

A CO₂-responsive pillar[5]arene: synthesis and self-assembly in water

Kecheng Jie, Yong Yao, Xiaodong Chi and Feihe Huang*

*State Key Laboratory of Chemical Engineering, Department of Chemistry, Zhejiang University, Hangzhou,
Zhejiang 310027, P. R. China*

Fax and Tel: +86-571-8795-3189; Email address: fhuang@zju.edu.cn.

Electronic Supplementary Information (12 pages)

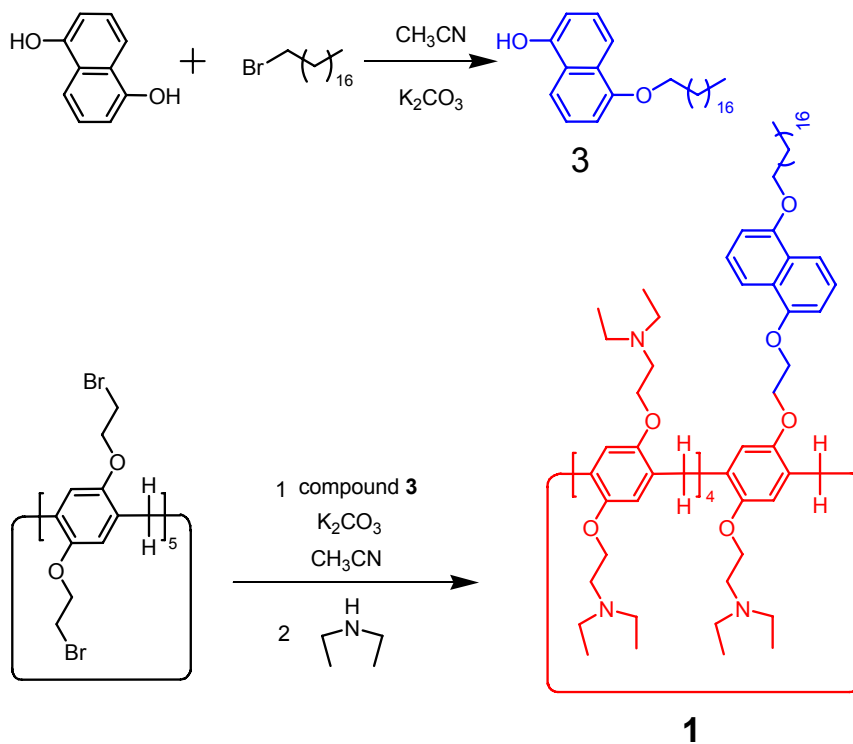
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|--|-----|
| 1. <i>Materials and methods</i> | S2 |
| 2. <i>Synthesis of compound 1</i> | S3 |
| 3. <i>Determination of critical aggregation concentration of protonated 1 in water</i> | S13 |
| 4. <i>Self-assembly of 1 (10⁻⁴ M) in water before and after adding HCl</i> | S13 |
| 5. <i>Self-assembly of 1 (10⁻⁴ M) in water switched by CO₂</i> | S14 |
| 6. <i>Transmittance study of CO₂-switch reversible process</i> | S15 |
| 7. <i>References</i> | S16 |

1. Materials and methods

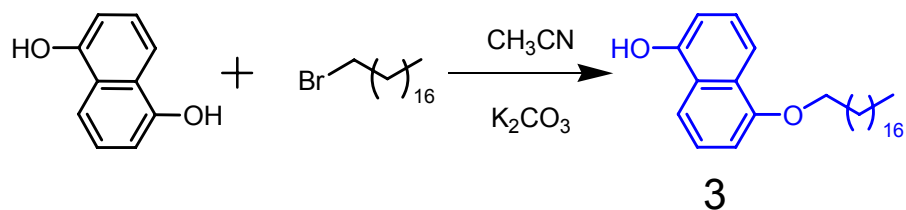
All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. 1-Bromooctadecane and 1,5-dihydroxy-naphthalene were purchased and used as supplied without further purification. Bromoethylpillar[5]arene^{S1} was prepared according to a published procedure. ¹H NMR and ¹³C HMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with IonSpec 4.7 Tesla FTMS. Transmission electron microscopy investigations were carried out on a JEM-1200EX instrument. Dynamic light scattering was carried out on a Malvern Nanosizer S instrument at room temperature. UV-vis spectra were taken on a PerkinElmer Lambda 35 UV-vis spectrophotometer.

2. Synthesis of compound 1

Scheme S1. Synthetic route to **1**.



2.1. Synthesis of compound **3**



Anhydrous potassium carbonate (27.6 g, 200 mmol) was added to a solution of 1,5-dihydroxynaphthalene (16.0 g, 100 mmol) and 1-bromooctadecane (33.3 g, 100 mmol) in dry acetonitrile (500 mL) under vigorous stirring. The mixture was stirred at 80 °C for 24 hours under nitrogen. After removal of the inorganic salt, the solvent was evaporated and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 100:1) to give **3** as a white solid. The yield of **3** was 75%. The melting point of **3** is 61.0 °C. The 1H NMR spectrum of **3** is shown in Fig. S1. 1H NMR (400 MHz, chloroform-*d*, 293 K) δ (ppm): 7.87 (d, $J = 4.0$ Hz, 1H), 7.69 (d, $J = 4$ Hz, 1H), 7.38 (t, $J = 6$ Hz, 1H), 7.27 (d, $J = 6$ Hz, 1H), 6.86–6.82 (m, 2H), 5.17 (s, 1H), 4.12 (t, $J = 6$ Hz, 2H), 1.95–1.88 (m, 2H), 1.40–1.26 (m, 30H), 0.90–0.86 (t, $J = 6$ Hz, 3H). The ^{13}C NMR spectrum of **3** is shown in Fig. S2. ^{13}C NMR (100 MHz, chloroform-*d*, 293 K) δ (ppm): 154.89, 151.10, 127.13, 125.37, 124.96, 114.94, 123.25, 109.37, 105.20, 77.34, 77.02, 76.70, 68.22, 31.94, 29.71, 29.64, 29.45, 29.38, 29.31, 26.28, 22.71, 14.14. LRESIMS is shown in Fig. S3: m/z 447.3 $[M + Cl]^-$. HRESIMS is shown in Fig. S4: m/z calcd for $[M + Cl]^-$ $C_{28}H_{44}O_2Cl^-$, 447.3030; found 447.3034; error 0.8 ppm.

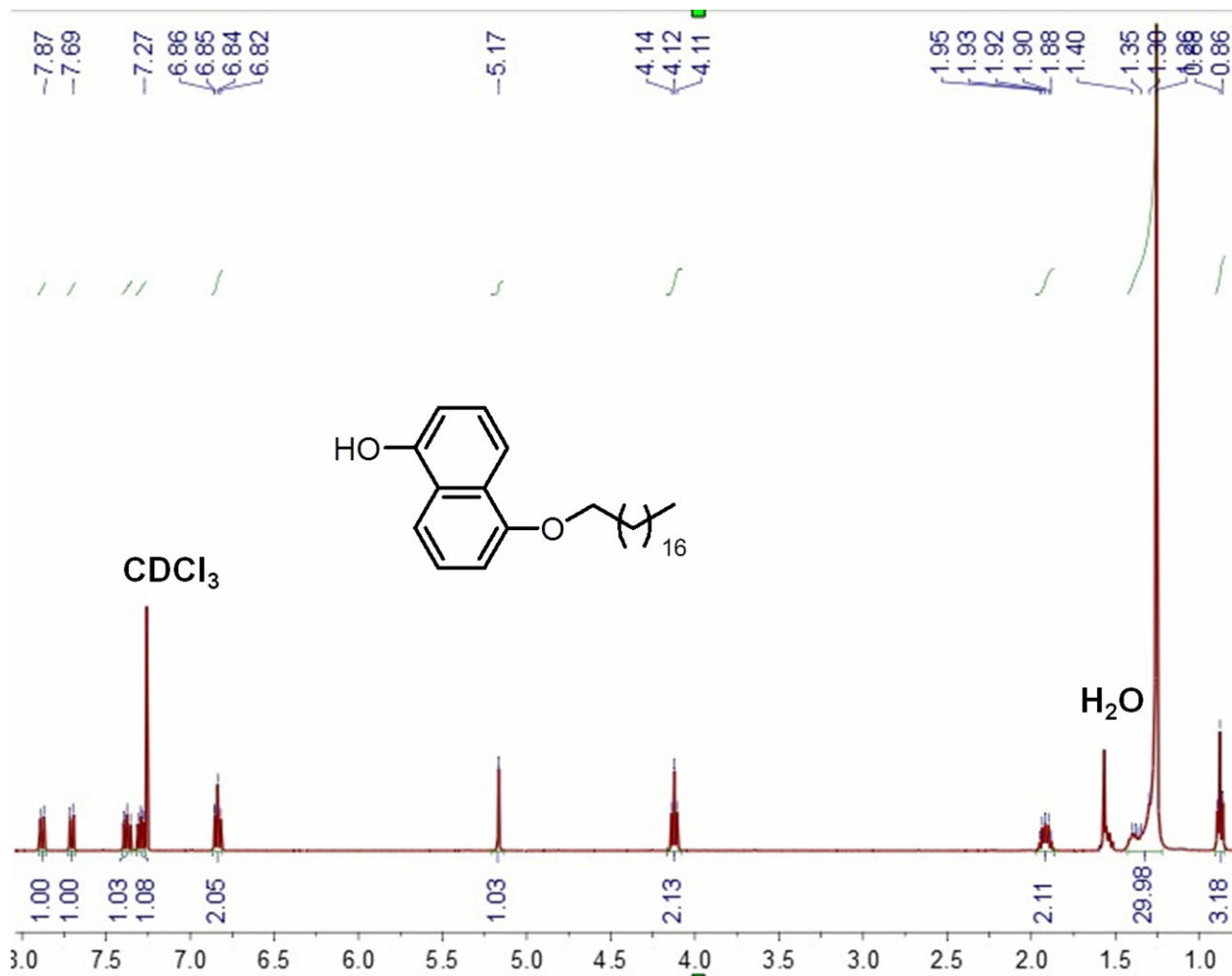


Fig. S1. ^1H NMR spectrum (400 MHz, chloroform-*d*, 293K) of **3**.

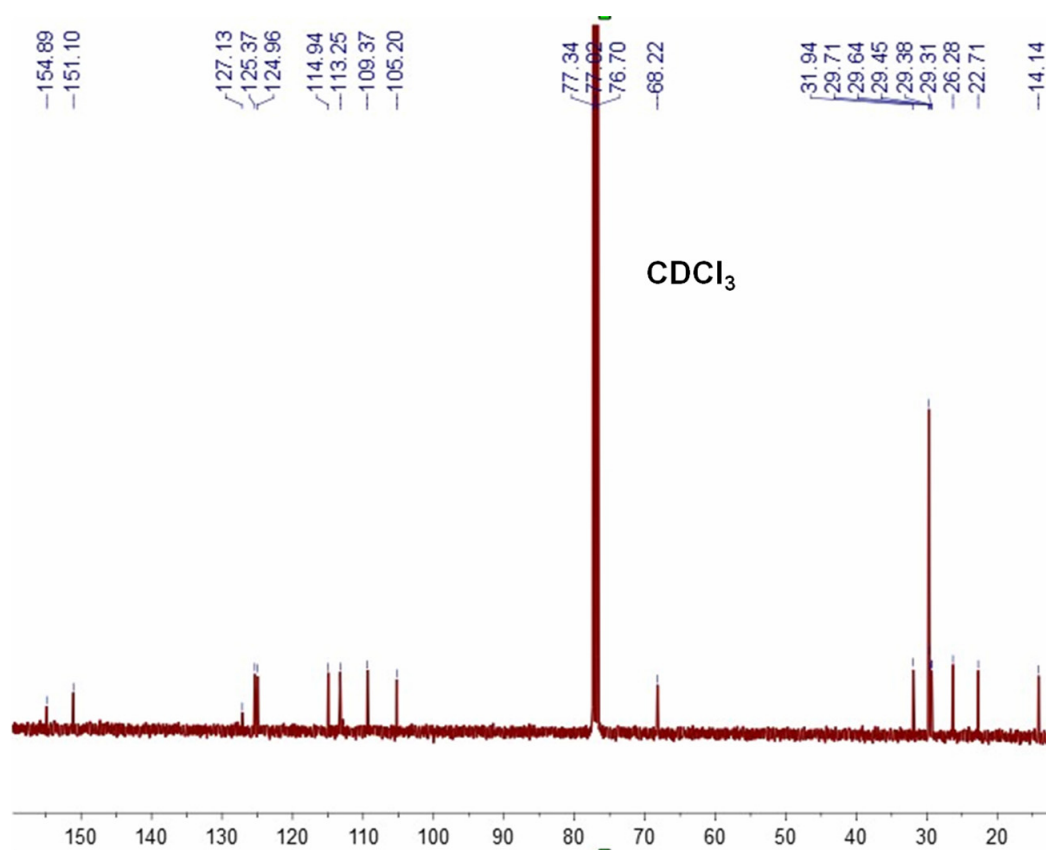


Fig. S2. ¹³C NMR spectrum (100 MHz, chloroform-*d*, 293K) of **3**.

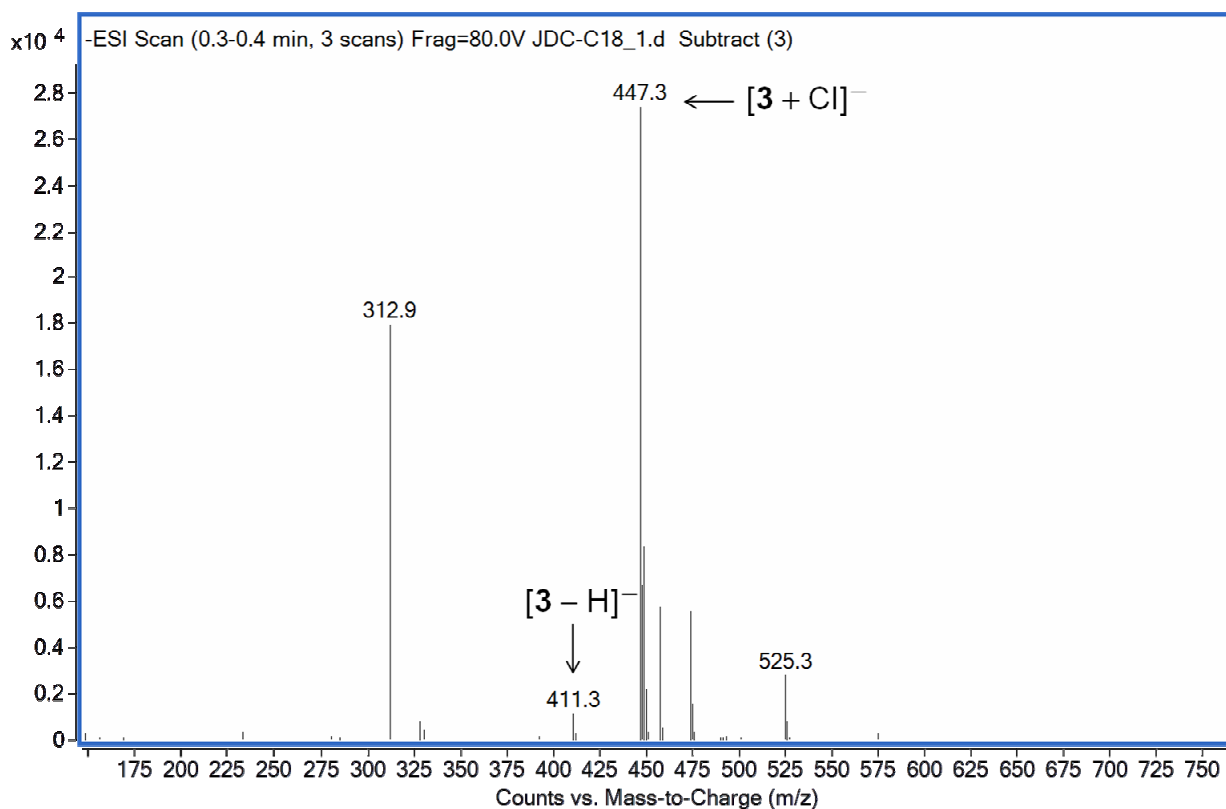


Fig. S3. Low resolution electrospray ionization mass spectrum of **3**.

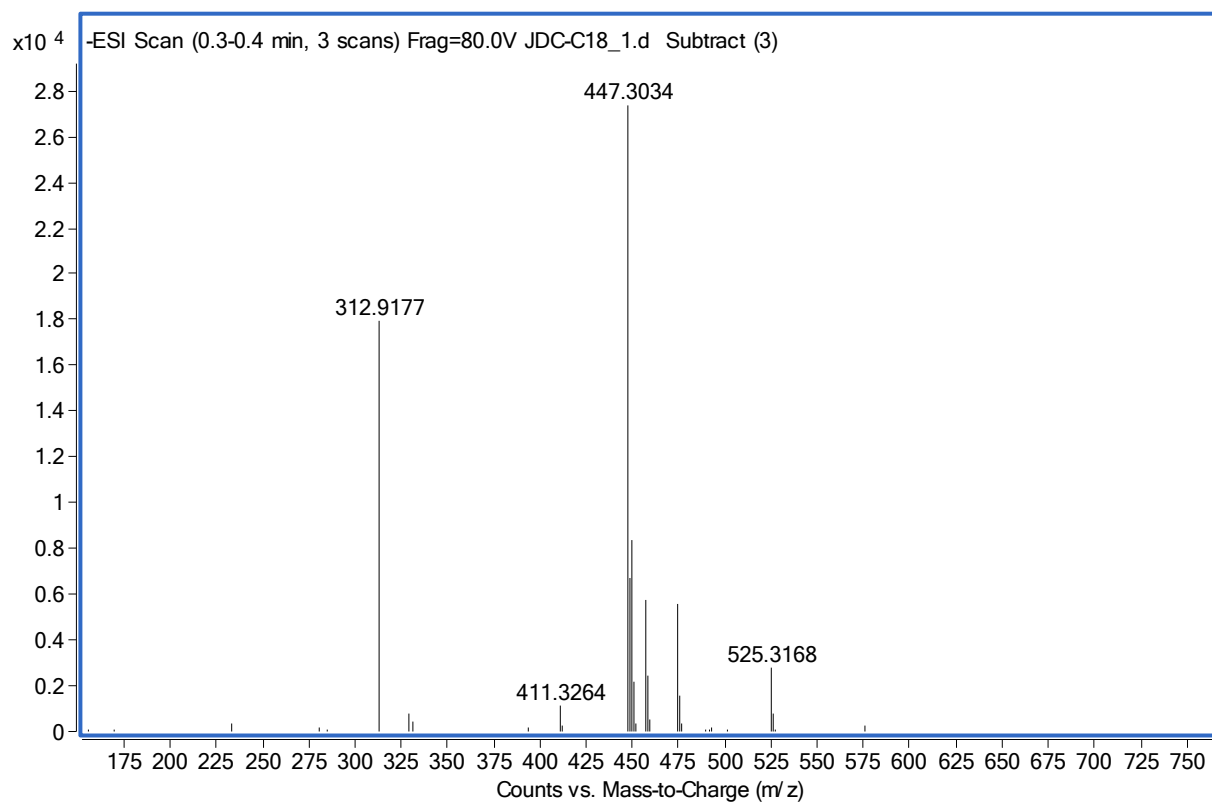
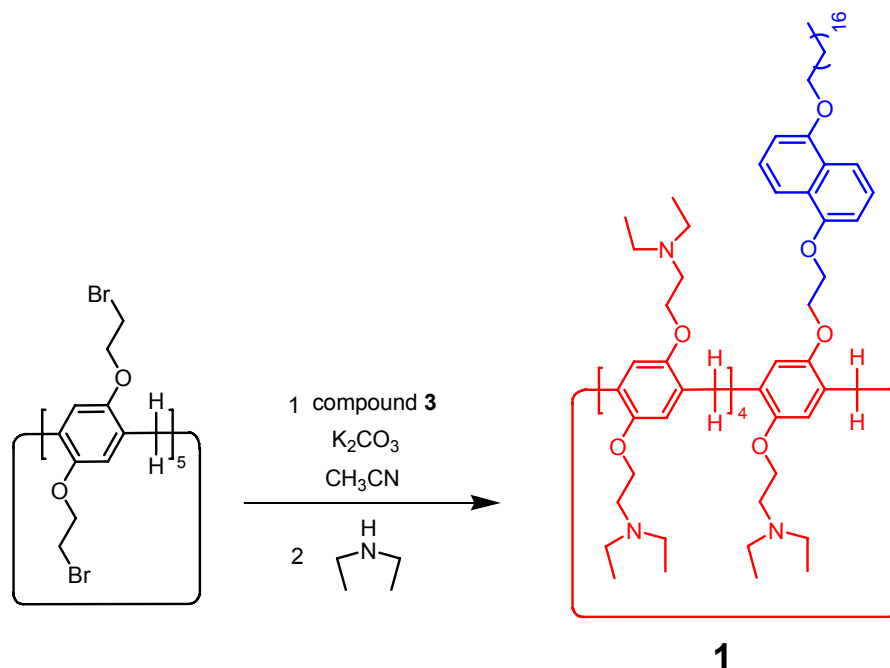


Fig. S4. High resolution electrospray ionization mass spectrum of **3**.

2.2. Synthesis of compound **1**



Anhydrous potassium carbonate (5.52 g, 40 mmol) was added to a solution of **3** (4.12 g, 10.0 mmol) and bromoethylpillar[5]arene (16.8 g, 10 mmol) in dry acetonitrile (250 mL) under vigorous stirring. The mixture was stirred at 80 °C for 24 hours. After removal of the inorganic salt, the solvent was evaporated and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) to give the crude product as a white solid. A mixture of the crude product with excess diethylamine (30 equiv) were dissolved in ethanol and refluxed for 24 h. The solvent was evaporated, and the residue was poured into a NaOH solution (1.00 M, 400 mL) and stirred. The solution was extracted with ethyl acetate (3 × 100 mL), and the organic phase was obtained. The oil yellow liquid was isolated after evaporation of the solution as the crude product, which was distilled in vacuo to give **1** as a solid.^{S2} The yield of **1** was 23.1%. The melting point of **1** is 75.2 °C. The ¹H NMR spectrum of **1** is shown in Fig. S5. ¹H NMR (400 MHz, chloroform-*d*, 293 K) δ (ppm): 7.93–7.89 (t, J = 6 Hz, 2H), 7.38 (t, J = 6 Hz, 1H), 7.33 (d, J = 6 Hz, 1H), 7.02–6.82 (m, 12H), 4.47 (d, J = 4 Hz, 4H), 4.13–4.08 (m, 10H), 3.93–3.74 (m, 18H), 3.00–2.91 (m, 16H), 2.49–2.43 (m, 4H), 1.93–1.89 (t, J = 6 Hz, 2H), 1.54 (s, 2H), 1.39 (s, 2H), 1.26–1.23 (m, 28H), 1.11–1.03 (m, 48H), 0.94 (t, J = 6 Hz, 6H), 0.88 (t, J = 6 Hz, 3H). The ¹³C NMR spectrum of **1** is shown in Fig. S6. ¹³C NMR (100 MHz, chloroform-*d*, 293 K) δ (ppm): 154.71, 151.43, 149.82, 149.76, 149.69, 128.42, 126.91, 126.81, 125.43, 124.88, 114.90, 114.13, 105.73, 105.32, 68.19, 67.46, 67.19, 67.10, 52.24, 51.93, 47.28, 47.55, 29.77, 29.36, 26.14, 22.68, 14.12, 12.13, 12.06. LRESIMS (done in chloroform-*d*) is shown in Fig. S7: m/z 1942.9 [M + D]⁻. HRESIMS (done in chloroform-*d*) is shown in Fig. S8: m/z calcd for [M + D]⁺ C₁₁₉H₁₉₃O₁₂N₉D⁺, 1942.4910; found 1942.4861; error 2.5 ppm.

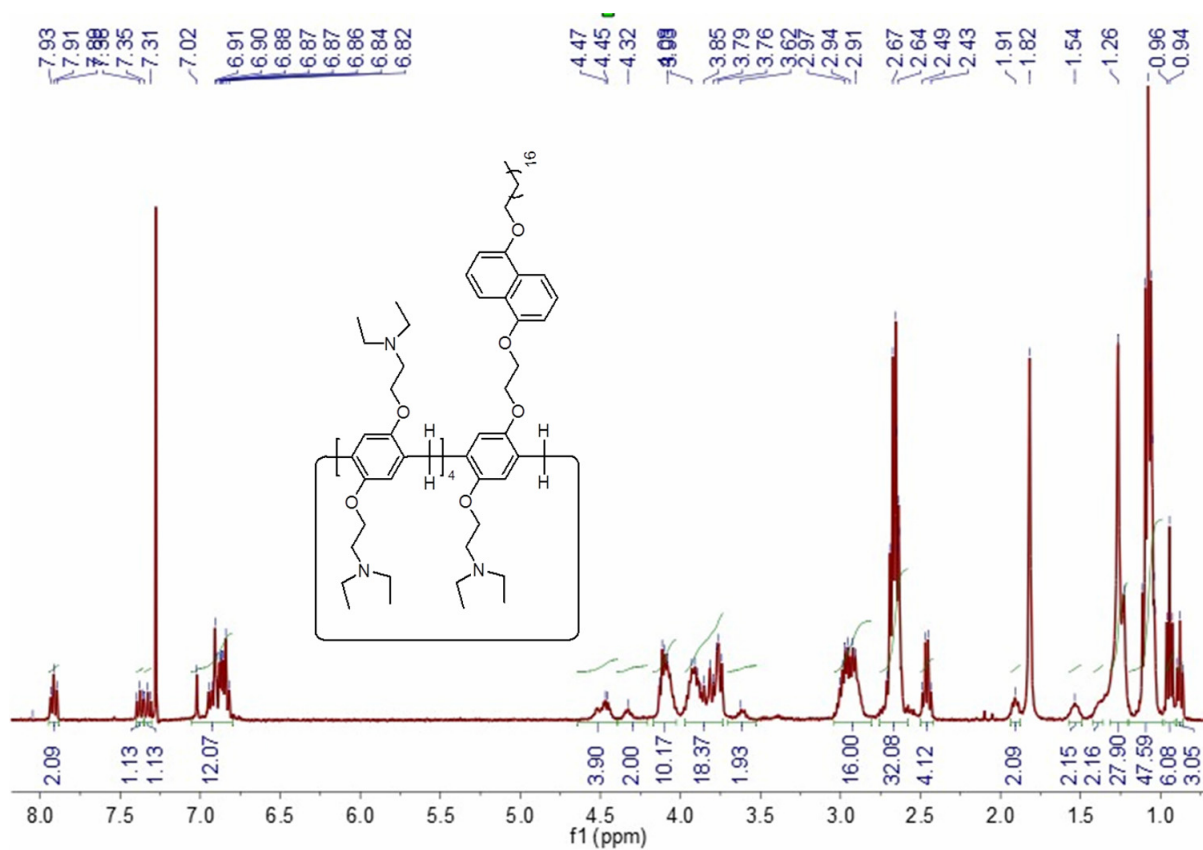


Fig. S5. ^1H NMR spectrum (400 MHz, CDCl_3 , 293K) of **1**.

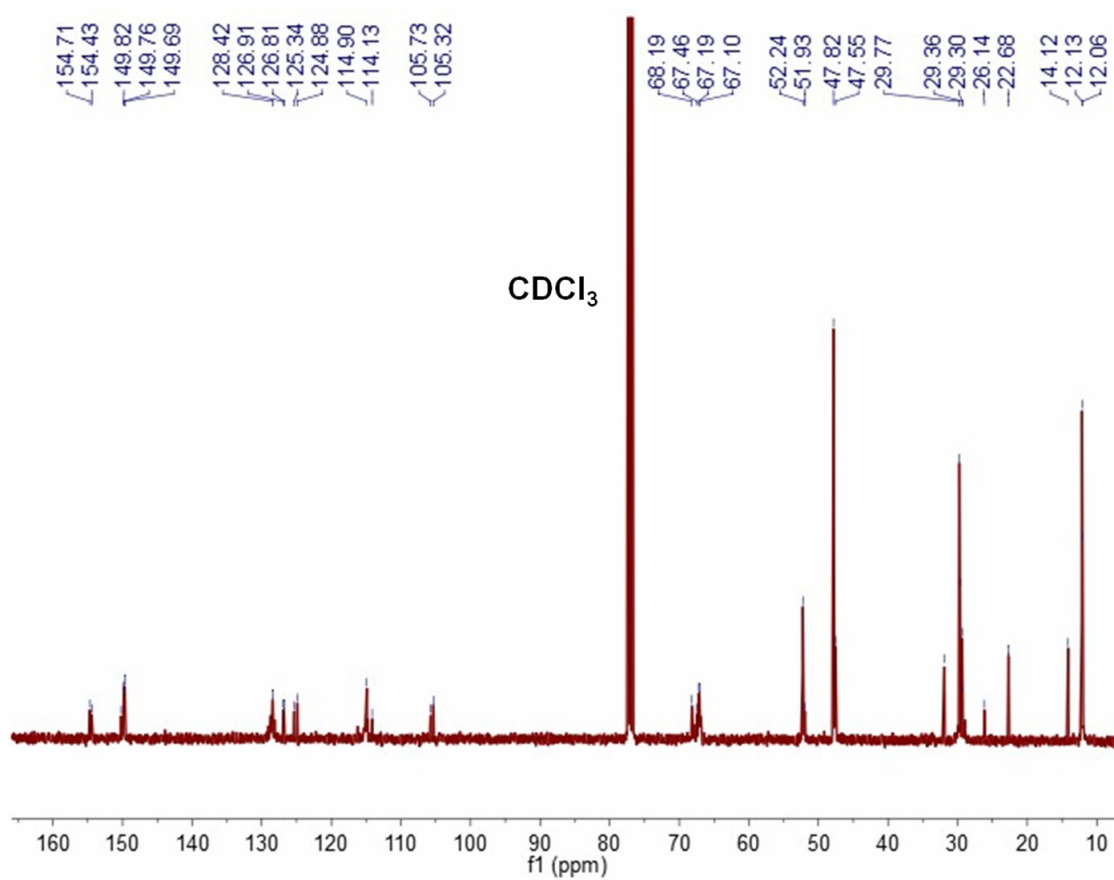


Fig. S6. ^{13}C NMR spectrum (100 MHz, CDCl_3 , 293K) of **1**.

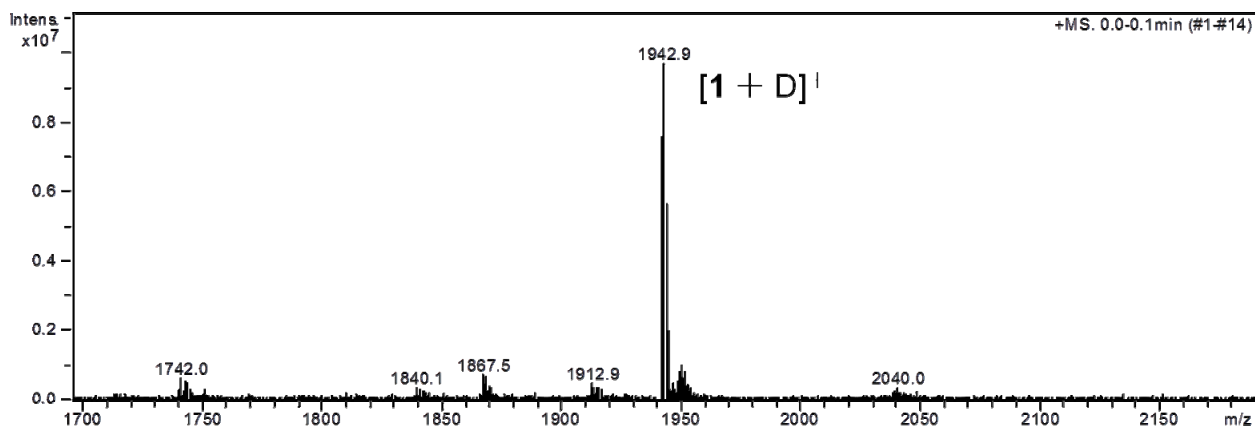


Fig. S7. Low resolution electrospray ionization mass spectrum of 1.

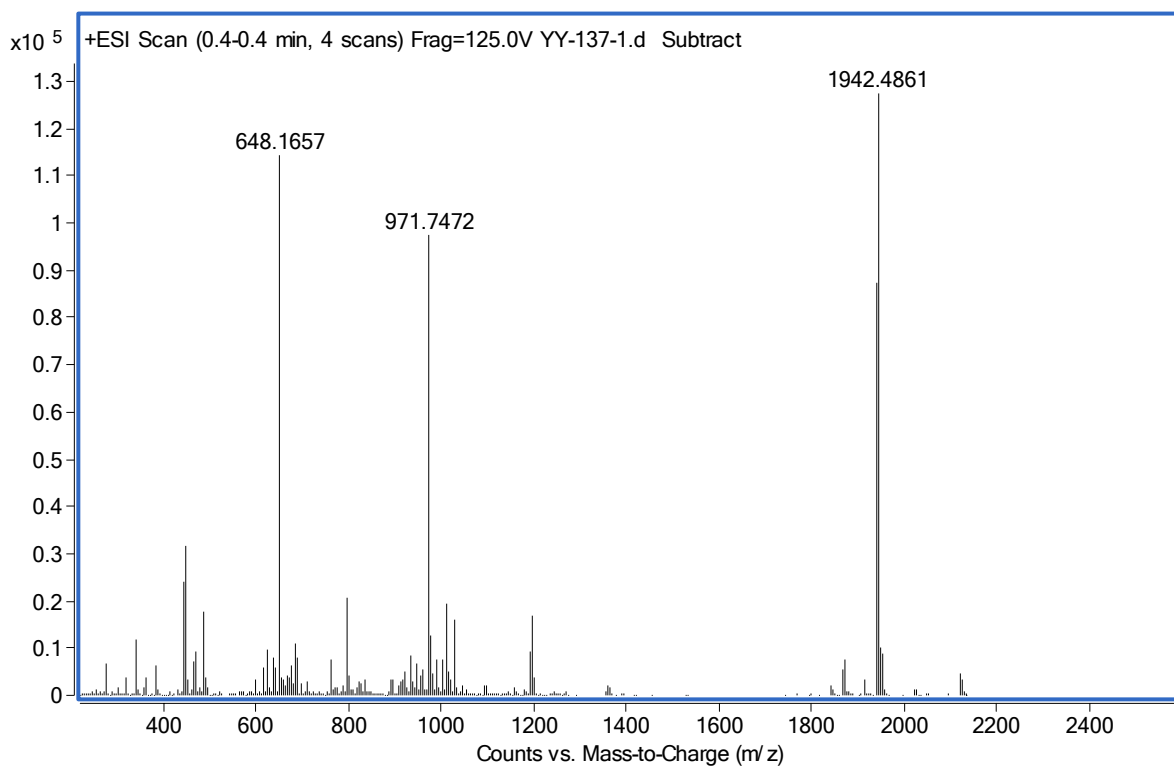


Fig. S8. High resolution electrospray ionization mass spectrum of 1.

2.3 Amphiphile **2** protonated by HCl

The ^1H NMR spectrum of **2** is shown in Fig. S9. ^1H NMR (400 MHz, DMSO- d_6 , 293 K) δ (ppm): 7.77–7.75 (d, 2H), 7.49–7.36 (m, 2H), 7.22 (d, $J = 4$ Hz, 2H), 7.03–6.87 (m, 12H), 4.56–4.43 (m, 18H), 4.12 (m, 4H), 3.78–3.67 (m, 24H), 3.32–3.10 (m, 33H), 1.84 (d, $J = 4$ Hz, 2H), 1.51–1.49 (m, 2H), 1.30–1.25 (m, 37H), 1.22–1.17 (m, 31H), 1.11–1.07 (t, $J = 6$ Hz, 4H), 0.86–0.82 (t, $J = 4$ Hz, 3H). The ^{13}C NMR spectrum of **2** is shown in Fig. S10. ^{13}C NMR (100 MHz, DMSO- d_6 , 293 K) δ (ppm): 130.15, 47.03, 28.59, 22.01, 13.89, 8.63, 8.42. LRESIMS (done in $\text{H}_2\text{O}-d$) is shown in Fig. S11: m/z 971.3 [$2 - 9\text{Cl}^- - 7\text{H}^+$] $^{2+}$.

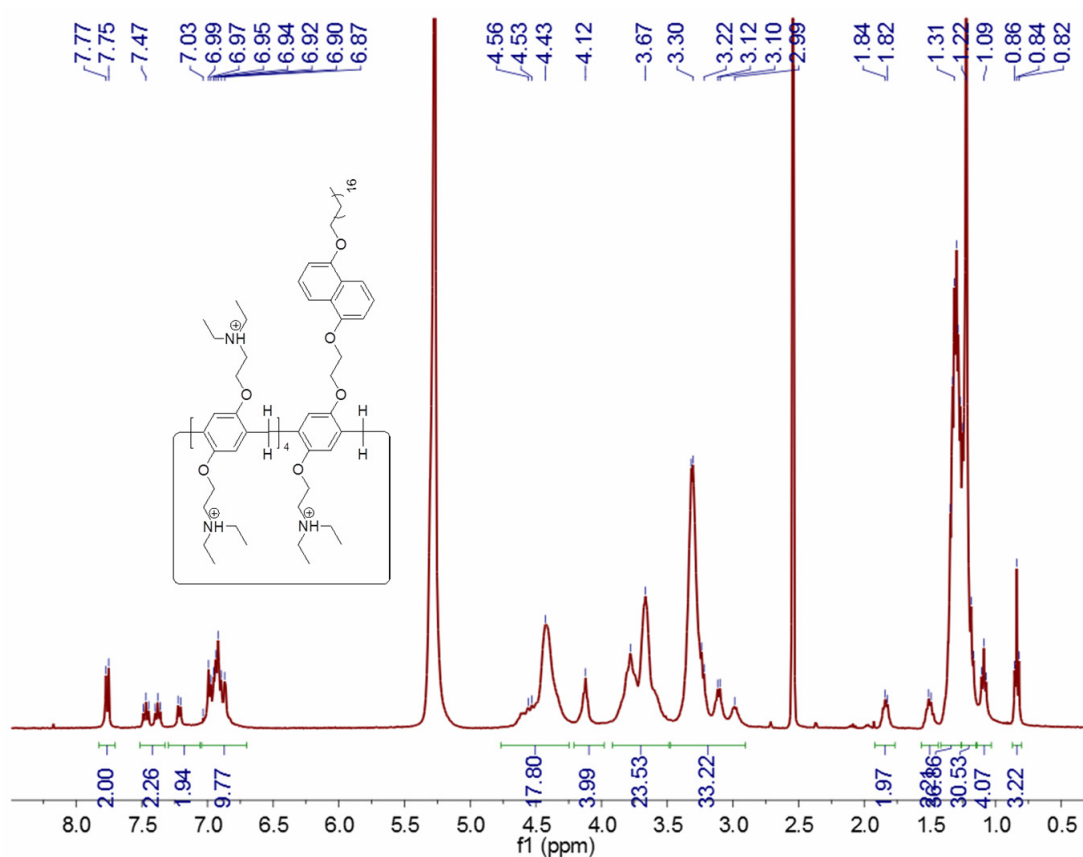


Figure S9. ^1H NMR spectrum (400 MHz, DMSO- d_6 , 293K) of **2**.

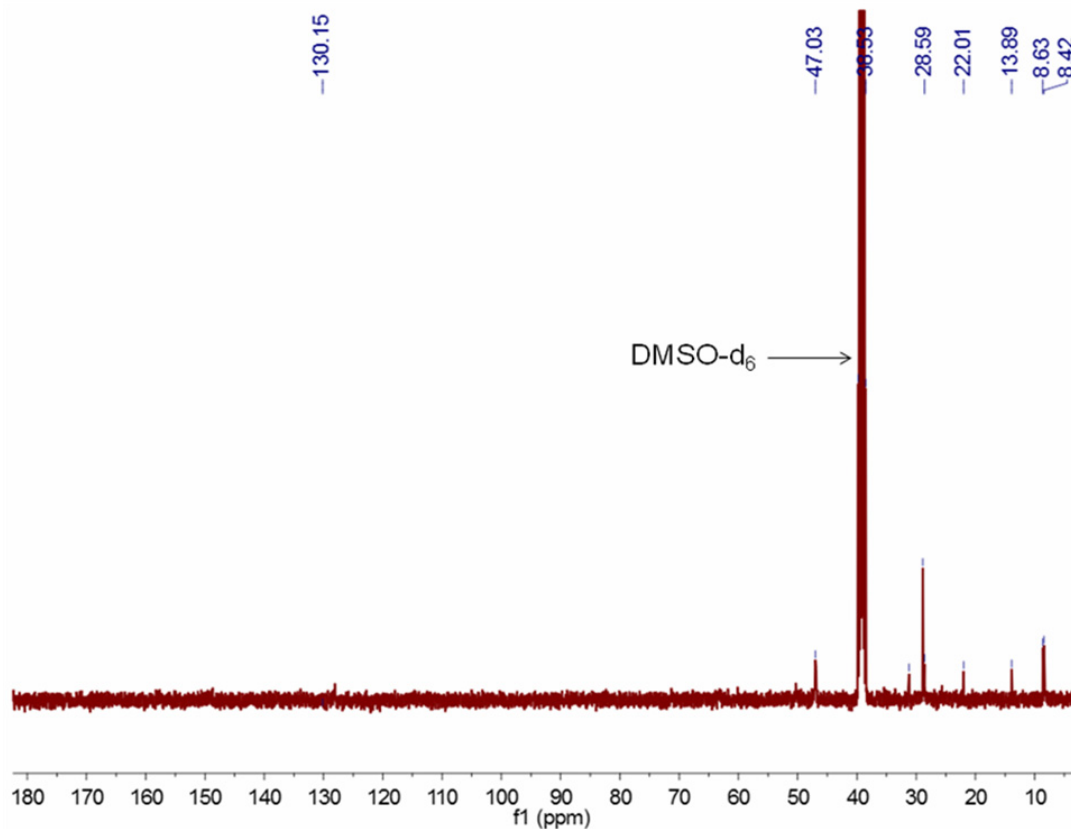


Fig. S10. ¹³C NMR spectrum (100 MHz, DMSO-d₆, 293K) of **2**.

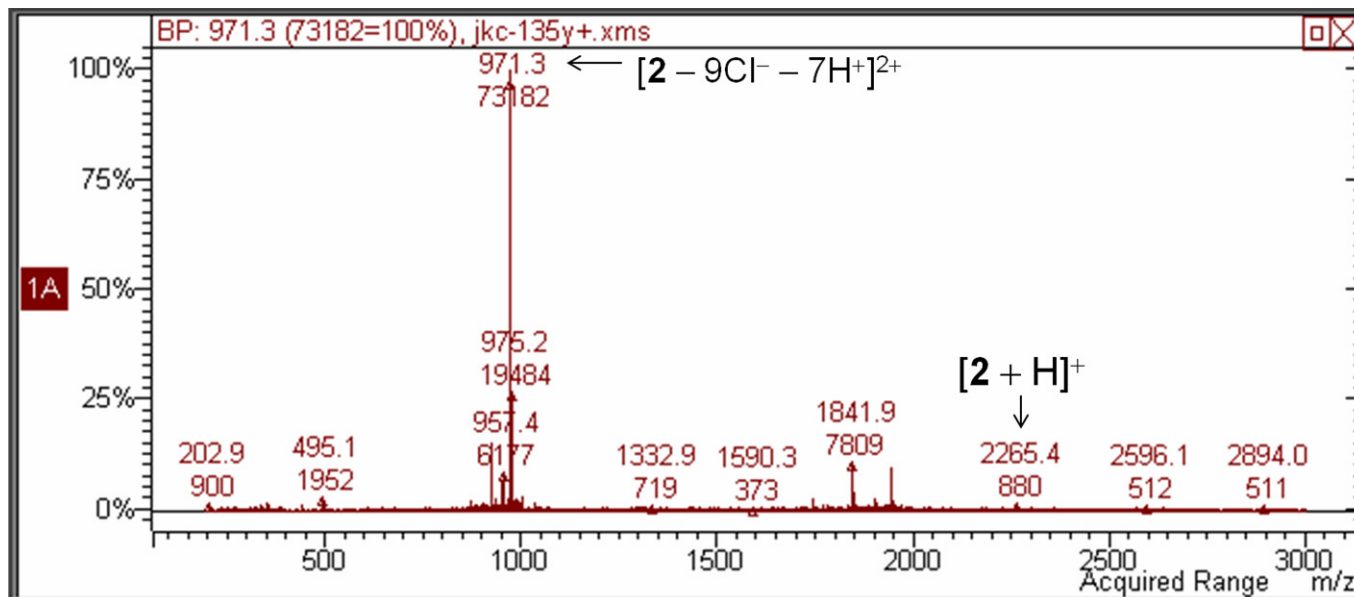


Fig. S11. Low resolution electrospray ionization mass spectrum of **2**.

3. Determination of critical aggregation concentration of protonated **1** in water

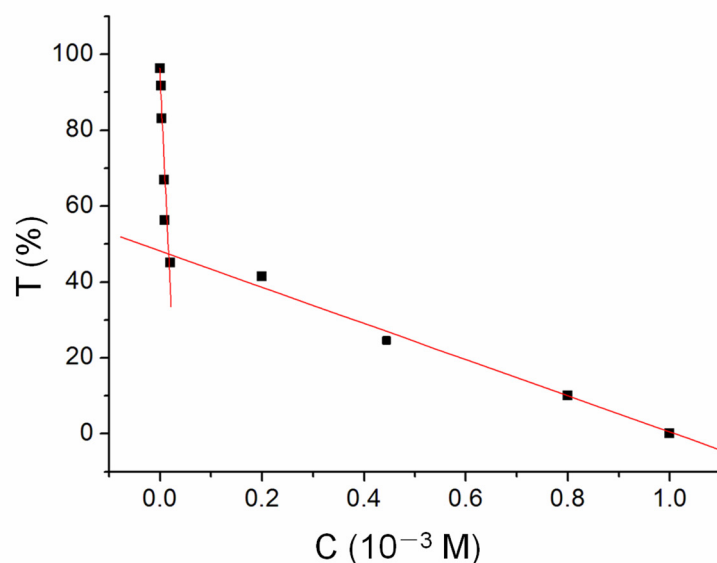


Fig. S12. Transmittance at 339 nm as a function of the amphiphilic pillar[5]arene **2** concentration. There are two linear segments in the curve and a sudden reduction of the slope, implying that the CAC of **2** is approximately 1.70×10^{-5} M.

4. Self-assembly of **1** (1.00×10^{-4} M) in water before and after adding HCl

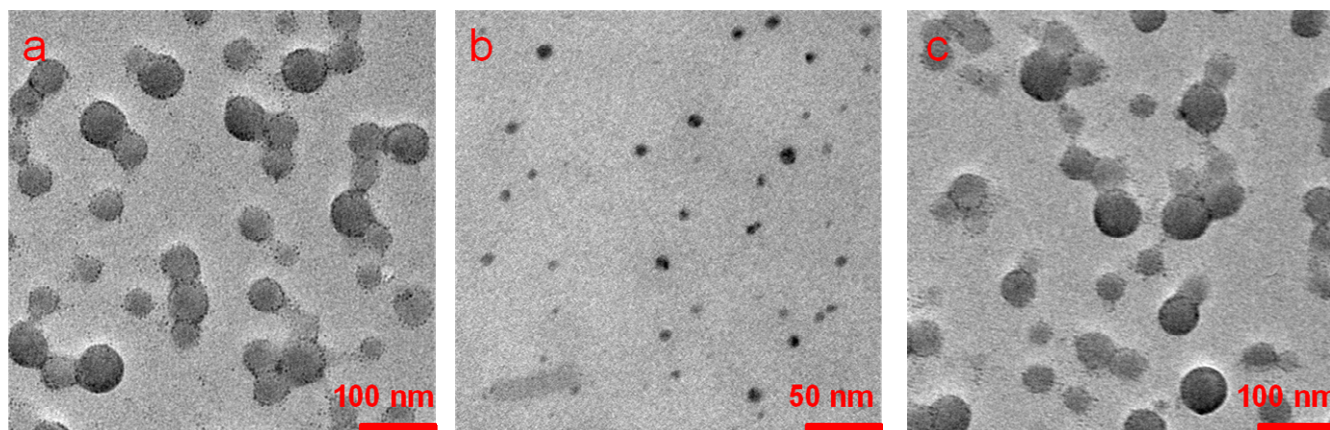


Fig. S13. TEM images of **1** (1.00×10^{-4} M) in water: (a) **1**; (b) after adjusting pH of (a) to 5.0 by adding HCl (1.00 M); (c) after adjusting pH of (b) to 8.0 by adding a NaOH aqueous solution (1.00 M).

5. Self-assembly of **1** (1.00×10^{-4} M) in water switched by CO_2

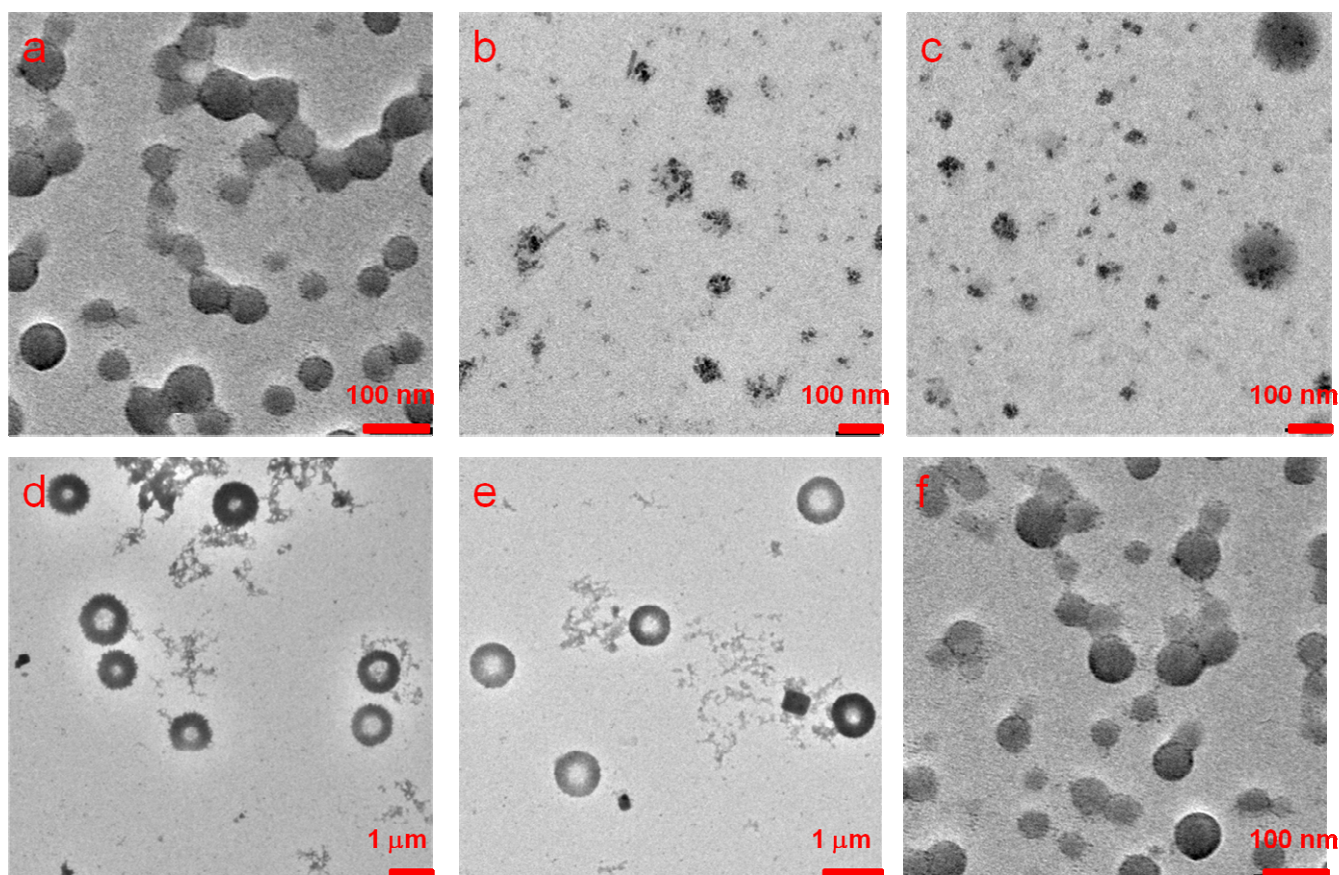


Fig. S14. TEM images of **1** (1.00×10^{-4} M) in water: (a) before bubbling CO_2 ; (b) after bubbling CO_2 for 30 s; (c) after bubbling CO_2 for 1 minute; (d) after bubbling CO_2 for 3 minutes; (e) after bubbling CO_2 for 5 minutes; (f) after bubbling N_2 to (b) or warming up for 5 minutes.

6. Transmittance study of CO₂-switch reversible process

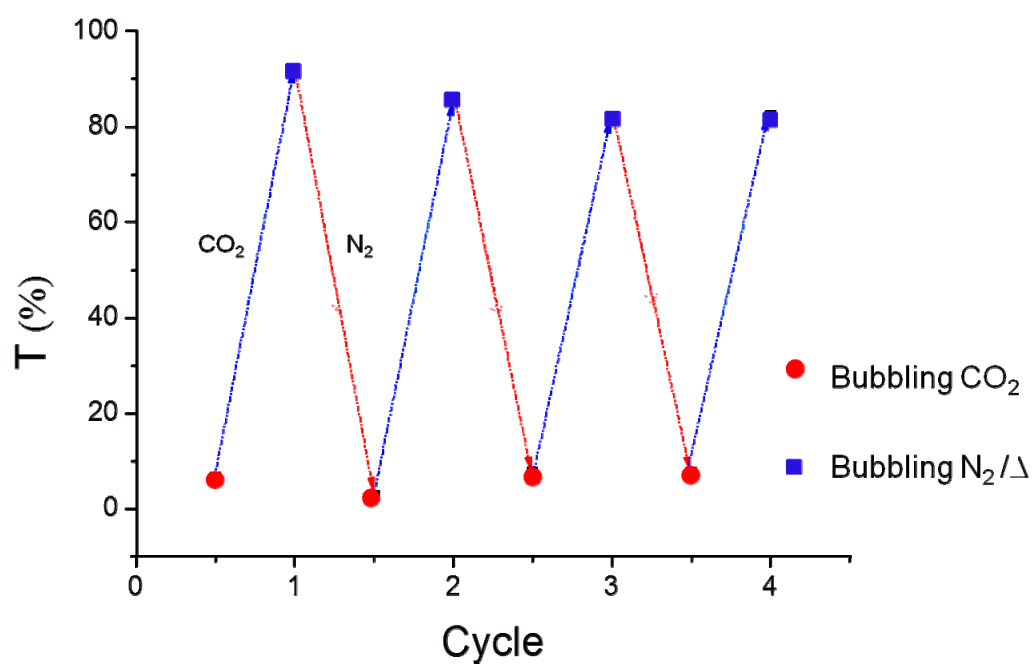


Fig. S15. The repeated cycles by bubbling CO₂ and bubbling N₂ or warming up to 70 °C.

References:

- S1. (a) X. Hu, L. Chen, W. Si, Y. Yu and J.-L. Hou, *Chem. Commun.*, 2011, **47**, 469–4696; (b) Y. Ma, X. Ji, F. Xiang, X. Chi, C. Han, J. He, Z. Abliz, W. Chen and F. Huang, *Chem. Commun.*, 2011, **47**, 12340–12342.
- S2. Q. Zhang, Z. Gao, F. Xu, S. Tai, X. Liu, S. Mo and F. Niu, *Langmuir*, 2012, **28**, 11979–11987.