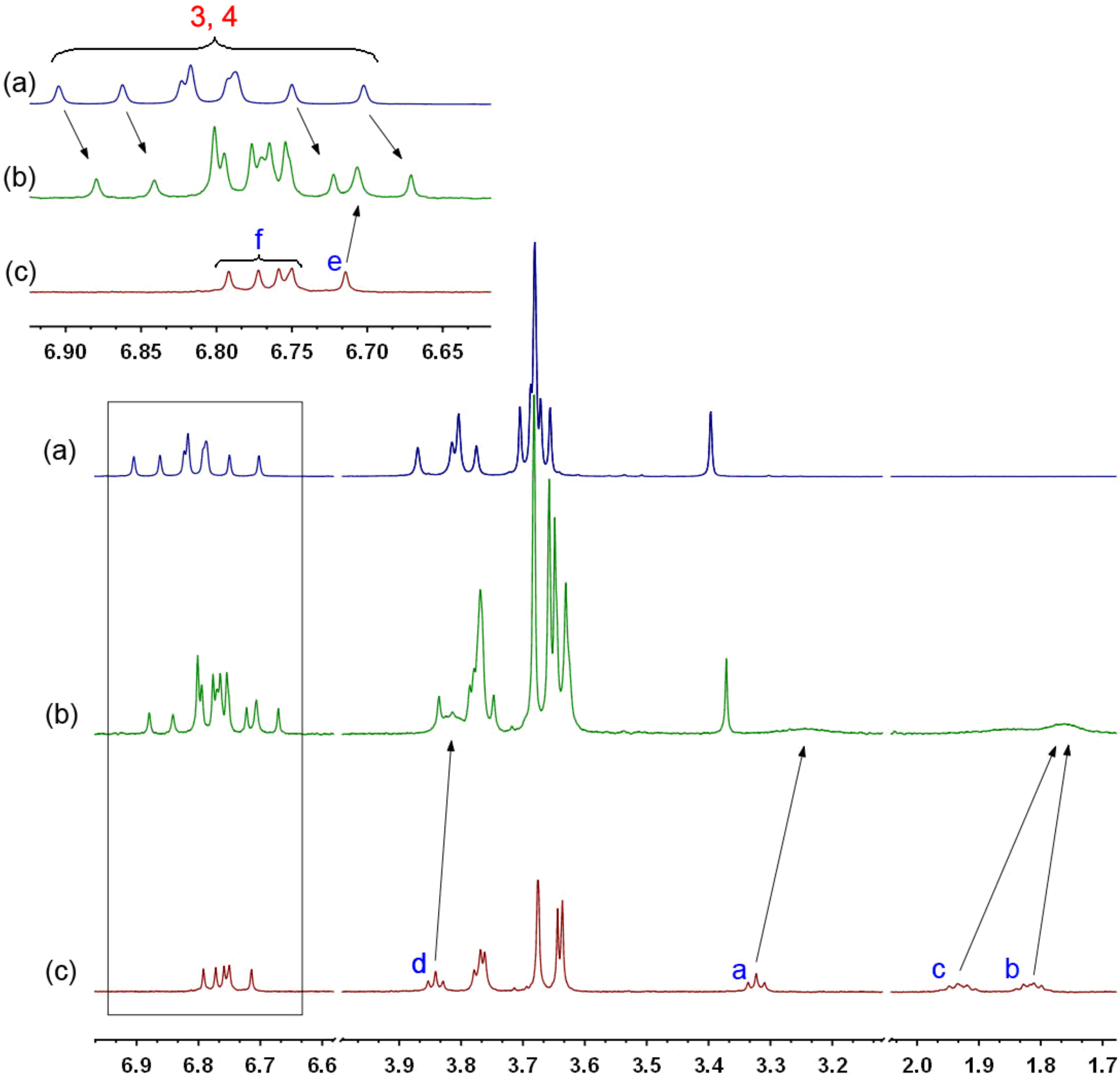

Figure S9. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K) of (a) *bis*-pillararene **2**, (b) 2 : 1 molar ratio of **1** and **2**, and (c) copillararene **1**. [**1**] = 1.0 mM, [**2**] = 0.50 mM.

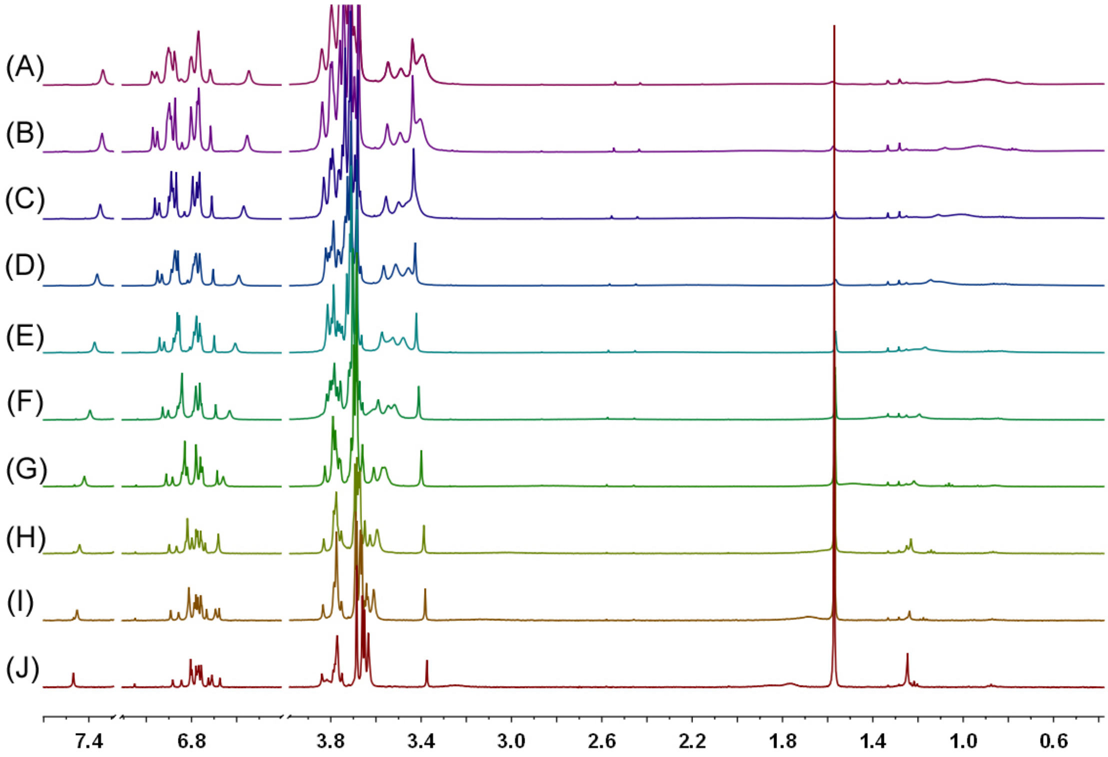

Figure S10. ^{1}H NMR spectra (500 MHz, CDCl$_3$, 298 K) of 2 : 1 molar ratio of **1** and **2** at different concentrations of **1**: (a) 200, (b) 150, (c) 100, (d) 60, (e) 40, (f) 20, (g) 10, (h) 5.0, (i) 3.0, and (j) 1.0 mM.

Variable-temperature (VT) ^{1}H NMR spectra.

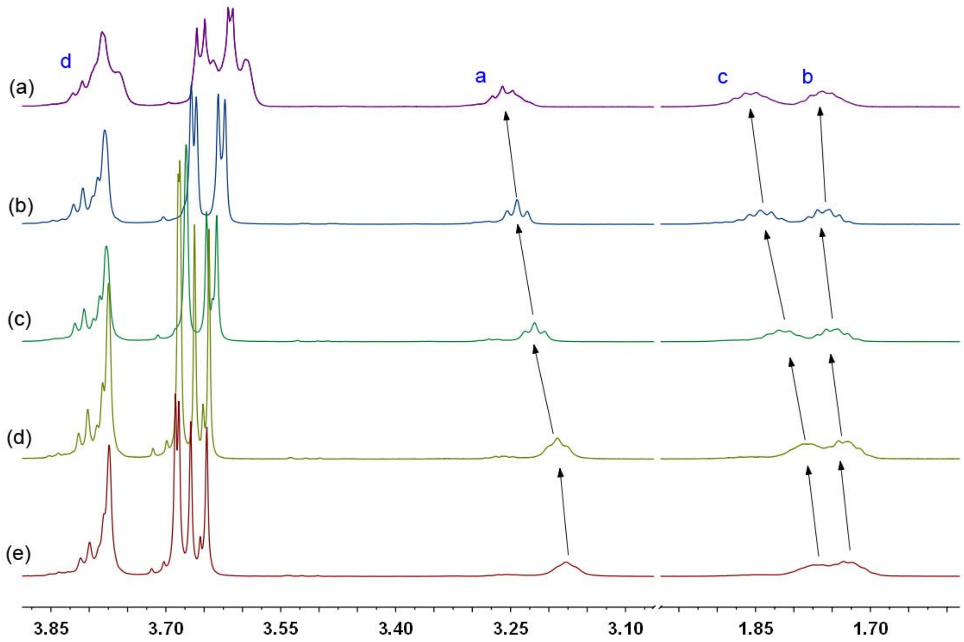

Figure S11. VT ^{1}H NMR (500 MHz, $CDCl_3$) spectra of **1** at 10 mM: (a) 313, (b) 308, (c) 303, (d) 300, and (e) 298 K.

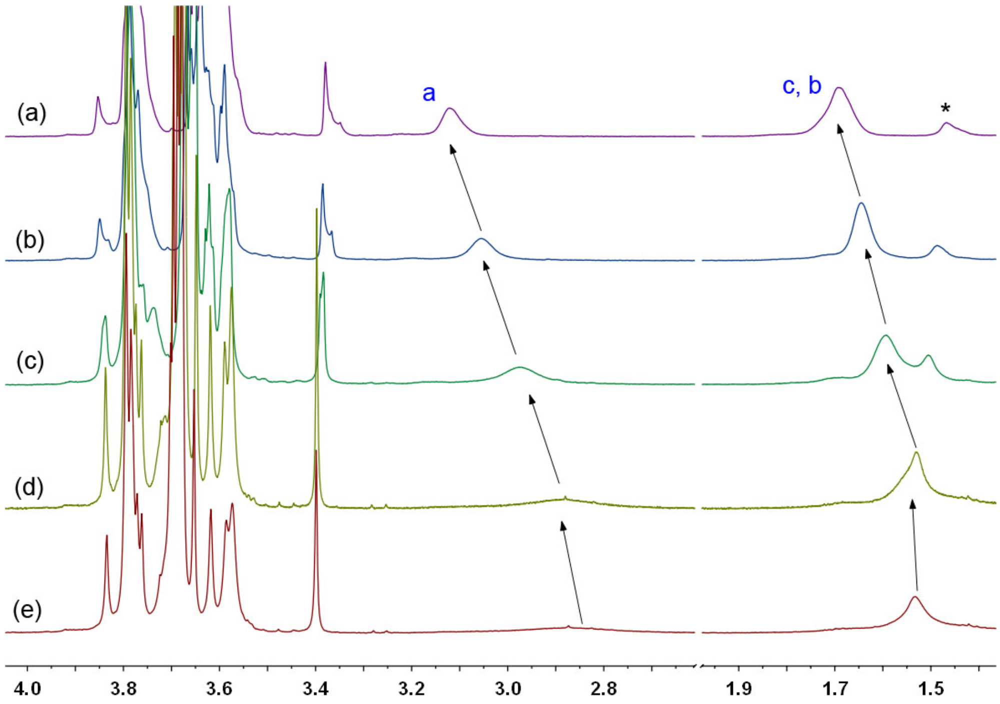

Figure S12. VT ^{1}H NMR spectra (500 MHz, $CDCl_3$) of 2 : 1 molar ratio of **1** and **2** at 10 mM of **1**: (a) 313, (b) 308, (c) 303, (d) 300, and (e) 298 K. Asterisk = water.

Calculated value of maximum polymerization degree $n_{\max}$.

$n_{\max}$ could be calculated using a well-defined method from $n_{\max} = 1/(1 - p)$, where p is the extent of complexation and can be calculated from $p = \Delta/\Delta_0$; the maximum chemical shift change (Δ_0) of H_3 was estimated to be 0.1106 ppm (Figure S13) using a $CDCl_3$ solution with 0.80 mM of pillar[5]arene dimer **2** and 160 mM of **1**. The maximum possible polymerization degree $n_{\max}$ of supramolecular alternating copolymer **1·1**⊂**2** with **1** concentration of 200 mM was calculated to be 15.4 (p = 93.5 %). That is to say, there are 15.4 pillar[5]arene dimer **2** and 15.4 [c2]daisy-chain dimer **1·1**, i.e. 61.6 (15.4 × 4) pillararene units, in the copolymer and the molar mass is 54.7 kDa.

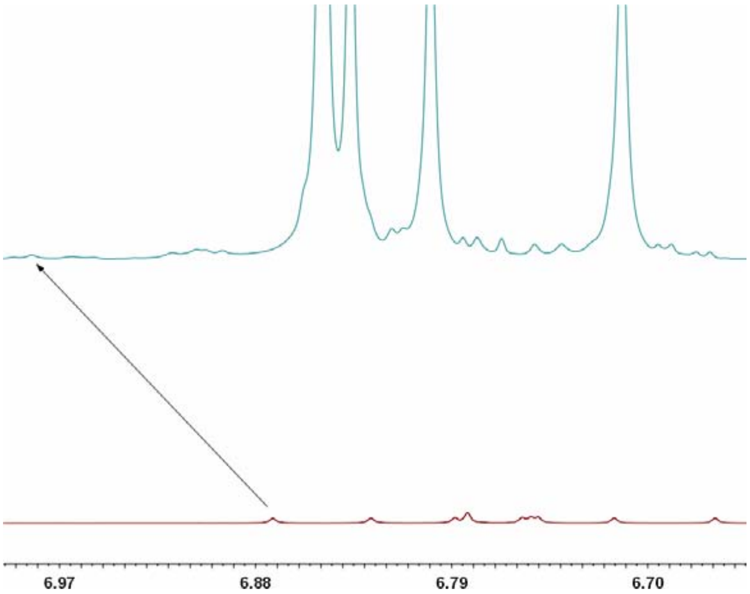

Figure S13. Partial ^1H NMR spectra (500 MHz, $CDCl_3$, 298 K): (a) 0.80 mM **2** and 160 mM **1**; (b) 0.80 mM **2**.

X-ray crystal data and crystal structures of [c2]daisy chain 1·1.

Crystallographic data: colorless, $C_{51}H_{60}Br_2O_{10}$, *FW* 992.81, Monoclinic, space group C2/c, $a = 37.756(4)$, $b = 11.9135(11)$, $c = 27.853(5)$, $\alpha = 90°$, $\beta = 129.9680(10)°$, $\gamma = 90°$, $V = 9602(2)$ Å^3, $Z = 8$, $D_c = 1.374$ g cm^{-3}, $T = 173(2)$ K, $\mu = 1.745$ mm^{-1}, 35435 measured reflections, 11390 independent reflections, 580 parameters, 6 restraint, $F(000) = 4128$, $R_1 = 0.0627$, $wR_2 = 0.1223$ (all data), $R_1 = 0.0413$, $wR_2 = 0.1136$ [$I > 2\sigma(I)$], max. residual density 0.557 e·Å^{-3}, and goodness-of-fit (F^2) = 1.065. CCDC 921428.

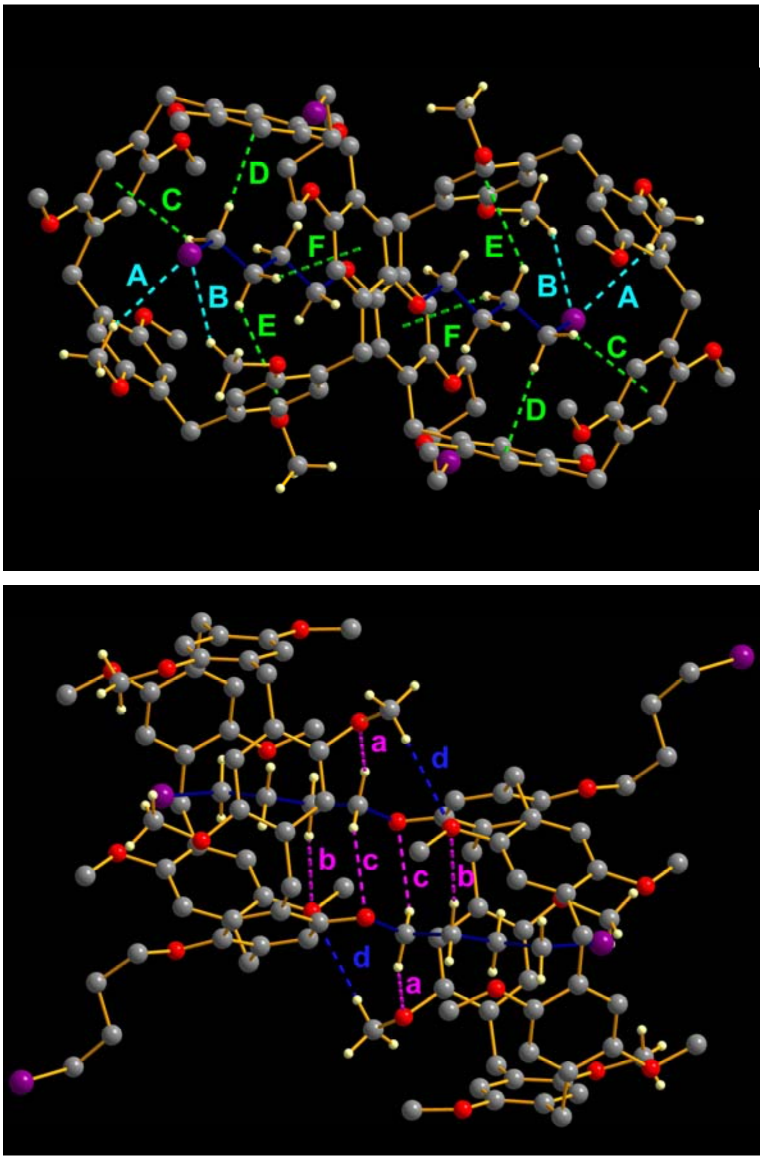

Figure S14. Crystal structure of [2]daisy chain **1·1**. Carbons are gray, Hydrogens are light yellow, oxygens are red, and bromines are violet. Dashes represent C−H···π interactions or hydrogen bonds.

C−H···Br hydrogen-bond parameters		
No.	H···Br distances (Å)	C−H···Br angles (deg)
A	2.97	148
B	3.23	157
C−H···π parameters		
No.	H···ring centre distances (Å)	C−H···ring angles (deg)
C	2.83	140
D	2.55	149
E	3.07	128
F	2.87	105
C−H···O hydrogen-bond parameters		
No.	H···O distances (Å)	C−H···O angles (deg)
a	2.93	129
b	2.89	129
c	2.76	136
d	2.71	161

References.

[S1]. C. Li, K. Han, J. Li, H. Zhang, J. Ma, X. Shu, Z. Chen, L. Weng, X. Jia, *Org. Lett.* **2012**, *14*, 42−45.

[S2]. M. Rahimizadeh, E. R. Seresht, N. Golari, M. Bakavoli, *Monatshefte für Chemie*, **2008**, *139*, 639−645.