Supplemental Information

Self-Organization of Rhombitruncated Cuboctahedral Hexagonal Columns from an Amphiphilic Janus Dendrimer

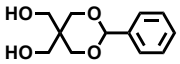
Ning Huang,[a] Qi Xiao,[a] Mihai Peterca,[a] Xiangbing Zeng,[b] and Virgil Percec[a,]*

[a]Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, United States

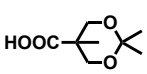
[b]Department of Materials Science and Engineering, University of Sheffield, Sheffield S1 3JD, United Kingdom

*E-mail: percec@sas.upenn.edu.

1. Synthesis and Characterization

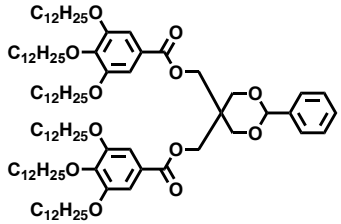


(2-Phenyl-1,3-dioxane-5,5-diyl)dimethanol (3): In a 250 mL round bottom flask charged with a stirring bar, 18.0 g (0.13 moles) of **1** and 130 mL of water were added. The mixture was heated to ~30 °C until all solids were fully dissolved. Benzaldehyde (**2**) (14.5 g, 0.14 moles) and HCl conc. (0.66 mL) were slowly introduced into the mixture. The reaction was kept at 23 °C for 3h. The white precipitate was collected by using a Büchner funnel and washed with cold water. Recrystallization was carried out with the white precipitate dissolved in hot water at 100 °C. After cooling for 10 min in the ice bath, the white precipitate was filtered and dried. The white precipitate was then dissolved in toluene at 110 °C and cooled in ice bath for 10 min. The white product was filtered and dried. Yield = 21.5 g, 73%. ^{1}H NMR (500 MHz, CDCl3): δ = 2.25 (s, 1H, O*H*), 2.38 (s, 1H, O*H*), 3.55 (s, 2H, -C*H*$_2$OH), 3.77 (d, J = 7 Hz, 2H, -C*H*$_2$OH), 4.15(m, 4H, -C*H*$_2$OCH-), 5.44 (s, 1H, -O$_2$C*H*-Ph), 7.37 (m, 3H, Ph), 7.48 (m, 2H, Ph); ^{13}C NMR (125 MHz, CDCl3): δ = 38.99, 64.36, 65.80, 70.15, 102.20, 126.17, 128.50, 129.24, 138.15. M.P. = 134 °C. [1,2]

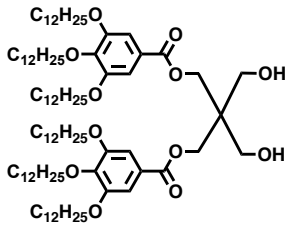


2,2,5-Trimethyl-1,3-dioxane-5-carboxylic acid (6): **4**, 10.00 g (74.55 mmol), and 13.8 mL (111.83 mmol) of 2,2-dimethoxypropane (**5**) and 0.71 g (3.73 mmol) of p-toluenesulfonic acid monohydrate were added

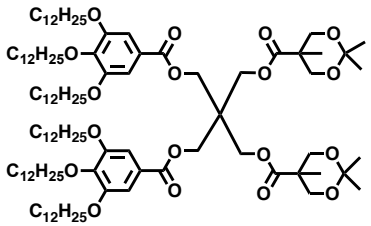
to a 250 mL round bottom flask filled with 50 mL acetone. The reaction mixture was stirred at 23 °C for 2h. 0.4 mL of a NH_3/EtOH (50:50) solution was introduced to the mixture solution to neutralize the catalyst. The solvent was removed by rotavaporator at 23 °C. 300 mL of DCM was added to dissolve the residue and was extracted with two portions of (20 mL) water. The organic phases were collected and the mixture solution was dried with $MgSO_4$ and evaporated to yield white crystals: 10.95 g (84%). ^{1}H NMR ($CDCl_3$): δ 1.21 (s, 3H, -CH_3), 1.42 (s, 3H, -CH_3), 1.45 (s, 3H, -CH_3), 3.69 (d, 2H, -CH_2O-), 4.18 (d, 2H, -CH_2O-). ^{13}C NMR ($CDCl_3$): δ 18.54, 21.99, 25.46, 41.87, 66.04, 98.50, 180.13. M.P. = 121 °C. [3]



(2-Phenyl-1,3-dioxane-5,5-diyl)bis(methylene) bis(3,4,5-tris(dodecyloxy)benzoate) (8): *N*,*N*'-dicyclohexylcarbodiimide (DCC) (6.91 g, 33.5 mmol) was added to 100 mL of dry dichloromethane (DCM) solution of 3,4,5-tris(dodecyloxy)benzoic acid (**7**) (10.0 g, 14.8 mmol), (2-phenyl-1,3-dioxane-5,5-diyl)dimethanol (**3)** (1.50 g, 6.7 mmol) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) [4] (4.36 g, 14.8 mmol) in a 250 mL round bottomed flask. The reaction was allowed to stir at 23 °C for 12 h. The solvent was then removed by rotary evaporator. The residue was redissolved with ethyl acetate (50 mL), filtered through Celite washed with ethyl acetate (10 mL × 3), and the filtrate was concentrated to dryness. The crude product was purified by column chromatography on silica gel with a mobile phase of hexane/ethyl acetate = 20/1 to provide Compound **6** as colorless oil (9.20 g, 6.0 mmol, 89%). ^{1}H NMR (500 MHz, CDCl3): δ = 0.88 (t, J = 6.8 Hz, 18H, 6×-CH_2CH_3), 1.21-1.40 (m, 96H, 6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.48 (m, 12H, 6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.74 (m, 4H, 2×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.80 (m, 8H, 4×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 4.00 (m, 14H, 6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$ + -OCH_2CCH_2O-), 4.24 (s, 2H, -OCH_2CCH_2O-), 4.31 (d, J = 11.7 Hz, 2H, -OCH_2CCH_2O-), 4.84 (s, 2H, -OCH_2CCH_2O-), 5.51 (s, 1H, -O_2CHPh), 7.22 (s, 2H, -Ar*H*), 7.22 (s, 2H, -Ar*H*), 7.37 (m, 3H, Ph), 7.51 (m, 2H, Ph); ^{13}C NMR (125 MHz, CDCl3): δ = 14.25, 14.40, 22.87, 23.01, 26.40, 26.46, 29.70, 29.77, 29.91, 29.98, 30.02, 30.04, 30.06, 30.07, 30.29, 30.69, 32.26, 38.27, 63.42, 64.17, 69.61, 69.62, 70.25, 73.84, 73.88, 102.64, 108.52, 108.62, 124.18, 124.71, 126.45, 128.69, 129.54, 137.98, 143.18, 143.36, 153.22, 253.30, 166.25, 166.32.; MALDI-TOF MS : (m/z): [M + Na]+ calcd for $C_{98}H_{168}NaO_{12}$: 1561.37; found 1560.86. [1]

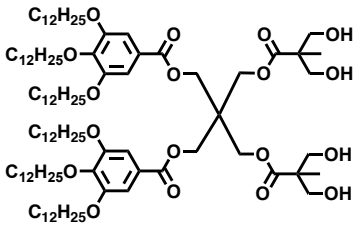


2,2-Bis(hydroxymethyl)propane-1,3-diyl bis(3,4,5-tris(dodecyloxy)benzoate) (9): **8** (9.20 g, 6.0 mmol) was dissolved with DCM (100 mL) and methanol (50 mL) in a 250 mL round bottomed flask. 10 % Palladium on carbon (300 mg) was added and the reaction was stirred under H_2 for 12 hours at 23 °C. The reaction was completed confirmed by TLC and was filtered with Celite. The filtrate was dried under rotary evaporator to obtain white solid (8.60 g, 5.9 mmol, 99%) without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 18H, 6×-CH_2CH_3), 1.20-1.40 (m, 96H, 6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.47 (m, 12H, 6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.76 (m, 4H, 2×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.82 (m, 8H, 4×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 3.00 (t, 2H, -O*H*), 3.71 (d, 4H, 2×-CH_2OH), 3.96-4.03 (m, 12H, 6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 4.47 (s, 4H, 2×-$OCH_2$C-), 7.23 (s, 4H, 2×Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.43, 23.03, 26.42, 26.47, 29.71, 29.79, 29.93, 30.00, 30.01, 30.04, 30.06, 30.08, 30.71, 32.28, 46.35, 63.20, 63.49, 69.67, 73.94, 108.72, 124.07, 143.53, 153.33, 167.45.; MALDI-TOF MS : (m/z): $[M + Na]^+$ calcd for $C_{91}H_{164}NaO_{12}$: 1472.21; found 1471.89. M. P. = 62 °C. [1]



2,2-Bis(((3,4,5-tris(dodecyloxy)benzoyl)oxy)methyl)propane-1,3-diyl bis(2,2,5-trimethyl-1,3-dioxane-5-carboxylate) (10): DCC (712 mg, 3.45 mmol) was added to 20 mL of dry DCM solution of **9** (1.0 g, 0.69 mmol), 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (**6)** (264 mg, 1.52 mmol) and DPTS (447 mg, 1.52 mmol) in a 100 mL round bottomed flask. The reaction was allowed to stir at 23 °C for 12 h. The solvent was then removed by rotary evaporator. The residue was redissolved with ethyl acetate (50 mL), filtered through Celite washed with ethyl acetate (10 mL × 3), and the filtrate was concentrated to dryness. The crude product was purified by column chromatography on silica gel with a mobile phase of hexane/ethyl acetate = 5/1 to provide Compound **10** as colorless oil (930 mg, 0.53 mmol, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 18H, 6×-CH_2CH_3), 1.08 (s, 6H, 2×-CH_3), 1.25-1.34 (m, 102H,

6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$ and 2×-CH_3), 1.40(s, 6H, 2×-CH_3), 1.43-1.50 (m, 12H, 6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.74 (m, 4H, 2×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.80 (m, 8H, 4×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 3.63 (d, J = 12 Hz, 4H, 2×-CCH_2O-), 3.97–4.00 (m, 12H, 6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 4.17 (d, J = 12 Hz, 4H, 2×-CCH_2O-), 4.39 (s, 4H, 2×-CCH_2O-), 4.48 (s, 4H, 2×-CCH_2O-), 7.20 (s, 4H, 2×Ar*H*). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1, 18.4, 21.6, 22.7, 25.5, 26.1, 26.1, 29.3– 29.7, 30.3, 31.9, 42.3, 43.5, 62.3, 62.4, 66.1, 69.2, 73.5, 98.2, 108.2, 123.9, 142.9, 152.9, 165.7, 173.6. MALDI-TOF MS: (m/z): $[M + Na]^+$ calcd for $C_{107}H_{188}NaO_{18}$:1784.37. Found 1784.28. [5]



Janus dendrimer **(3,4,5)12G1-PE-BMPA-G1-$(OH)_4$ (11)**: **10** (930 g, 0.53 mmol) was dissolved with DCM (20 mL) and methanol (20 mL) in a 100 mL round bottomed flask. 2M HCl aqueous solution (2 mL) was added and the reaction was stirred at 23 °C for 12 hours. The reaction was completed confirmed by TLC. The reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution (10 mL), and then extract with DCM (25 mL × 3). The mixture oil was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate = 1/2) and recrystallization with hot methanol for two times to obtain white solid (760 mg, 0.45 mmol, 86%). ^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 18H, 6×-CH_2CH_3), 1.08 (s, 6H, 2×-CH_3), 1.25-1.34 (m, 96H, 6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.43-1.50 (m, 12H, 6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.74 (m, 4H, 2×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.80 (m, 8H, 4×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 3.15 (t, J = 6.4 Hz, 4H, 4×-O*H*), 3.75 (m, 4H, -CCH_2OH), 3.88 (m, 4H, -CCH_2OH), 3.96–4.00 (m, 12H, 6×-$OCH_2CH_2CH_2(CH_2)_8CH_3$), 4.35 (s, 4H, 2×-$CCH_2O$-), 4.49 (s, 4H, 2×-$CCH_2O$-), 7.21 (s, 4H, 2×Ar*H*).^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3, 17.3, 22.8, 26.2, 26.3, 29.5–29.9, 30.5, 32.1, 43.8, 50.0, 61.7, 62.1, 68.4, 69.4, 73.7, 108.3, 123.8, 143.2, 152.1, 166.1, 175.3. MALDI-TOF MS: (m/z): $[M + Na]^+$ calcd $C_{101}H_{180}NaO_{18}$: 1704.31. Found 1706.84. M.P.= 91 °C (isotropic transition temperature by DSC, first scan, 10 °C/min). [5]

2. Supplemental Figures

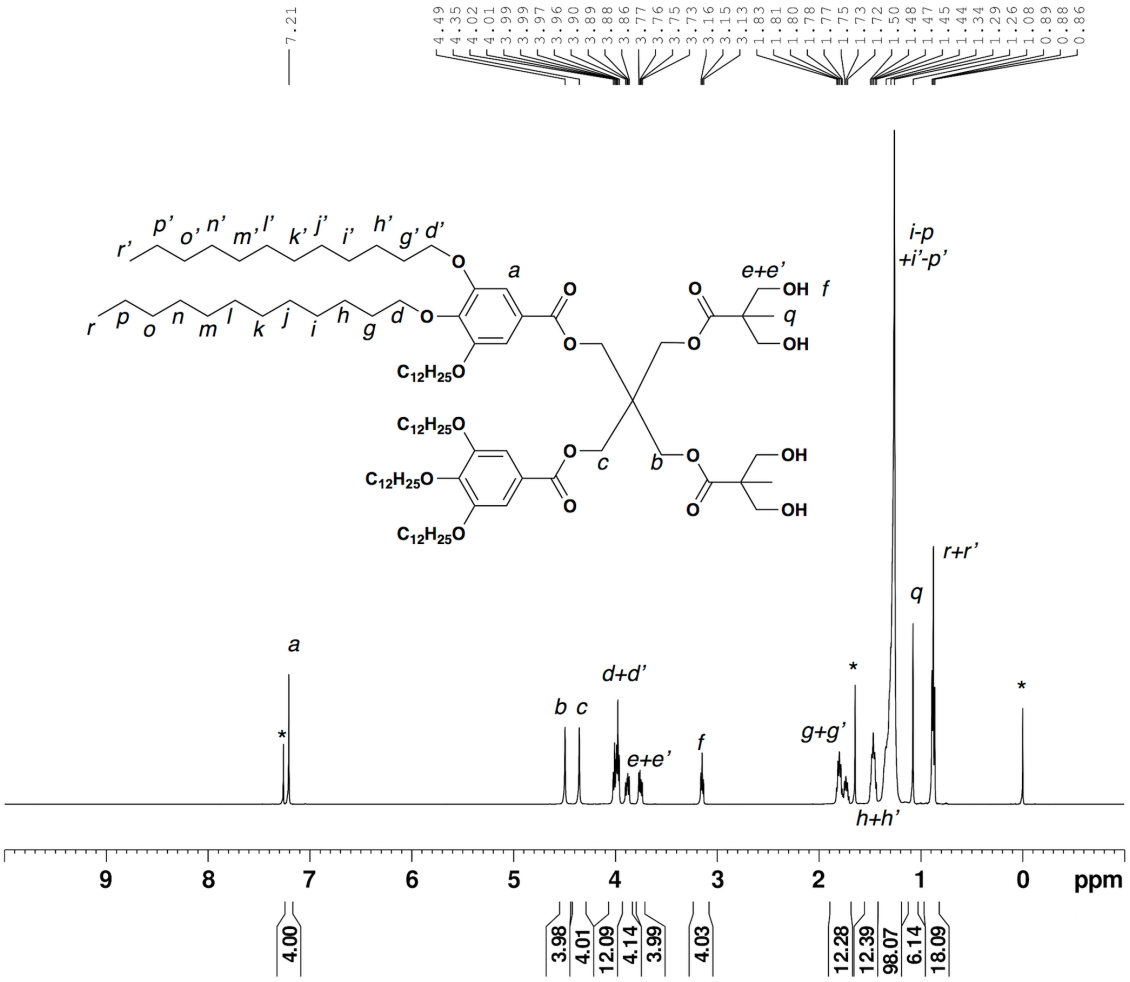


Figure S1. ^{1}H NMR of **11** in $CDCl_3$ (500 MHz). Asterisked signals at δ 7.26 ppm, 1.65 ppm, and 0 ppm are due to partially nondeuterated residues of $CDCl_3$, water, and tetramethylsilane (TMS), respectively.

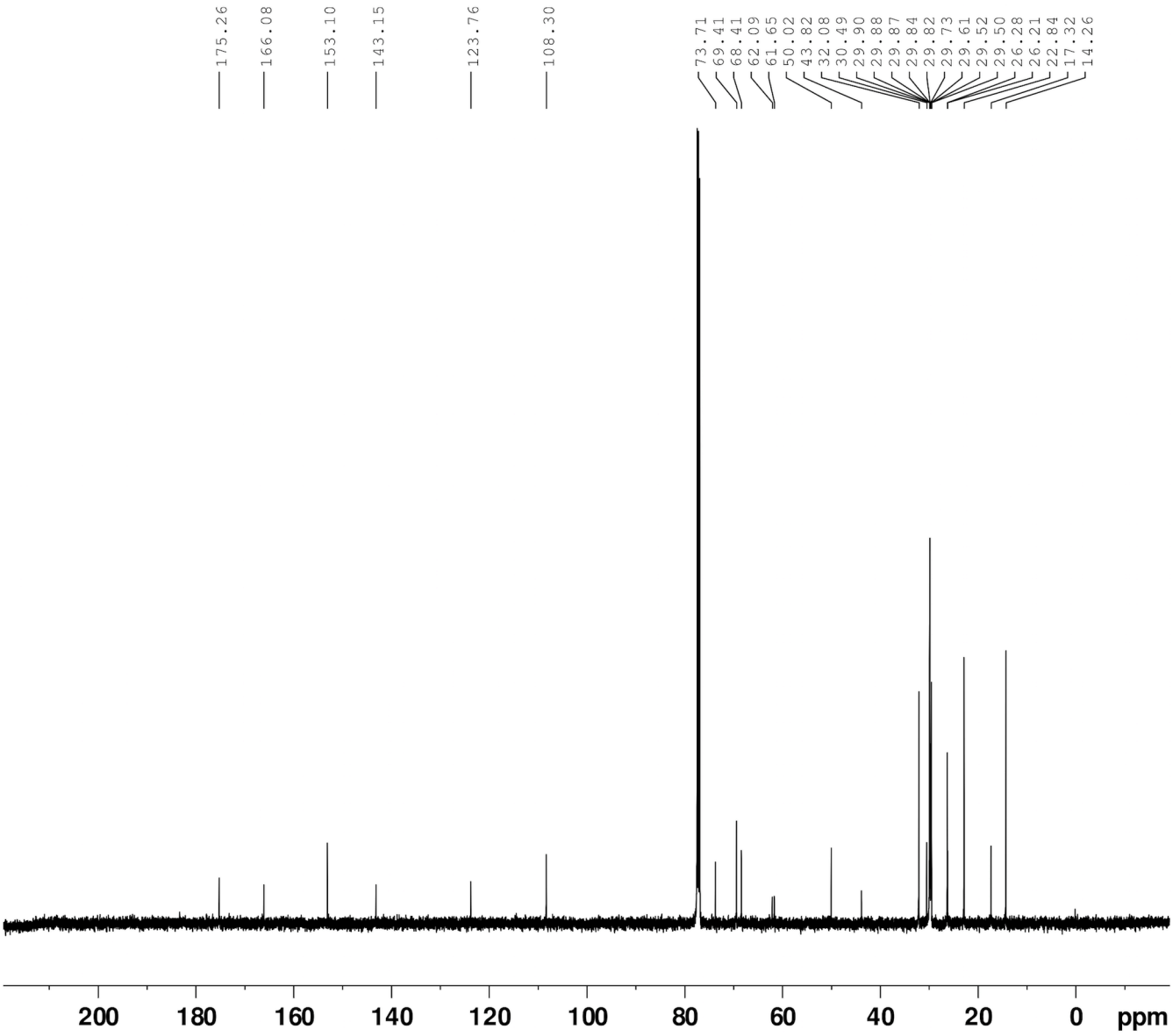


Figure S2. ^{13}C NMR of **11** in $CDCl_3$ (126 MHz).

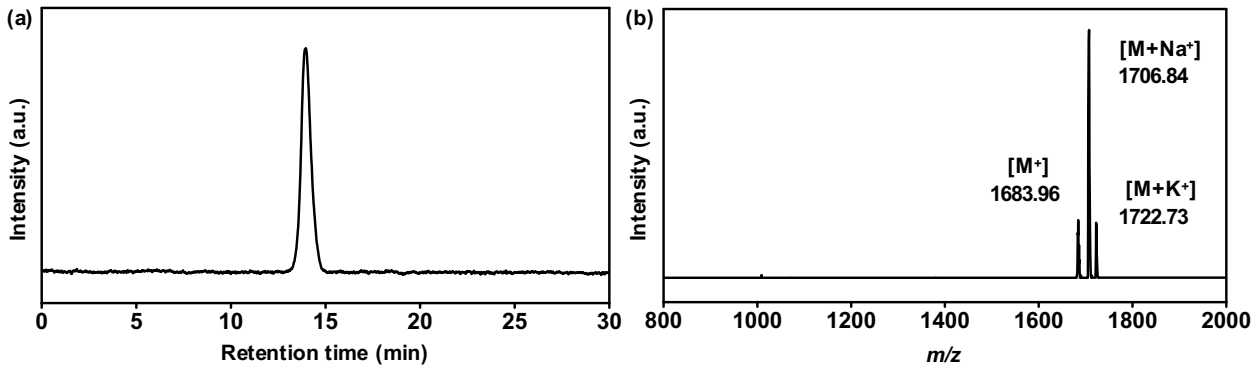


Figure S3. (a) HPLC traces of **11** (eluent: THF; detector: λ = 254 nm). (b) MALDI-TOF mass spectrum of **11** (matrix: 2,5-dihydroxylbenzoic acid).

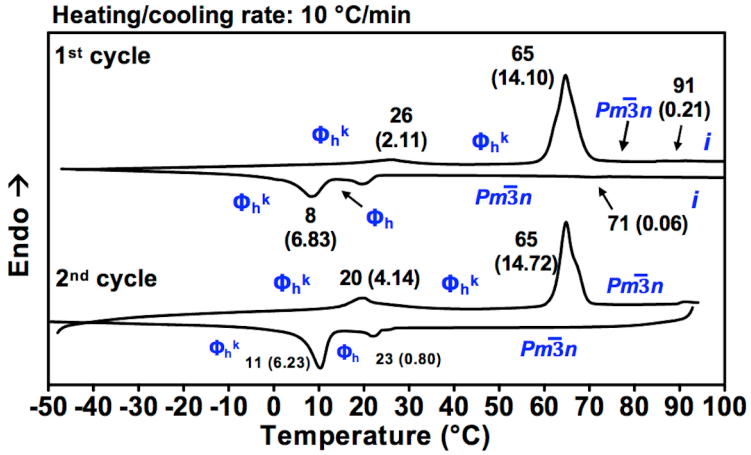


Figure S4. Thermal analysis of **11** by DSC. DSC traces of the first (upper) and the second (lower) heating and cooling scans of **11** at the rate of 10 °C/min. Phases indexed by XRD, transition temperatures (in °C), and associated enthalpy changes (in parentheses in kcal/mol) are indicated.

3. Supplemental References

[1] V. Percec, D.A. Wilson, P. Leowanawat, C.J. Wilson, A.D. Hughes, M.S. Kaucher, D.A. Hammer, D.H. Levine, A.J. Kim, F.S. Bates, K.P. Davis, T.P. Lodge, M.L. Klein, R.H. DeVane, E. Aqad, B.M. Rosen, A.O. Argintaru, M.J. Sienkowska, K. Rissanen, S. Nummelin, and J. Ropponen, Science **328**, 1009 (2010).).

[2] H. Issidorides, and R. Gulen, Org. Synth. **38**, 65 (1958).

[3] H. Ihre, A. Hult, J.M.J. Fréchet, and I. Gitsov, Macromolecules **31**, 4061 (1998).

[4] J.S. Moore and S.I. Stupp, Macromolecules **23**, 65 (1990).

[5] J. Ropponen, S. Nummelin, and K. Rissanen, Org. Lett. **6**, 2495 (2004).