Supplementary Information

Discotic liquid crystals stabilized by interionic interactions: imidazolium ion–anchored paraffinic triphenylene

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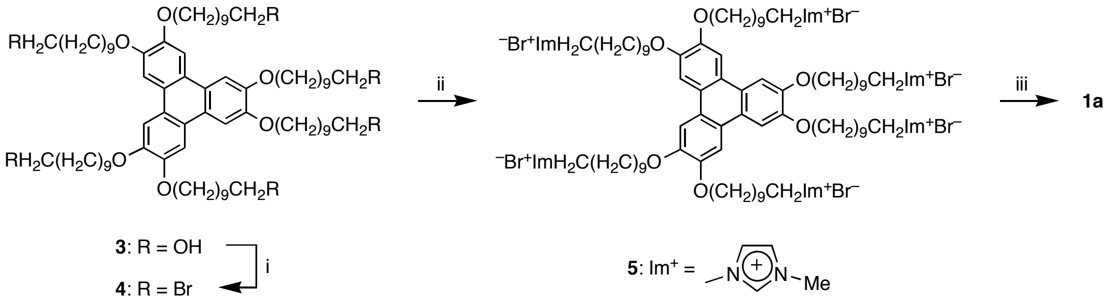
Measurements.

^{1}H and ^{13}C NMR spectra were recorded at 293 K in $CDCl_3$ and CD_3CN on a JEOL Type GSX–270 spectrometer, operating at 270.05 and 67.80 MHz, respectively, using residual non–deuterated or partially deuterated solvents as internal references. Differential scanning calorimetry (DSC) was performed on a Mettler–Toledo model DSC 822^e difference scanning calorimeter, where temperature and enthalpy were calibrated with In (430 K, 3.3 J mol^{-1}) and Zn (692.7 K, 12 J mol^{-1}) standard samples using sealed Al sample pans. Cooling and heating profiles were recorded and analyzed using the Mettler–Toledo STAR^e software system. X–ray diffraction measurements were performed on a Cu substrate using a Rigaku model RINT2500PC system with monochromated CuKα radiation. Optical microscopy was performed on a Nikon model OPTIPHOT optical polarizing microscope equipped with a Mettler FP–82HT hot–stage. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI–TOF–MS) was performed on an Applied Biosystems BioSpectrometry Workstation^{TM} model Voyager–DE^{TM} STR spectrometer using 9-nitroanthracene as a matrix. Electrospray–ionization mass spectroscopy (ESI–MS) was performed on a JEOL model AccuTOF JMS–T 100L spectrometer.

Materials.

Unless otherwise noted, reagents and solvents were used as received from Tokyo Kasei Co. (TCI) [10-bromo-1-decanol (85%), 2,3,6,7,10,11-hexahydroxytriphenylene (95%), tetrabromomethane (99%), triphenylphosphine (95%), $AgBF_4$ (98%) and imidazole (98%)], Acros Organics [1-methylimidazole (99%)] and Kanto Chemicals [anhydrous THF (99.5%)]. 2,3,6,7,10,11-Hexakis(10-hydroxydecyloxy)triphenylene was prepared according to a literature[1] with some modifications. Anhydrous solvents for reactions were purchased from Kanto Chemicals.

Preparation of 1a and 1b.



Scheme 1 *Regents and conditions*: (i) CBr_4, PPh_3, THF, r.t.; (ii) 1-methyl-imidazole, 90 °C; (iii) $AgBF_4$, CH_3CN, r.t..

Compound 4. To a dry THF solution of a mixture of 2,3,6,7,10,11-hexakis(10-hydroxydecyloxy)triphenylene (**3**) (500 mg, 0.40 mmol) and CBr_4 (2.65 g, 8.0 mmol) was added PPh_3 (2.6g, 10 mmol) at 0 °C under Ar, and the mixture was stirred for 15 min at room temperature under Ar. The reaction mixture was then poured into water and extracted with CH_2Cl_2. The combined extract was evaporated to dryness, and the residue was chromatographed on silica gel with CH_2Cl_2/hexane (CH_2Cl_2; gradient 30–50%) as an eluent, where the first fraction was collected and evaporated to dryness, affording **4** as white solid (309 mg) in 48% yield. ^1H NMR ($CDCl_3$): δ 7.81 (s, 6H), 4.20 (t, $J = 6.4$ Hz, 12H), 3.38 (t, $J = 6.8$ Hz, 12H), 1.94–1.78 (m, 24H), 1.69–1.19 (m, 72H). ^{13}C NMR ($CDCl_3$): δ 148.79, 123.49, 107.28, 69.66, 34.11, 32.88, 29.62, 29.54, 29.49, 28.88, 28.25, 26.24. MALDI–TOF–MS: Calcd. for $C_{78}H_{126}Br_6O_6$ $[M]^+$: m/z = 1632.47; Found: 1632.56.

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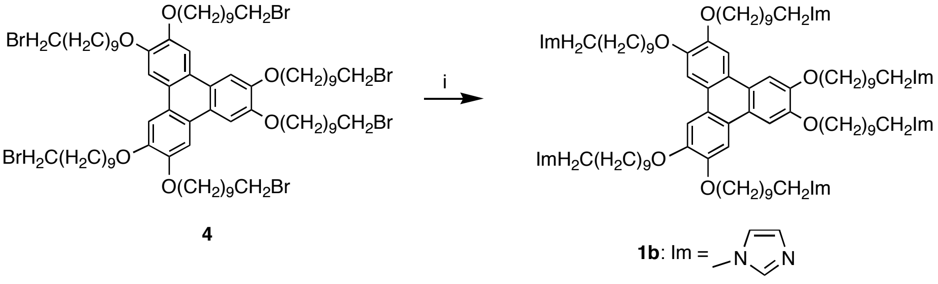
[1] G. Cooke, A. Radhi, N. Boden, R. J. Bushby, Z. Lu, S. Brown and S. L. Heath, *Tetrahedron*, 2000, **56**, 3385.

Compound 5. To 1-methylimidazole (10 mL, 250 mmol) was added compound **4** (300 mg, 0.18 mmol), and the mixture was stirred for 20 h at 90 °C under Ar. The reaction mixture was then evaporated to dryness, and the residue was washed with ether, affording **5** as colorless oil (336 mg) in 83% yield. ^{1}H NMR (CD_3CN): δ 9.04 (s, 6H), 7.89 (s, 6H), 7.42 (dd, J = 1.7, 1.7 Hz, 6H), 7.34 (dd, J = 1.7, 1.7 Hz, 6H), 4.24 (t, J = 6.3 Hz, 12H), 4.13 (t, J = 7.2 Hz, 12H), 3.84 (s, 18H), 1.98–1.73 (m, 24H), 1.63–1.18 (m, 72H). ^{13}C NMR (CD_3CN): δ 149.44, 124.31, 123.83, 122.89, 107.35, 69.94, 50.30, 36.75, 30.55, 30.18, 30.02, 29.59, 26.81, 26.66. ESI–TOF–MS: Calcd. for $C_{102}H_{162}Br_6N_{12}O_6$ $[M - Br]^+$: m/z = 2051.86; Found: 2051.83.

Compound 1a. To a dry MeCN (10 mL) solution of compound **5** (304 mg, 0.14 mmol) was added a dry MeCN (5 mL) solution of $AgBF_4$ (29 mg, 0.15 mmol), and the mixture was stirred for 8 h at room temperature. The reaction mixture was then filtrated off from an insoluble fraction. To the resulting supernatant solution was added an active carbon and an Al_2O_3 gel, and the mixture was stirred at room temperature for 4 h. Then the mixture was filtrated off from an insoluble fraction, and evaporated to dryness. The residue was washed with ether and dried at 70 °C under reduced pressure for 12 h, affording **1a** as colorless oil (164 mg) in 54% yield. ^{1}H NMR (CD_3CN): δ 8.39 (s, 6H), 7.88 (s, 6H), 7.33 (dd, J = 1.7, 1.7 Hz, 6H), 7.31 (dd, J = 1.7, 1.7 Hz, 6H), 4.23 (t, J = 6.3 Hz, 12H), 4.06 (t, J = 7.3 Hz, 12H), 3.79 (s, 18H), 1.93–1.69 (m, 24H), 1.63–1.18 (m, 72H). ^{13}C NMR (CD_3CN): δ 149.64, 136.60, 124.37, 123.91, 122.97, 107.48, 69.94, 50.36, 36.72, 30.54, 30.19, 30.13, 30.04, 30.01, 29.57, 26.86, 26.64. ESI–TOF–MS: Calcd. for $C_{102}H_{162}B_6F_{24}N_{12}O_6$ $[M - BF_4]^+$: m/z = 2086.29; Found: 2086.23. Anal. Calcd. for: C 56.37, H 7.51, N 7.73; Found: C 56.13, H 7.49, N 7.53.



Scheme 2 *Regents and conditions*: (i) NaH, imidazole, DMF, r.t..

Compound 1b. To a dry DMF solution of imidazole (383 mg, 5.63 mmol) were successively added compound **4** (100 mg, 61 μmol) and NaH (162 mg, 6.75 mmol) at 0 °C under Ar, and the mixture was stirred for 8 h at room temperature under Ar. The reaction mixture was poured into water and extracted with CH_2Cl_2. The combined extract was evaporated to dryness, affording **1b** as white solid (60 mg) in 63% yield. ^{1}H NMR ($CDCl_3$): δ 7.80 (s, 6H), 7.42 (brs, 6H), 7.02 (brs, 6H), 6.86 (s, 6H), 4.19 (t, J = 6.3 Hz, 12H), 3.88 (t, J = 7.3 Hz, 12H), 1.97–1.65 (m, 24H), 1.61–1.17 (m, 72H). ^{13}C NMR ($CDCl_3$): δ 148.96, 137.07, 129.34, 123.60, 118.69, 107.43, 69.67, 47.01, 31.05, 29.47, 29.44, 29.40, 29.38, 29.07, 26.53, 26.10. MALDI–TOF–MS: Calcd. for $C_{96}H_{144}N_{12}O_6$ $[M]^+$: m/z = 1561.13; Found: 1561.79.

Preparation of samples from 1a and [C$_6$mim][BF$_4$].

Dry MeCN solutions of **1a** (100 mM) and [C$_6$mim][BF$_4$] (50 mM) were mixed together at varying ratios, and the resulting solutions were evaporated to dryness under reduced pressure at 80 °C for 12 h, affording waxy solid samples with mole fractions of [C$_6$mim][BF$_4$] ranging from 0 to 1.0.

DSC traces of compound 1b.

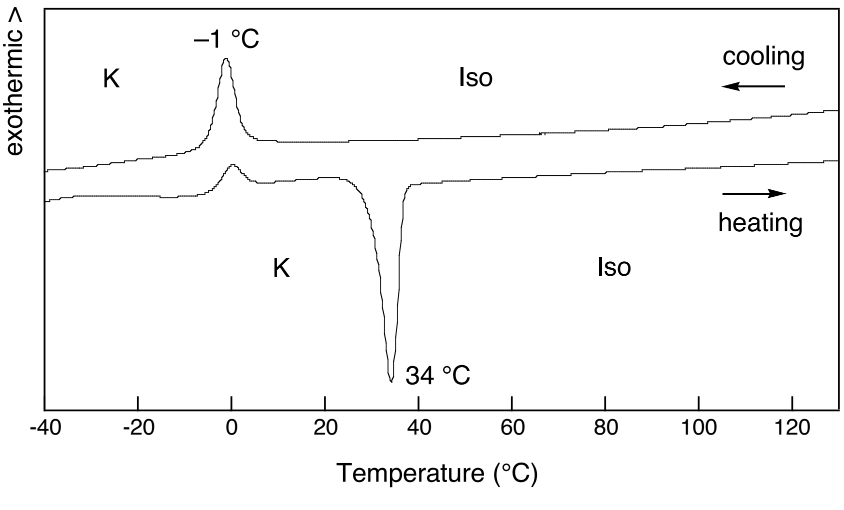


Fig. S1 DSC trace on second heating/cooling cycle of **1b** (scan rate 10 °C min^{-1}). K, crystalline state; Iso, isotropic liquid.