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Supporting Information

Shape Induced Sorting via Rim-to-Rim Complementarity in the Formation of Pillar[5,6]arene-based Supramolecular Organogels

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1. Materials and Methods

General. Starting materials were purchased from Sigma-Aldrich, Alfa Aesar, TCI, Cambridge Isotope Laboratories, and Bio-Lab Ltd and used as received. Chemical reactions were monitored by TLC (Merck, silica gel 60 F254) and the compounds were purified by SiO_2 flash chromatography (Merck Kieselgel 60). ^1H and ^{13}C NMR spectra were recorded on 400 and 500 MHz Bruker Avance III NMR spectrometers. Chemical shifts (δ) are given in part per millions (ppm), and spin-spin coupling (*J*) in Hz. The chemical shifts are quoted relative to residual $CHCl_3$ signals (at δ 7.26 ppm for the ^1H NMR and 77.2 ppm for the ^{13}C NMR) when the solvent is $CDCl_3$, or to residual DMSO-d_5 (at δ 2.50 ppm for the ^1H NMR and 39.5 ppm for the ^{13}C NMR) when the solvent is DMSO-d_6. Abbreviations for multiplicities used: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, br = broad signal.

Diffusion NMR measurements were performed on the above NMR instruments which are equipped with gradient systems capable of producing pulsed-gradients of up to ~50 G/cm. in the z-direction These diffusion NMR experiments were performed using the eddy currents delays (LED) pulse sequence with 4ms sine-shaped pulse gradients. The gradient pulses were incremented from 0.7 to 32.2 G/cm (effective gradient strength (G * 2/π)) in 10 steps, and the pulse gradient separation was 50ms. The diffusion coefficients were extracted from: $\ln I/I_0 = -\gamma^2\delta^2G^2(2/\pi)^2(\Delta-\delta/4)D = -bD$, where I and I_0 are the echo intensity, in the presence and absence of gradient pulse, respectively, γ is the gyromagnetic ratio, *G* is the pulse gradient strength, 2/π is a geometrical correction factor due to the sine shape of the pulse gradients used, δ is the duration of the pulse gradient, Δ is the time interval between the leading edges of the pulse gradients used, and *D* is the diffusion coefficient. The diffusion coefficients were extracted from the slope of the plot of $\ln(I/I_0)$ against the b-values. All diffusion NMR experiments were collected at 298 K and were measured in triplicates. The given values represent means ± the standard deviation of the means.

High-resolution electrospray mass-spectra were recorded on a Waters Synapt instrument. The morphology of the coated (few nm gold/palladium) xerogels was imaged by scanning electron microscopy (Quanta 200-FEG ESEM). SEM samples were prepared by casting

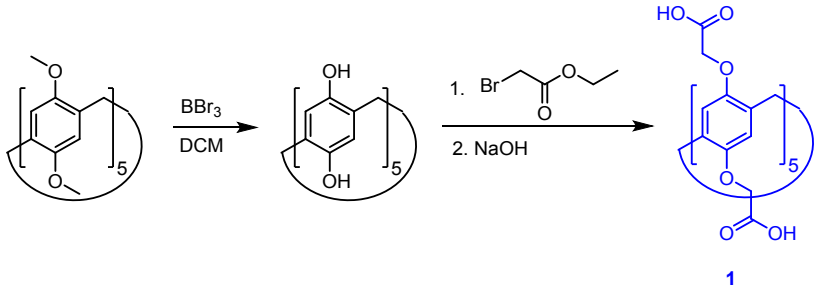
the gel on top of a silicon chip, placed on a specimen holder and imaged. The gel was dried under reduced pressure using a lyophilizer.

Gelation Procedure. The two components percarboxylated pillar[n]arenes **1** and **2** and peraminopillar[n]arenes **3a-c** and **4a-c** (2.5 μmol) were dissolved in two separate 4 mL vials in the appropriate solvent. All gels were produced with the use of DMSO as a co-solvent. Chlorinated solvents were used for gelation (chloroform, dichloromethane, dichloroathane, dichlorobenzene and tetrachloroethane). Gels were produced by mixing Pillar[n]arene **1** and **2** dissolved in 100 μL DMSO with pillar[n]arenes **3a** and **4b** dissolved in 1000 μL Chlorinated solvent. Solutions were mixed using Pasteur or Gilson pipettes, and vigorously vortexed for 15 min. The time required for gelation upon resting depends on the mixture concentration; however, in all cases the gels were characterized after a minimum of 24 h resting period.

***T*$_{gel}$ Measurments.**[1] The gel-to-solution (or precipitation) transition temperature (T_{gel}) was measured by a test tube inverting method following the procedure described by Smith et al.[2] The gel sample was heated in an oil bath at a rate of ca. 1 ^{o}C/min. The gel was carefully removed from the oil bath and turned upside down as the temperature was increased (in intervals of 1°C). In all cases, the transparent (or translucent) gel becomes opaque upon heating, until it collapses into a turbid solution, at a temperature that was determined as T_{gel}. It should be noted that a procedure in which the vial was placed upside down inside the oil bath and slowly heated gave similar T_{gel} value (for 2mM $CHCl_3$-DMSO gel ±2^{o}C).[2]

2. Experimental procedures and characterization

The known compounds **1**,[3] **2**,[4] **3a-c**[2] and **4a**[2] were synthesized according to previously described procedures[2-4], while the new compounds **4b-c** were prepared by simple modifications of these procedures.[5-6] All compounds were thoroughly purified and analyzed by NMR. NMR data of the known compounds was consistent with literature.



Scheme S1. Synthesis of compound **1.**

Decacarboxylatopillar[5]arene (1). Full detailed procedures and characterizations of compound **1** and its precursors were previously reported by our group.[3] ^{1}H NMR (500 MHz, DMSO-d$_6$): δ 12.93 (s, CO_2H, 10H), 7.09 (s, Ar*H*, 10H), 4.69 (d, *J* = 15 Hz, ArOC*H*HCO, 10H), 4.41 (d, *J* = 15 Hz, ArOCH*H*CO, 10H), 3.74 (s, $ArCH_2Ar$, 10H) ppm.

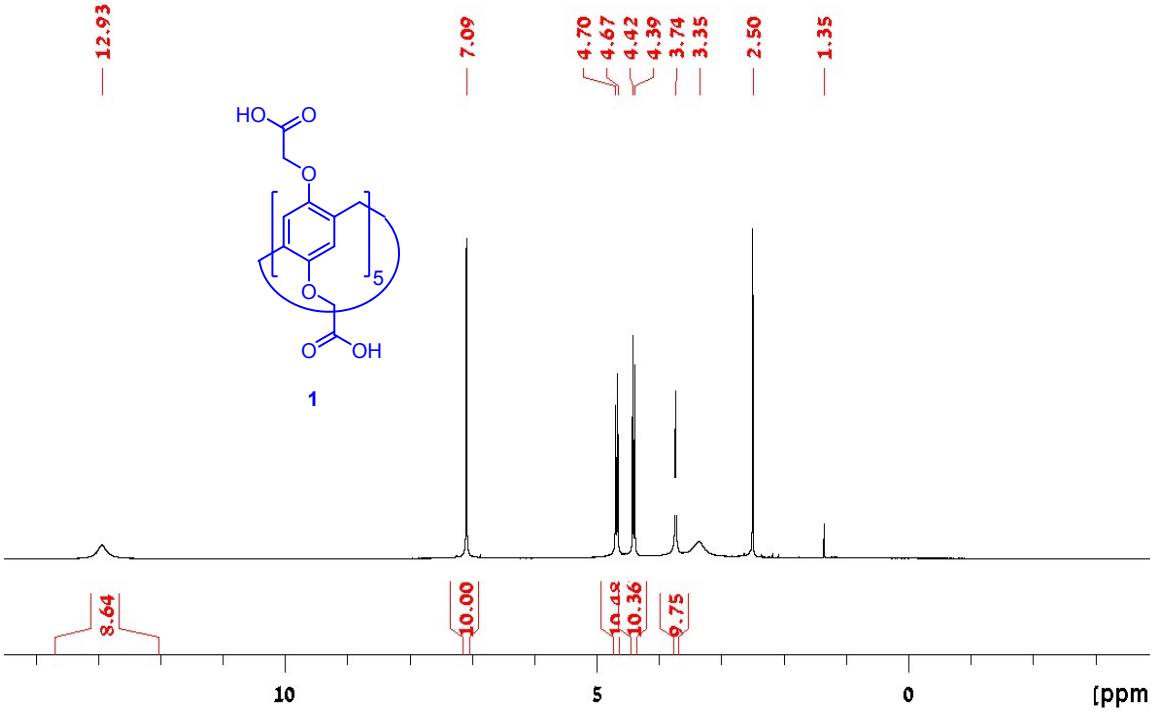
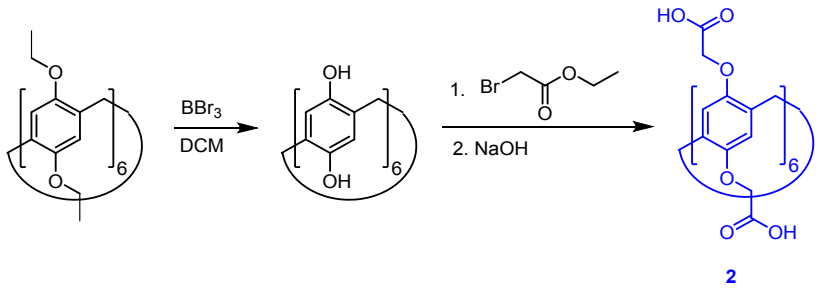


Figure S1. ^{1}H NMR spectrum of **1** in DMSO-d$_6$ (500 MHz). (*) Represent H_2O.



Scheme S2. Synthesis of compound **2.**

Dodecacarboxylatopillar[6]arene (2). Full detailed procedures and characterizations of compound **2** and its precursors were previously reported.[4] ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.88 (s, CO_2H, 12H), 6.83 (s, Ar*H*, 12H), 4.49 (d, *J* = 7.2 Hz, ArOCH_2CO, 24H), 3.71 (s, ArCH_2Ar, 12H) ppm.

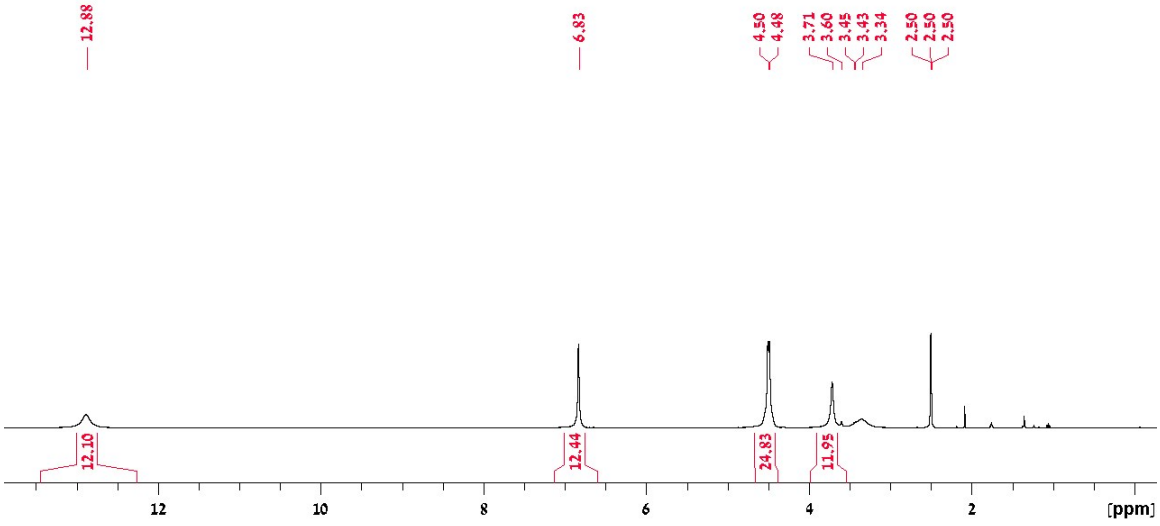
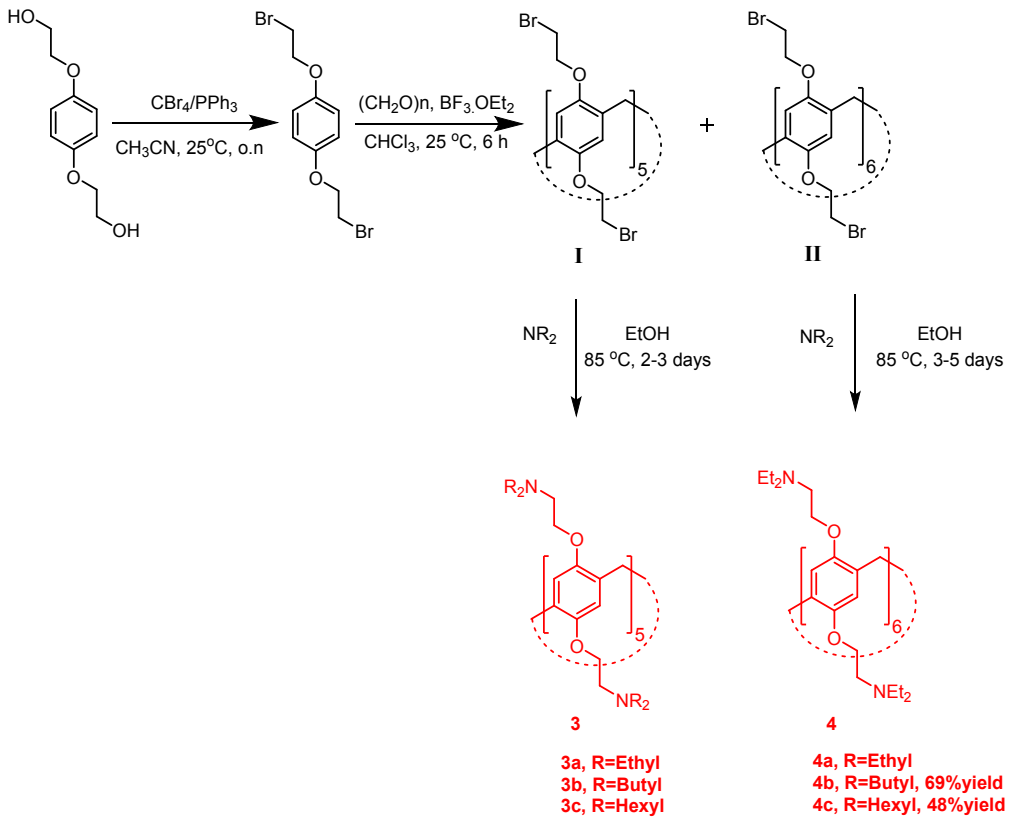
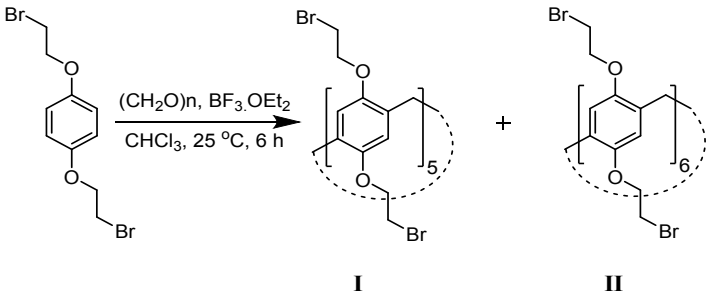


Figure S2. ^{1}H NMR spectrum of **2** in DMSO-d_6 (400 MHz). (*) Represent H_2O

The amine substituted pillar[n]arenes **3a-c** and **4a-c** used in this study were prepared according to Scheme S3.



Scheme S3. Structures of precursors and the synthesis of compounds **3a-c** and **4a-c.**



Decabromoethoxypillar[5]arene (I). Compound **I** was synthesized and characterized according to the reported procedure.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 (s, Ar*H*, 10H), 4.23 (t, *J* = 5.7 Hz, ArOC*H*$_2$CH$_2$Br, 20H), 3.85 (s, ArC*H*$_2$Ar, 10H), 3.64 (t, *J* = 5.7 Hz, ArOCH$_2$C*H*$_2$Br, 20H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 129.2, 116.2, 69.1, 30.9, 29.5 ppm.

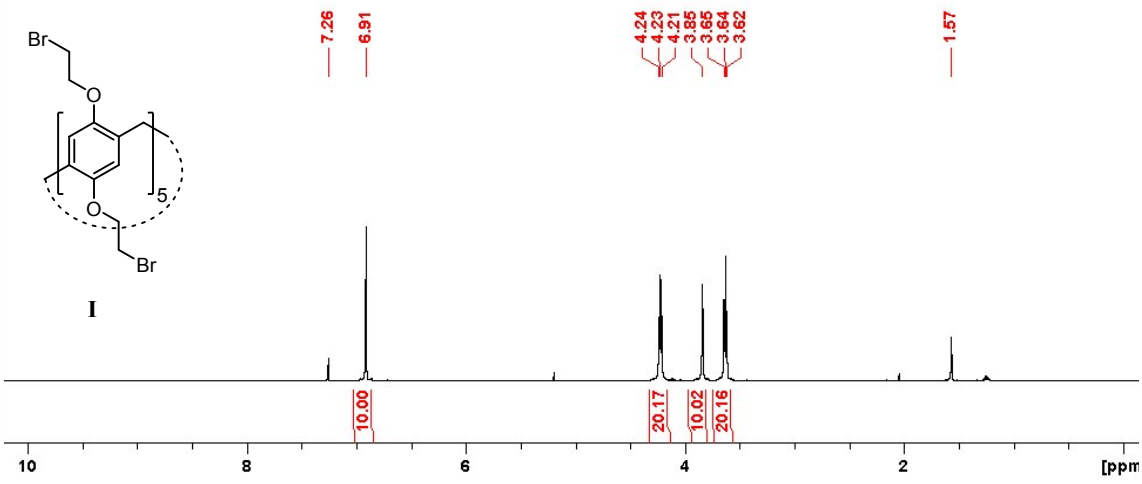


Figure S3. ^{1}H NMR spectrum of **I** in $CDCl_3$ (400 MHz). (*) Represent H_2O.

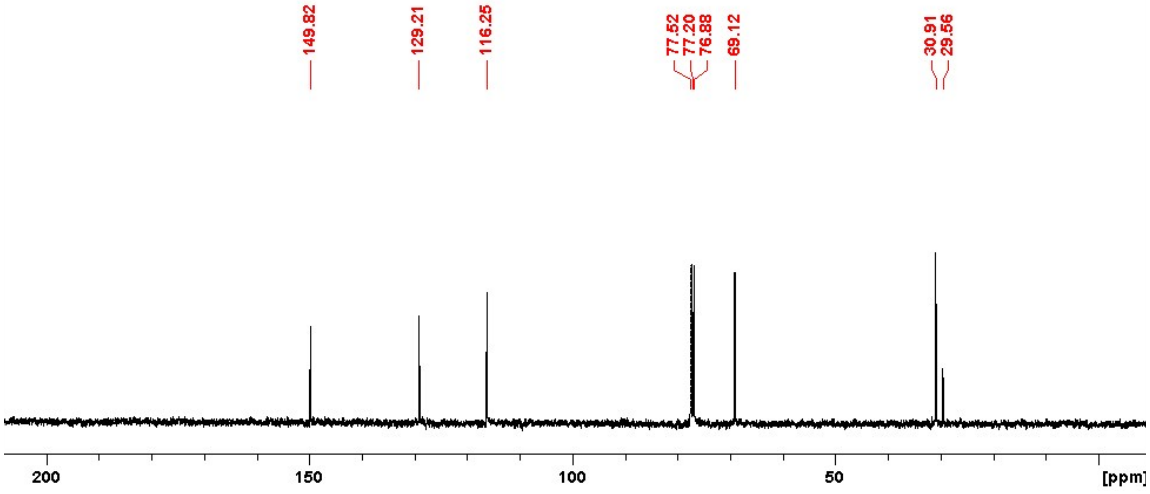


Figure S4. ^{13}C NMR spectrum of **I** in $CDCl_3$ (100 MHz).

Dodecabromoethoxypillar[6]arene (II). Compound **II** was synthesized and characterized according to the reported procedure.[7] ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78 (s, Ar*H*, 12H), 4.16 (t, *J* = 6.2 Hz, ArOC*H*$_2$CH$_2$Br, 24H), 3.86 (s, ArC*H*$_2$Ar, 12H), 3.55 (t, *J* = 6.2 Hz, ArOCH$_2$C*H*$_2$Br, 24H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.3, 128.6, 115.9, 69.1, 30.7, 30.4 ppm. HRMS: m/z calcd. for $C_{66}H_{72}O_{12}Br_{12}$ $[M+Na]^+$ 2038.4999, found 2038.5018.

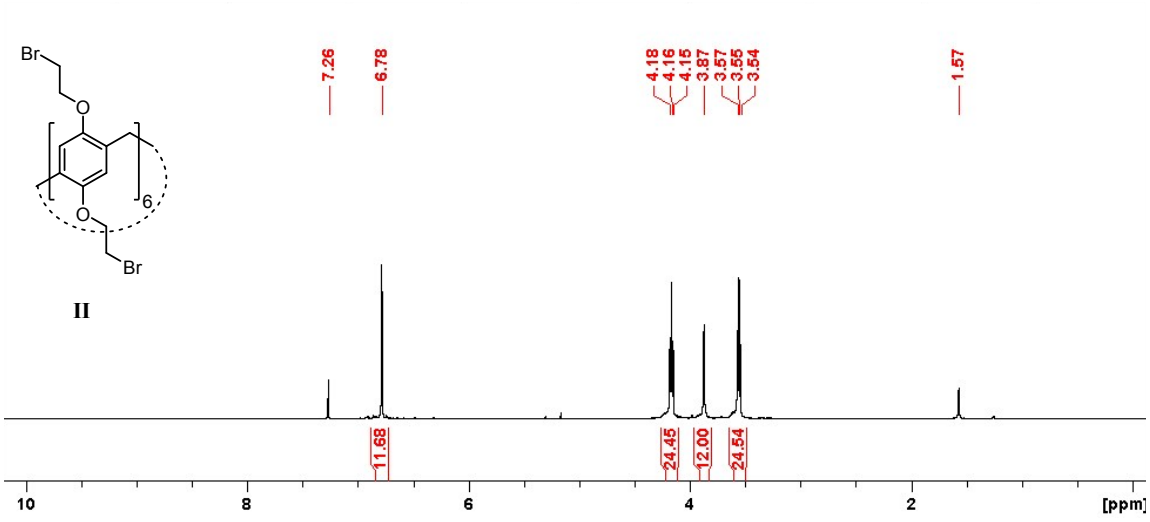


Figure S5. ^{1}H NMR spectrum of **II** in $CDCl_3$ (500 MHz).

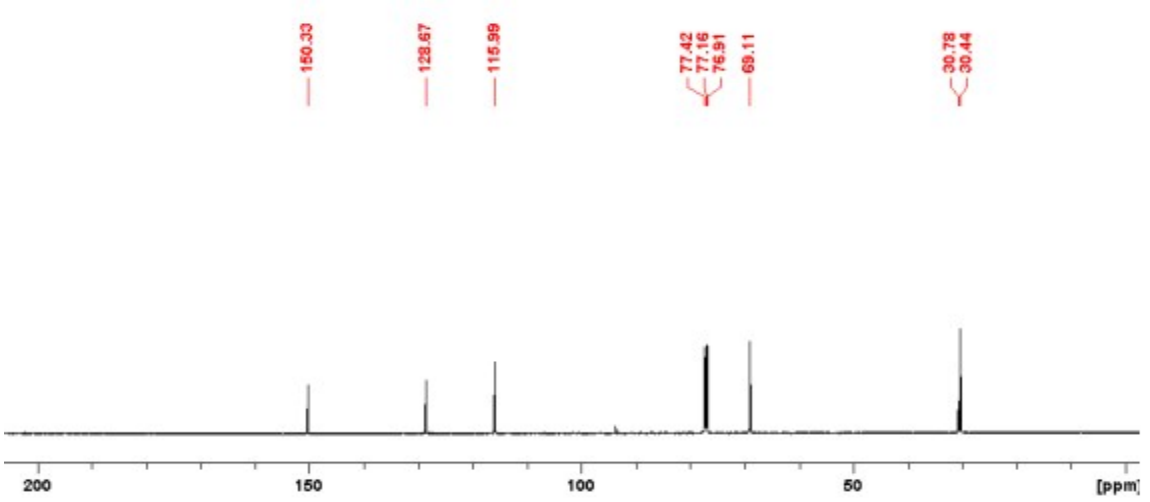
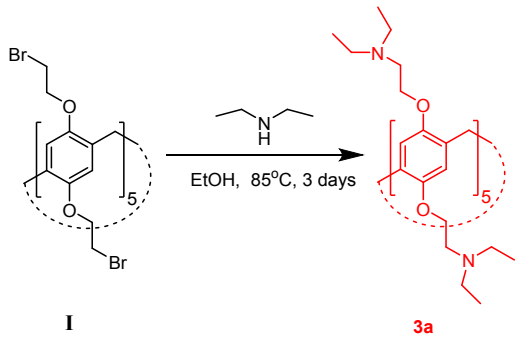


Figure S6. ^{13}C NMR spectrum of **II** in $CDCl_3$ (125 MHz).



Deca(diethylaminoethoxy)pillar[5]arene (3a). Compound **3a** was synthesized and characterized according to reported procedure.[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (s, Ar*H*, 10H), 4.06 (m, ArOC*H*HCH$_2$N, 10H), 3.88 (m, ArOCH*H*CH$_2$N, 10H) 3.74 (s,

ArCH_2Ar, 10H), 2.91 (m, ArOCH_2CH_2N, 20H), 2.63 (q, J =7.1 Hz, NCH_2CH$_3$, 40H), 1.05 (t, J =7.1 Hz, 60H) ppm.

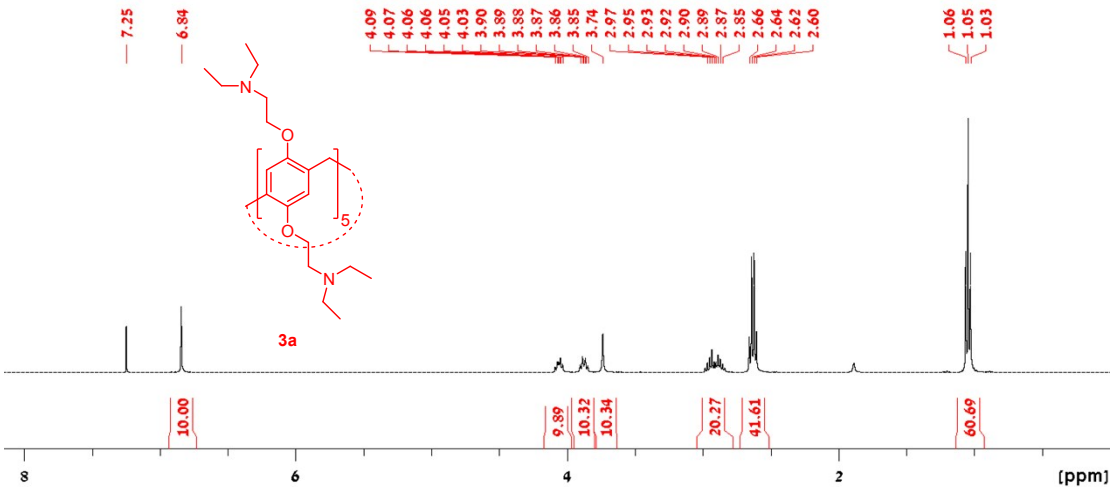
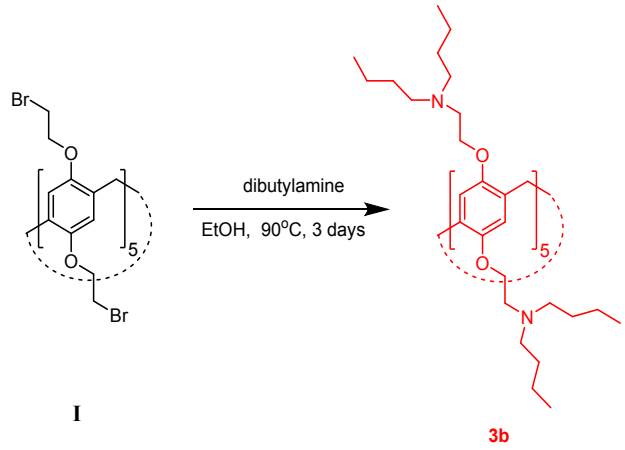


Figure S7. ^{1}H NMR spectrum of **3a** in $CDCl_3$ (400 MHz).



Deca(dibutylaminoethoxy)pillar[5]arene (3b).[2] Dibutylamine (2.43 mL, 14.40 mmol) was added to a solution of decabromoethylpillar[5]arene (**I**) (0.87 g, 0.52 mmol) in ethanol (5.5 mL). The resulting mixture was heated to 90°C in a pressure tube for 3 days. After cooling to 25°C, the solvent was removed under reduced pressure to obtain an orange powder. A saturated K_2CO_3 aqueous solution (4 mL) was added to the residue and the turbid mixture was stirred for 1h. The product was extracted with ethyl acetate (30 mL), and washed with brine. The organic phase was dried with magnesium sulfate and evaporated to afford an orange solid. The crude product was purified by column chromatography (silica gel; gradient 10% NH_4OH in methanol / chloroform) to afford **3b** as an orange dense oil (280 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, ArH,

10H), 4.04 (m, ArOC*H*HCH$_2$N, 10H), 3.91 (m, ArOCH*H*CH$_2$N, 10H), 3.75 (s, ArC*H*$_2$Ar, 10H), 2.97 (m, ArOCH$_2$C*H*HN, 10H), 2.86 (m, ArOCH$_2$CH*H*N, 10H), 2.54 (t, *J* = 7.4 Hz, NC*H*$_2$(CH$_2$)$_2$CH$_3$, 40H), 1.44 (m, NCH$_2$C*H*$_2$CH$_2$CH$_3$, 40H), 1.28 (sex, *J* = 7.3 Hz, N(CH$_2$)$_2$C*H*$_2$CH$_3$, 40H), 0.87 (t, *J* = 7.2 Hz, N(CH$_2$)$_3$C*H*$_3$, 60H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 149.8, 128.5, 114.8, 67.2, 54.9, 53.6, 29.8, 29.4, 20.8, 14.2 ppm. MS: m/z Calcd. for C$_{135}$H$_{241}$O$_{10}$N$_{10}$ [M+H]$^+$ 2162.8657, found 2162.8635.

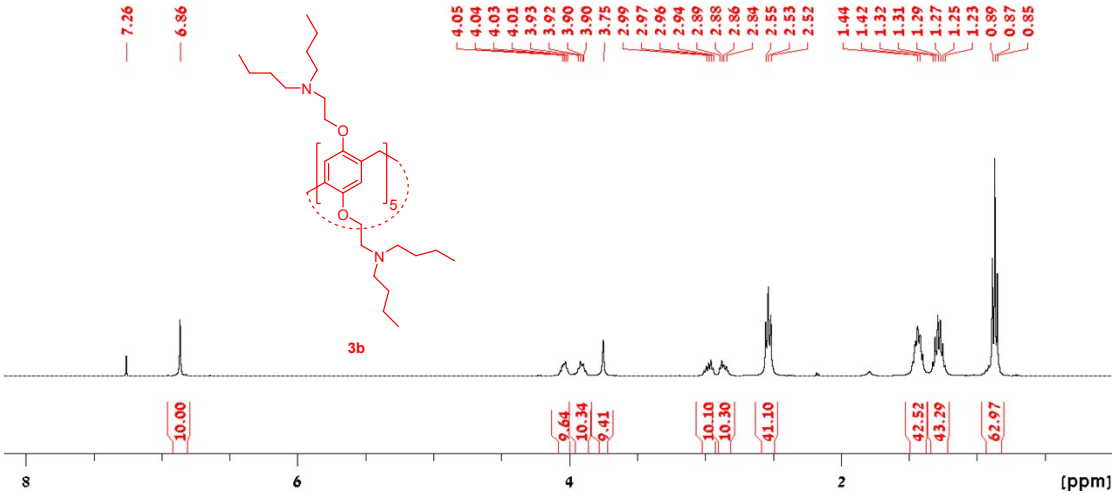


Figure S8. ^{1}H NMR spectra of **3b** in CDCl$_3$ (400 MHz)

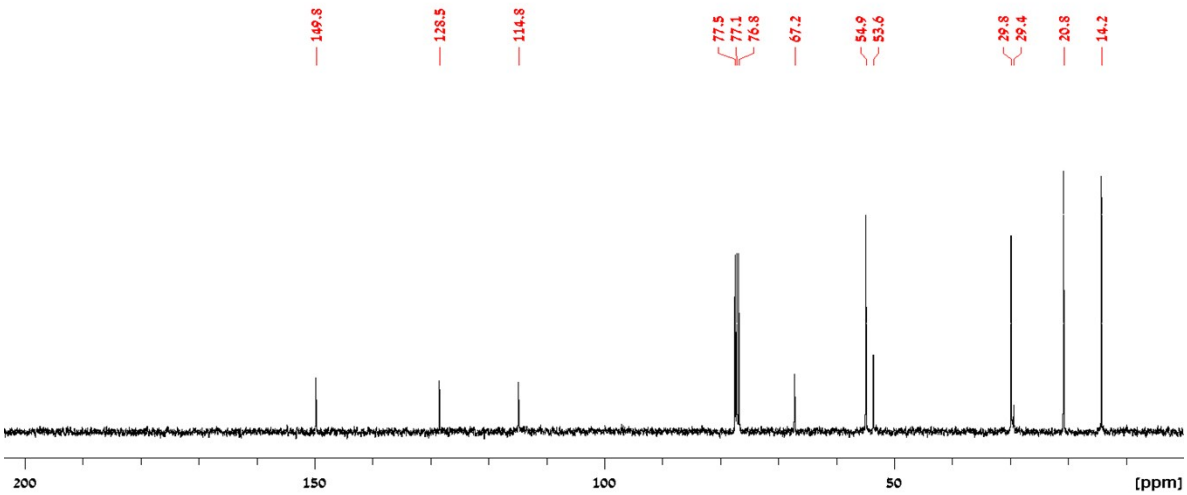
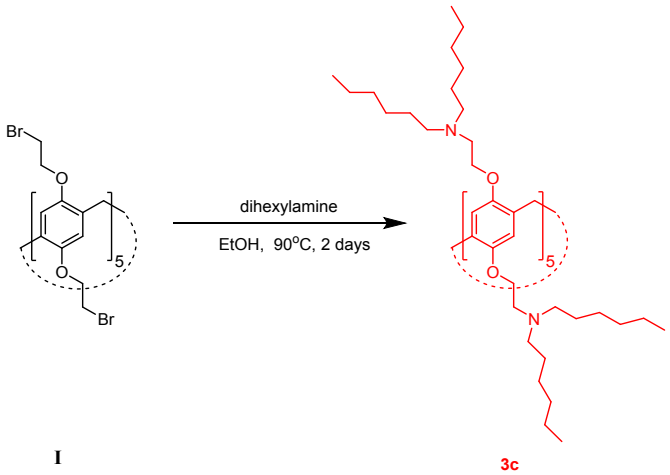


Figure S9. ^{13}C NMR spectra of **3b** in CDCl$_3$ (100 MHz)



I 3c

Deca(dihexylaminoethoxy)pillar[5]arene (3c).[2] Dihexylamine (5.5 mL, 23.8 mmol) was added to a solution of decabromoethylpillar[5]arene (**I**) (0.8 g, 0.48 mmol) in ethanol (10 mL). The resulting mixture was heated to 90°C in a pressure tube for 2 days. After cooling to 25°C, the solvent was removed under reduced pressure, and a NaOH solution (5.5M, 4.5 mL) was added to the residue before the turbid mixture was stirred for 1h. The product was extracted with ethyl acetate (25 mL), and washed with water. The organic phase was evaporated to afford a yellow liquid. The product was purified by trituration with methanol to afford **3c** as a yellow dense oil (984 mg, 75.2 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87 (s, Ar*H*, 10H), 3.96 (br, ArOCH_2CH$_2$N, 20H), 3.74 (s, ArCH_2Ar, 10H), 2.99 (m, ArOCH$_2$C*H*HN, 10H), 2.83 (m, ArOCH$_2$CH*H*N, 10H), 2.52 (t, *J* =7.4 Hz, NCH_2(CH$_2$)$_4$CH$_3$, 40H), 1.42 (m, NCH$_2$CH_2(CH$_2$)$_3$CH$_3$, 40H), 1.19 (m, N(CH$_2$)$_2$CH_2(CH$_2$)$_2$CH$_3$ & N(CH$_2$)$_3$CH_2CH$_2$CH$_3$ & N(CH$_2$)$_4$CH_2CH$_3$, 120H), 0.82 (t, *J* = 6.7 Hz, N(CH$_2$)$_5$CH_3, 60H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 128.3, 114.5, 67.1, 55.2, 53.5, 32.0, 29.4, 27.5, 27.4, 22.8, 14.2 ppm. MS: m/z Calcd. for $C_{175}H_{321}O_{10}N_{10}$ $[M+H]^+$ 2723.4917, found 2723.4912.

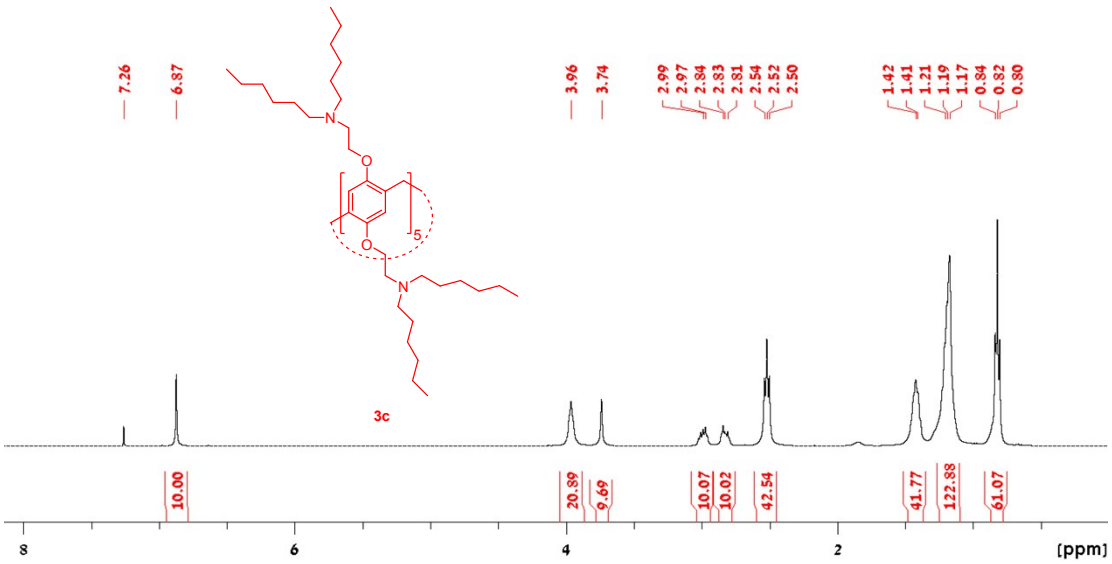


Figure S10. ^{1}H NMR spectra of **3c** in $CDCl_3$ (400 MHz)

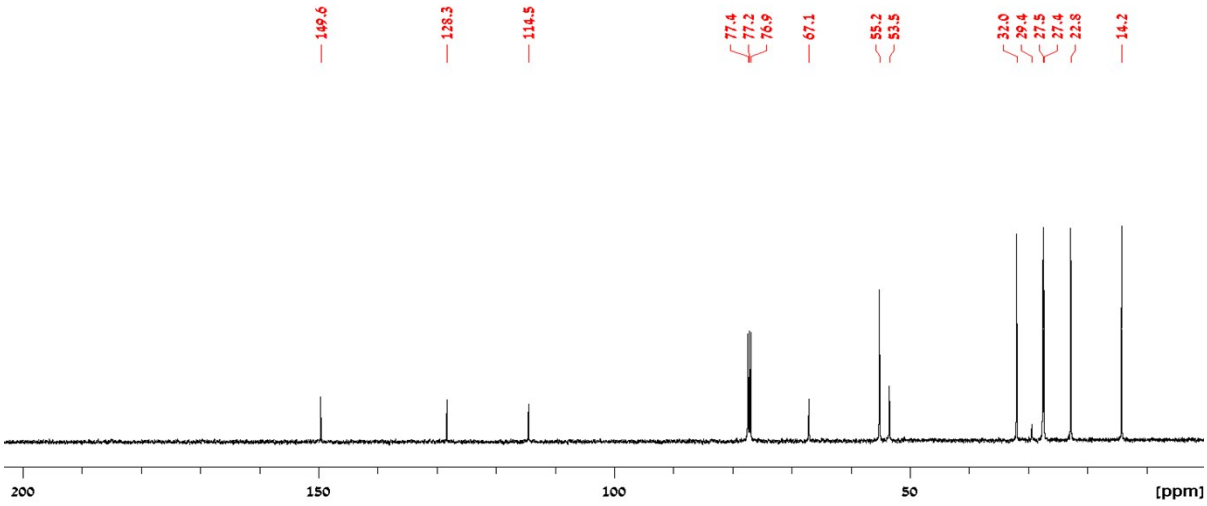
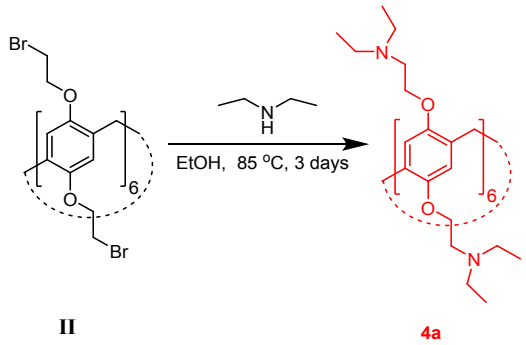


Figure S11. ^{13}C NMR spectra of **3c** in $CDCl_3$ (125 MHz)



II **4a**

Dodeca(diethylaminoethyl)pillar[6]arene (4a).[2] Diethylamine (4.2 mL, 40.6 mmol) was added to a solution of Dodecabromoethylpillar[6]arene **II** (700 mg, 0.35 mmol) in ethanol (5 mL) under vigorous stirring. The mixture was refluxed for 3 days. After cooling to 25°C, the solution was evaporated to obtain an orange powder. A saturated $K_2CO_{3(aq)}$ (10 mL) was then added to the residue and the turbid solution was stirred. The product was extracted with ethyl acetate (3 × 50 mL), and the organic phase was evaporated to give an orange oil. The product was purified by column chromatography (silica gel; gradient 10% NH_4OH in methanol/ chloroform) to afford **4a** as a yellow oil (0.54 g, 80%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.75 (s, Ar*H*, 12H), 3.87 (t, *J*=6.3 Hz, ArO*CH*$_2$CH$_2$, 24H), 3.77 (s, ArC*H*$_2$Ar, 12H), 2.77 (t, *J*=6.3 Hz, ArOCH$_2$*CH*$_2$N, 24H), 2.53 (q, *J*=7.1 Hz, N*CH*$_2$CH$_3$, 48H), 0.98 (s, NCH$_2$*CH*$_3$, 72H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 150.5, 128.1, 115.3, 67.5, 52.3, 47.9, 30.8, 12.3 ppm. HRMS: m/z Calcd. for $C_{114}H_{193}O_{12}N_{12}$ $[M+H]^+$ 1922.4861, found 1922.4849.

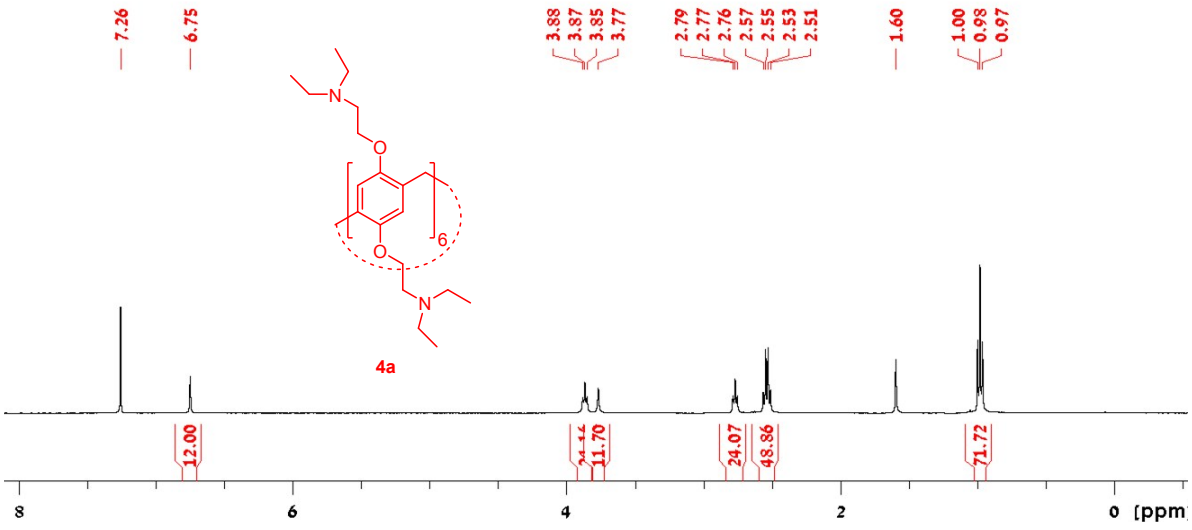


Figure S12. ^{1}H NMR spectrum of **4a** in $CDCl_3$ (400 MHz).

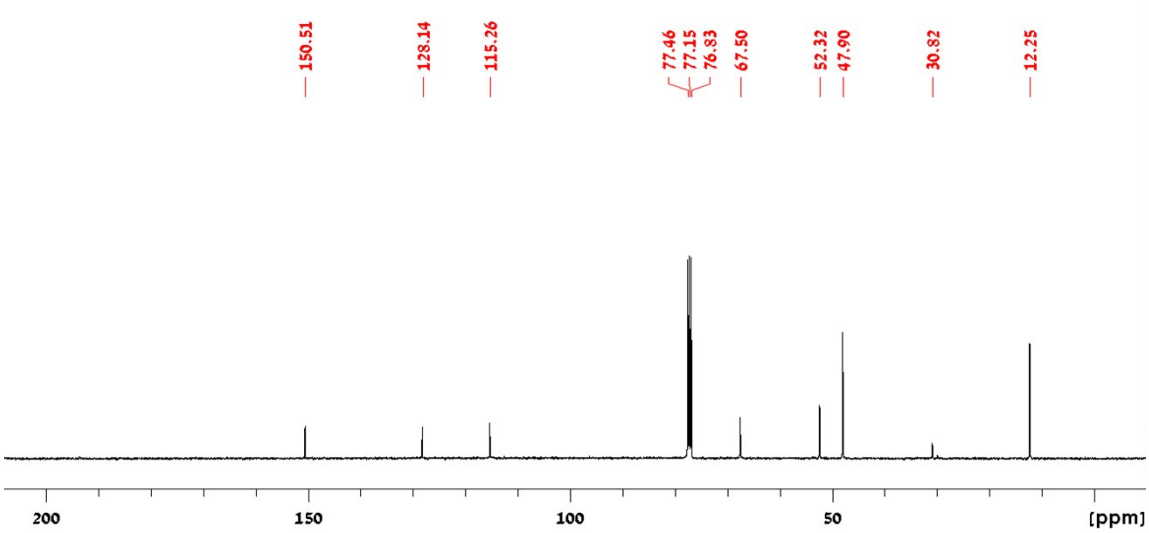
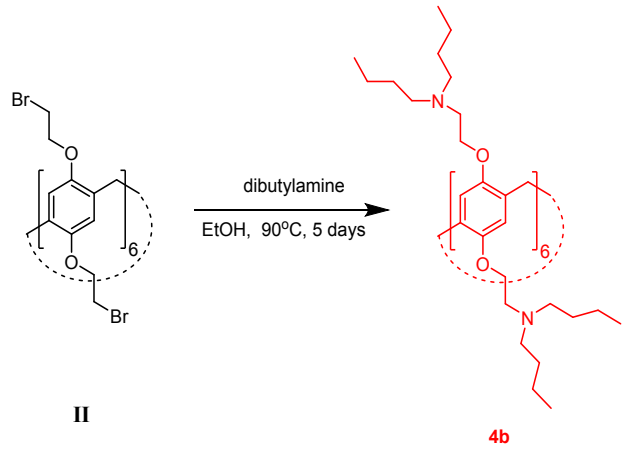


Figure S13. ^{13}C NMR spectrum of **4a** in $CDCl_3$ (100 MHz).



II **4b**

Deca(dibutylaminoethoxy)pillar[6]arene (4b). Dibutylamine (6.0 mL, 35.40 mmol) was added to a solution of decabromoethylpillar[6]arene **II** (550 mg, 0.25 mmol) in ethanol (3 mL). The resulting mixture was heated to 90°C in a pressure tube for 5 days. After cooling to 25°C, the solvent was removed under reduced pressure to obtain an orange powder. A saturated K_2CO_3 aqueous solution (4 mL) was added to the residue and the turbid mixture was stirred for 1h. The product was extracted with ethyl acetate (30 mL), and washed with brine. The organic phase was dried with magnesium sulfate and evaporated to afford an orange solid. The crude product was purified by column chromatography (silica gel; gradient 10% NH_4OH in methanol / chloroform) to afford **4b** as an orange dense oil (530 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78 (s, Ar*H*, 12H), 3.89 (t, *J* = 5.0 Hz, $ArOC\mathit{H}_2CH_2N$, 12H), 3.76 (s, $ArC\mathit{H}_2Ar$, 12H), 2.82 (t, *J* = 6.0 Hz, $ArOCH_2C\mathit{H}_2N$, 12H), 2.49 (t, *J* = 7.4 Hz, $NC\mathit{H}_2(CH_2)_2CH_3$, 48H), 1.41 (m, $NCH_2C\mathit{H}_2CH_2CH_3$, 48H), 1.29 (m, $N(CH_2)_2C\mathit{H}_2CH_3$, 48H), 0.89 (t, *J* = 7.3 Hz,

$N(CH_2)_3CH_3$, 72H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4, 127.9, 115.0, 67.4, 54.7, 53.6, 30.9, 29.8, 20.8, 14.3 ppm. MS: m/z Calcd. for $C_{162}H_{289}O_{12}N_{12}$ $[M+H]^+$ 2595.2373, found 2595.2397.

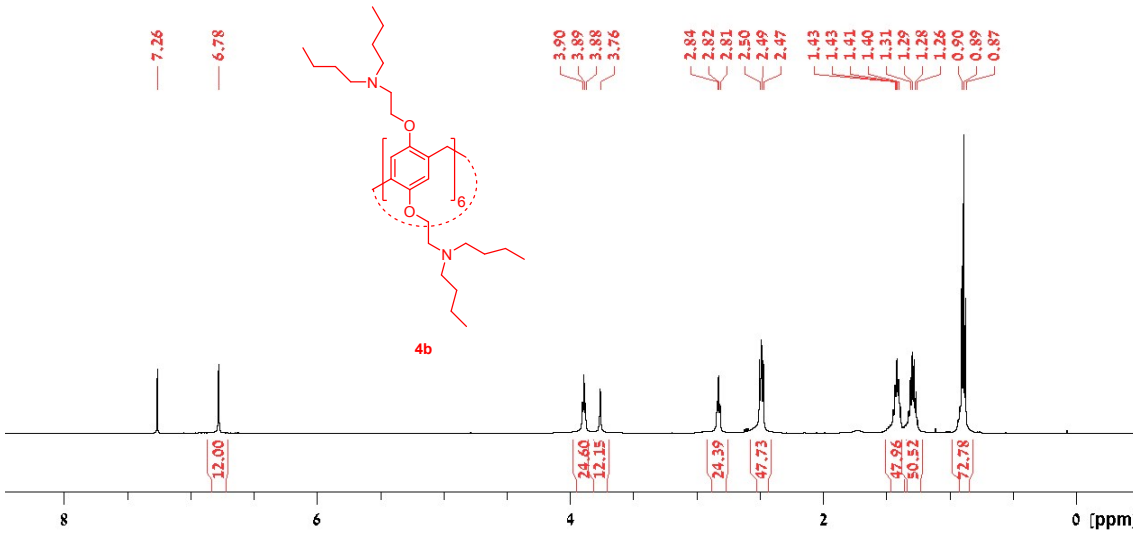


Figure S14. ^1H NMR spectra of **4b** in $CDCl_3$ (500 MHz)

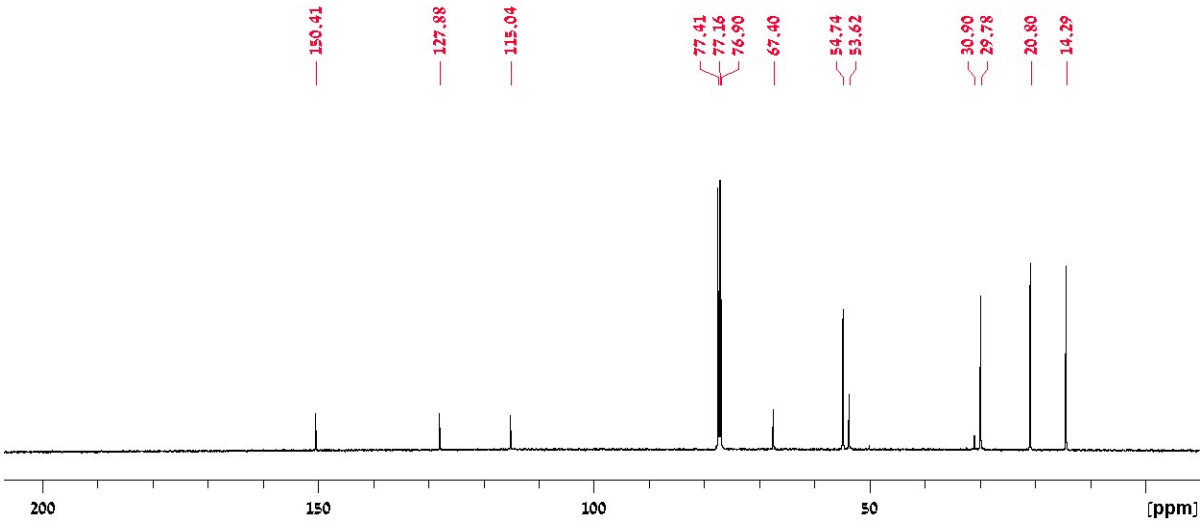
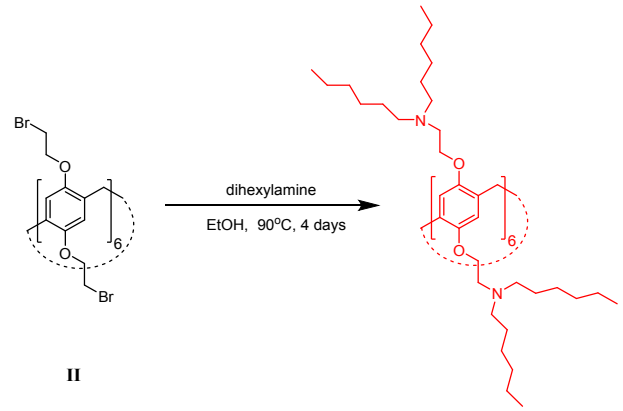


Figure S15. ^{13}C NMR spectra of **4b** in $CDCl_3$ (125 MHz)



II

4c

Deca(dihexylaminoethoxy)pillar[6]arene (4c). Dihexylamine (7 mL, 30.0 mmol) was added to a solution of decabromoethylpillar[6]arene **II** (500 mg, 0.25 mmol) in ethanol (10 mL). The resulting mixture was heated to 90°C in a pressure tube for 4 days. After cooling to 25°C, the solvent was removed under reduced pressure, and a NaOH solution (0.2M, 10 mL) was added to the residue before the turbid mixture was stirred for 1h. The product was extracted with ethyl acetate (10 mL), and washed with water. The organic phase was evaporated to afford a yellow liquid. The product was purified by trituration with methanol to afford **4c** as a yellow dense oil (387 mg, 48 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.75 (s, Ar*H*, 12H), 3.88 (t, *J* = 5.8 Hz, $ArOC\mathit{H}_2CH_2N$, 24H), 3.75 (s, $ArC\mathit{H}_2Ar$, 12H), 2.83 (t, *J* = 5.7 Hz, $ArOCH_2C\mathit{H}_2N$, 12H), 2.49 (t, *J* =7.5 Hz, $NC\mathit{H}_2(CH_2)_4CH_3$, 48H), 1.43 (m, $NCH_2C\mathit{H}_2(CH_2)_3CH_3$, 48H), 1.25 (m, $N(CH_2)_2C\mathit{H}_2(CH_2)_2CH_3$ & $N(CH_2)_3C\mathit{H}_2CH_2CH_3$ & $N(CH_2)_4C\mathit{H}_2CH_3$, 144H), 0.87 (t, *J* = 6.9 Hz, $N(CH_2)_5C\mathit{H}_3$, 72H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4, 127.8, 115.1, 67.4, 55.0, 53.7, 32.1, 31.1, 27.6, 27.4, 22.9, 14.2 ppm. MS: m/z Calcd. for $C_{210}H_{385}O_{12}N_{12}$ $[M+H]^+$ 3267.9885, found 3267.9839.

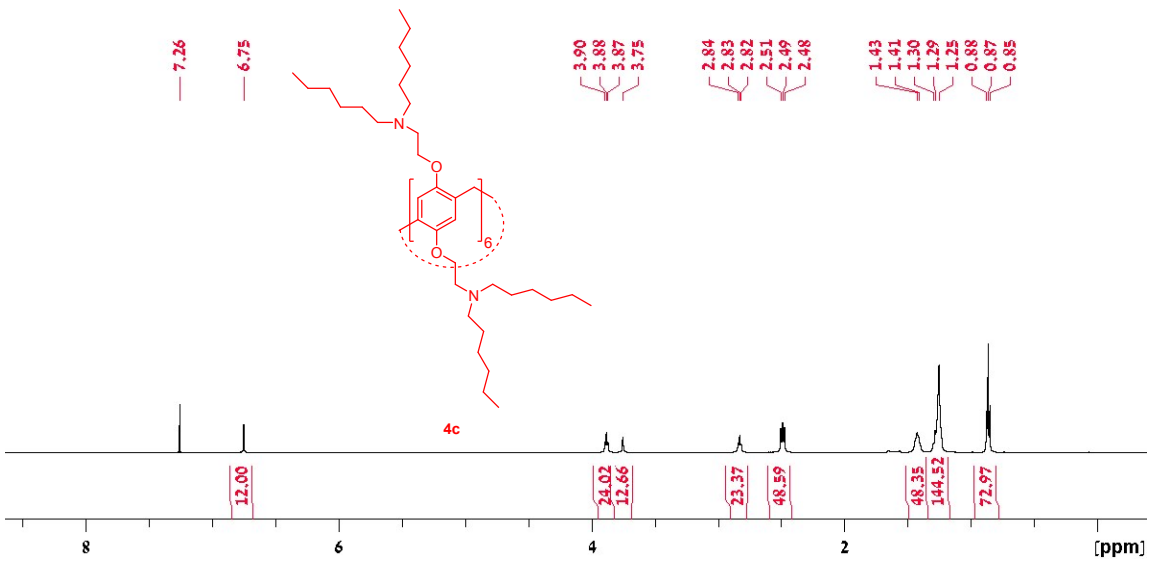


Figure S16. ^{1}H NMR spectra of **4c** in $CDCl_3$ (500 MHz)

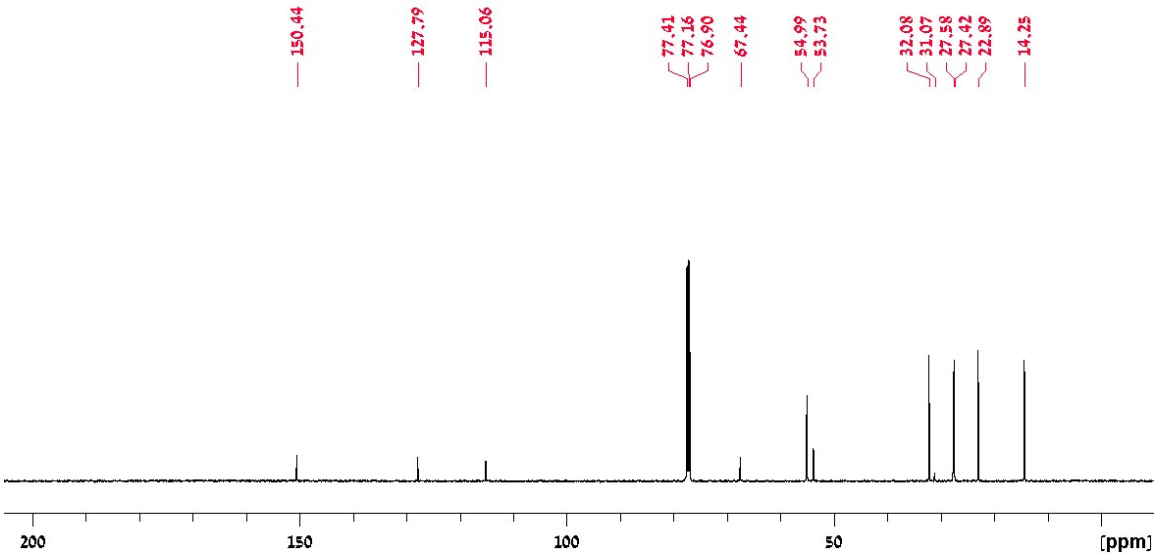


Figure S17. ^{13}C NMR spectra of **4c** in $CDCl_3$ (125 MHz)

3. Variable temperature measurements of 4b and 3a

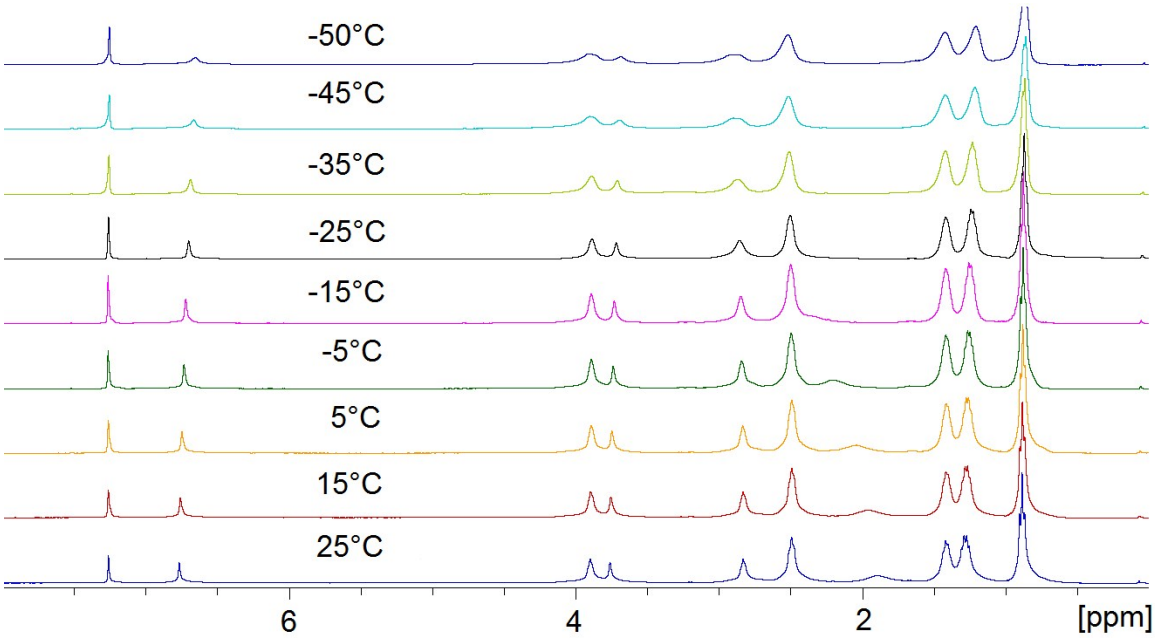


Figure S18. Temperatures controlled ^{1}H NMR spectra in $CDCl_3$ (500 MHz) of **4b**.

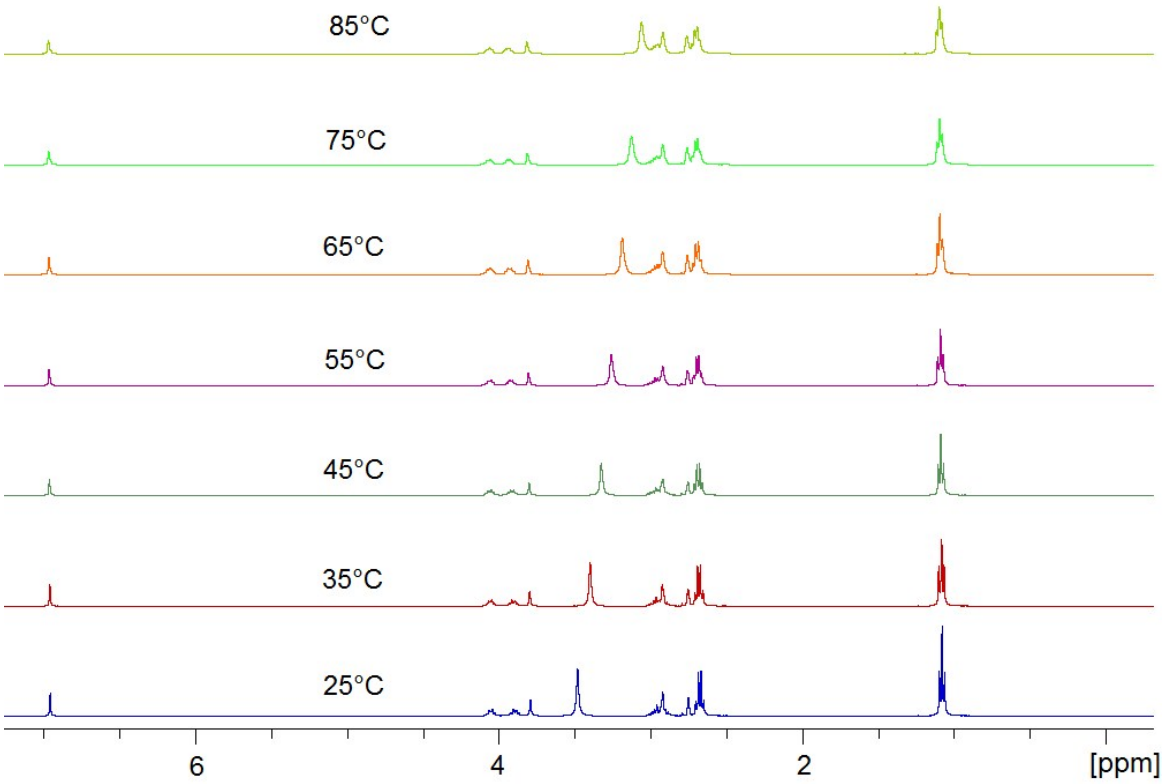


Figure S19. Temperatures controlled ^{1}H NMR spectra in DMF-*d7* (400 MHz) of **3a**.

4. Diffusion NMR

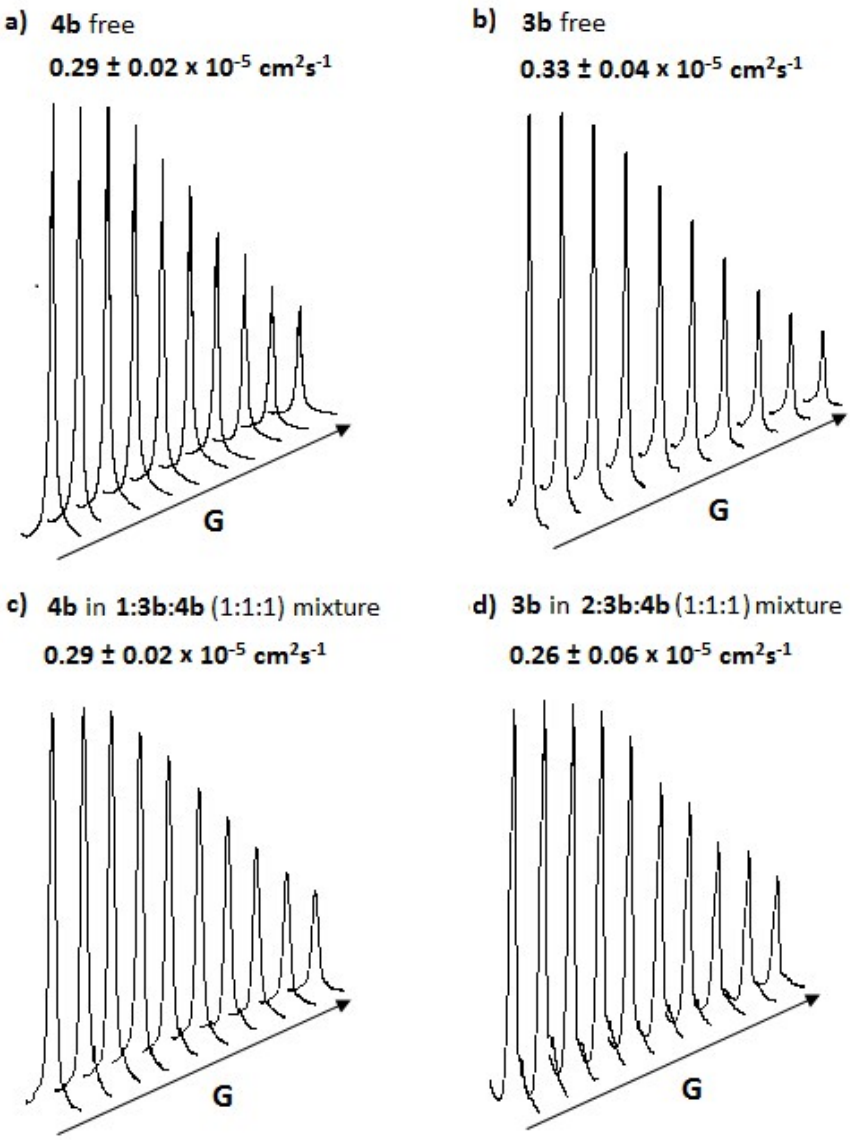


Figure S20. ^{1}H NMR signal decay as a function of the gradient strength (G) for 2.5 mM 10:1 $CDCl_3$-$DMSO_{d6}$ solutions, along the diffusion coefficients extracted, for (a) **4b**, (b) **3b**, (c) **4b** in the 1:1 mixture of **1**:**3b**, and (d) **3b** in the 1:1 mixture of **2**:**4b**.

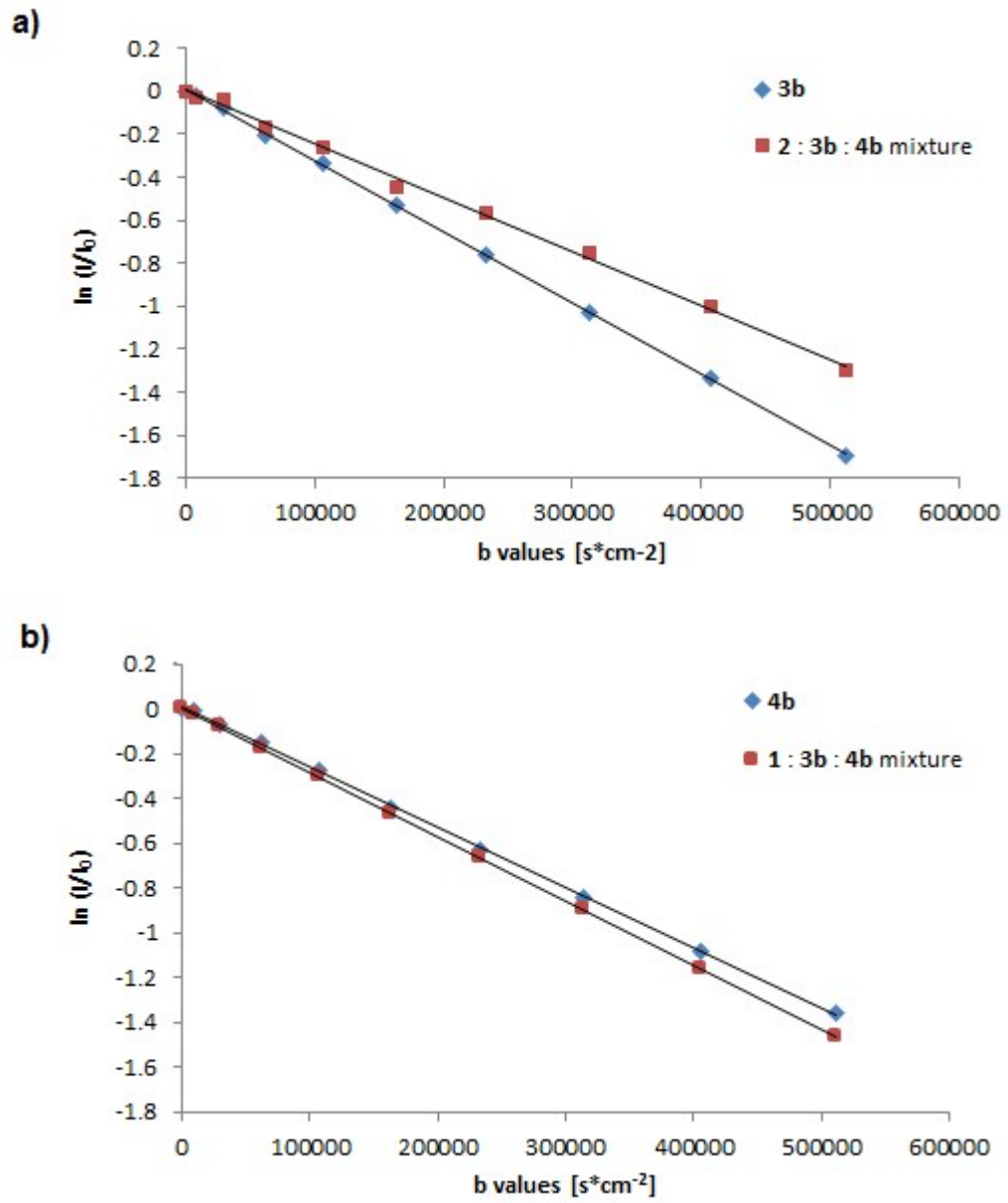


Figure S21. The natural log of the normalized signal decay (ln I/I_0) as a function of the b values ($b = -\gamma^2G^2\delta^2 2/\pi)^2(\Delta-\delta/4)$) for the experiments shown in Figure S20, for one representative peak of **3b** alone and in the 1:1 **2**:**4b** mixture (a) and of **4b** alone and in the 1:1 **1**:**3b** mixture (b).

5. ^{1}H-NMR spectra of three-component mixture

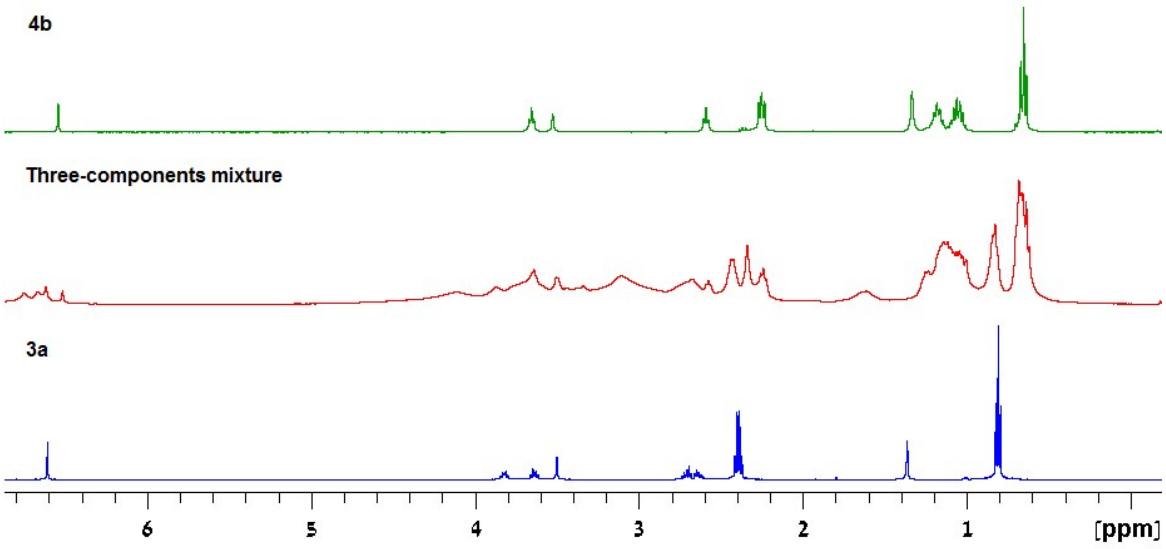


Figure S22. ^{1}H NMR spectra of **3a** (bottom), **4b** (upper) and the 1:1:1 three component mixture (solution) of **2**:**4b**:**3a** (middle) in $CDCl_3$-DMSO (9:1)

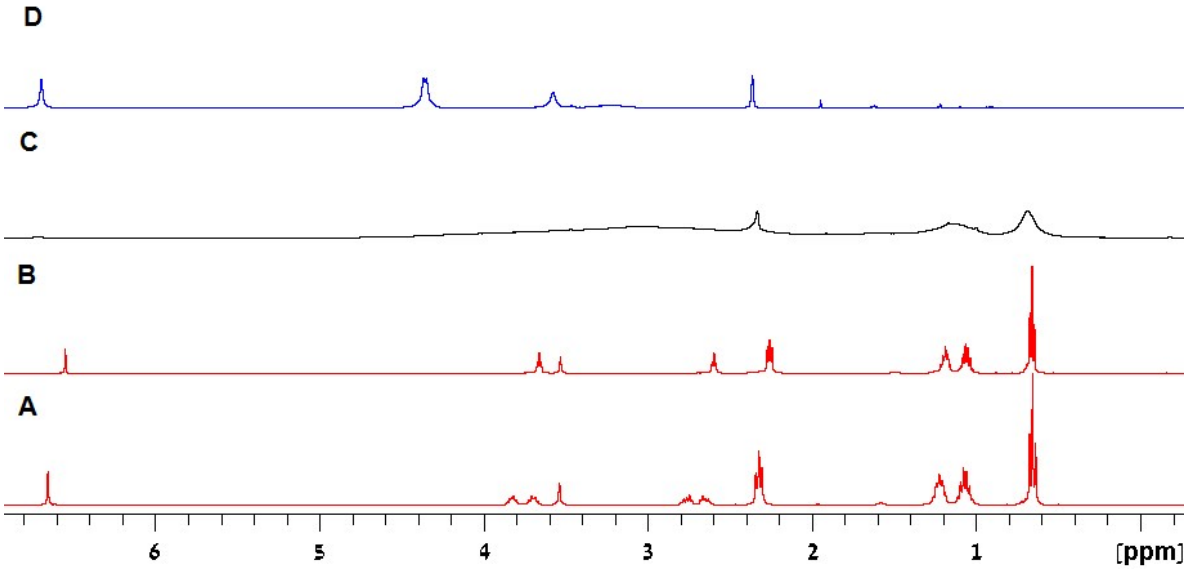


Figure S23. ^{1}H NMR spectra (3.8 mM, 298K, 400 MHz) of (A) **3b** in $CDCl_3$, (B) **4b** in $CDCl_3$, (C) a mixture of **2**, **3b**, **4b** (2 : 1 : 1) in $CDCl_3$-DMSO-d_6 (9:1) (gel with T_{gel} of 78°C and t_{gel} of about 12 hours, (D) **2** in DMSO-d_6.

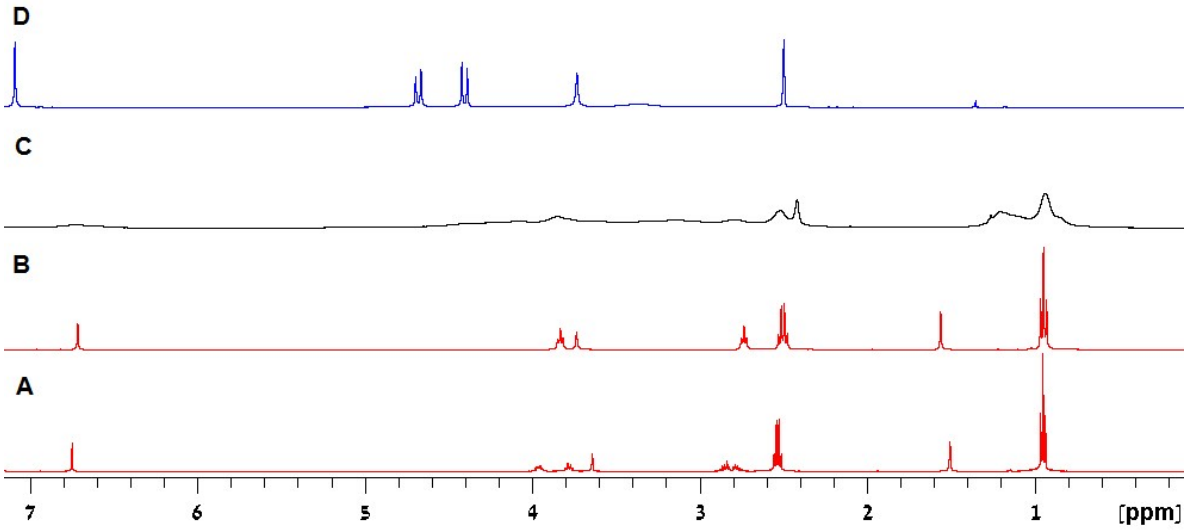


Figure S24. ^{1}H NMR spectra (3.8 mM, 298K, 400 MHz) of (A) **3a** in $CDCl_3$, (B) **4a** in $CDCl_3$, (C) a mixture of **1**, **3a**, **4a** (2 : 1 : 1) in $CDCl_3$-DMSO-d_6 (9:1) (gel with T_{gel} of 95°C and t_{gel} of few minutes) (D) **1** in DMSO-d_6.

6. ^{1}H NMR spectra of "four-component" gel

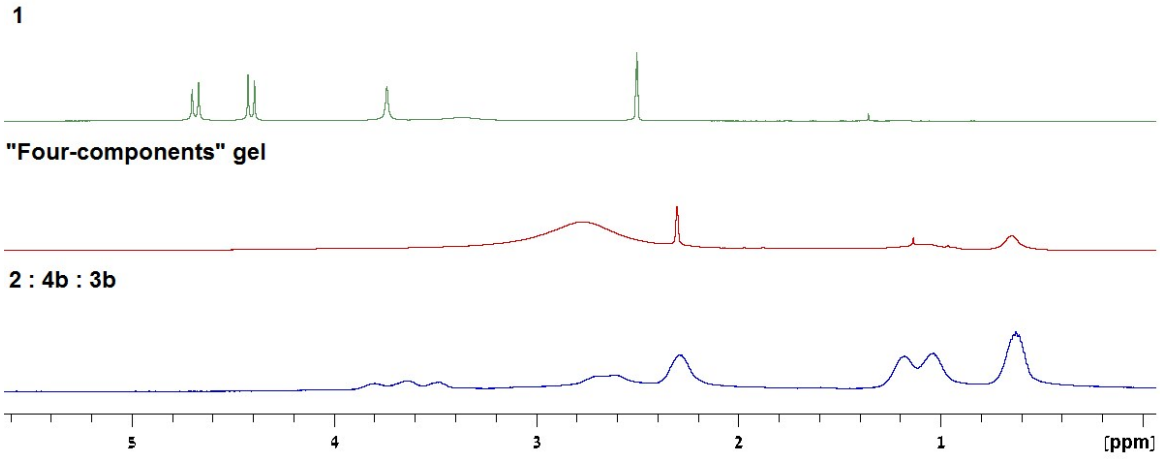


Figure S25. ^{1}H NMR spectra (3.8 mM, 298K, 500 MHz) of **1** DMSO-d_6 (top), a mixture of **2**, **3b**, **4b** in $CDCl_3$-DMSO-d_6 (9:1) (bottom) (solution), and a mixture of **1**, **2**, **3b**, **4b** in $CDCl_3$-DMSO-d_6 (9:1) (middle) (gel).

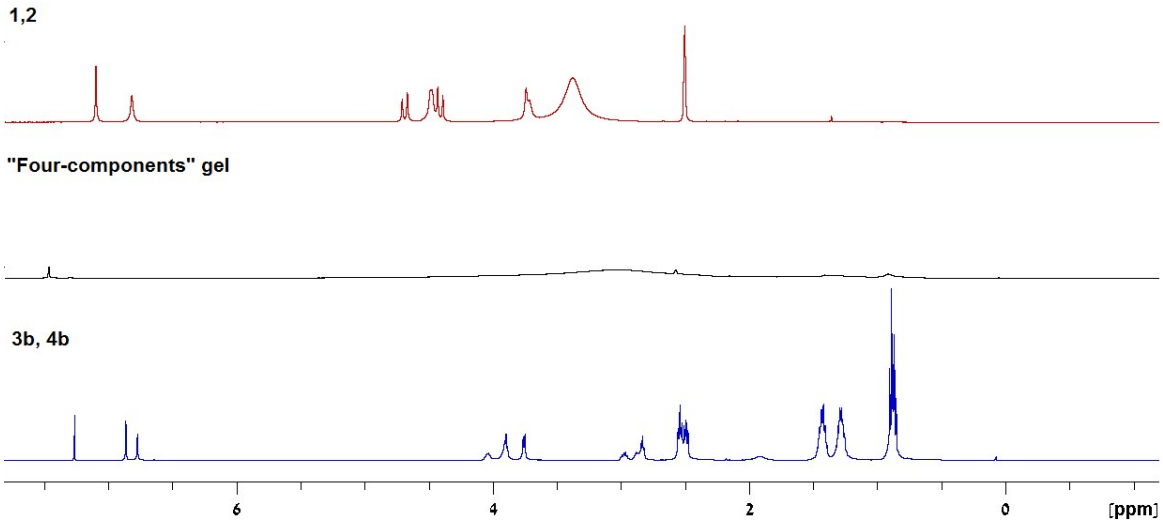


Figure S26. ^{1}H NMR spectra (3.8 mM, 298K, 500 MHz) of **1** and **2** in DMSO-d_6 (top) (solution), **3b** and **4b** in $CDCl_3$ (bottom) (solution), and a mixture of **1**, **2**, **3b**, **4b** in $CDCl_3$-DMSO-d_6 (9:1) (middle) (gel).

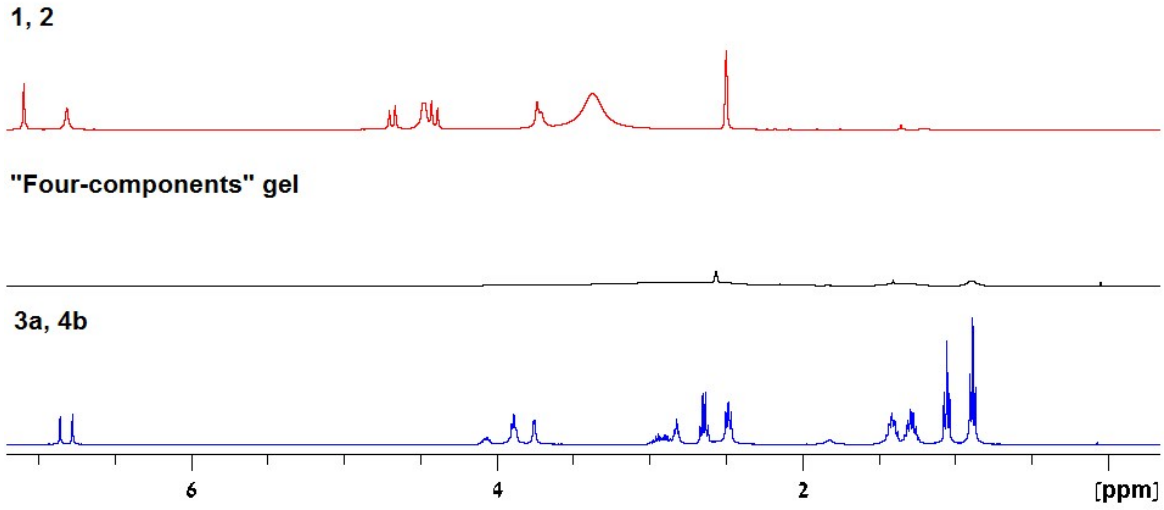


Figure S27. ^{1}H NMR spectra (3.8 mM, 298K, 500 MHz) of **1** and **2** in DMSO-d_6 (top) (solution), **3a** and **4b** in $CDCl_3$ (bottom) (solution), and a mixture of **1**, **2**, **3a**, **4b** in $CDCl_3$-DMSO-d_6 (10:1) (middle) (gel).

7. References.

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