Supporting Information

Antiaromatic twinned triphenylene discotics showing nematic phases
Liang Zhang, Hemant Gopee, David L. Hughes and Andrew N. Cammidge*
School of Chemistry, University of East Anglia, Norwich NR4 7TJ, UK.
General procedures:
Pyridine was dried over calcium hydride before use and all the other solvents were used as purchased. NMR spectra were recorded on Varian Gemini 300 MHz and Varian Unity Plus 400MHz spectrometers. $^1$H and $^{13}$C NMR signals are reported in ppm. $^1$H signals are referenced to the residual proton of a deuterated solvent 7.26 ppm for CDCl$_3$ and 5.32 ppm for CD$_2$Cl$_2$. $^{13}$C NMR signals are referenced to the solvent signal CDCl$_3$ at 77.0 ppm and CD$_2$Cl$_2$ at 53.8 ppm. EI and HRMS analyses were performed at the EPSRC National Mass Spectrometry Service Centre at Swansea University. MALDI-MS analyses were recorded on AXIMA-CFRplus equipment. UV spectra were recorded on an HITACHI U300 instrument. Fluorescence spectra were recorded on a PerkinElmer LS45 instrument. Elemental analyses were performed in the Science Centre at London Metropolitan University.

2,7,10,11-Tetrakis(hexyloxy)-3,6-bis(3-methyl-3-hydroxybutynyl)triphenylene 5a

\[
\begin{align*}
\text{H}_3\text{C}_6\text{O} & \quad \text{OC}_6\text{H}_{13} \\
\text{H}_3\text{C}_6\text{O} & \quad \text{OC}_6\text{H}_{13}
\end{align*}
\]

3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (3.00 g, 3.81 mmol), Cul (0.10 g, 0.52 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.16 g, 0.22 mmol) and PPh$_3$ (0.24 g, 0.91 mmol) were stirred in refluxing triethylamine (50 mL) under an atmosphere of nitrogen for 15 min. The heating source was then removed and 2-methyl-but-3-yn-2-ol (1.60 g, 20 mmol) was added dropwise to the mixture. The solution was heated under reflux for a further 24 h. The mixture was cooled to room temperature and water was added. The mixture was extracted with DCM (3×100 mL) and the solvent removed in vacuo to leave a dark-brown solid which was purified by column chromatography (ethyl acetate/petroleum ether=1:4) to give the pure title compound (2.44 g, 81%) as a pale yellow solid.

Mp I 190 °C Colh 90 °C Cr; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.45 (s, 2 H), 7.76 (s, 2 H), 7.61 (s, 2 H), 4.28-4.22 (m, 8 H), 2.45 (br, 2 H), 1.98-1.91 (m, 8 H), 1.71 (s, 12 H), 1.67-1.37 (m, 24 H), 0.95-0.92 (m, 12 H); $^{13}$C NMR (CDCl$_3$, 75.45 MHz): $\delta$ 157.8, 150.0, 129.8, 128.4, 124.5, 122.3, 112.4, 107.6, 104.4, 98.4, 79.1, 69.7, 69.0, 65.8, 31.8, 31.7, 31.6, 29.4, 25.9, 25.8, 22.8, 22.7, 14.1, 14.0; MS (EI): m/z 792.6 (M$, 100\%$); HRMS: Calcd. For C$_{52}$H$_{72}$O$_6$: 792.5323. Found: 792.5326.
3,6-Diethynyl-2,7,10,11-tetrakis(hexyloxy)triphenylene 6a

2,7,10,11-Tetrakis(hexyloxy)-3,6-bis(3-methyl-3-hydroxybutynyl)triphenylene 5a (3.0 g, 3.78 mmol) was dissolved in refluxing dry toluene (50 mL) under an atmosphere of nitrogen. NaH (60% dispersion in oil) (0.67 g, 17.0 mmol NaH) was added in small portions and the mixture heated under reflux for 2 h. The solution was then poured onto ice-cold water and the organic layer was extracted with DCM (3×100 mL). The solvent was removed in vacuo to leave a dark-brown oil which was purified by column chromatography (ethyl acetate/petroleum ether=1:9) to give the pure title compound (1.82 g, 71%) as a pale yellow solid.

Mp 140 °C; \( ^1H \) NMR (CDCl\(_3\), 400 MHz): \( \delta \) 8.57 (s, 2 H), 7.82 (s, 2 H), 7.70 (s, 2 H), 4.27-4.23 (m, 8 H), 3.38 (s, 2 H), 1.99-1.92 (m, 8 H), 1.60-1.36 (m, 24 H), 0.95-0.92 (m, 12 H); \( ^{13}C \) NMR (CDCl\(_3\), 75.45 MHz): \( \delta \) 158.4, 150.3, 130.4, 129.5, 124.6, 122.2, 111.8, 107.6, 104.5, 81.5, 80.6, 69.6, 69.2, 31.8, 31.7, 29.4, 29.3, 25.9, 25.8, 22.8, 22.7, 14.0; MS (EI): \( m/z \) 676.6 (M\(^+\), 100%); HRMS: Calcd. For C\(_{46}\)H\(_{60}\)O\(_4\): 676.4486. Found: 676.4478.
Absorption spectrum
4.3×10⁻⁶ M in DCM
Synthesis of Twin 3a and higher oligomers

6a

Fluorescence spectrum
14.8×10⁻⁸ M in DCM
Excitation wavelength= 280 nm
A mixture of CuCl (300 mg, 30.0 mmol) and Cu(OAc)$_2$·H$_2$O (600 mg, 30.0 mmol) in freshly distilled pyridine (100 mL) was stirred and heated at 60 °C. Compound 6a (677 mg, 1.0 mmol) in pyridine (13 mL) was added over 18 h, and the mixture was stirred at 60 °C for another 24 h. The solvent was evaporated and the residue was dissolved in DCM, washed with water (3×300 mL), dried over MgSO$_4$, evaporated under vacuo to dryness and subjected to purification by silica gel chromatography (DCM/cyclohexane=3:7-2:3) to yield compound 3a (185 mg, 27%), 8a (175 mg, 26%) and 9 (40 mg, 6%) as solids.

Compound 3a: Mp Cr1 153 °C Cr2 209 °C N$_D$ > 280 °C (Decomp); $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 9.32 (s, 4 H), 7.81 (s, 4 H), 7.67 (s, 4 H), 4.28 (t, J=6.4 Hz, 8 H), 4.24 (t, J=6.4 Hz, 8 H), 1.99-1.89 (m, 16 H), 1.60-1.56 (m, 16 H), 1.45-1.40 (m, 32 H), 0.99-0.93 (m, 24 H); UV-Vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log $\varepsilon$) 336 (4.71), 355 (4.55), 375 (4.77), 400 (4.29), 424(4.54) nm; Anal. Calcd. For C$_{92}$H$_{118}$O$_8$: C, 81.86; H, 8.66; Found: C, 81.79; H, 8.68; MS (MALDI): m/z 1349.86 (M$^+$, 100%).
Compound 8a: Mp > 300 °C; \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.81 (s, 6 H), 6.92 (s, 6 H), 6.85 (s, 6 H), 4.30-3.90 (m, 24 H), 2.18-2.10 (m, 12 H), 2.02-1.94 (m, 12 H), 1.76-1.61 (m, 24 H), 1.56-1.40 (m, 48 H), 0.99 (t, \(J\) = 6.8 Hz, 18 H), 0.90 (t, \(J\) = 7.2 Hz, 18 H); \(^{13}\)C NMR (75 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 158.7, 149.6, 129.7, 129.1, 123.9, 121.5, 111.3, 106.5, 103.0, 79.8, 79.5, 69.5, 69.3, 32.3, 30.1, 29.8, 26.4, 26.3, 23.2, 23.1, 14.2, 14.1; UV-Vis (CH\(_2\)Cl\(_2\)) \(\lambda\)\(_{\text{max}}\) (log \(\varepsilon\)) 319 (5.07), 376 (5.35), 395 (5.11), 418(5.31) nm; Anal. Calcd. For C\(_{138}\)H\(_{174}\)O\(_{12}\): C, 81.86; H, 8.66; Found: C, 81.78; H, 8.71; MS (MALDI): \(m/z\) 2024.79 (M\(^+\), 100%).
Compound 9: Mp > 300 °C; \(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 8.50 (s, 8 H), 7.71 (s, 8 H), 7.61 (s, 8 H), 4.28 (t, \(J = 8.4\) Hz, 16 H), 4.22 (t, \(J = 8.4\) Hz, 16 H), 2.05-1.88 (m, 32 H), 1.64-1.55 (m, 32 H), 1.54-1.33 (m, 64 H), 0.95-0.86 (m, 48 H); \(^{13}\)C NMR (75 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 159.3, 150.4, 130.8, 129.7, 124.5, 122.1, 111.7, 107.2, 104.2, 79.5, 78.8, 69.7, 69.4, 32.09, 32.07, 29.8, 29.6, 26.2, 26.1, 23.0, 14.2, 14.1; UV-Vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) (log \(\varepsilon\)) 304 (5.73), 352 (5.50), 378 (5.36), 402 (5.26) nm; MS (MALDI): \(m/z\) 2699.65 (M\(^+\),100%).
3-Bromophenol (17.30 g, 0.10 mol) was heated at reflux with 1-bromodecane (44.24 g, 0.20 mol) and potassium carbonate (27.64, 0.20 mol) in ethanol (200 mL) for 24 h. The solution was filtered and the filter cake was washed thoroughly with ethanol. The solvent was evaporated under vacuum to yield the title compound 10 as a colourless oil (30.39g, 97%).

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.16-7.10 (m, 1 H), 7.08-7.04 (m, 2 H), 6.84-6.80 (m, 1 H), 3.92 (t, $J$=6.6 Hz, 2 H),
1.81-1.72 (m, 2 H), 1.46-1.25 (m, 14 H), 0.89 (t, J=6.6 Hz, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 160.1, 130.5, 123.6, 122.8, 117.7, 113.6, 68.2, 31.8, 29.5, 29.3, 29.2, 29.0, 25.9, 22.6, 14.0; HRMS: Calcd. For C$_{16}$H$_{25}$OBr: 312.1083. Found: 312.1082.
1-Bromo-3-decyloxybenzene 10 (25.06 g, 0.08 mol) was added slowly to the mixture of magnesium turnings (2.30 g, 0.096 mol) and freshly distilled THF (100 mL). The mixture was then heated at reflux for 3 h before it was transferred to a solution of trimethyl borate (16.63 g, 0.16 mol) in freshly distilled THF (200 mL) at -78 °C. After addition the mixture was stirred and allowed to warm gradually to room temperature overnight. 10% Hydrochloride was added slowly and the solution was extracted with diethyl ether. The organic layer was dried over MgSO₄ and evaporated to give a solid that can recrystallized from hexane to give 11 as a white solid (17.8 g, 80%).

1H NMR (300 MHz, CD₃OD) δ 7.23-7.19 (m, 3 H), 6.92-6.89 (m, 1 H), 3.94 (t, J=4.8 Hz, 2 H), 1.77-1.70 (m, 2 H), 1.49-1.26 (m, 14 H), 0.89 (t, J=5.1 Hz, 3 H); 13C NMR (75 MHz, CD₃OD) δ 164.5, 159.9, 129.7, 126.9, 120.3, 117.4, 68.8, 33.1, 30.8, 30.7, 30.6, 30.5, 27.2, 23.8, 14.5; HRMS: Calcd. For [C₁₆H₂₇O₃B+F]⁺: 297.2046. Found: 297.2045.
1,2-Didecoxy-4,5-bis(3-decoxyphenyl)benzene 12

1,2-Dibromo-4,5-bis(3-decoxyphenyl)benzene (10.97 g, 0.02 mol), 3-decoxy-phenylboronic acid 11 (16.69 g, 0.06 mol), PdCl₂ (283.7 mg, 1.6 mmol), PPh₃ (1.68 g, 6.4 mmol) and Na₂CO₃ (10.6 g, 0.1 mol) were heated at reflux in toluene-ethanol-water (3:3:1) (140 mL) for 72 h. The mixture was evaporated to dryness, DCM was added and it was washed with water. After drying over MgSO₄ and evaporation, the residue was subjected to chromatography (DCM/petroleum ether = 1:4) on silica gel to yield the title compound 12 as colourless oil (14.54 g, 85%).

¹H NMR (300 MHz, CDCl₃) δ 7.10 (t, J=7.8 Hz, 2 H), 6.95 (s, 2 H), 6.73-6.65 (m, 6 H), 4.05 (t, J=6.6 Hz, 4 H), 3.73 (t, J=6.6 Hz, 4 H), 1.89-1.79 (m, 4 H), 1.70-1.57 (m, 4 H), 1.52-1.23 (m, 56 H), 0.90-0.86 (m, 12 H); ¹³C NMR (75 MHz, CDCl₃) δ 158.7, 148.4, 143.0, 133.1, 128.8, 122.2, 116.0, 113.0, 69.4, 68.0, 31.8, 29.5, 29.33, 29.25, 29.0, 26.0, 25.9, 25.5, 22.6, 14.0, 13.98; HRMS: Calcd. For C₅₈H₉₄O₄: 854.7147. Found: 854.7155.
Iron (III) chloride (4.87 g, 30 mmol) was added to compound 12 (5.13 g, 6.0 mmol) in DCM (200 mL). The blue suspension was stirred at room temperature for 20 min and then methanol was added. The mixture was extracted with DCM (3×200 mL) and the organic layer was dried over MgSO$_4$ and evaporated. The title compound 13 was recrystallized from DCM and methanol to yield a pale yellow solid (4.56 g, 89%).

Mp 86 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J$=9.0 Hz, 2 H), 7.90 (s, 2 H), 7.85 (d, $J$=2.4 Hz, 2 H), 7.19 (dd, $J$=2.4 Hz, $J$=9.0 Hz, 2 H), 4.23 (t, $J$=6.6 Hz, 4 H), 4.16 (t, $J$=6.6 Hz, 4 H), 2.00-1.84 (m, 8 H), 1.62-1.50 (m, 8 H), 1.42-1.22 (m, 48 H), 0.89 (t, $J$=6.3 Hz, 12 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.5, 149.4, 129.9, 124.3, 124.2, 123.2, 114.4, 107.0, 106.9, 69.4, 68.2, 31.92, 31.90, 29.7, 29.62, 29.59, 29.51, 29.49, 29.47, 29.4, 29.3, 26.1, 22.7, 14.1; HRMS: Calcd. For C$_{58}$H$_{92}$O$_4$: 852.6990. Found: 852.6985.

2,3,6,11-Tetrakis(decyloxy)triphenylene 13
3,6-Dibromo-2,7,10,11-tetrakis(decyloxy)triphenylene 4b

Bromine (1.66 g, 10.4 mmol) was added dropwise to the solution of compound 13 (4.22 g, 4.95 mmol) stirred in DCM (200 mL) at 0 °C. After addition, the reaction was stirred at 0 °C for 2 h. Saturated aqueous sodium metabisulfite was added. The mixture was extracted with DCM (3×200 mL) and the organic layer was dried over MgSO4 and evaporated. The title compound 4b was recrystallized from DCM and methanol to give a pale yellow sticky solid (4.55 g, 91%).

Mp Cr 65 °C Colh 132 °C l; 1H NMR (300 MHz, CDCl3) δ 8.26 (s, 2 H), 7.72 (s, 2 H), 7.55 (s, 2 H), 4.25 (t, J=6.6 Hz, 4 H), 4.19 (t, J=6.6 Hz, 4 H), 2.00-1.84 (m, 8 H), 1.62-1.52 (m, 8 H), 1.45-1.22 (m, 48 H), 0.89 (t, J=6.6 Hz, 12 H); 13C NMR (100 MHz, CDCl3) δ 153.6, 149.6, 128.8, 127.2, 123.6, 122.7, 112.2, 106.2, 104.8, 69.4, 69.2, 31.9, 29.73, 29.65, 29.62, 29.6, 29.5, 29.41, 29.37, 29.3, 26.4, 26.2, 22.7, 14.1; MS (MALDI): m/z 1010.11 (M⁺, 100%).
2,7,10,11-Tetrakis(decyloxy)-3,6-bis(3-methyl-3-hydroxybutynyl)triphenylene 5b

Compound 4b (2.50 g, 2.47 mmol), Pd(PPh3)2Cl2 (173.5 mg, 0.247 mmol) and CuI (94.1 mg, 0.494 mmol) in triethylamine (40 mL) was heated at reflux for 15 min. 2-Methyl-3-butyn-2-ol (841 mg, 10 mmol) was added dropwise to the mixture. The solution was heated under reflux for a further 24 h. The mixture was cooled to room temperature and water was added. The mixture was extracted with DCM (3×100 mL) and the solvent removed in vacuo to leave a dark-brown solid which was purified by column chromatography (ethyl acetate/petroleum ether=1:4) to yield the title compound 5b as a yellow sticky solid (2.26 g, 90%).

Mp Cr 44 °C Colb 109 °C I; 1H NMR (300 MHz, CDCl3) δ 8.14 (s, 2 H), 7.48 (s, 2 H), 7.29 (s, 2 H), 4.18-4.12 (m, 8 H), 3.45 (s, 2 H), 2.00-1.92 (m, 8 H), 1.73 (s, 12 H), 1.67-1.61 (m, 8 H), 1.45-1.25 (m, 48 H), 0.92-0.88 (m, 12 H); 13C NMR (100 MHz, CDCl3) δ 157.2, 149.4, 129.1, 127.8, 124.1, 121.8, 111.8, 107.0, 103.9, 98.2, 78.8, 69.4, 68.7, 65.5, 31.92, 31.89, 31.5, 29.74, 29.66, 29.65, 29.48, 29.45, 29.40, 29.36, 26.2, 22.7, 14.1; MS (MALDI): m/z 1016.42 (M+, 100%).
3,6-Diethynyl-2,7,10,11-tetrakis(decyloxy)triphenylene 6b

Compound 5b (1.85 g, 1.82 mmol) was heated at reflux with excess of sodium hydroxide in toluene for 2 h. The mixture was filtered and the solvent was evaporated. The title compound 6b was recrystallized from DCM and methanol (1.56 g, 95%).

Mp Cr 59 °C Colh 91 °C l; H NMR (300 MHz, CDCl3) δ 8.56 (s, 2 H), 7.80 (s, 2 H), 7.69 (s, 2 H), 4.27-4.22 (m, 8 H), 3.38 (s, 2 H), 2.00-1.90 (m, 8 H), 1.61-1.52 (m, 8 H), 1.48-1.26 (m, 48 H), 0.88 (t, J=6.6 Hz, 12 H); C NMR (75 MHz, CDCl3) δ 158.3, 150.1, 130.3, 129.4, 124.5, 122.1, 111.7, 107.4, 104.4, 81.3, 80.4, 69.5, 69.1, 31.8, 29.6, 29.54, 29.49, 29.44, 29.38, 29.29, 29.27, 29.20, 29.0, 22.6, 14.0; Anal. Calcd. For C62H92O4: C, 82.61; H, 10.29; Found: C, 82.67; H, 10.26; HRMS: Calcd. For C62H92O4: 900.6990. Found: 900.6991.
Synthesis of 3b and 8b
A mixture of CuCl (300 mg, 30.0 mmol) and Cu(OAc)$_2$·H$_2$O (600 mg, 30.0 mmol) in freshly distilled pyridine (100 mL) was stirred and heated at 60 °C. Compound 6b (901 mg, 1.0 mmol) in pyridine (13 mL) was added over 18 h and the mixture was stirred at 60 °C for another 24 h. The solvent was evaporated and the residue was dissolved in DCM, washed with water (3×300 mL), dried over MgSO$_4$, evaporated under vacuo to dryness and subjected to purification by silica gel chromatography (DCM/cyclohexane=3:7-4:6) to yield the title compound 3b (224 mg, 25%) and 8b (207 mg, 23%) as solids.

Compound 3b: Mp Cr 110 °C N D 131 °C I; $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 9.32 (s, 4 H), 7.81 (s, 4 H), 7.67 (s, 4 H), 4.28 (t, $J$=6.4 Hz, 8 H), 4.24 (t, $J$=6.4 Hz, 8 H), 1.99-1.89 (m, 16 H), 1.60-1.56 (m, 16 H), 1.45-1.40 (m, 32 H), 0.99-0.93 (m, 24 H); UV-Vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log ε) 336 (4.71), 355 (4.55), 375 (4.77), 400 (4.29), 424(4.54) nm; Anal. Calcd. For C$_{124}$H$_{180}$O$_8$: C, 82.80; H, 10.09; Found: C, 82.78; H, 10.03; MS (MALDI): m/z 1797.78 (M$^+$, 100%).

Compound 8b: Mp > 300 °C; $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 7.70 (brs, 6 H), 6.89 (brs, 6 H), 6.78 (brs, 6 H), 4.40-3.90 (brm, 24 H), 2.20-2.05 (brm, 12 H), 2.02-1.85 (brm, 12 H), 1.78-0.6 (brm, 108 H); $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) δ 158.7, 149.6, 129.7, 129.1, 123.9, 121.5, 111.3, 106.5, 103.0, 79.8, 79.5, 69.5, 69.3, 32.3, 30.1, 29.8, 26.4, 26.3, 23.2, 23.1, 14.2, 14.1; Anal. Calcd. For C$_{186}$H$_{270}$O$_{12}$: C, 82.80; H, 10.09; Found: C, 82.71; H, 9.97; MS (MALDI): m/z 2697.64 (M$^+$, 100%).
Stepwise synthesis of 7

\[
\begin{align*}
5a & \quad \text{NaH (1eq) \quad Toluene} \\
14 & \quad \text{Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}} \quad \text{CuI} \quad \text{PPh\textsubscript{3}} \quad \text{TEA}
\end{align*}
\]

11-Ethynyl-3,6,7,10-tetrakis(hexyloxy)-2-(3-methyl-3-hydroxybutynyl)triphenylene 14

\[
\begin{align*}
\text{C}_6\text{H}_{13}\text{O} \quad \text{NaH} \quad \text{Toluene} \\
\text{C}_6\text{H}_{13} \quad \text{C}_6\text{H}_{13} \\
\text{C}_6\text{H}_{13} \quad \text{C}_6\text{H}_{13} \\
\text{C}_6\text{H}_{13} \quad \text{C}_6\text{H}_{13} \\
\text{C}_6\text{H}_{13} \quad \text{C}_6\text{H}_{13} \\
\text{C}_6\text{H}_{13} \quad \text{C}_6\text{H}_{13} \\
\text{C}_6\text{H}_{13} \quad \text{C}_6\text{H}_{13} \\
\text{C}_6\text{H}_{13} \quad \text{C}_6\text{H}_{13}
\end{align*}
\]

2,7,10,11-Tetrakis(hexyloxy)-3,6-bis(3-methyl-3-hydroxybutynyl)triphenylene 5a (1.50 g, 1.89 mmol) was dissolved in refluxing dry toluene (30 mL) under an atmosphere of nitrogen. NaH (60% dispersion in oil) (0.075 g, 1.89 mmol NaH) was added in one portion and the mixture heated under reflux for 30 min. The solution was the poured onto ice-cold water and the organic layer was extracted with DCM (3×100 mL). The solvent was removed in vacuo to leave a dark-brown oil which was purified by column chromatography (ethyl acetate/petroleum ether=1:9) to give the pure title compound (0.50 g, 35%) as a yellow solid.

Mp 164 °C Colh 72 °C K; \(^1\)H NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta\) 8.61 (s, 1 H), 8.52 (s, 1 H), 7.84 (s, 1 H), 7.83 (s, 1 H), 7.73 (s, 1 H), 7.70 (s, 1 H), 4.28-4.22 (m, 8 H), 3.39 (s, 1 H), 2.17 (br, 1 H), 1.98-1.92 (m, 8 H), 1.72 (s, 6 H), 1.61-1.34 (m, 24 H), 0.96-0.88 (m, 12 H); \(^{13}\)C NMR (CDCl\textsubscript{3}, 75.45 MHz): \(\delta\) 157.9, 157.5, 149.7, 149.6, 129.9, 129.5, 129.0, 128.1, 124.3, 123.9, 121.8, 121.7, 112.0, 111.3, 107.3, 107.1, 104.1, 103.9, 97.9, 80.9, 80.1, 79.2, 69.2, 68.7, 68.5, 65.4, 31.2, 31.1, 31.0, 29.2, 28.8, 28.7, 25.3, 25.2, 22.2, 22.1, 13.6, 13.5; MS (ES): \(m/z\) 735.5 (M\(^+\), 100%); HRMS: Calcd. For [C\(_4\)H\(_{60}\)O\(_5\)+NH\(_4\)]\(^+\): 752.5249. Found: 752.5257.
Dimer 15

Compound 14 (0.40 g, 0.54 mmol), Cul (0.05 g, 0.26 mmol), Pd(PPh₃)₂Cl₂ (0.10 g, 0.14 mmol), PPh₃ (0.12 g, 0.45 mmol) were stirred in refluxing triethylamine (50 mL) under an atmosphere of nitrogen for 24 h. The mixture was cooled to room temperature and water added. The mixture was extracted with DCM (3×100 mL) and solvent was removed in vacuo to leave a dark-brown solid which was purified by column chromatography (ethyl acetate/petroleum ether=1:4) to give the pure title compound (0.23 g, 58%) as an off-white solid.

Mp 185 °C; ¹H NMR (CDCl₃, 300 MHz): δ 8.59 (s, 2 H), 8.45 (s, 2 H), 7.76 (s, 4 H), 7.65 (s, 2 H), 7.61 (s, 2 H), 4.29-4.22 (m, 16 H), 2.48 (br, 2 H), 2.03-1.93 (m, 16 H), 1.73 (s, 12 H), 1.60-1.25 (m, 48 H), 0.98-0.85 (m, 24 H); ¹³C NMR (CDCl₃, 75.45 MHz): δ 157.8, 156.9, 149.3, 149.0, 129.4, 128.9, 127.5, 123.8, 123.4, 121.5, 111.6, 110.9, 106.7, 106.5, 103.6, 103.4, 97.5, 78.0, 77.5, 68.7, 68.6, 68.4, 67.9, 64.8, 30.7, 30.6, 28.7, 28.4, 28.3, 24.9, 24.8, 21.7, 13.1, 13.0; MS (MALDI): m/z 1468 (M⁺, 100%).
Dimer 15 (0.23 g, 0.16 mmol) was dissolved in refluxing dry toluene (50 mL) under an atmosphere of nitrogen. NaH (60% dispersion in oil) (0.067 g, 1.7 mmol NaH) was added in small portions and the mixture heated under reflux for 2 h. The solution was poured onto ice-cold water and the organic layer was extracted with DCM (3×100 mL). The solvent was removed in vacuo to leave a dark-brown oil which was purified by column chromatography (ethyl acetate/petroleum ether=1:9) to give the pure title compound (0.16 g, 75%) as a pale yellow solid.

Mp 153 °C; \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 8.64 (s, 2 H), 8.60 (s, 2 H), 7.82 (s, 4 H), 7.72 (s, 4 H), 4.31-4.24 (m, 16 H), 3.39 (s, 2 H), 1.99-1.92 (m, 16 H), 1.65-1.40 (m, 48 H), 0.99-0.83 (m, 24 H); \(^{13}\)C NMR (CDCl\(_3\), 75.45 MHz): \(\delta\) 158.4, 157.8, 149.6, 129.8, 129.2, 124.1, 121.7, 111.5, 111.2, 106.9, 103.9, 80.9, 79.0, 78.4, 77.0, 69.1, 68.8, 31.2, 29.2, 28.9, 28.7, 25.4, 25.3, 22.2, 13.6, 13.5; MS (MALDI): \(m/z\) 1351.9 (M\(^+\), 100%).