**Electronic Supplementary Material**

**Copillar[5]arene-based supramolecular polymer gels**

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1. Materials and methods

1,4-Dimethoxybenzene, boron trifluoride ethyl ether complex, 1-Bromohexadecane, and 1-Bromododecane were reagent grade and used as received. Solvents were either employed as purchased or dried by CaCl₂. ¹H NMR spectra were recorded on a Mercury-600BB spectrometer at 600 MHz and ¹³C NMR spectra were recorded on a Mercury-600BB spectrometer at 150 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. XRD patterns were recorded at a scanning rate of 5°/min in the 2θ range of 2° to 50° with Cu-Kα radiation.

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 (0.83 g, 5 mmol), 1-Bromohexadecane (19.85 g, 65.0 mmol) and acetone (300.0 mL) were added. The reaction mixture was stirred at reflux for 6 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 (yield: 89%) as a white solid. m.p. 68 °C. $^1$H NMR (600 MHz, CDCl$_3$, 275 K) $\delta$ (ppm): 6.83 (s, 4H), 3.91-3.88 (t, $J$=18, 2H), 3.77 (s, 3H), 1.77-1.73 (m, 2H), 1.44-1.40 (m, 2H), 1.26 (m, 24H), 0.89-0.86 (t, $J$=18, 3H).
**Figure S1** $^1$H NMR spectra of 1-methoxy-4-cetylbenzene.
To a solution of 1-methoxy-4-cetylbenzene (1.74 g, 5 mmol) and 1,4-dimethoxybenzene (2.76 g, 20 mmol) in 1,2-dichloroethane (80 mL), paraformaldehyde (0.75 g, 25 mmol) was added. Then, boron trifluoride diethyl etherate (3.2 mL, 25 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 = 0.45). The fractions containing the product were combined and concentrated under vacuum to
give COP5-16 (0.86 g, 18%) as a white solid, m.p. 108 °C. The proton NMR spectrum of COP5-16 is shown in Figure S2. $^1$H NMR (600 MHz, chloroform–d, 293K) δ (ppm): 7.03–7.01 (m, 10H), 4.04-4.03 (t, J=12, 2H), 3.98-4.00 (m, 10H), 3.89–3.87 (m, 27H), 1.97–1.96 (m, 2H), 1.62–1.60 (m, 2H), 1.42–1.40 (m, 2H), 1.32–1.29 (m, 2H), 1.23–0.98 (m, 20H), 0.92-0.90 (t, J=12, 3H). The $^{13}$C NMR spectrum of COP5-16 is shown in Figure S3. The $^{13}$C NMR (150 MHz, chloroform–d, 293K) δ (ppm): 150.60, 150.57, 150.50, 150.02, 128.24, 128.16, 128.11, 128.05, 114.70, 113.74, 113.62, 68.46, 55.58, 55.52, 55.51, 55.45, 31.73, 29.92, 29.89, 29.87, 29.80, 29.72, 29.61, 29.56, 29.50, 29.47, 29.29, 26.28, 22.52, 14.11. IR (KBr, cm$^{-1}$) v: 2929 (CH), 2852 (CH), 1212 (C-O-C). HRMS m/z: (M+Na)$^+$ Calcd for C$_{60}$H$_{76}$O$_{10}$Na$^+ 983.57; $ Found 983.56, error : 1 ppm. (M+K)$^+$ Calcd for C$_{60}$H$_{76}$O$_{10}$K$^+ 999.54; $ Found 999.53, error : 1 ppm.
Figure S2 $^1$H NMR spectra of monomer COP5-16.
Figure S3 $^{13}$C NMR spectra of monomer COP5-16.
Figure S4 High resolution mass data of monomer COPS-16.

![Chemical diagram]

In a 500 mL round–bottom flask, 4-Methoxyphenol (7.44 g, 60.0 mmol), K₂CO₃ (33.1 g, 240 mmol), KI (0.83 g, 5 mmol), 1-Bromododecane (16.18 g, 65.0 mmol) and acetone (300.0 mL) were added. The reaction mixture was stirred at reflux for 6 days. After the solid was filtered off, the solvent was removed. The solid was dissolved in CHCl₃ (150 mL) and washed twice with H₂O (200 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated to afford the crude product, which was recrystallized with CH₃CN to give 1-methoxy-4-dodecylbenzene (yield 83%) as a white solid. m.p. 62 °C. ¹H NMR (600 MHz, CDCl₃, 275 K) δ (ppm): 6.83 (s, 4H), 3.91-3.88 (t, J=18, 2H), 3.77 (s, 3H), 1.77-1.73 (m, 2H), 1.45-1.42 (m, 2H), 1.26 (m, 16H), 0.90-0.86 (t, J=24, 3H).
Figure S5: $^1$H NMR spectra of 1-methoxy-4-dodecylbenzene.
To a solution of 1-methoxy-4-dodecylbenzene (1.5 g, 5 mmol) and 1,4-
dimethoxybenzene (2.76 g, 20 mmol) in 1,2-dichloroethane (80 mL),
paraformaldehyde (0.75 g, 25 mmol) was added. Then, boron trifluoride diethyl
etherate (3.2 mL, 25 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 CHCl$_3$ (150 mL)
and the insoluble part was filtered off. The resulting solid dissolved in CHCl$_3$ and
washed twice with H$_2$O (100 mL). The organic layer was dried over anhydrous
Na$_2$SO$_4$ and evaporated to afford the crude product, which was isolated by flash
column chromatography using petroleum ether/ethyl acetate (50:1) (R$_f$ = 0.45). The
fractions containing the product were combined and concentrated under vacuum to
give COP5-12 (0.72 g, 16%) as a white solid, m.p. 78 °C. The proton NMR spectrum
of COP5-12 is shown in Figure S6. $^1$H NMR (600 MHz, chloroform-$d$, 293K) δ
(ppm): 6.83–6.80 (m, 10H), 3.87-3.85 (t, J=12, 2H), 3.82–3.78 (m, 10H), 3.69–3.67
(m, 27H), 1.80–1.77 (m, 2H), 1.46–1.43 (m, 2H), 1.28–1.24 (m, 2H), 1.16–1.14 (m, 2H), 1.07–0.90 (m, 12H), 0.77–0.75 (t, J=12, 3H). The $^{13}$C NMR spectrum of COP5-12 is shown in Figure S7. The $^{13}$C NMR (150 MHz, chloroform–d, 293K) δ (ppm): 150.63, 150.60, 150.52, 150.02, 128.24, 128.17, 128.14, 128.05, 114.77, 113.87, 113.83, 113.80, 113.77, 113.75, 113.72, 68.44, 55.63, 55.57, 55.55, 55.50, 31.72, 29.76, 29.65, 29.61, 29.59, 29.52, 29.47, 29.36, 29.31, 26.61, 22.50, 14.07. IR (KBr, cm$^{-1}$) ν: 2930 (CH), 2852 (CH), 1212 (C-O-C). HRMS m/z: (M+Na)$^+$ Calcd for C$_{56}$H$_{68}$O$_{10}$Na$^+$ 927.50; Found 927.50, error : 0 ppm. (M+K)$^+$ Calcd for C$_{56}$H$_{68}$O$_{10}$K$^+$ 943.47; Found 943.47, error : 0 ppm.
Figure S6 $^1$H NMR spectra of monomer COP5-12.
Figure S7 $^{13}$C NMR spectra of monomer COP5-12.
Figure S8 High resolution mass data of monomer COP5-12.
Table 1 Gelation properties of COP5-12 and COP5-16

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G: gel, S: sol, E: emulsion, P: precipitate. COP5-16: 6.2 wt%; COP5-12: 8.5 wt%.
Figure S9 Partial $^1$H NMR spectra (600 MHz, CDCl$_3$, 293 K) of COP5-12 at different monomer concentrations: 1) 0.5 mg, 2) 1.0 mg, 3) 5.0 mg, 4) 10.0 mg, 5) 50.0 mg, 6) 100.0 mg in 0.5 ml CDCl$_3$.

Figure S10 NOESY NMR spectrum (600 MHz, CDCl$_3$, 293 K) of COP5-12 at a concentration of 0.22 M.
Figure S11 Partial $^1$H NMR spectra (600 MHz, CDCl$_3$, 293 K) of COP5-16 at different monomer concentrations: 1) 0.5 mg, 2) 1.0 mg, 3) 5.0 mg, 4) 10.0 mg, 5) 50.0 mg, 6) 100.0 mg in 0.5 ml CDCl$_3$.

Figure S12 NOESY NMR spectrum (600 MHz, CDCl$_3$, 293 K) of COP5-16 at a concentration of 0.21 M.
Figure S13 (a), (b), (c): SEM images of COP5-12 gels of phase B (Supramolecular Organic Framework); (d), (e), (f): SEM images of COP5-16 gels of phase B (Supramolecular Organic Framework).

Figure S14 XRD diagrams of the gel of COP5-16.