

Amphiphilic pillar[5]arenes: chemical structure influence on self-assembly morphology and application in gas responsiveness and λ -DNA condensation

Yong Yao, Peifa Wei, Shiyu Yue, Jinying Li, and Min Xue *

Department of Chemistry,

Zhejiang University, Hangzhou 310027, P. R. China;

Email: xuemin@zju.edu.cn

Electronic Supplementary Information (28 pages)

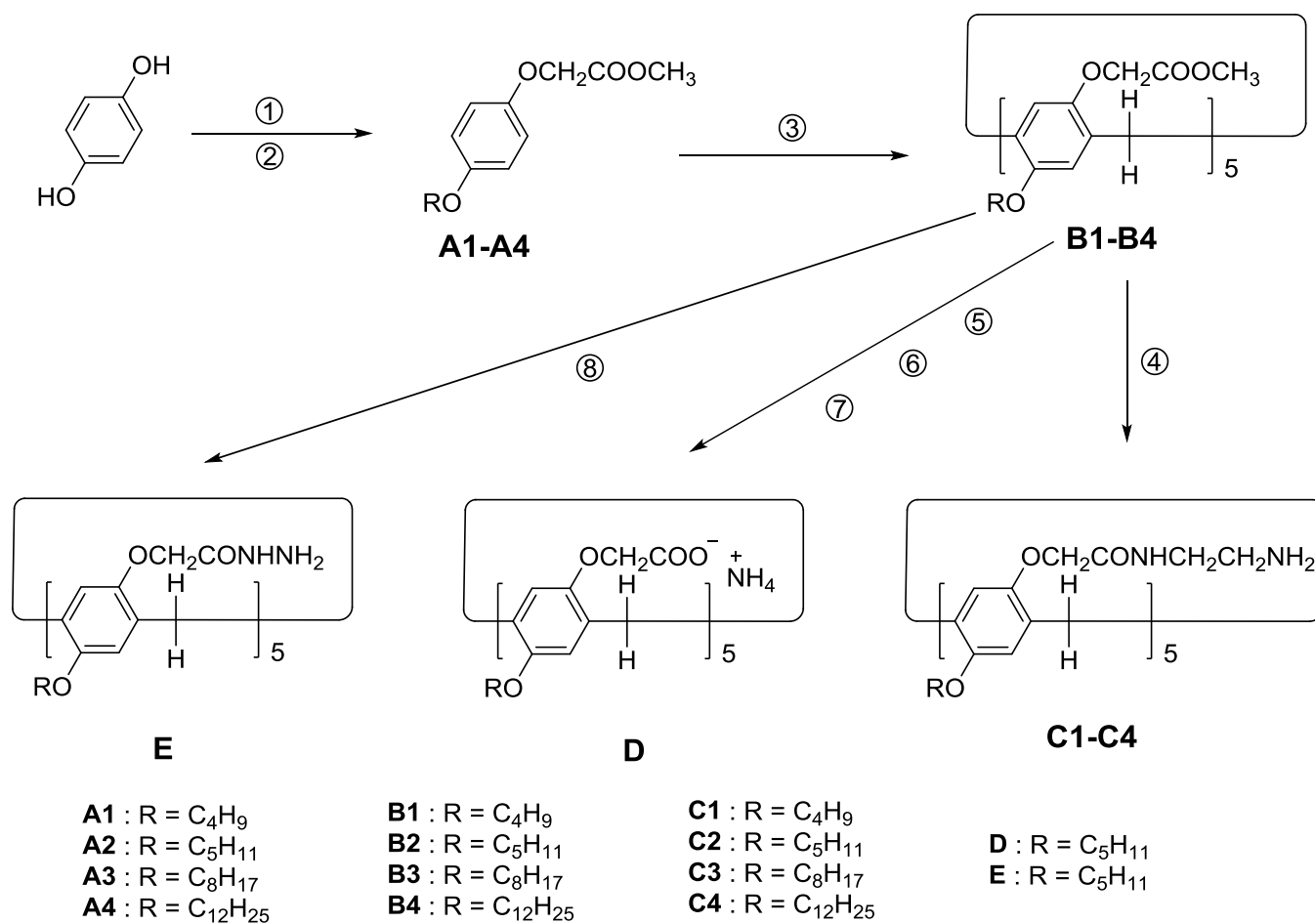
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1. *Materials and methods*

HCl, NaOH, hydroquinone, methyl chloroacetate, $\text{NH}_3 \cdot \text{H}_2\text{O}$, 1-bromobutane, hydrazine hydrate, 1-bromopentane, 1-bromoheptane, 1-bromododecane, ethanediamine, $\text{BF}_3 \cdot \text{Et}_2\text{O}$, trioxymethylene, $\text{ClCH}_2\text{CH}_2\text{Cl}$, CH_3CN were obtained from Beijing Chemical Reagents Co. All the chemicals involved in our experiments were of analytical grade and used as received. Amphiphilic pillar[5]arenes were synthesized according to our previous work. The TEM images were obtained using a Hitachi instrument with an accelerating voltage of 100 kV. The samples were prepared by drop-coating this solution on a carbon-coated copper grid. The ultrathin section of microtube was placed on copper grids coated with formvar. SEM was applied to investigate the morphology, which was carried out with a Hitachi S-4800 scanning electron microscope. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance DMX-400 spectrometer. Mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. Dynamic light scattering measurements were performed on a Nano-ZS ZEN3600 instrument. UV-Vis spectra were taken on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. FT-IR spectra were taken with potassium bromide pellets on a TENSOR 27 spectrometer. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.

2. Syntheses of amphiphilic pillar[5]arenes

Scheme S1. Synthetic route to amphiphilic pillar[5]arenes

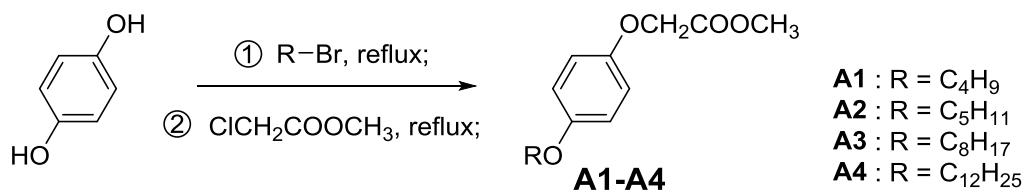


①. R-Br, reflux; ②. ClCH₂COOCH₃, reflux; ③. trioxymethylene, BF₃·Et₂O; ④. NH₂CH₂CH₂NH₂, reflux;

⑤. NaOH, H₂O, reflux; ⑥. HCl, filtration; ⑦. NH₃·H₂O; ⑧. NH₂NH₂·H₂O, reflux.

2.1. Syntheses of noncyclic monomers **A1–A4**

Scheme S2. Syntheses of compounds **A1–A4**



Anhydrous potassium carbonate (55.2 g, 400 mmol) was added to a solution of hydroquinone (44.0 g, 400 mmol) and alkyl bromide (400 mmol) in dry acetonitrile (500 mL) under vigorous stirring. The mixture was stirred at 80 °C for 24 hours under nitrogen atmosphere.^{S1} Then methyl chloroacetate (43.2 g, 400 mmol) and additional anhydrous potassium carbonate (55.2 g, 400 mmol) were added into the reaction mixture. The mixture was stirred for another 24 hours. After removal of the inorganic salt by filtration, the solvent was evaporated and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, *v/v* 10:1) to give **A1–A4** as white solids (43%–51%).

A1: Mp: 79.2–77.9 °C. The proton NMR spectrum of **A1** is shown in Figure S1. ¹H NMR (400 MHz, chloroform-*d*, 293K) δ (ppm): 6.86–6.80 (m, 4H), 4.58 (s, 2H), 3.90 (t, *J* = 6.0 Hz, 2H), 3.79 (s, 3H), 1.77–1.70 (m, 2H), 1.50–1.43 (m, 2H), 0.92 (t, *J* = 6.0 Hz, 3H). The ¹³C NMR spectrum of **A1** is shown in Figure S2. ¹³C NMR (100 MHz, chloroform-*d*, 293K) δ (ppm): 169.70, 154.17, 151.86, 115.83, 115.40, 68.23, 66.27, 52.16, 31.40, 19.24, 13.85. LRESIMS is shown in Figure S7: *m/z* 261.0 [**A1** + Na]⁺. HRESIMS: *m/z* calcd for [**A1** + Na]⁺ C₁₃H₁₈NaO₄, 261.1103; found 261.1103; error 0 ppm.

The characterization data of **A2** were reported in our previous work.^{S1}

A3: Mp: 74.8–74.1 °C. The proton NMR spectrum of **A3** is shown in Figure S3. ¹H NMR (400 MHz, chloroform-*d*, 293K) δ (ppm): 6.86–6.81 (m, 4H), 4.58 (s, 2H), 3.89 (t, *J* = 6.0 Hz, 2H), 3.80 (s, 3H), 1.78–1.71 (m, 2H), 1.42–1.28 (m, 10H), 0.88 (t, *J* = 6.0 Hz, 3H). The ¹³C NMR spectrum of **A3** is shown in Figure S4. ¹³C NMR (100 MHz, chloroform-*d*, 293K) δ (ppm): 169.71, 154.17, 151.86, 115.83, 115.41, 68.57, 66.29, 52.18, 31.81, 29.36, 29.34, 29.24, 26.05, 22.65, 14.09. LRESIMS is shown in Figure S8: *m/z* 316.9 [**A3** + Na]⁺. HRESIMS: *m/z* calcd for [**A3** + Na]⁺ C₁₇H₂₆NaO₄, 317.1729; found 317.1731; error 0.6 ppm.

A4: Mp: 70.1–69.3 °C. The proton NMR spectrum of **A4** is shown in Figure S5. ¹H NMR (400 MHz, chloroform-*d*, 293K) δ (ppm): 6.86–6.81 (m, 4H), 4.58 (s, 2H), 3.93 (t, *J* = 6.0 Hz, 2H), 3.80 (s, 3H), 1.78–1.71 (m, 2H), 1.41–1.26 (m, 18H), 0.88 (t, *J* = 6.0 Hz, 3H). The ¹³C NMR spectrum of **A4** is shown in Figure S6. ¹³C NMR (100 MHz, chloroform-*d*, 293K) δ (ppm): 169.72, 154.18, 151.86, 115.84, 115.42, 68.59, 66.30, 52.20, 29.63,

29.60, 29.58, 29.41, 29.35, 26.05, 22.69, 14.12. LRESIMS is shown in Figure S9: m/z 373.2 [**A4** + Na]⁺.

HRESIMS: m/z calcd for [**A4** + Na]⁺ C₁₇H₂₆NaO₄, 373.2455; found 373.2478; error 6 ppm.

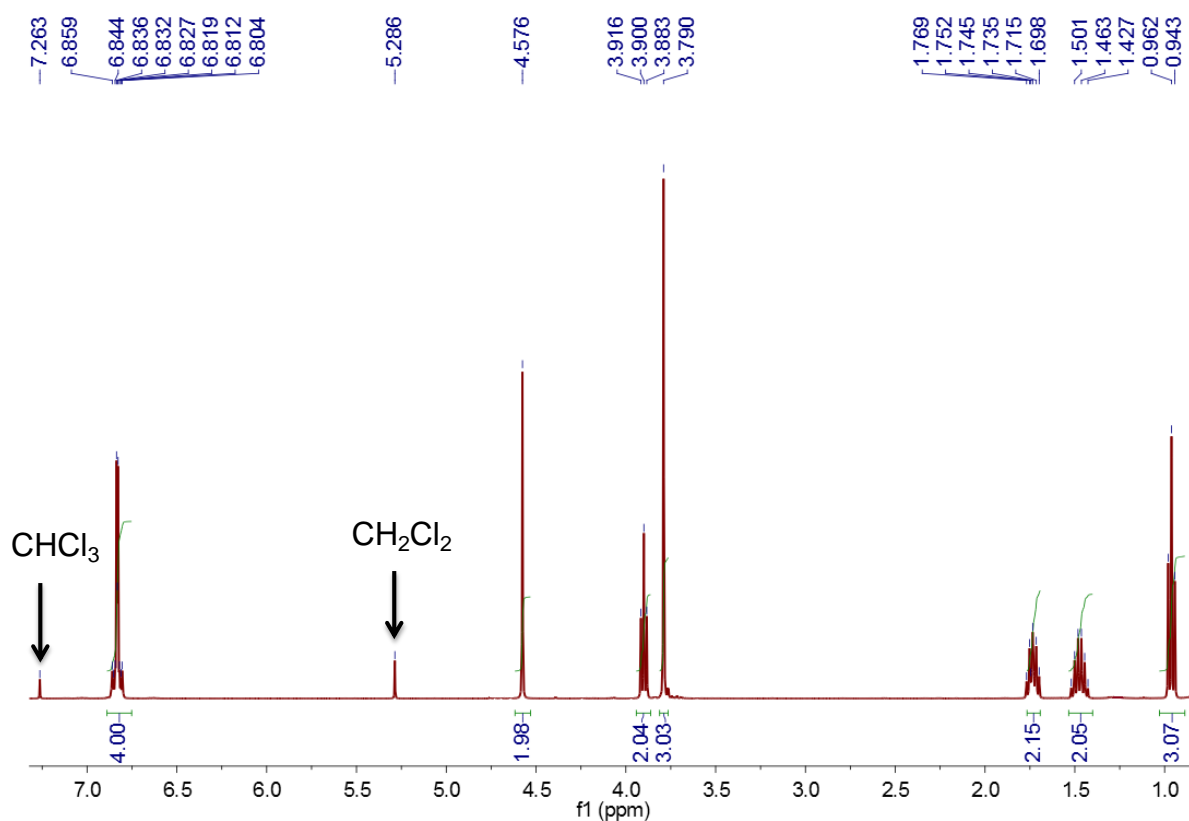


Fig. S1 ¹H NMR spectrum (400 MHz, CDCl₃, 293 K) of monomer **A1**.

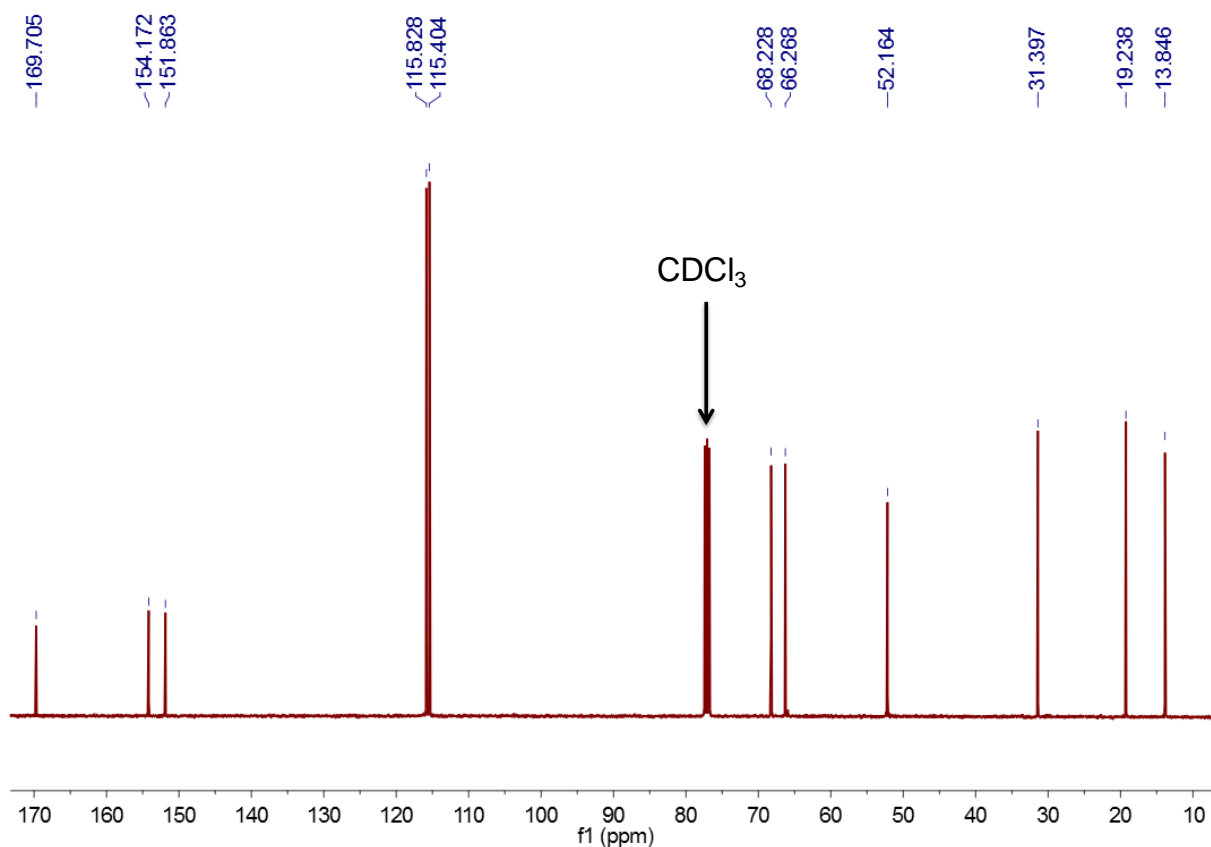


Fig. S2 ^{13}C NMR spectrum (100 MHz, CDCl₃, 293 K) of monomer A1.

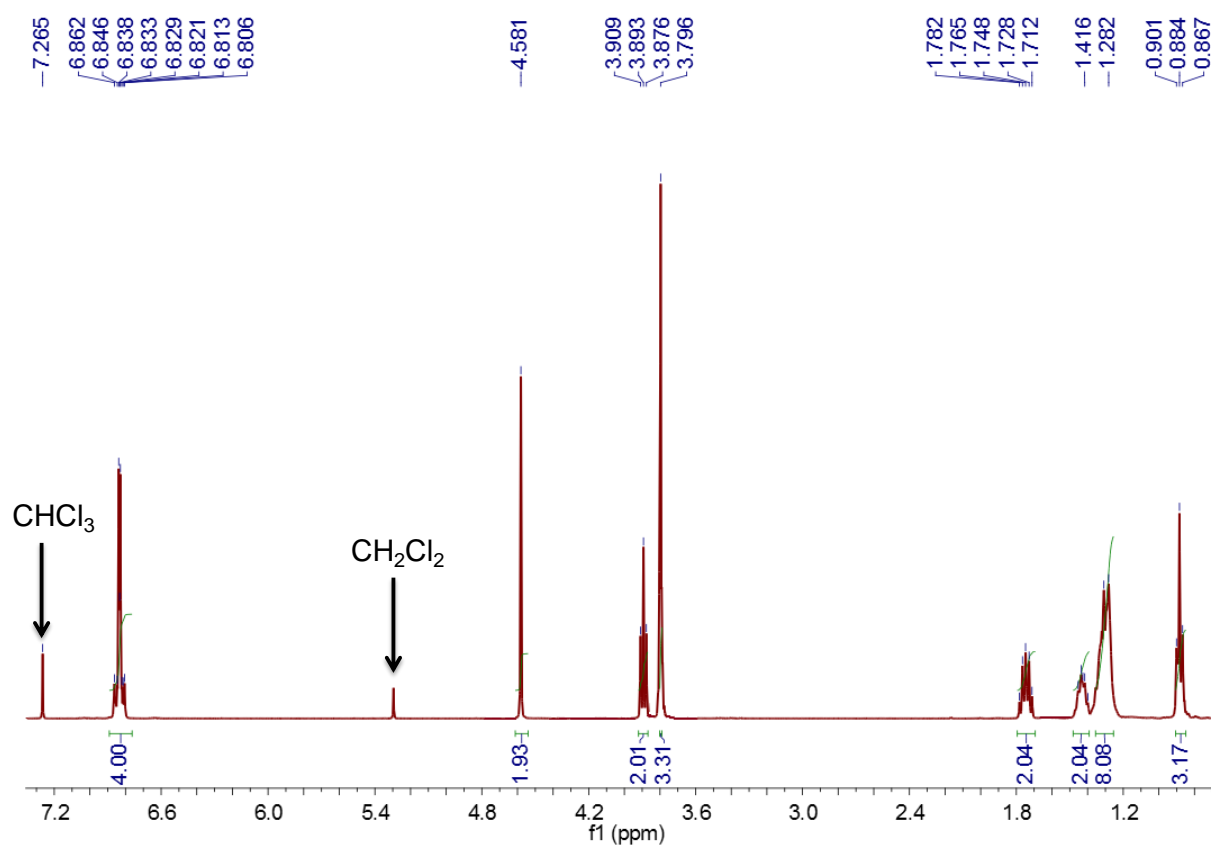


Fig. S3 ^1H NMR spectrum (400 MHz, CDCl₃, 293 K) of monomer A3.

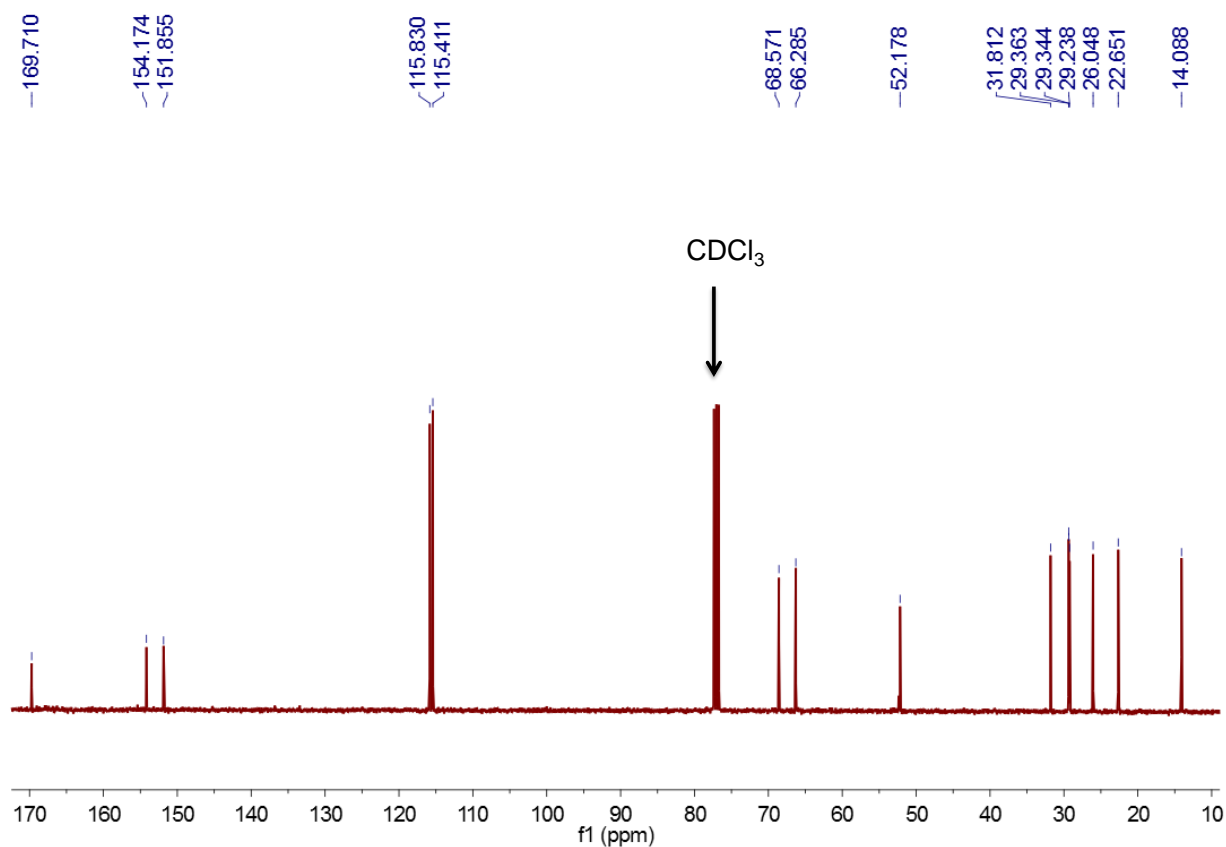


Fig. S4 ^{13}C NMR spectrum (100 MHz, CDCl_3 , 293 K) of monomer A3.

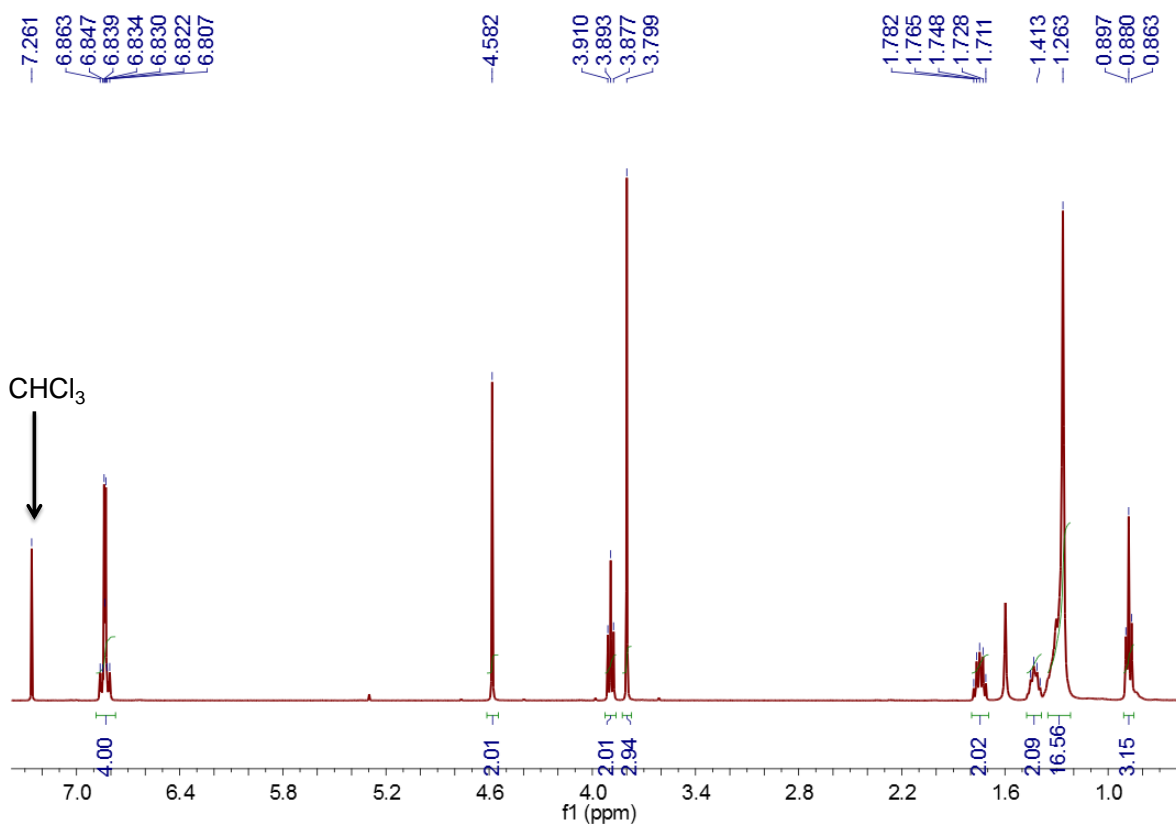


Fig. S5 ^1H NMR spectrum (400 MHz, CDCl_3 , 293 K) of monomer A4.

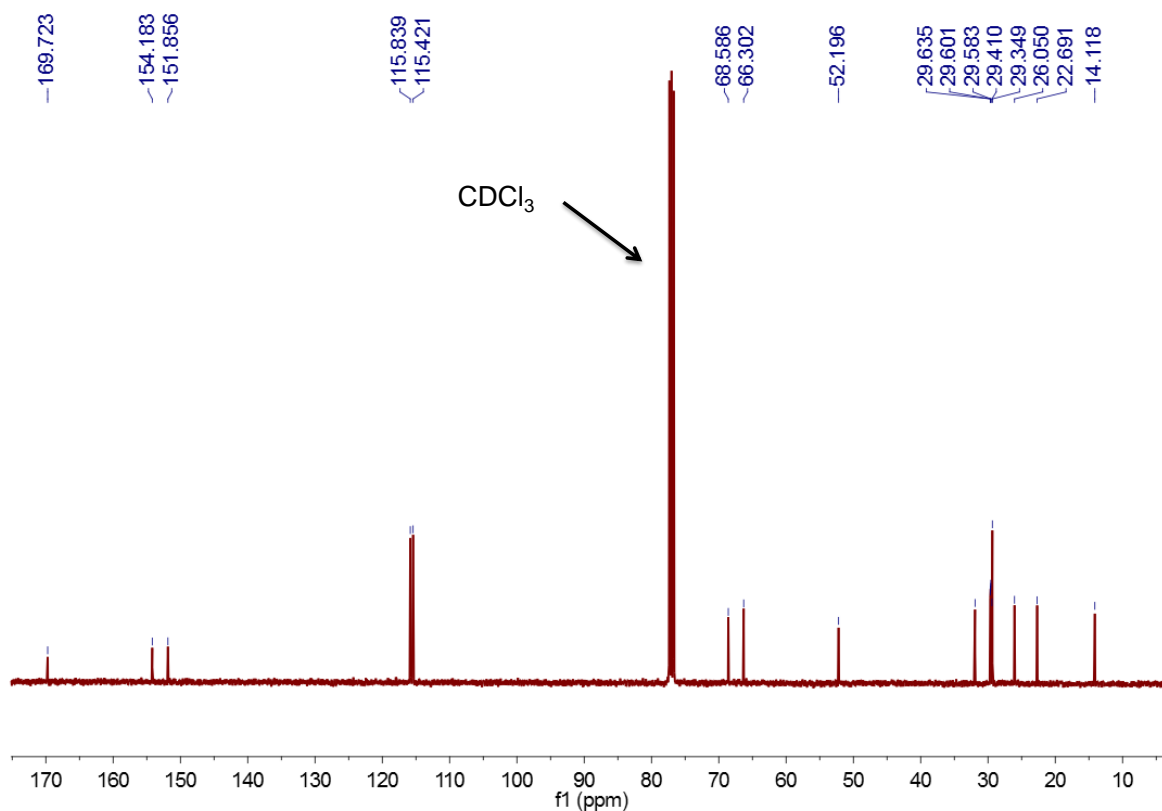


Fig. S6 ^{13}C NMR spectrum (100 MHz, CDCl_3 , 293 K) of monomer **A4**.

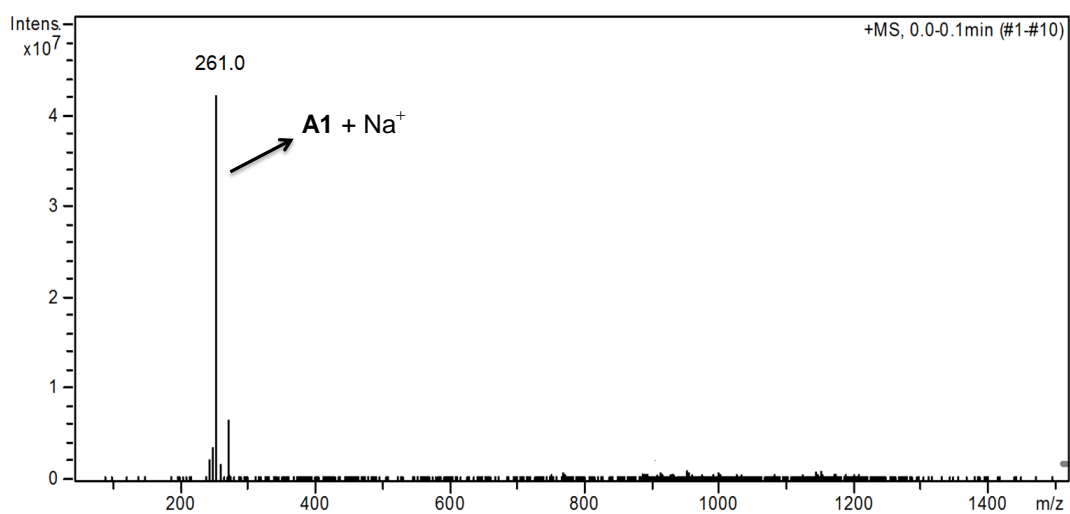


Fig. S7 Electrospray ionization mass spectrum of monomer **A1**. Assignment of the main peak: m/z 261.0 [**A1** + Na^+] (100%).

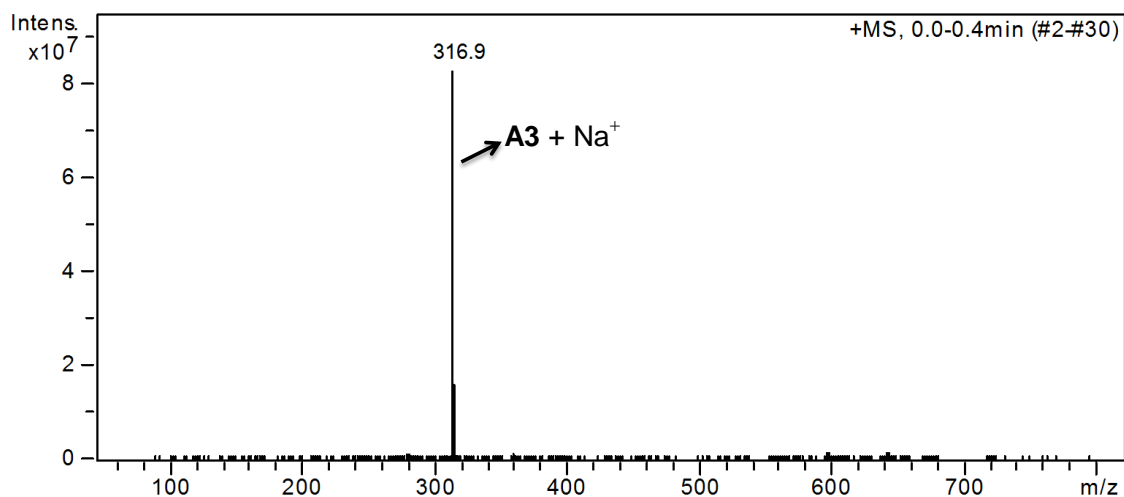


Fig. S8 Electrospray ionization mass spectrum of monomer **A3**. Assignment of the main peak: m/z 316.9 [**A3** + Na^+] (100%).

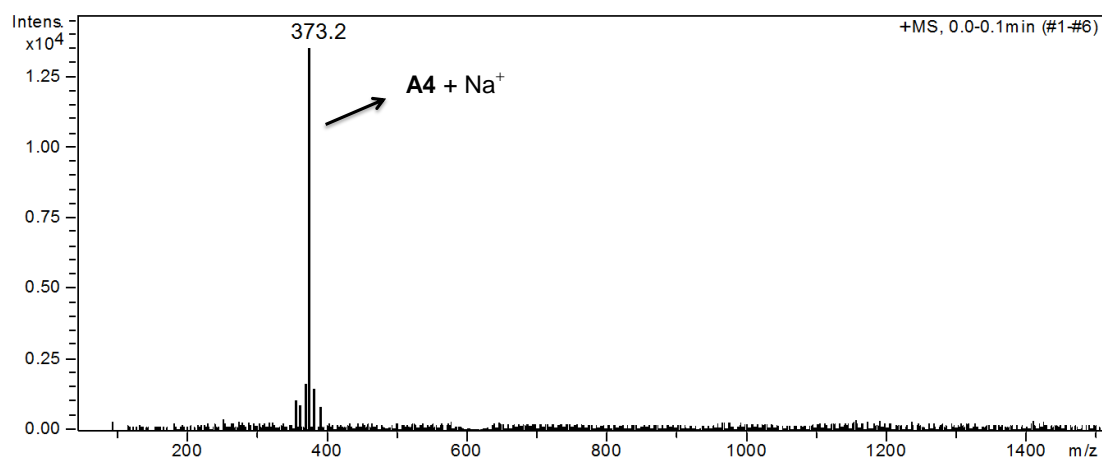
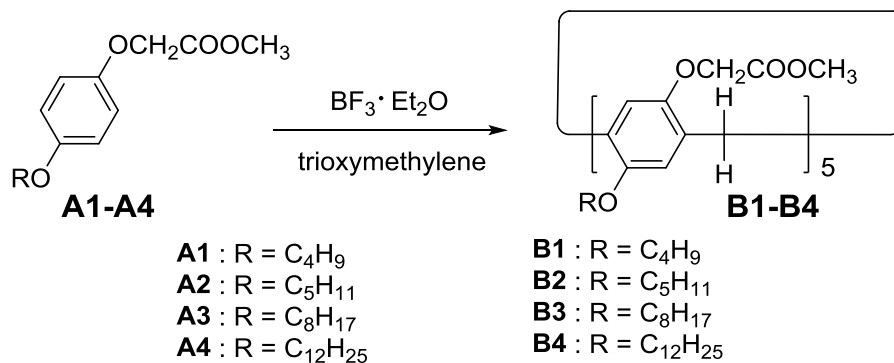


Fig. S9 Electrospray ionization mass spectrum of monomer **A4**. Assignment of the main peak: m/z 373.2 [**A4** + Na^+] (100%).

2.2. Syntheses of nonsymmetric pillar[5]arenes **B1–B4**

Scheme S3. Syntheses of pillar[5]arenes **B1–B4**



A solution of **A1–A4** (11.5 mmol) and trioxymethylene (0.349 g, 11.5 mmol) in 1,2-dichloroethane (50 mL) were cooled with ice bath. Boron trifluoride etherate (3.26 g, 23.0 mmol) was added to the solution and the mixture was stirred at room temperature for 1 hour. The reaction mixture was then washed by water (50 mL × 2) and dried with Na₂SO₄. The solvent was evaporated to provide a crude product, which was purified by column chromatography (eluent: petroleum ether/ethyl acetate, 10:1) to give white solids **B1–B4** (1.8%–2.4%).

B1: Mp: 111.3–112.1 °C. The proton NMR spectrum of **B1** is shown in Figure S10. ¹H NMR (400 MHz, chloroform-*d*, 293K) δ (ppm): 6.65 (s, 5H), 6.31 (s, 5H), 4.55 (t, *J* = 6.0 Hz, 5H), 4.06–4.02 (m, 5H), 3.79 (s, 20H), 3.64 (s, 15H), 1.86–1.81 (m, 10H), 1.38–1.34 (m, 10H), 0.94 (t, *J* = 6.0 Hz, 15H). The ¹³C NMR spectrum of **B1** is shown in Figure S11. ¹³C NMR (100 MHz, chloroform-*d*, 293K) δ (ppm): 170.06, 155.57, 154.86, 128.28, 127.53, 126.31, 99.59, 68.28, 55.52, 51.21, 37.01, 35.21, 21.07, 14.29. LRESIMS is shown in Figure S16: *m/z* 1346.1 [**B1** + Cl][−]. HRESIMS: *m/z* calcd for [**B1** + Na]⁺ C₇₀H₉₀NaO₂₀, 1273.5923; found 1273.5918; error −0.4 ppm.

The characterization data of **B2** were reported in our previous work.^{S1}

B3: Mp: 96.7–96.5 °C. The proton NMR spectrum of **B3** is shown in Figure S12. ¹H NMR (400 MHz, chloroform-*d*, 293K) δ (ppm): 7.05 (s, 5H), 6.80 (s, 5H), 4.52 (s, 10H), 3.88–3.81 (m, 20H), 3.59 (s, 15H), 1.82 (s, 10H), 1.58–1.52 (m, 10H), 1.37–1.27 (m, 40H), 0.87 (t, *J* = 6.0 Hz, 15H). The ¹³C NMR spectrum of **B3** is shown in Figure S13. ¹³C NMR (100 MHz, chloroform-*d*, 293K) δ (ppm): 169.99, 150.23, 148.30, 128.34, 128.19, 114.23, 68.17, 65.50, 51.83, 31.89, 29.95, 29.66, 29.34, 26.42, 22.67, 14.09. LRESIMS is shown in Figure S17: *m/z* 1614.0 [**B3** + Na]⁺. HRESIMS: *m/z* calcd for [**B3** + Na]⁺ C₉₀H₁₃₀NaO₂₀, 1553.9053; found 1553.9069; error 1 ppm.

B4: Mp: 89.3–88.6 °C. The proton NMR spectrum of **B4** is shown in Figure S14. ¹H NMR (400 MHz, chloroform-*d*, 293K) δ (ppm): 7.07 (s, 5H), 6.83 (s, 5H), 4.70 (s, 10H), 3.80–3.77 (m, 20H), 3.69 (s, 15H), 1.83 (s, 10H), 1.54–1.26 (m, 30H), 1.21 (s, 60H), 0.86 (t, *J* = 6.0 Hz, 15H). The ¹³C NMR spectrum of **B4** is shown in Figure S15. ¹³C NMR (100 MHz, chloroform-*d*, 293K) δ (ppm): 169.96, 167.49, 128.34, 128.19, 114.13, 68.10, 68.06, 65.46, 63.76, 52.46, 51.88, 29.74, 29.72, 29.69, 29.43, 26.38, 22.70, 14.04. Anal. Calcd. for C₁₁₀H₁₇₀O₂₀: C 72.89, H 9.45. Found: C 72.92, H 9.49.

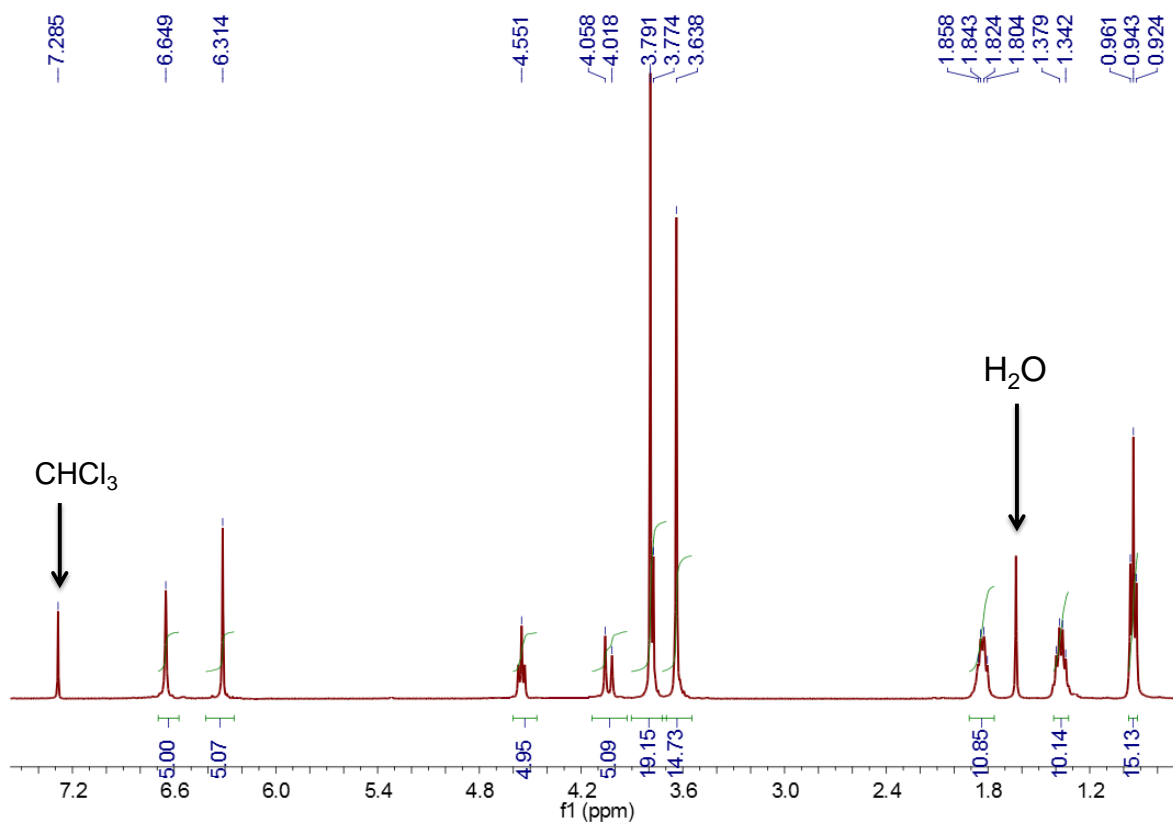


Fig. S10 ¹H NMR spectrum (400 MHz, CDCl₃, 293 K) of pillar[5]arene **B1**.

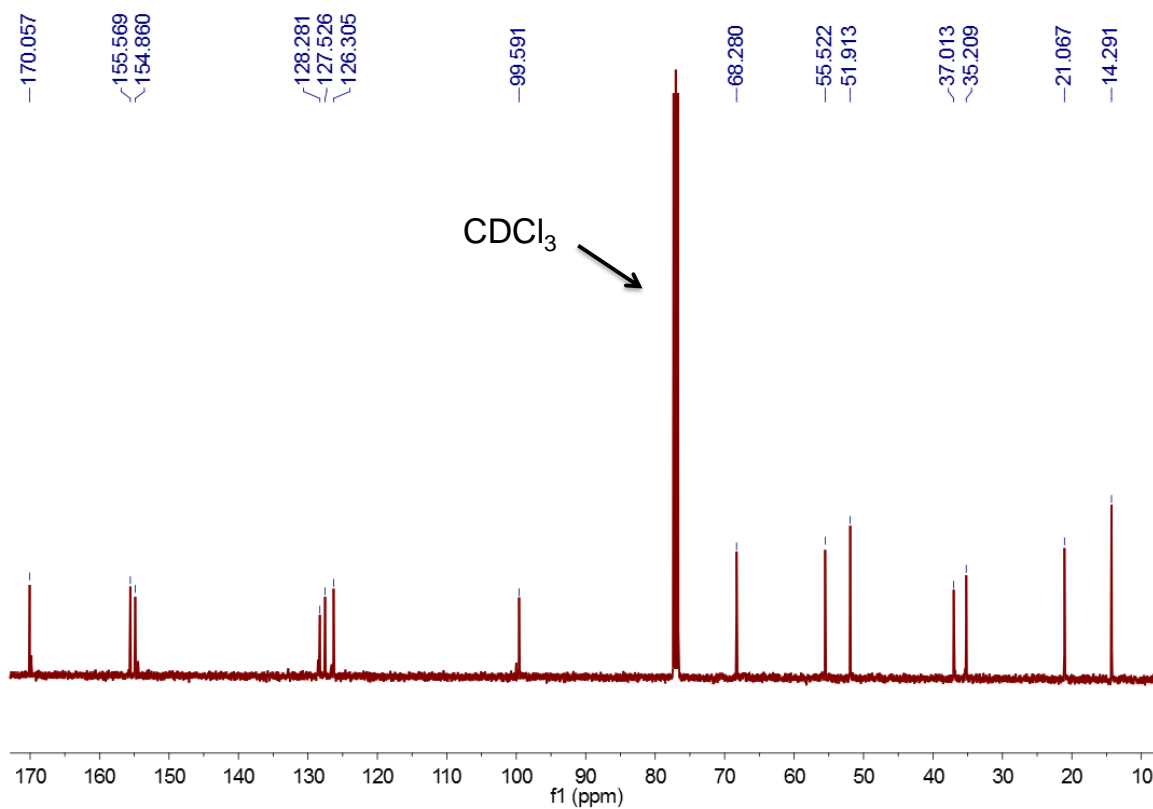


Fig. S11 ¹³C NMR spectrum (100 MHz, CDCl₃, 293 K) of pillar[5]arene **B1**.

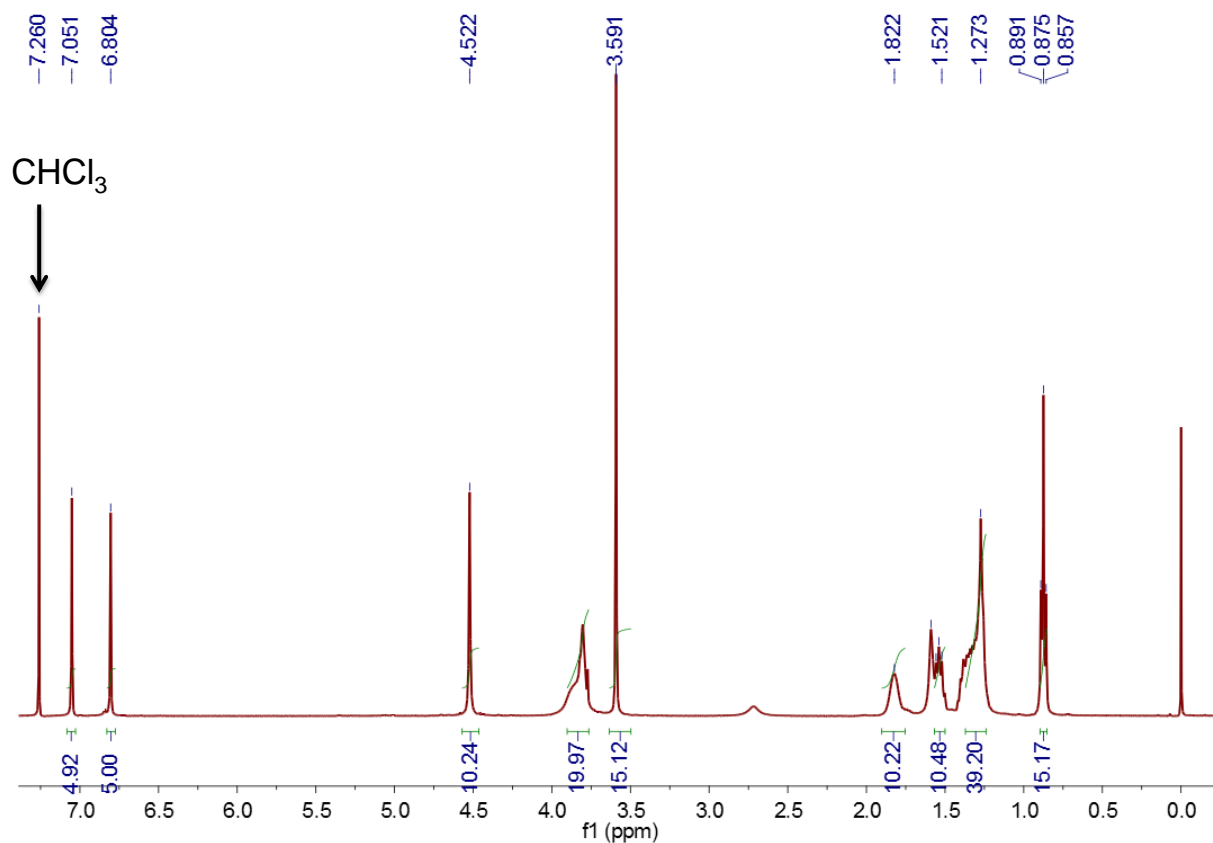


Fig. S12 ^1H NMR spectrum (400 MHz, CDCl_3 , 293 K) of pillar[5]arene **B3**.

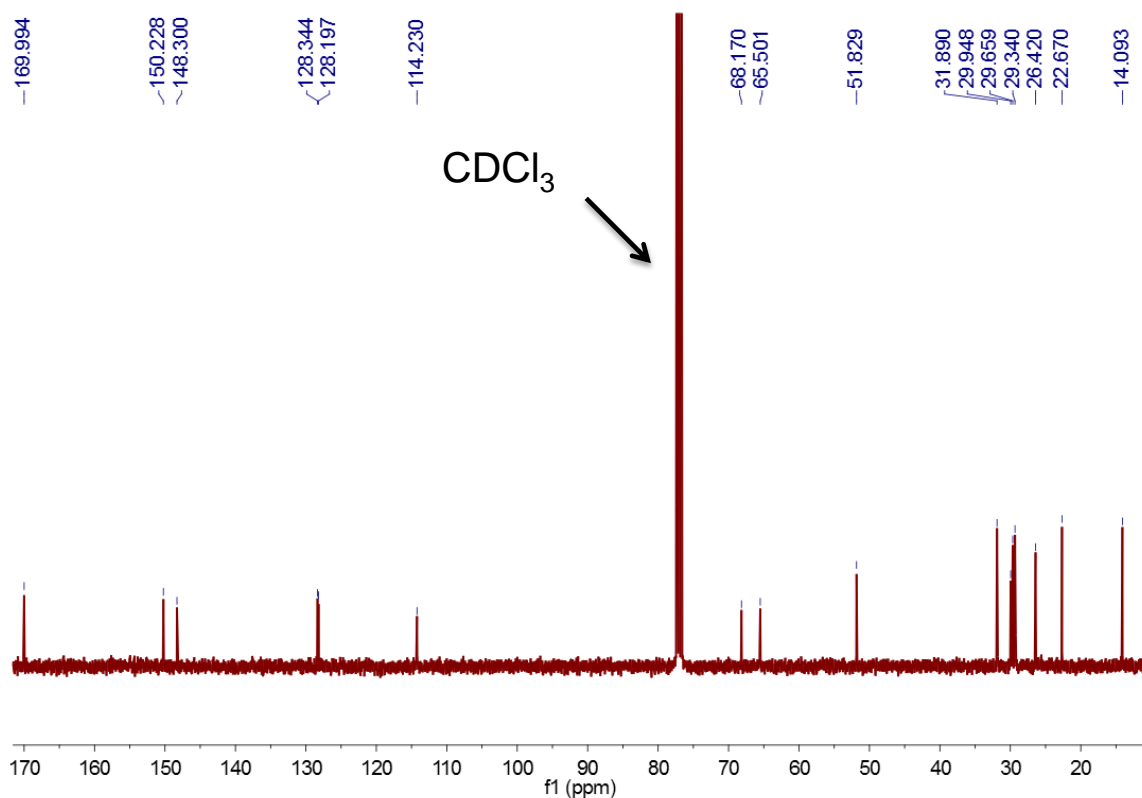


Fig. S13 ^{13}C NMR spectrum (400 MHz, CDCl_3 , 293 K) of pillar[5]arene **B3**.

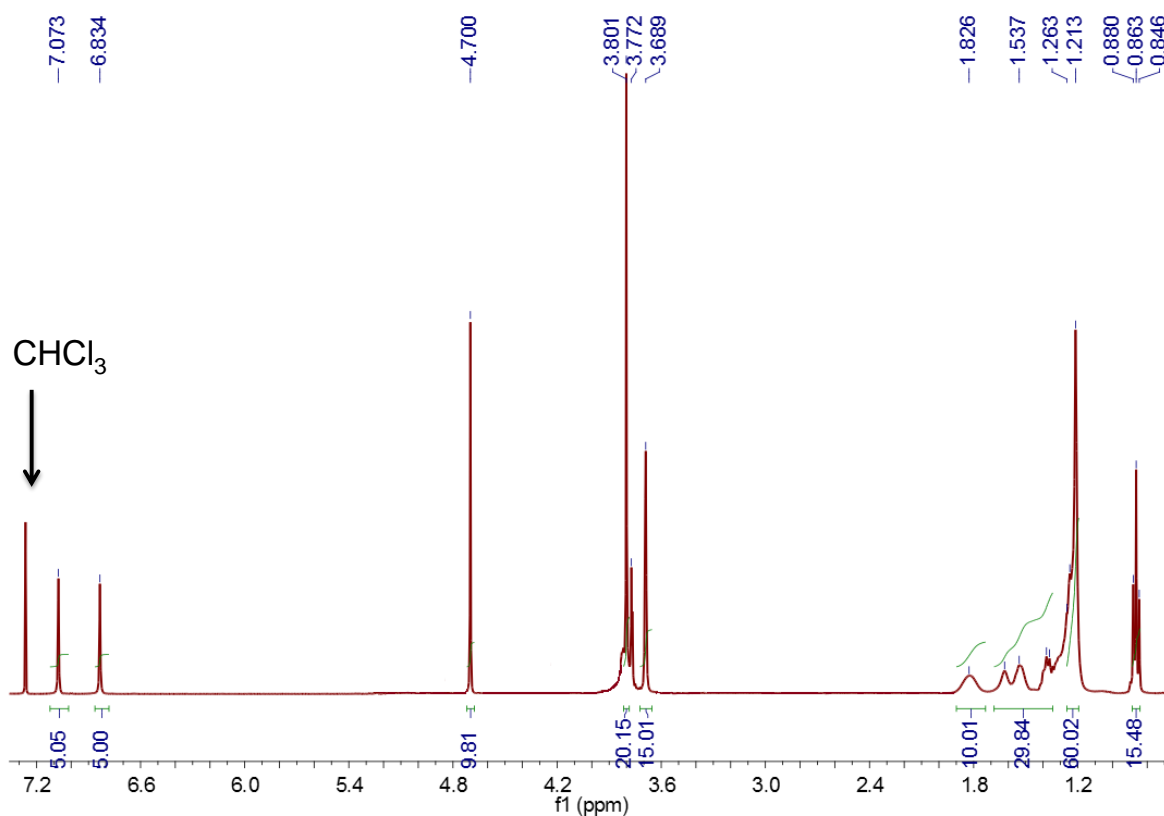


Fig. S14 ¹H NMR spectrum (400 MHz, CDCl₃, 293 K) of pillar[5]arene **B4**.

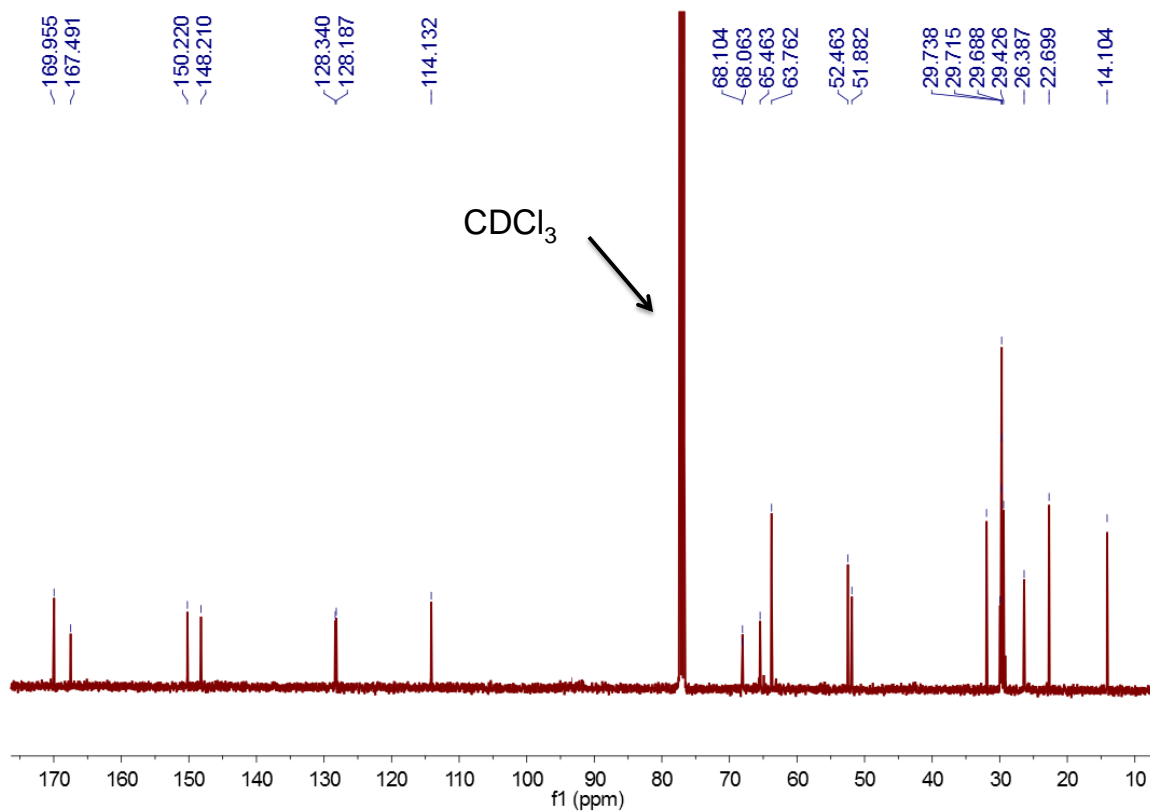


Fig. S15 ¹³C NMR spectrum (400 MHz, CDCl₃, 293 K) of pillar[5]arene **B4**.

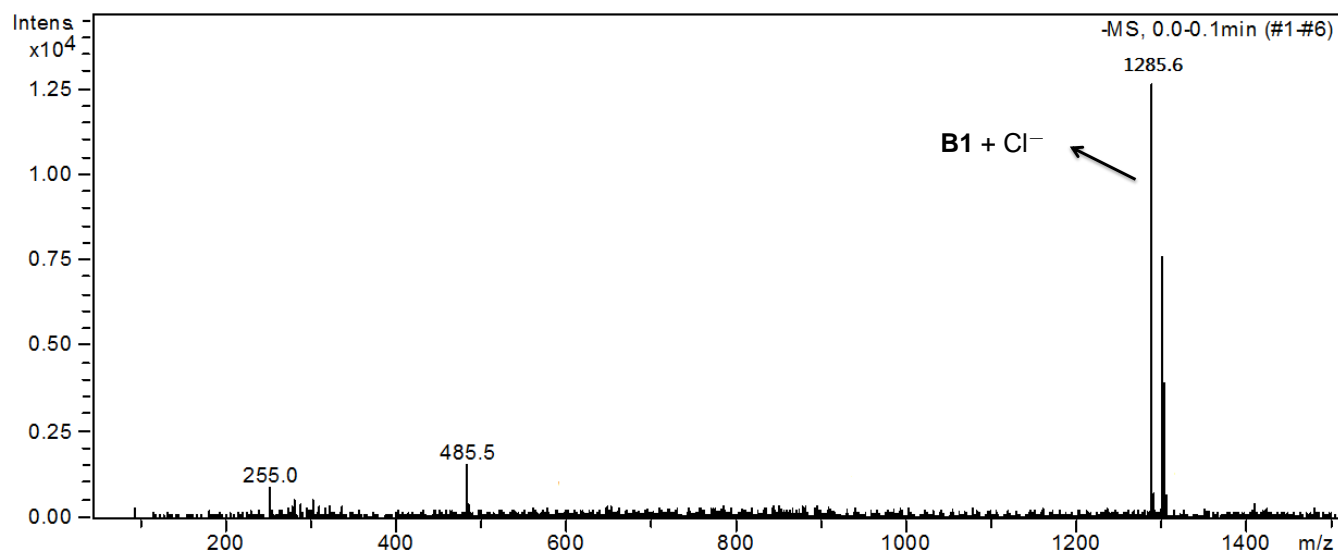


Fig. S16 Electrospray ionization mass spectrum of monomer **B1**. Assignment of the main peak: m/z 1285.6 [**B1** + Cl]⁻ (100%).

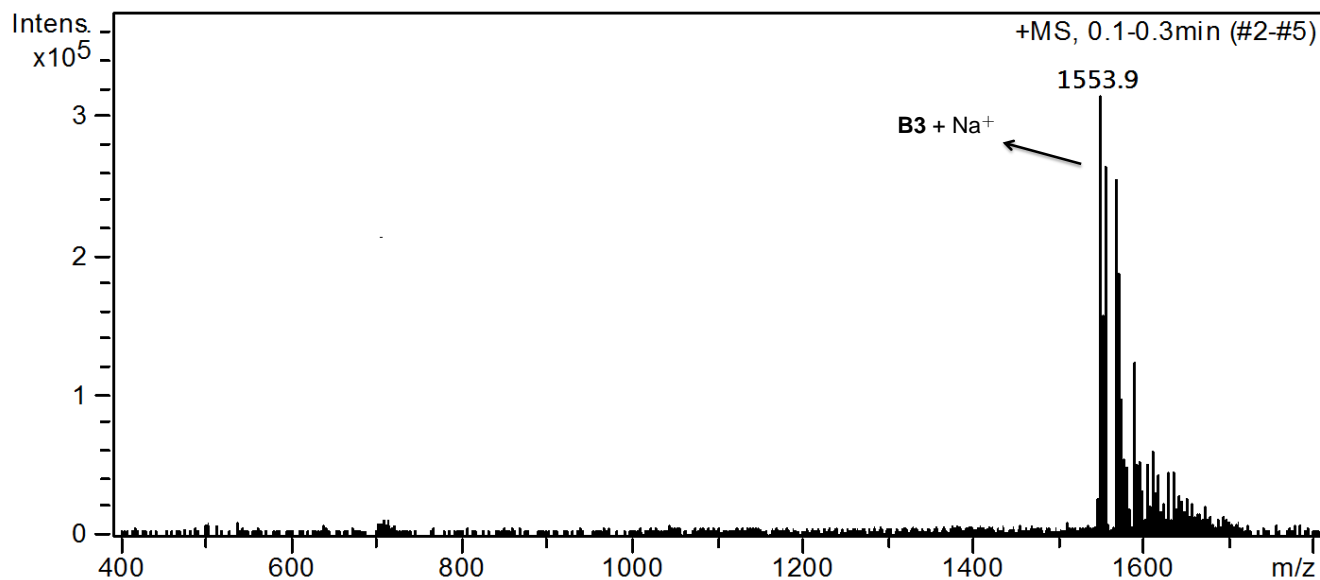
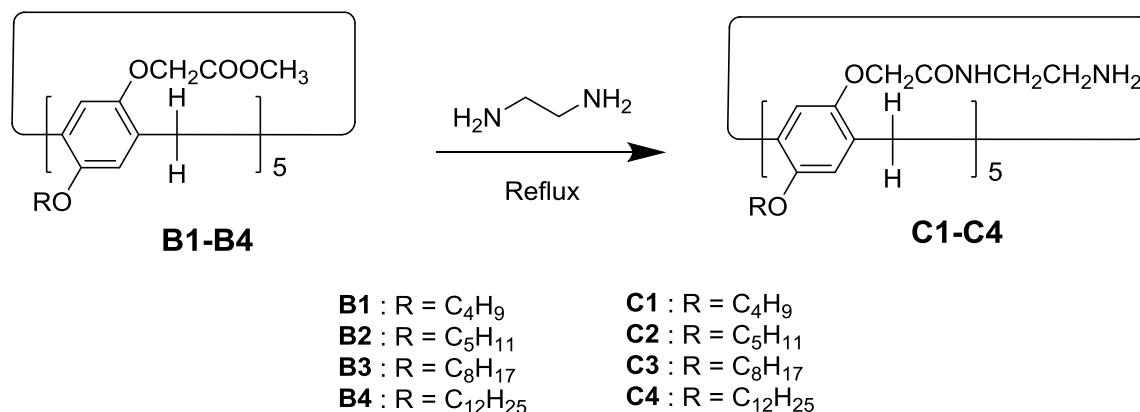


Fig. S17 Electrospray ionization mass spectrum of monomer **B3**. Assignment of the main peak: m/z 1553.9 [**B3** + Na]⁺ (100%).

2.3. Syntheses of amphiphilic pillar[5]arenes **C1–C4**

Scheme S4. Syntheses of amphiphilic pillar[5]arenes **C1–C4**



A mixture of **B1–B4** (1.00 mmol) and ethanediamine (5 mL) in ethanol (25 mL) was stirred in a 100 mL round-bottom flask at 90 °C for 24 hours. After cooling, the solvent was removed and the residue was poured into saturated brine (50 mL) to give white solids **C1–C4** (51–55%).

C1: Mp: 222.7–221.9 °C. The proton NMR spectrum of **C1** is shown in Figure S18. ¹H NMR (400 MHz, DMSO-*d*₆, 293 K) δ (ppm): 7.21 (s, 5H), 7.02 (s, 5H), 6.82 (s, 5H), 4.55 (s, 10H), 4.12 (s, 10H), 3.98 (s, 10H), 3.69–3.62 (m, 10H), 3.52 (s, 10H), 2.81 (s, 10H), 1.83 (s, 10H), 1.57 (s, 10H), 1.05 (t, *J* = 5.6 Hz, 15H). The ¹³C NMR spectrum of **C1** is shown in Figure S19. ¹³C NMR (100 MHz, DMSO-*d*₆, 293 K) δ (ppm): 169.75, 150.86, 150.78, 133.54, 132.96, 117.35, 116.84, 70.64, 67.92, 41.79, 41.05, 37.93, 31.61, 30.51, 19.94, 14.02. Anal. Calcd. for C₇₅H₁₁₀N₁₀O₁₅: C 64.73, H 7.97, N 10.06. Found: C 64.69, H 7.92, N 10.04.

The characterization data of **C2** were reported in our previous work.^{S1}

C3: Mp: 196.8–196.3 °C. The proton NMR spectrum of **C3** is shown in Figure S20. ¹H NMR (400 MHz, DMSO-*d*₆, 293 K) δ (ppm): 7.36 (s, 5H), 7.31 (s, 5H), 7.20 (s, 5H), 4.57(s, 10H), 4.09 (s, 10H), 4.08–4.07 (m, 15H), 3.92–3.91 (m, 5H), 3.04–3.01 (m, 10H), 1.84–1.83 (m, 10H), 1.55–1.51 (m, 10H), 1.37–1.29 (m, 40H), 0.97 (t, *J* = 5.6 Hz, 15H). The ¹³C NMR spectrum of **C3** is shown in Figure S21. ¹³C NMR (100 MHz, DMSO-*d*₆, 293 K) δ (ppm): 169.72, 150.83, 150.75, 133.51, 132.93, 117.38, 116.81, 70.32, 67.88, 41.78, 41.01, 37.90, 37.90, 29.04, 26.47, 22.91, 13.99. Anal. Calcd. for C₉₅H₁₅₀N₁₀O₁₅: C 68.23, H 9.04, N 8.38. Found: C 68.26, H 9.12, N 8.36.

C4: Mp: 181.2–178.9 °C. The proton NMR spectrum of **C4** is shown in Figure S22. ¹H NMR (400 MHz, DMSO-*d*₆, 293 K) δ (ppm): 7.34 (s, 5H), 7.26 (s, 5H), 7.21 (s, 5H), 4.64 (s, 10H), 4.17–4.13 (m, 20H), 3.59–3.58 (m, 10H), 3.31–3.25 (m, 10H), 1.86–1.81 (m, 10H), 1.43–1.41 (m, 10H), 1.34–1.26 (m, 80H), 0.95 (t, *J* = 5.6 Hz, 15H). The ¹³C NMR spectrum of **C4** is shown in Figure S23. ¹³C NMR (100 MHz, DMSO-*d*₆, 293 K) δ (ppm): 169.75, 150.86, 150.78, 133.54, 132.96, 117.35, 116.84, 70.35, 67.92, 41.79, 41.05, 37.93, 29.06, 29.49, 22.94, 14.02. Anal. Calcd. for C₁₁₅H₁₉₀N₁₀O₁₅: C 70.73, H 9.81, N 7.17. Found: C 70.82, H 9.82, N 7.15.

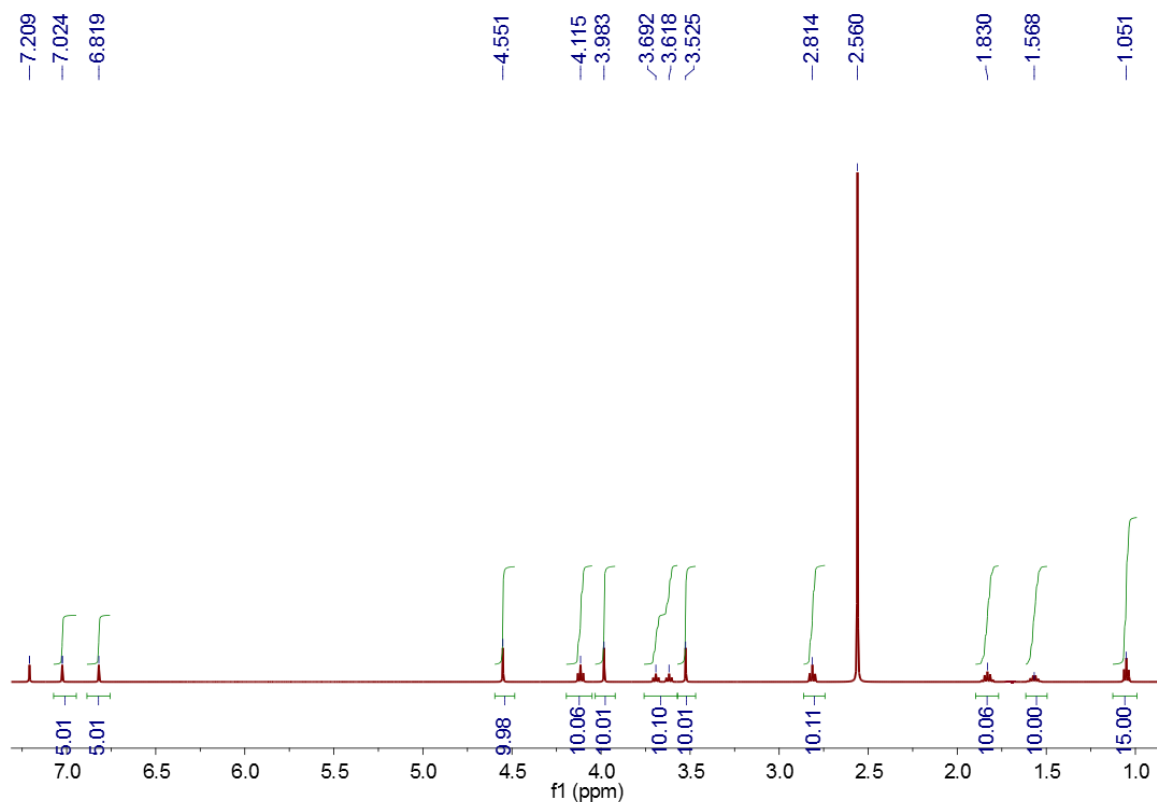


Fig. S18 ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 293 K) of amphiphilic pillar[5]arene **C1**.

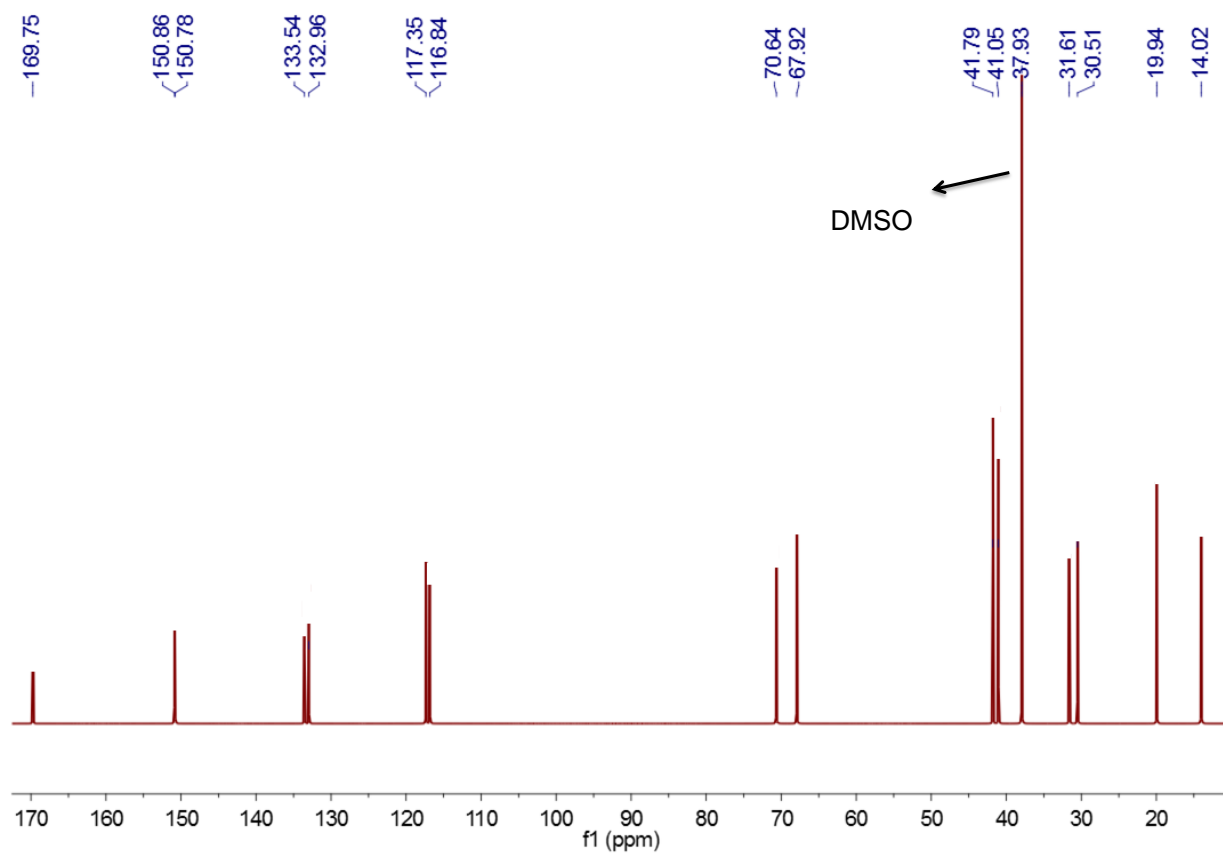


Fig. S19 ^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6$, 293 K) of amphiphilic pillar[5]arene **C1**.

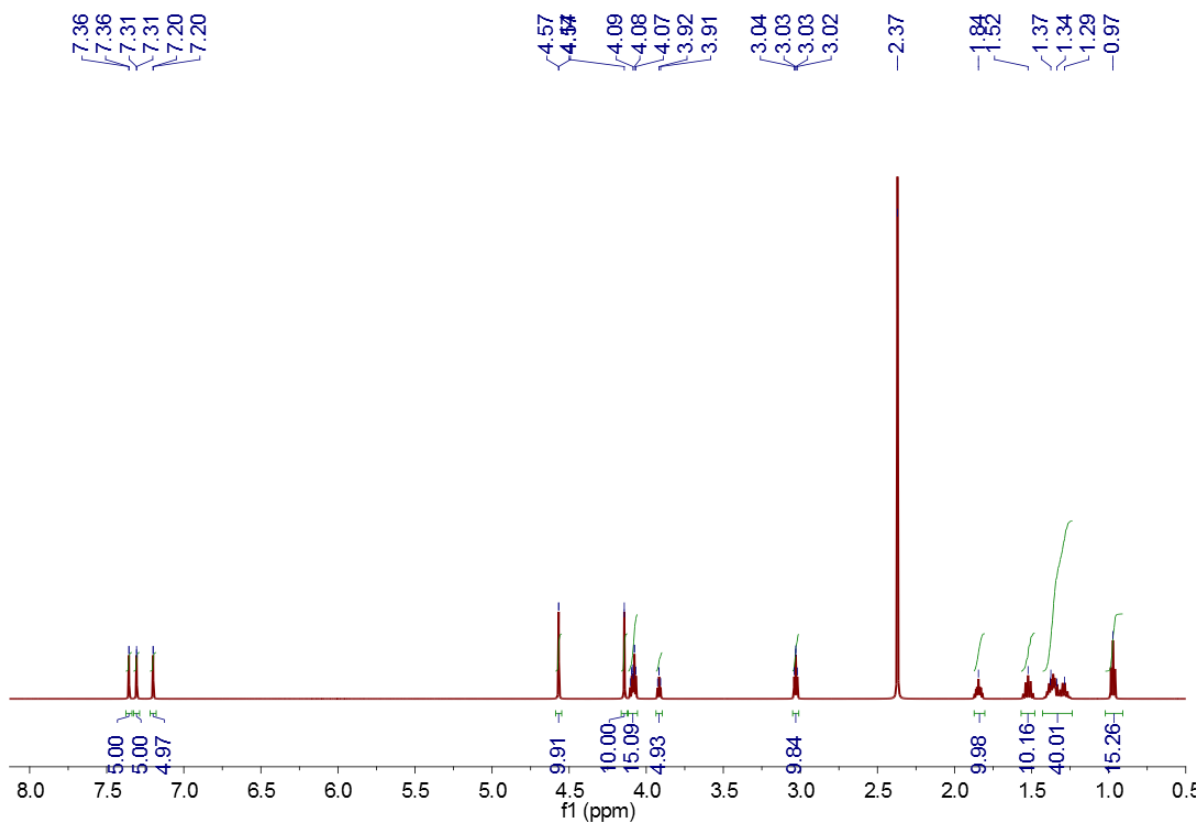


Fig. S20 ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 293 K) of amphiphilic pillar[5]arene **C3**.

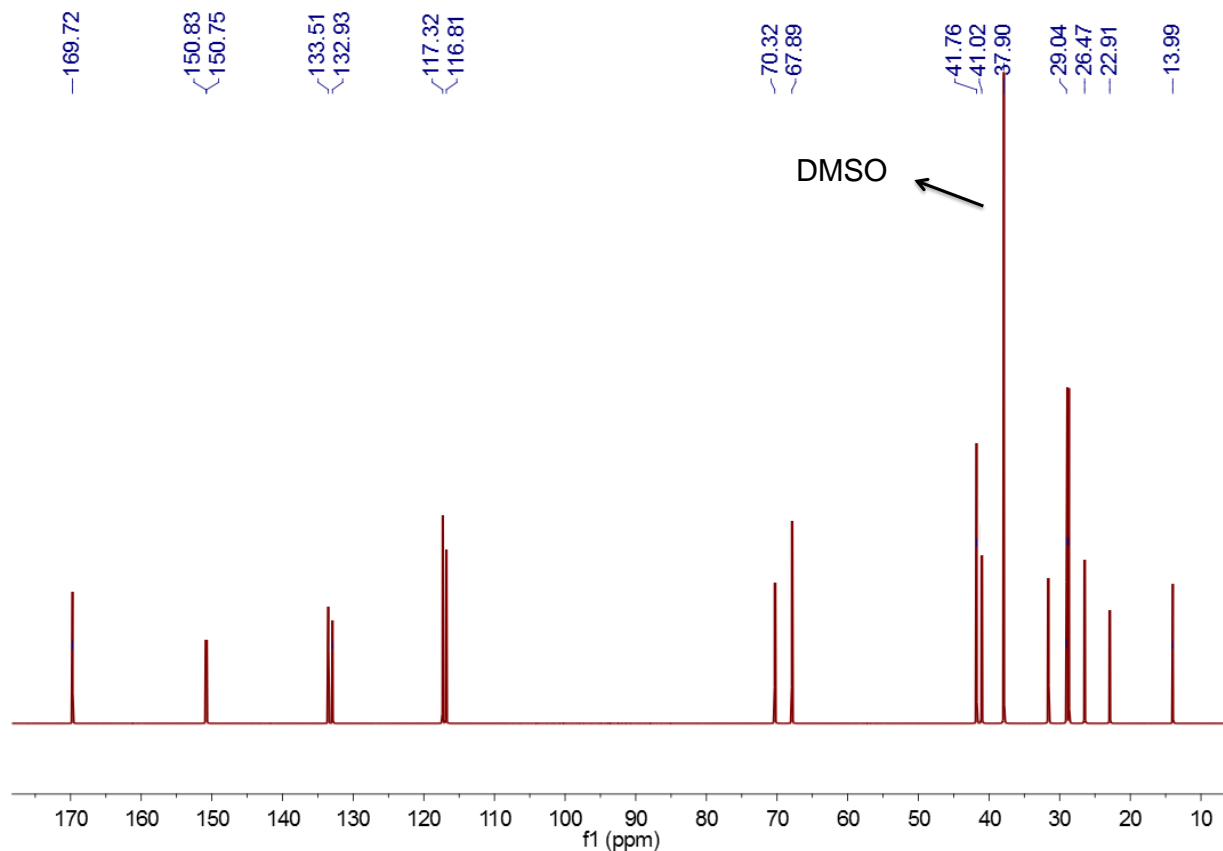


Fig. S21 ^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6$, 293 K) of amphiphilic pillar[5]arene **C3**.

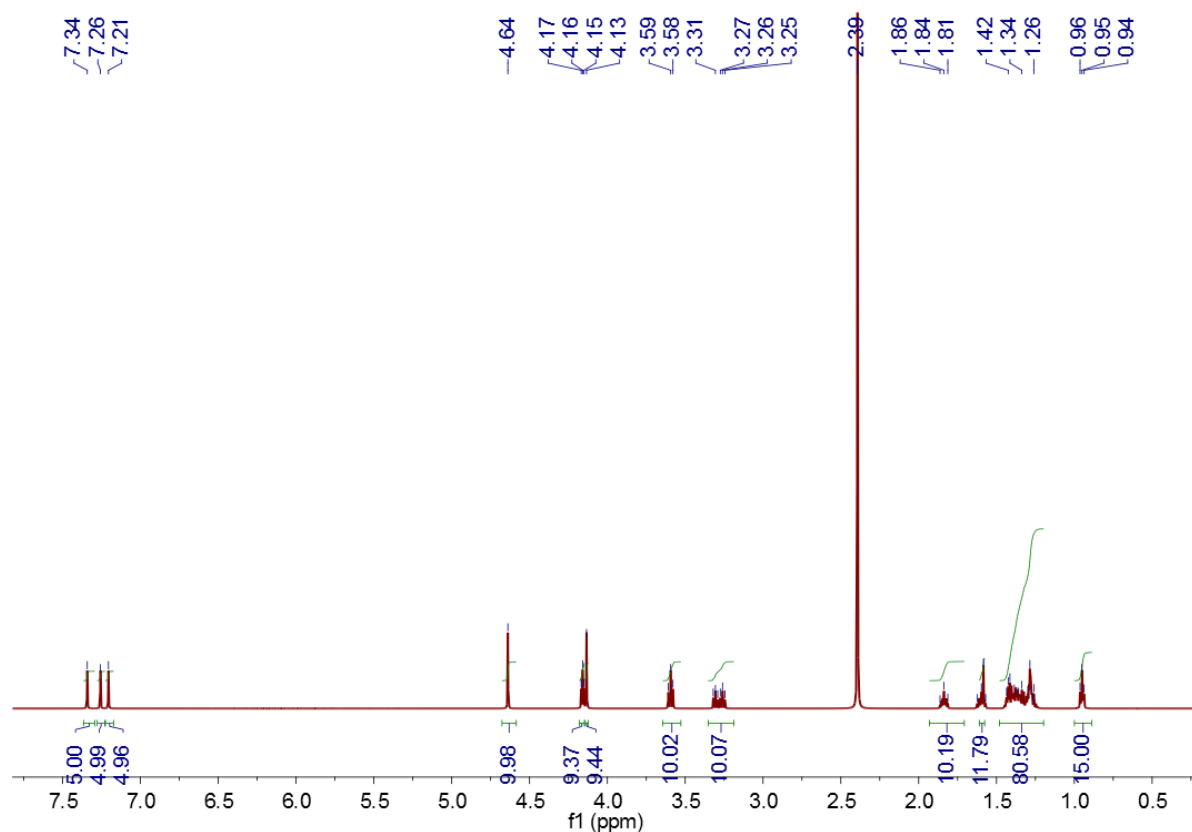


Fig. S22 ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$, 293 K) of amphiphilic pillar[5]arene **C4**.

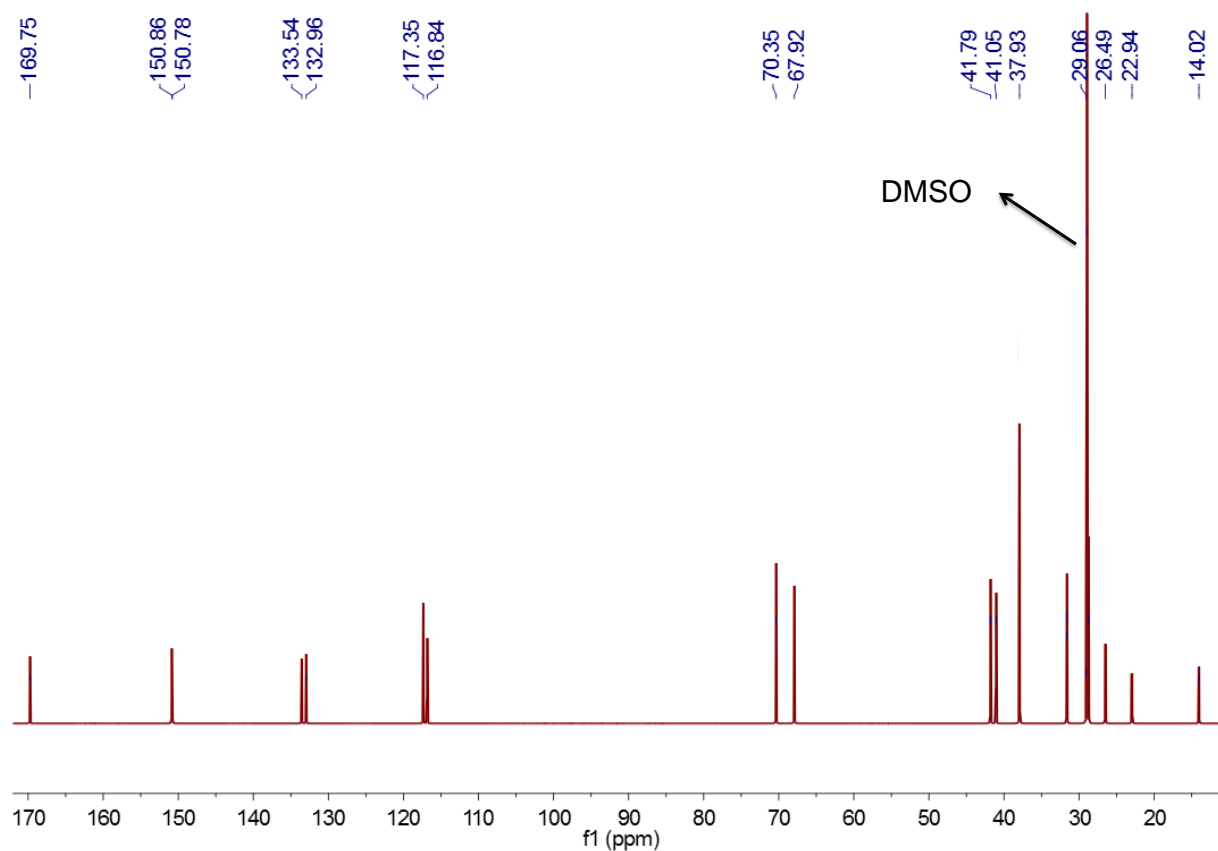
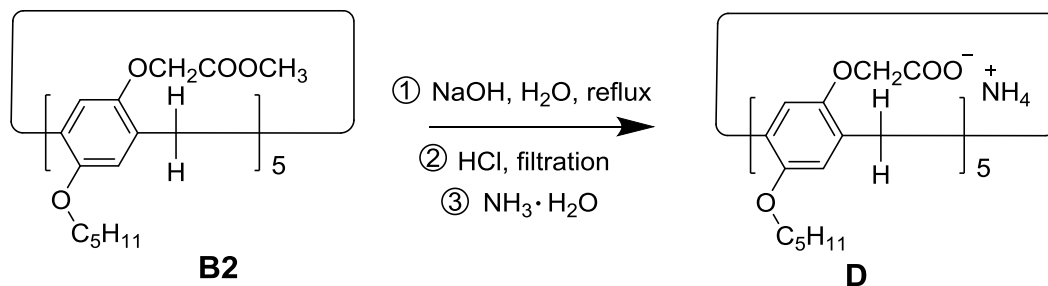


Fig. S23 ^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6$, 293 K) of amphiphilic pillar[5]arene **C4**.

2.4. Synthesis of amphiphilic pillar[5]arene **D**

Scheme S5. Synthesis of amphiphilic pillar[5]arene **D**



A mixture of **B2** (1.43 g, 5.00 mmol) and NaOH (100 mmol) in water (25 mL) was stirred in a 100 mL round-bottom flask at 100 °C for 24 hours. After cooling, HCl was added to the mixture until the pH of the system was 4. Then the solvent was removed and the residue was washed with water (2 × 50 mL). At last, excess NH₃·H₂O was added to the residue to obtain **D** as a white solid (1.33 g, 89%). Mp: > 230 °C. The ¹H NMR spectrum of **D** is shown in Figure S24. ¹H NMR (400 MHz, DMSO-*d*₆, 293 K) δ (ppm): 7.10 (s, 5H), 6.80 (s, 5H), 4.49 (s, 10H), 3.83 (s, 10H), 3.69 (s, 10H), 1.82 (s, 10H), 1.47–1.39 (m, 20H), 0.94 (t, *J* = 6.0 Hz, 15H). The ¹³C NMR spectrum of **D** is shown in Figure S25. ¹³C NMR (100 MHz, DMSO-*d*₆, 293 K) δ (ppm): 175.65, 151.06, 150.98, 133.75, 133.16, 117.56, 117.05, 70.55, 68.47, 28.65, 23.15, 14.23. LRESIMS is shown in Figure S26: *m/z* 315.9 [(**D** - 4 NH₄⁺)/4]⁻, 427.2 [(**D** - 3 NH₄⁺)/3]⁻, 649.8 [(**D** - 2 NH₄⁺)/2]⁻, 1317.7 [**D** - NH₄⁺]⁻. HRESIMS: *m/z* calcd for [(**D** - 2 NH₄⁺)/2]⁻ C₇₀H₉₇N₃O₂₀²⁻, 649.8338; found 649.8365; error 4 ppm.

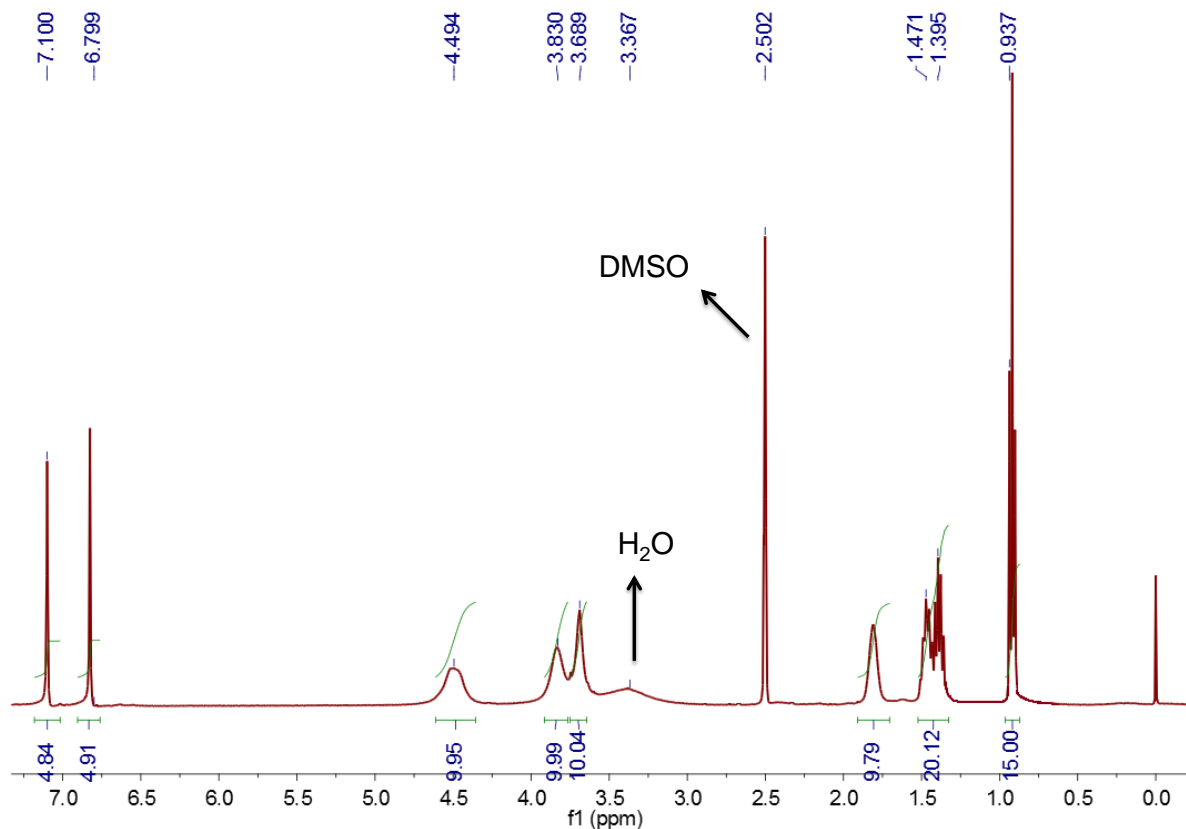


Fig. S24 ¹H NMR spectrum (400 MHz, DMSO-*d*₆, 293 K) of amphiphilic pillar[5]arene **D**.

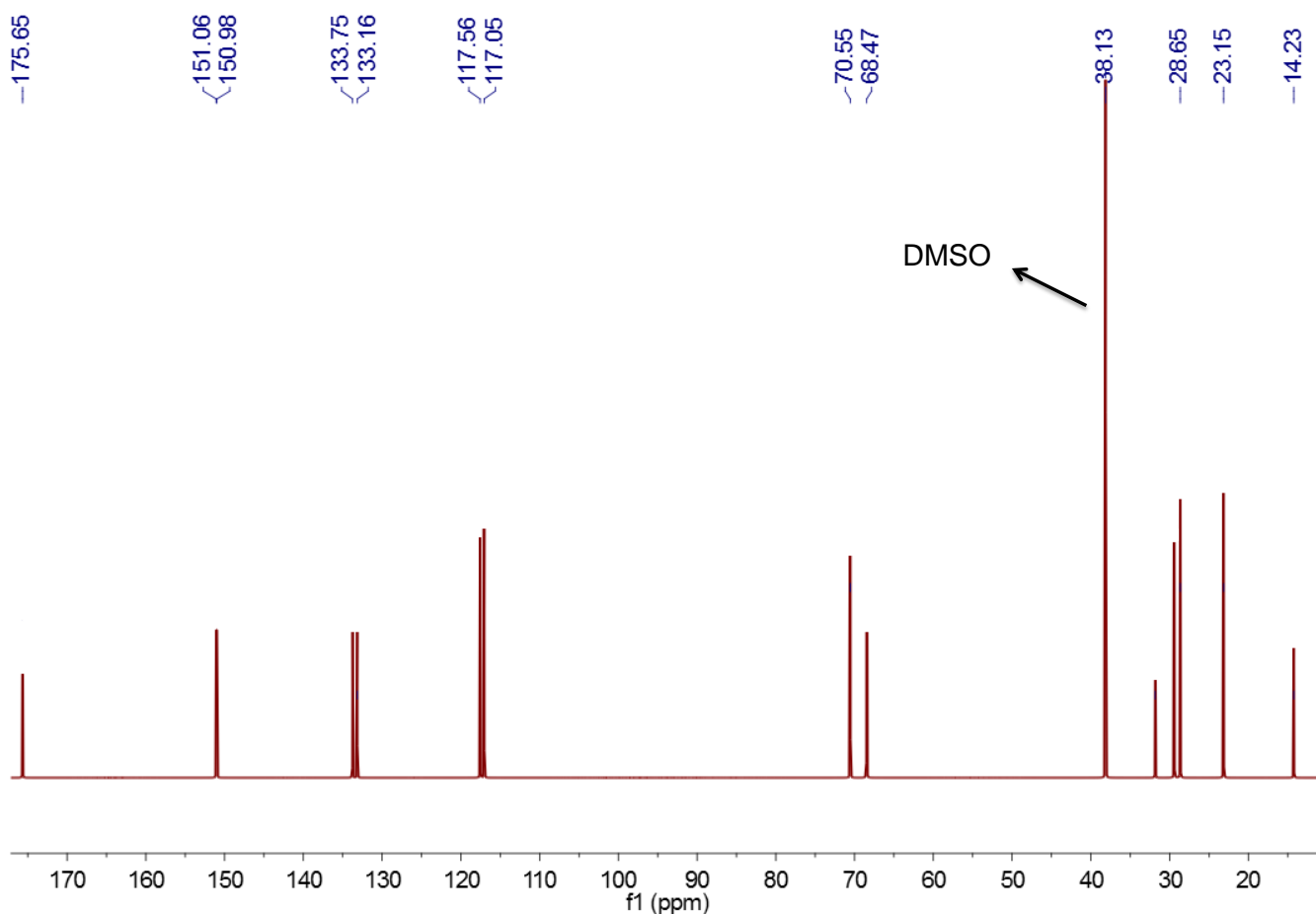


Fig. S25 ^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6$, 293 K) of amphiphilic pillar[5]arene **D**.

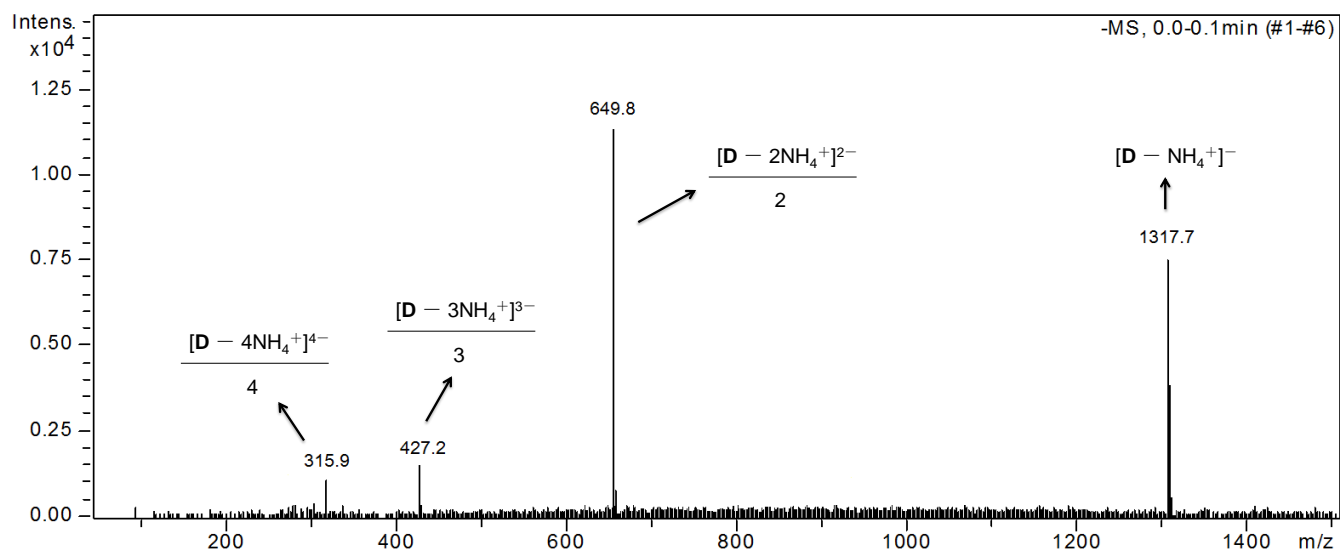
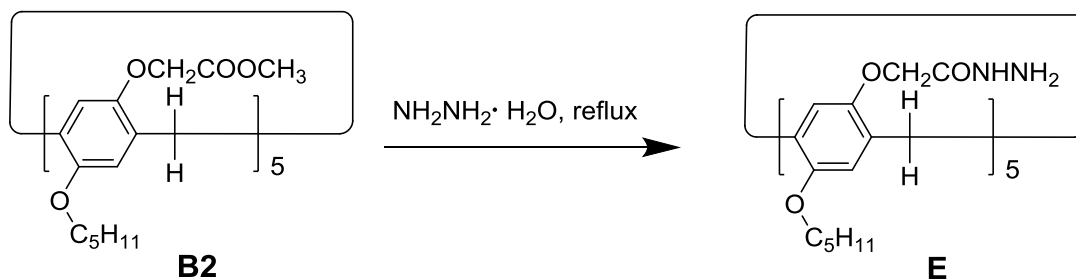


Fig. S26 Electrospray ionization mass spectrum of amphiphilic pillar[5]arene **D**. Assignment of the main peaks: m/z 315.9 $[\text{D} - 4\text{NH}_4^+]^{4+}$ (10%), m/z 427.2 $[\text{D} - 3\text{NH}_4^+]^{3-}$ (15%), m/z 649.8 $[\text{D} - 2\text{NH}_4^+]^{2-}$ (100%), 1317.7 $[\text{D} - \text{NH}_4^+]^-$ (70%).

2.5. Synthesis of amphiphilic pillar[5]arene **E**

Scheme S6. Synthesis of amphiphilic pillar[5]arene **E**



A mixture of **B2** (1.00 mmol) and NH₂NH₂·H₂O (5 mL) in ethanol (25 mL) was stirred in a 100 mL round-bottom flask at 90 °C for 2 hours.^{S2} After cooling, the solvent was removed and the residue was washed with ethanol (2 × 10 mL) to give **E** as a white solid (91%). Mp: > 230 °C. The proton NMR spectrum of **E** is shown in Figure S27. ¹H NMR (400 MHz, CDCl₃, 293 K) δ (ppm): 8.91 (s, 5H), 7.54 (s, 5H), 7.39 (s, 5H), 4.68 (s, 10H), 4.32 (s, 10H), 4.05 (t, *J* = 5.6 Hz, 10H), 3.86–3.81 (m, 20H), 1.82–1.77 (m, 10H), 0.985 (t, *J* = 5.6 Hz, 15H). The ¹³C NMR spectrum of **E** is shown in Figure S28. ¹³C NMR (100 MHz, CDCl₃, 293 K) δ (ppm): 150.91, 150.83, 133.60, 133.01, 117.41, 116.90, 70.04, 64.61, 31.67, 29.26, 28.50, 23.00, 14.08. LRESIMS is shown in Figure S29: *m/z* 1343.7 [**E** + Na]⁺ (100%). HRESIMS: *m/z* calcd for [**E** + Na]⁺ C₇₀H₁₀₀N₁₀O₁₅Na, 1343.7267; found 1343.7289; error 2 ppm.

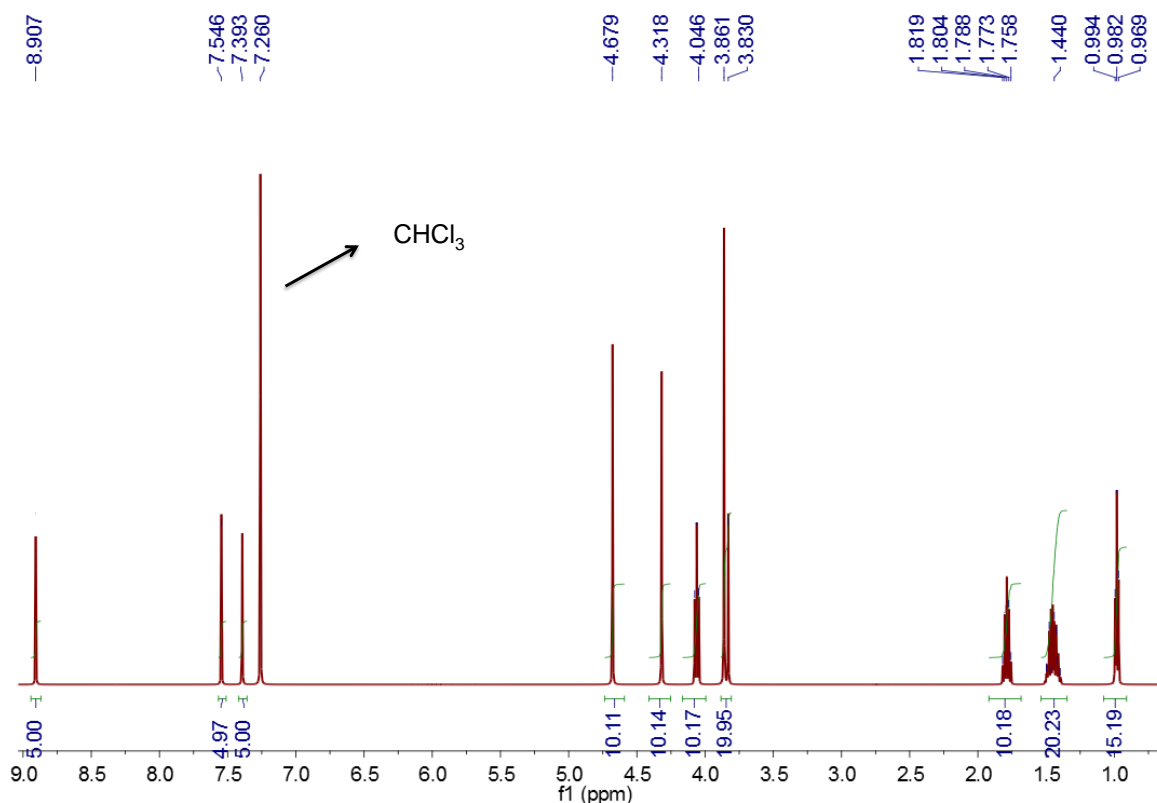


Fig. S27 ¹H NMR spectrum (400 MHz, CDCl₃, 293 K) of amphiphilic pillar[5]arene **E**.

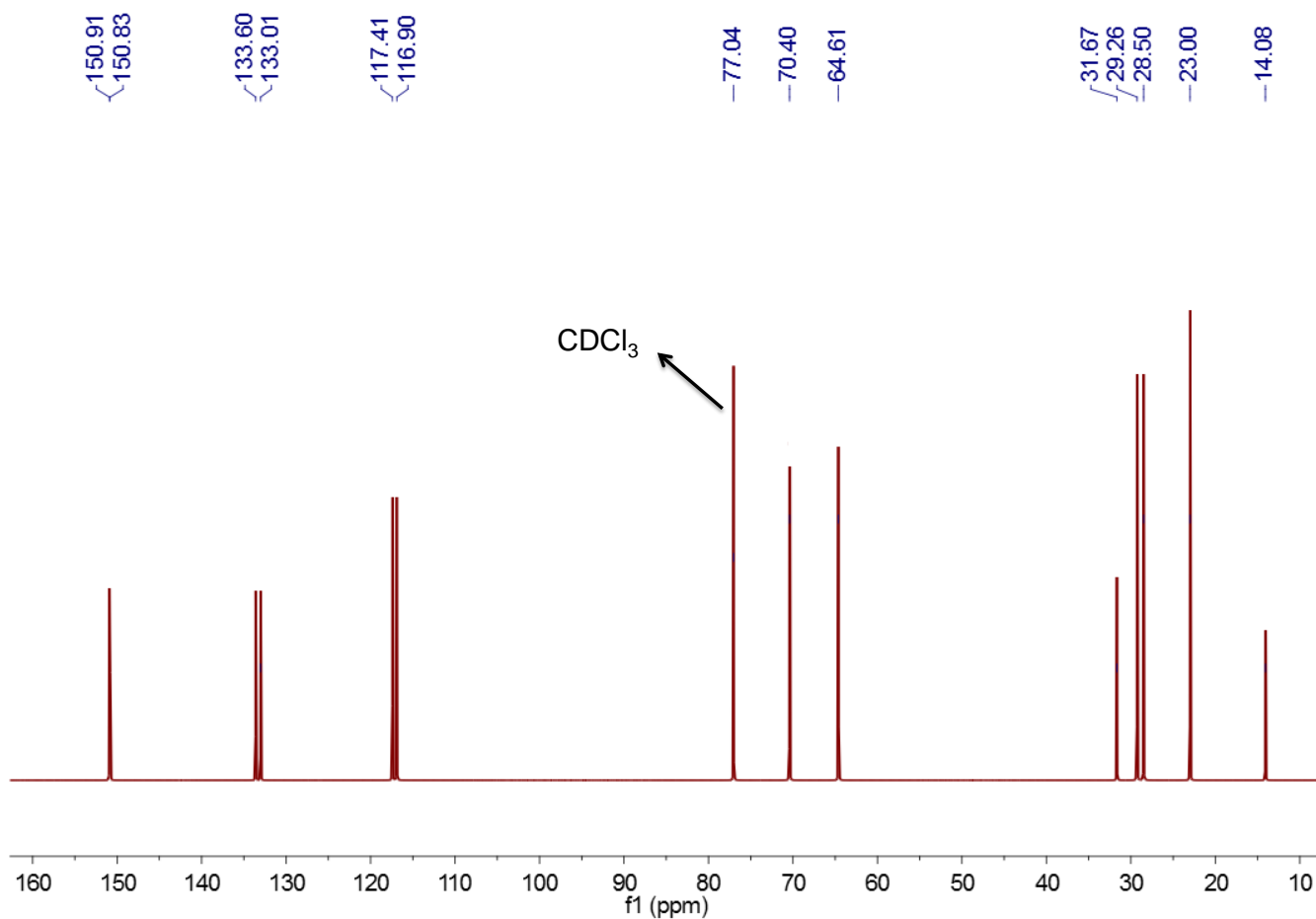


Fig. S28 ^{13}C NMR spectrum (100 MHz, CDCl_3 , 293 K) of amphiphilic pillar[5]arene **E**.

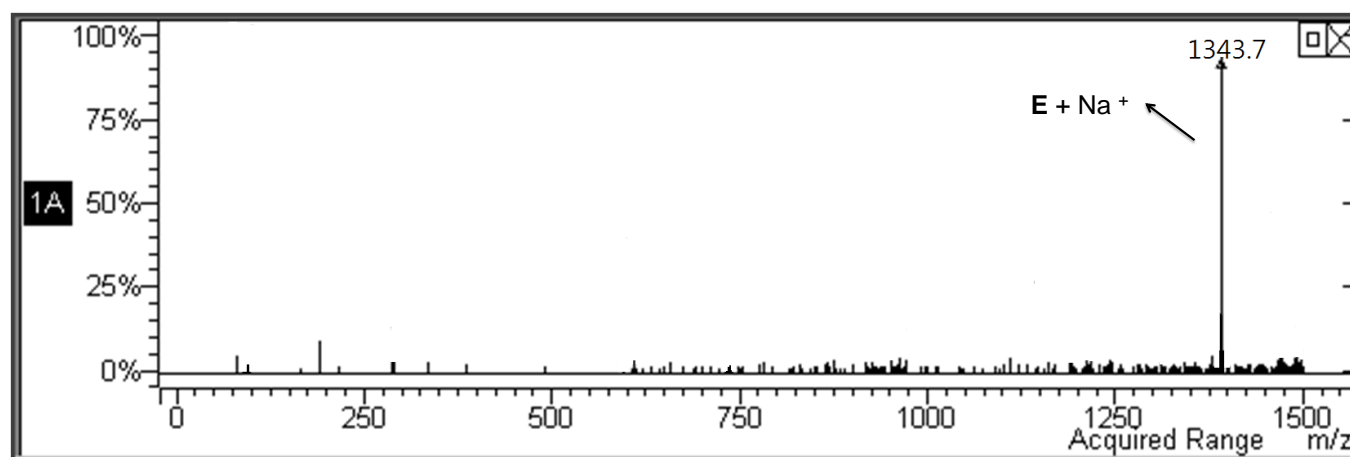


Fig. S29 Electrospray ionization mass spectrum of the **E**. Assignment of the main peak: m/z 1343.7 [**E** + Na] $^+$.

3. Self-assembly of amphiphilic pillar[5]arenes in water

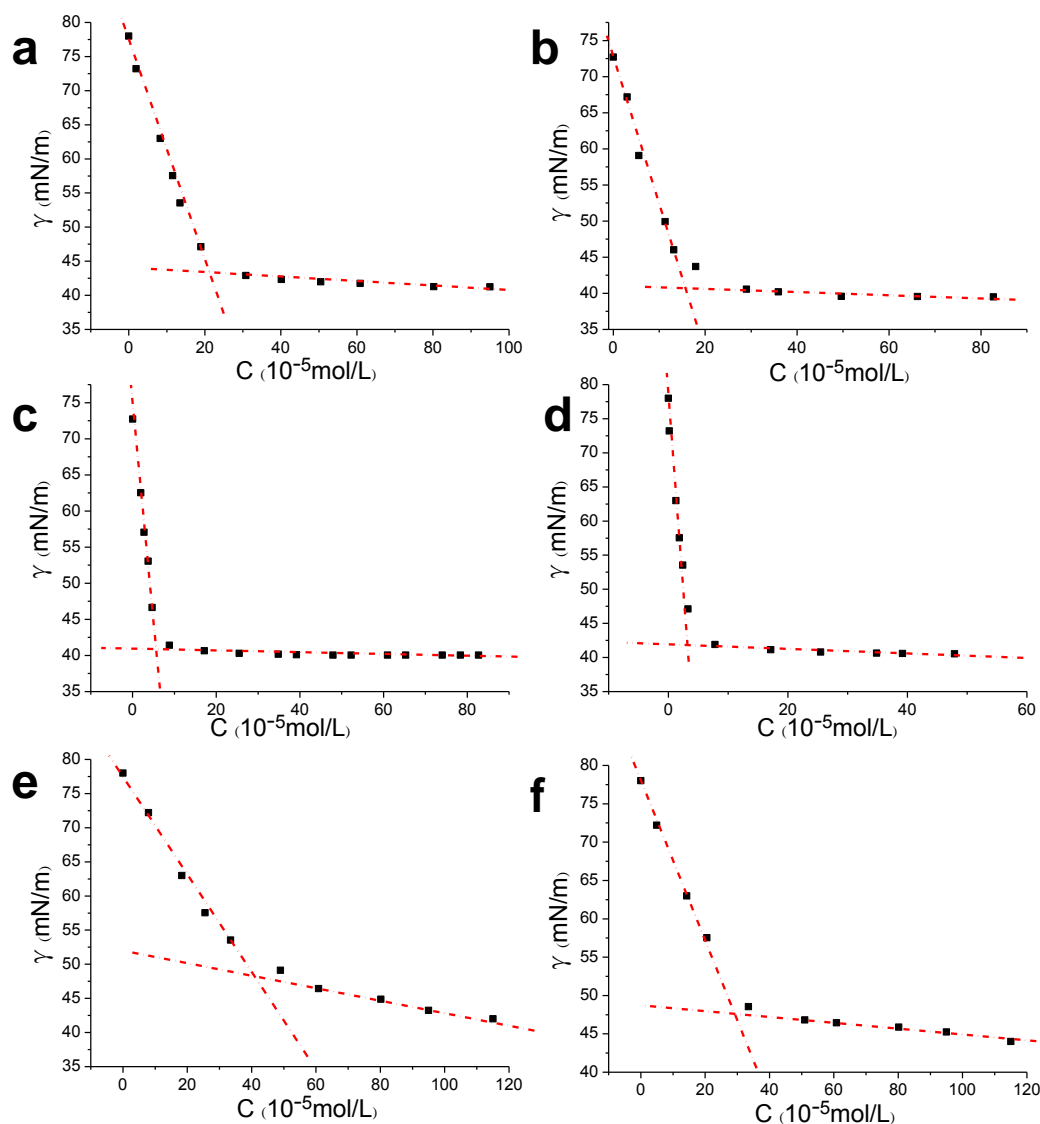


Fig. S30 Surface tension of water as a function of the amphiphilic pillar[5]arene concentration: (a) C1; (b) C2; (c) C3; (d) C4; (e) D; (f) E. There are two linear segments in the curve and a sudden reduction of the slope for every amphiphilic pillar[5]arene. The breaking points indicate the CMC values of these amphiphilic pillar[5]arenes in water.^{S3}

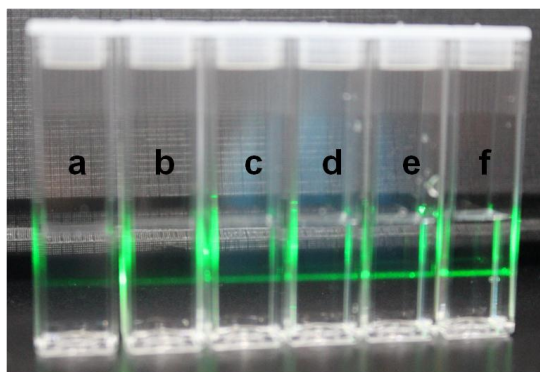


Fig. S31 Tyndall effects of amphiphilic pillar[5]arenes: (a) C1; (b) C2; (c) C3; (d) C4; (e) D; (f) E. $[C1] = [C2] = [C3] = [C4] = [D] = [E] = 2.00 \times 10^{-4}$ M.

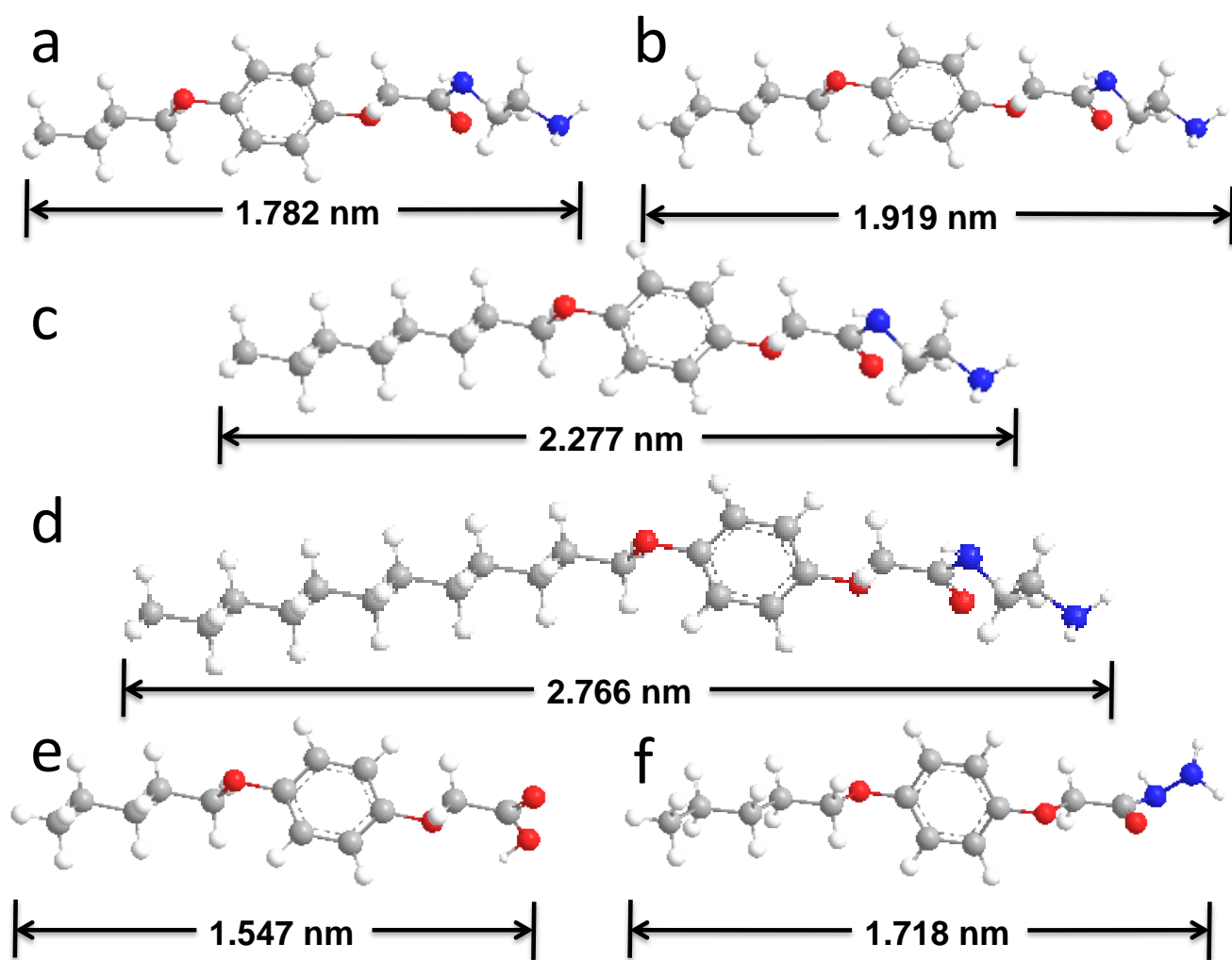


Fig. S32 Models of repeating units of amphiphilic pillar[5]arenes: (a) **C1**; (b) **C2**; (c) **C3**; (d) **C4**; (e) **D**; (f) **E**. (Carbon atoms are gray, oxygen atoms are red, nitrogen atoms are blue, and hydrogen atoms are white.)

4. Further self-assembly of amphiphilic pillar[5]arenes in water

Table S1. Evolution of UV–Vis intensities of 2.00×10^{-5} M **C1**, **C2**, **C3** and **C4** aqueous solutions.

amphiphilic pillar[5]arenes	Absorbance _{fresh prepared}	Absorbance _{aging for 1 week}	Absorbance _{aging for 2 months}
C1	1.73	1.05	0.04
C2	1.92	1.32	0.07
C3	1.64	1.14	0.11
C4	1.83	1.17	0.10

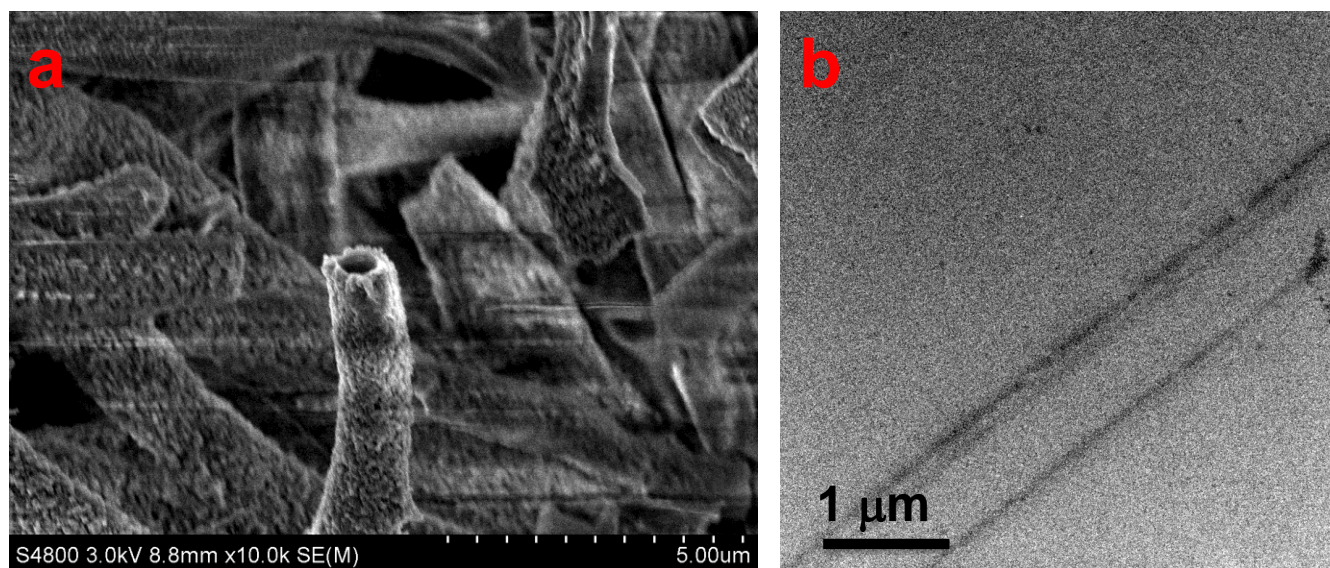


Fig. S33 (a) SEM image of the cross-section of a microtube self-assembled from amphiphilic pillar[5]arene **C4**. (b) TEM image of the vertical-section of a microtube self-assembled from amphiphilic pillar[5]arene **C4**.

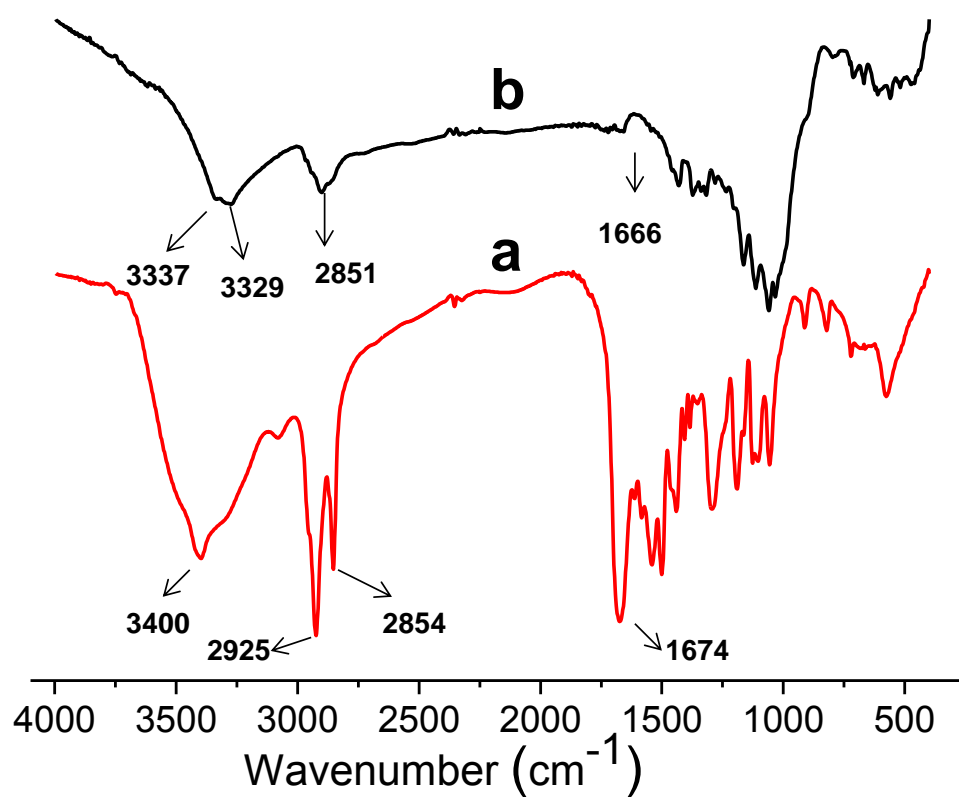


Fig. S34 Comparison of the Fourier transform IR spectra of a powder sample of amphiphilic pillar[5]arene **C4** with that of a microtube sample of **C4**.

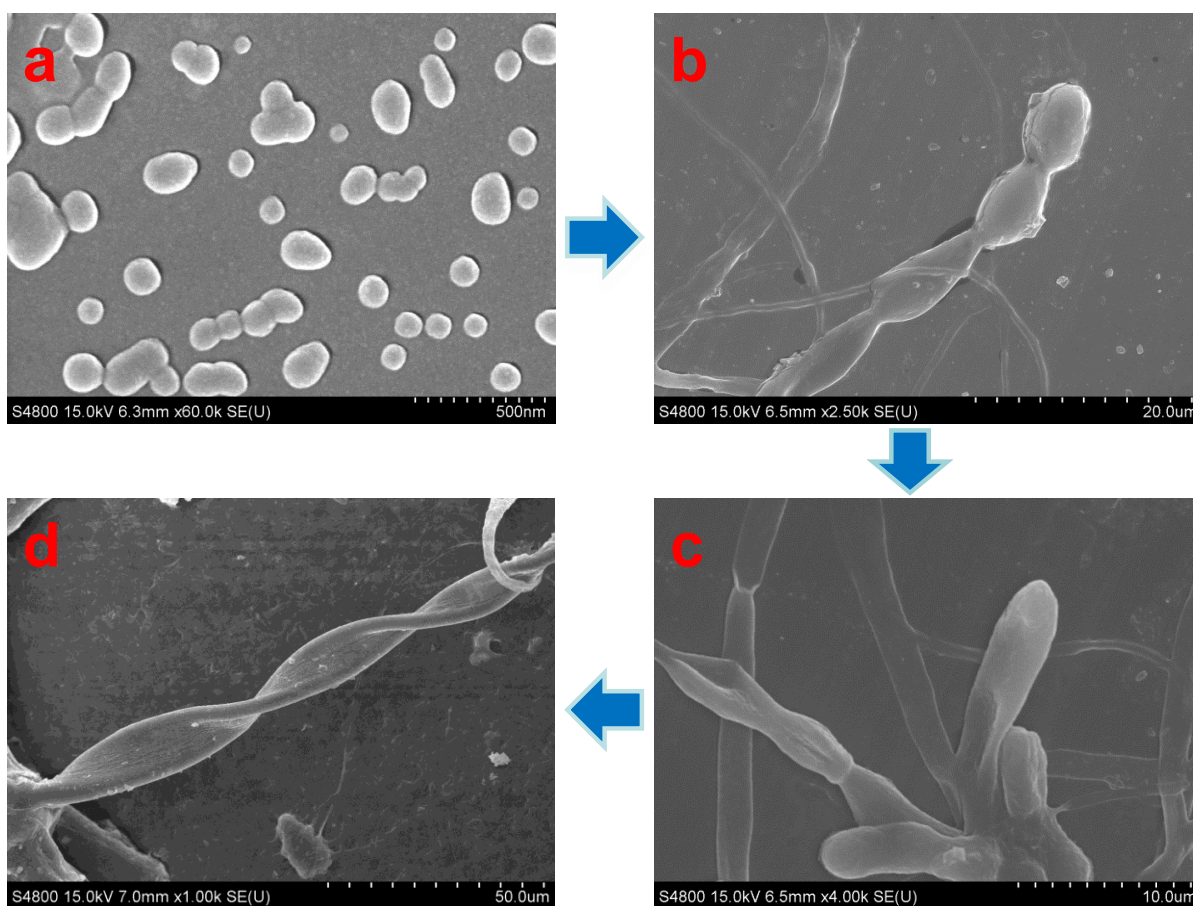


Fig. S35 TEM images of the intermediate structures self-assembled from amphiphilic pillar[5]arene **C4**: (a) vesicles; (b) fused vesicles; (c) further fused vesicles; (d) helical microtubes.

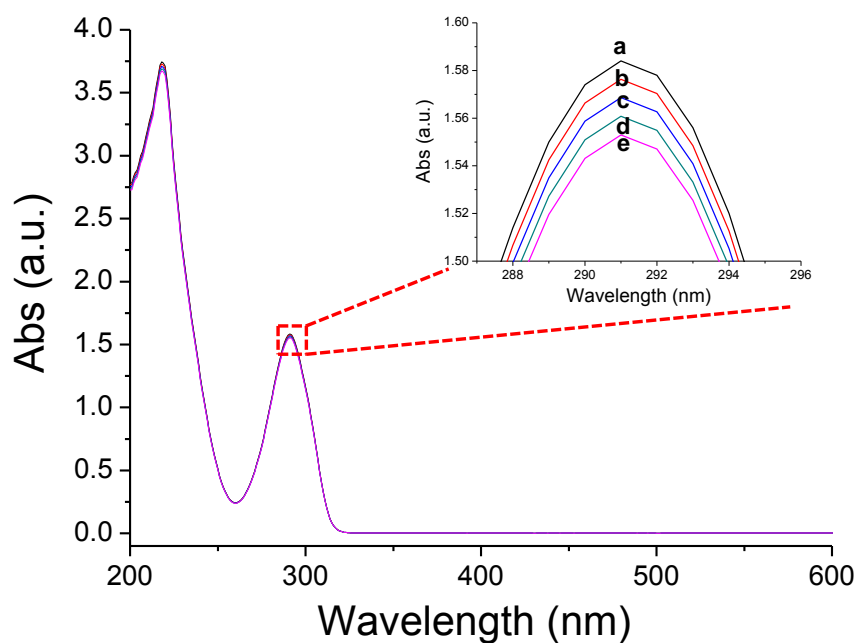


Fig. S36 UV-Vis spectra of amphiphilic pillar[5]arene **D** in water at different aging times: (a) 1 day; (b) 2 days; (c) 1 week; (d) 1 month; (e) 2 months.

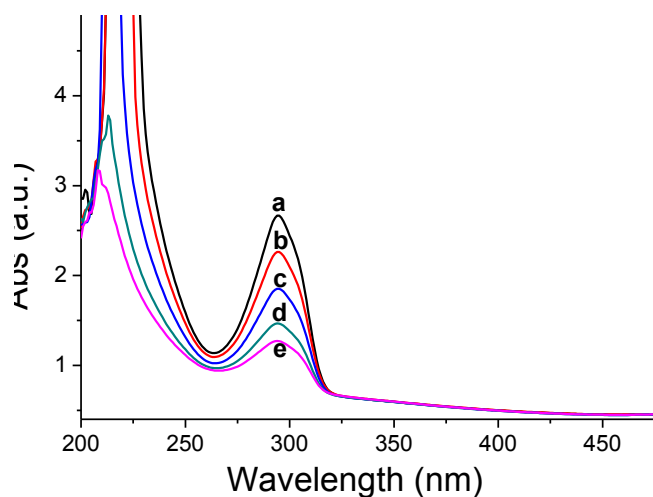


Fig. S37 UV-Vis spectra of amphiphilic pillar[5]arene **E** in water at different aging times: (a) 1 day; (b) 2 days; (c) 1 week; (d) 1 month; (e) 2 months.

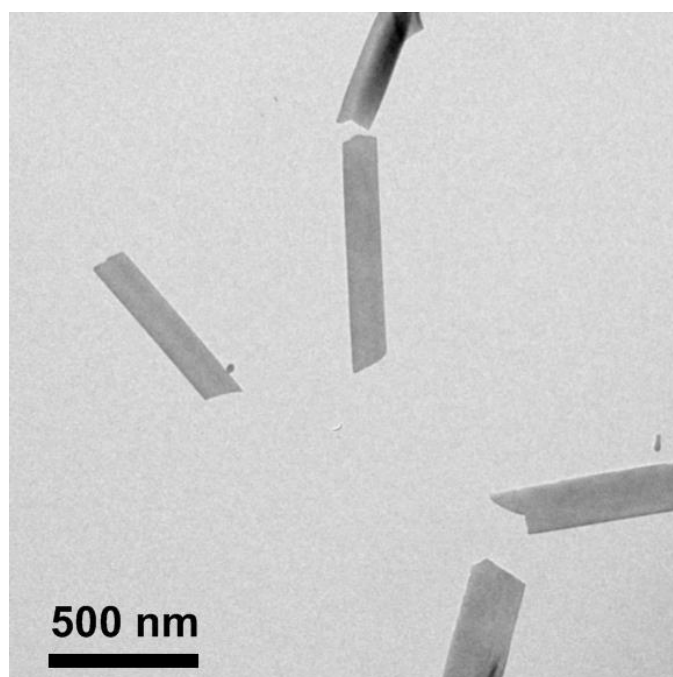


Fig. S38 TEM image of the nanosheets self-assembled from amphiphilic pillar[5]arene **E** after 2 months.

5. Application of the microtubes self-assembled from **C4** in the capture of λ -DNA

The peak at around 260 nm was attributed to the absorbance of λ -DNA.^{S4} A decrease in the characteristic absorbance of λ -DNA from 0.982 to 0.155 after the microtubes of **C4** were immersed into an aqueous solution of λ -DNA confirmed that λ -DNA was captured by the microtubes (Figure S38, spectra a and b).

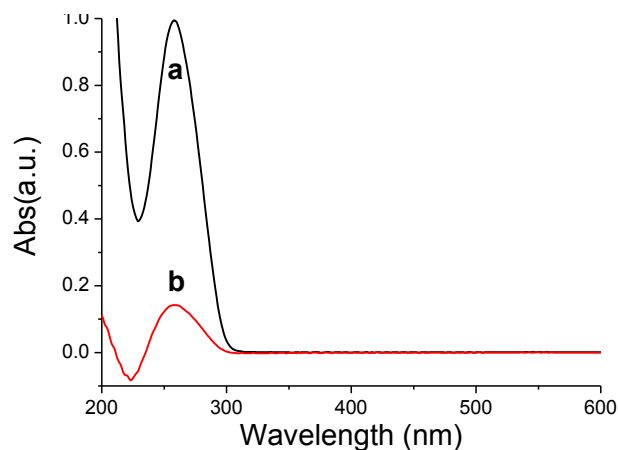


Fig. S39 The UV-Vis spectra: (a) λ -DNA; (b) after microtubes of **C4** were immersed into an aqueous solution of λ -DNA.

References:

- S1. Y. Yao, M. Xue, J. Chen, M. Zhang, F. Huang, *J. Am. Chem. Soc.* 2012, **134**, 15712.
- S2. C. Yan, W. Chen, J. Chen, T. Jiang, Y. Yao, *Tetrahedron* 2007, **63**, 9614.
- S3. Y. Sun, C-G. Yan, Y. Yao, Y. Han, M. Shen, *Adv. Funct. Mater.* 2008, **18**, 3981.
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