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General methods
All reagents were commercially available and used as supplied without further purification. $^1$H or $^{13}$C NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. The melting points were collected on a SHPSIC WRS–2 automatic melting point apparatus. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 25.0 °C in deionized water. Scanning electron microscopy investigation was carried out on a JEOL 6390LV instrument. Transmission electron microscopy investigations were carried out on a JEM-1200EX instrument.

SEM sample preparation
SEM samples were prepared by dissolving monomer 1 in deionized water at high concentration via the natural withering methodology for the supramolecular polymer.

Preparation of rod–like micro fiber
The high concentration supramolecular polymers (600 mM) of 1 were firstly prepared in water. Then a rod–like micro fiber can be drawn from the high concentration supramolecular polymers by using a glass bar.
In a 500 mL round–bottom flask, 4-methoxyphenol (7.44 g, 60.0 mmol), K$_2$CO$_3$ (33.1 g, 240 mmol), KI (0.830 g, 5.00 mmol), 1-bromohexadecane (19.9 g, 65.0 mmol) and acetone (300 mL) were added. The reaction mixture was stirred at reflux for 3 days. After the solid was filtered off, the solvent was removed. The solid was dissolved in CHCl$_3$ (150 mL) and washed twice with H$_2$O (200 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated to afford the crude product, which was recrystallized with CH$_3$CN to give 1-methoxy-4-cetylbenzene (18.6 g, 89 %) as a white solid. m.p. 68.8~69.6 °C. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ (ppm): 6.83 (s, 4H), 3.89 (t, $J$ = 6 Hz, 2H), 3.77 (s, 3H), 1.77–1.73 (m, 2H), 1.44–1.40 (m, 2H), 1.26 (m, 24H), 0.88 (t, $J$ = 6 Hz, 3H). The $^{13}$C NMR (100 MHz, CDCl$_3$, 298K) $\delta$ (ppm): 153.66, 153.33, 115.43, 114.61, 68.68, 55.74, 31.94, 29.69, 29.66, 29.62, 29.61, 29.44, 29.42, 29.37, 26.08, 22.71, 14.14.
Fig. S1 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of 1-methoxy-4-cetylbenzene.

Fig. S2 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$, 298K) of 1-methoxy-4-cetylbenzene.
To a solution of 1-methoxy-4-cetylbenzene (1.74 g, 5.00 mmol) and 1,4-
bis(bromomethoxy)benzene (6.48 g, 20.0 mmol) in 1,2-dichloroethane (80.0 mL),
paraformaldehyde (0.750 g, 25.0 mmol) was added. Then, boron trifluoride diethyl
etherate (3.20 mL, 25.0 mmol) was added to the solution and the mixture was stirred
at room temperature for 8 h. The solution was poured into methanol and the resulting
precipitate was collected by filtration. The solid was dissolved in CHCl₃ (150 mL)
and the insoluble part was filtered off. The resulting solid dissolved in CHCl₃ and
washed twice with H₂O (100 mL). The organic layer was dried over anhydrous
Na₂SO₄ and evaporated to afford the crude product, which was isolated by flash
column chromatography using petroleum ether/ethyl acetate (50:1) (Rf = 0.5). The
fractions containing the product were combined and concentrated under vacuum to
give 2 (0.850 g, 10 %) as a white solid, m.p. 136.6~137.8 °C. The proton NMR
spectrum of 2 is shown in Fig. S3. ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 6.90–
6.82 (m, 10H), 4.24–3.92 (m, 16H), 3.89 (t, J = 4 Hz, 2H), 3.83–3.76 (m, 13H), 3.64–
3.58 (m, 16H), 1.83–1.80 (m, 2H), 1.54–1.50 (m, 2H), 1.38–1.36 (m, 2H), 1.25–1.18 (m, 20H), 0.87 (t, \( J = 8 \) Hz, 3H). The \(^{13}\text{C}\) NMR spectrum of 2 is shown in Fig. S4. The \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\), 298K) \( \delta \) (ppm): 150.51, 150.03, 149.70, 129.52, 129.40, 129.02, 128.99, 128.72, 127.94, 116.22, 116.09, 115.58, 115.18, 113.91, 68.96, 68.81, 59.01, 31.96, 30.63, 30.48, 30.35, 29.88, 29.78, 29.73, 29.65, 29.59, 29.51, 26.28, 22.73, 14.18. Anal. Calcd for C\(_{68}\)H\(_{88}\)Br\(_8\)O\(_{10}\): C, 47.91; H, 5.20; Found C, 47.90; H, 5.18.
Fig. S3 $^1$H NMR spectrum (400 MHz, CDCl$_3$, 298K) of pillar[5]arene 2.

Fig. S4 $^{13}$C NMR spectrum (125 MHz, CDCl$_3$, 298K) of pillar[5]arene 2.
Compound 2 (1.0 g, 0.600 mmol) and trimethylamine (33.0 % in ethanol, 6.43 mL, 23.8 mmol) were added to ethanol (50.0 mL). The solution was refluxed 12 hours. Then the solvent was removed by evaporation to obtain 1 as a light yellow solid (1.29 g, 100 %). m.p.: >250 °C. The $^1$H NMR spectrum of 1 is shown in Fig. S5. $^1$H NMR (400 MHz, DMSO–$d_6$, 298K) δ(ppm): 7.06–6.79 (m, 10H), 4.65–4.38 (m, 17H), 4.17–3.75 (m, 33H), 3.39–3.34 (s, 76H), 1.81–1.80 (m, 2H), 1.50 (s, 2H), 1.24 (m, 28H), 0.86 (t, $J = 6$ Hz, 3H). The $^{13}$C NMR spectrum of 1 is shown in Fig. S6. $^{13}$C NMR (125 MHz, DMSO–$d_6$, 298K) δ (ppm): 149.92, 149.06, 148.67, 128.18, 128.10, 127.77, 127.44, 115.75, 114.87, 113.31, 68.38, 64.57, 64.39, 62.81, 62.57, 59.50, 55.91, 54.31, 53.19, 53.10, 52.88, 31.26, 29.13, 29.11, 29.07, 29.05, 28.68, 22.07 and 13.95. Anal. Calcd for C$_{92}$H$_{160}$Br$_8$N$_8$O$_{10}$: C, 50.74; H, 7.41; N, 5.15; Found C, 50.71; H, 7.42; N, 5.17.
Fig. S5 $^1$H NMR spectrum (400 MHz, DMSO–$d_6$, 298K) of pillar[5]arene 1.

Fig. S6 $^{13}$C NMR spectrum (125 MHz, DMSO–$d_6$, 298K) of pillar[5]arene 1.
**Fig. S7** Partial $^1$H NMR spectrum (400 MHz, D$_2$O, 298K) of 1 at different concentrations: (a) 0.460 mM; (b) 0.920 mM; (c) 4.58 mM; (d) 9.18 mM; (e) 25.9 mM; (f) 61.9 mM; (g) 138 mM; (h) 184 mM.

**Fig. S8** Partial $^1$H NMR spectrum (400 MHz, D$_2$O, 298K) of 1 at different concentrations: (a) 0.460 mM; (b) 0.920 mM; (c) 4.58 mM; (d) 9.18 mM; (e) 25.9 mM; (f) 61.9 mM; (g) 138 mM; (h) 184 mM.
Fig. S9  Partial $^1$H NMR spectrum (400 MHz, D$_2$O, 298K) of 1 at different concentrations: (a) 0.460 mM; (b) 0.920 mM; (c) 4.58 mM; (d) 9.18 mM; (e) 25.9 mM; (f) 61.9 mM; (g) 138 mM; (h) 184 mM.

Fig. S10  Partial $^1$H NMR spectrum (400 MHz, D$_2$O, 298K) of 1 at different concentrations: (a) 0.460 mM; (b) 0.920 mM; (c) 4.58 mM; (d) 9.18 mM; (e) 25.9 mM; (f) 61.9 mM; (g) 138 mM; (h) 184 mM.
Fig. S11 ¹H NMR spectra of 1 (400 MHz, D₂O, 298 K) and 1-methoxy-4-(cetyl)benzene (400 MHz, CDCl₃, 298 K) at a concentration of 1.00 mM.
Fig. S12 Partial NOESY NMR spectrum (500 MHz, D$_2$O, 298K) of 1 at a concentration of 150 mM.

Fig. S13 Full NOESY NMR spectrum (500 MHz, D$_2$O, 298 K) of 1 at a concentration of 150 mM.
**Fig. S14** TEM images of 1 (1.5 × 10^{-4} M) in water.

**Fig. S15** The concentration-dependent conductivity of 1. The critical aggregation concentration (CAC) was determined to be 0.62 × 10^{-4} M.