A CO\textsubscript{2}-responsive pillar[5]arene: synthesis and self-assembly in water

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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 was prepared according to a published procedure. $^1$H NMR and $^{13}$C NMR 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-dihydroxy-naphthalene (16.0 g, 100 mmol) and 1-bromo-1-hexadecane (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 13C NMR spectrum of 3 is shown in Fig. S2. 13C 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. $^1$H NMR spectrum (400 MHz, chloroform-$d$, 293K) of 3.
**Fig. S2.** $^{13}$C 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. The yield of 1 was 23.1%. The melting point of 1 is 75.2 °C. The $^1$H NMR spectrum of 1 is shown in Fig. S5. $^1$H NMR (400 MHz, chloroform-$d$, 293 K) $\delta$ (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 $^{13}$C NMR spectrum of 1 is shown in Fig. S6. $^{13}$C NMR (100 MHz, chloroform-$d$, 293 K) $\delta$ (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]$^+$ C$_{119}$H$_{193}$O$_{12}$N$_9$D$^+$, 1942.4910; found 1942.4861; error 2.5 ppm.
**Fig. S5.** $^1$H NMR spectrum (400 MHz, chloroform-$d$, 293K) of 1.

**Fig. S6.** $^{13}$C NMR spectrum (100 MHz, chloroform-$d$, 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 $^1$H NMR spectrum of 2 is shown in Fig. S9. $^1$H NMR (400 MHz, DMSO-$d_6$, 293 K) $\delta$ (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) $\delta$ (ppm): 130.15, 47.03, 28.59, 22.01, 13.89, 8.63, 8.42. LRESIMS (done in H$_2$O-$d_6$) is shown in Fig. S11: $m/z$ 971.3 [2 – 9Cl$^-$ – 7H$^+$]$^{2+}$.

Figure S9. $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, 293K) of 2.
**Fig. S10.** $^{13}$C NMR spectrum (100 MHz, DMSO-$d_6$, 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 $1.70 \times 10^{-5}$ M.

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

**Fig. S13.** TEM images of 1 (1.00 $\times 10^{-4}$ 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 CO2

**Fig. S14.** TEM images of 1 (1.00 × 10^{-4} M) in water: (a) before bubbling CO2; (b) after bubbling CO2 for 30 s; (c) after bubbling CO2 for 1 minute; (d) after bubbling CO2 for 3 minutes; (e) after bubbling CO2 for 5 minutes; (f) after bubbling N2 to (b) or warming up for 5 minutes.
6. Transmittance study of CO$_2$-switch reversible process

*Fig. S15.* The repeated cycles by bubbling CO$_2$ and bubbling N$_2$ or warming up to 70 °C.
References:
