Supplementary Information

Systematical study on the influences of linkage length on phase behaviors and charge carrier mobilities of discotic dimers

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1. Materials and Methods

Materials

All solvents employed were purchased from Aldrich and used without further purification unless stated otherwise. Column and thin layer chromatography were performed on silica gel (200–300 mesh ASTM) and Silica Gel 60 glass backed sheets, respectively.

Methods

$^1$H-NMR spectra were measured in CDCl$_3$ on Bruker NMR spectrometers (DMX 300 MHz), chemical shifts are given in parts per million (δ) and are referenced from tetramethylsilane (TMS). Multiplicities of the peaks are given as s = singlet, d = doublet, t = triplet, m = multiplet. Fourier transform infrared spectroscopy was carried out on a Shimadzu FTIR-8400 spectrometer using KBr pellets. High resolution mass spectrum was recorded on a Bruker Apex IV FTMS mass spectrometer. Polarising optical microscopy was carried out on a leica DM4500P microscope equipped with a linkam TMS94 hot stage. Differential scanning calorimetry was carried out on a Netzsch DSC 200. X-ray diffraction studies were conducted on a Brucker D8 advance diffractrometer equipped with a variable temperature controller. All of the measurements were carried out at heating and cooling rates of 10°C min$^{-1}$.

Compounds 1-3 and 5-7 were prepared according to literature procedures and characterized by $^1$H-NMR and FT-IR; compounds T3D3-T3D12 and T5D3-T5D12 were synthesised from 3 and appropriate α,ω-dibromoalkane according to our previous work dimers of HAT4.

Charge mobility was measured using a time-of-flight (TOF) devices. The LC cells with a thickness of 15 μm were purchased from E.H.C. company with semi-transparent indium tin oxide (ITO) electrodes. The purified compounds were capillary-filled into the cell at the temperature 10°C higher than their clear point, and then slowly cooled to their mesophases at a rate of 0.1°C min$^{-1}$ in order to obtain a well defined homeotropic alignment. The cell was placed on the hotstage and illuminated by light pulses from a N$_2$ laser (USHO KEC 160, wavelength 337nm, and the pulse width is 600 ps). The transient photocurrent across the cell was amplified by using a NF low-noise current preamplifier (model 5307) and monitored using a digital phosphor oscilloscope (Tektronix TDS 3032c). The bias voltage was applied to the sample with a power supply unit (Kikusui PAN110-3A). Measurements were carried out under atmospheric conditions.

The products were purified by flash chromatography and recrystallized from ethanol and dichloromethane.
2. Synthesis and characterization

Scheme 1: Syntheses of triphenylene dimers T3D3-T3D12 (a) and T5D3-T5D12 (b)

1, 2-dipropoxybenzene (1)

1-Bromopropane (184.3g, 1.5mol) was added to a vigorously stirred solution of catechol (44 g, 0.4mol) and potassium carbonate (220.9g) in ethanol (600ml) under nitrogen. The reaction mixture was stirred under reflux for 24 h and filtered with copious washings of ethanol. The filtrate was concentrated in vacuo and subjected to a silica gel column chromatography on silica, eluting with 1:1 dichloromethane: light petroleum to give the product as pale yellow oil. (50 g, 95 %); TLC Rf: 0.6 (dichloromethane-hexane 1:1); IR (KBr): v_{max}/cm^{-1} 1257 (C-O-C); δH (300MHZ, CDCl₃) 6.90 (4H, s, ArH), 4.0 (4H, t, OCH₂), 1.91 (4H, m, OCH₂CH₂), 1.05 (t, 6H, CH₃).

2, 3, 6, 7, 10, 11-hexapropoxytriphenylene (2)

Compound 1 (15g, 0.077mol) was added to a vigorously stirred suspension of Iron(III) chloride (37.6g, 0.232mol) in dichloromethane (100ml). The reaction occurred with vigorous evolution of gas and was quenched with methanol (150ml) after 70 min. The reaction mixture was filtered and the filtrate concentrated in vacuo to give a pale yellow powder which was subjected to a silica gel column chromatography, eluting with 1:1 dichloromethane: light petroleum to give 2 as pale yellow powder which was recrystallized from ethanol. (11.6g, 77%); TLC Rf: 0.44 (ethyl acetate - hexane 1:6); IR (KBr): v_{max}/cm^{-1} 1263 (C-O-C); δH (300MHZ, CDCl₃) 7.85 (6H, s, ArH), 4.22 (12H, t, OCH₂), 2.0 (12H, m, OCH₂CH₂), 1.2 (18H, t, CH₃).
2-hydroxy -3, 6, 7, 10, 11-Pentapropyoxiphenylene (3)

To a cooled suspension of catechol (11g, 0.1mol) in CH₂Cl₂ (50 mL), a solution (0 °C) of BBr₃(28.6g, 0.11mol) in CH₂Cl₂ (10 ml) was added slowly with stirring 3h under nitrogen. The mixture was brought to room temperature, the solvent removed and the product distilled under vacuum to give B-Bromocatecholboronane as white solid (16g, 80%). The solid was then used to make a 0.5 M solution by mixing with CH₂Cl₂ (160 ml) and this was used for next ether cleavage reactions. A solution of 2 (26.6g, 0.0462mol) was dissolved in anhydrous CH₂Cl₂ (200 ml) and cooled to 0°C. To this was added (110.8ml, 0.055mol) of B-Bromocatecholboronane solution in CH₂Cl₂ under argon and the mixture was stirred at room temperature for 24h. After that it was poured over ice-water and extracted with CH₂Cl₂, the combined extract was dried with anhydrous Na₂SO₄ overnight, solvent was removed under vacuum and the crude product was purified by a silica gel column chromatography, eluting with 1: 30 ethyl acetate: light petroleum to give B-Bromocatecholboronane as white solid (16g, 80%). The solid was subjected to a silica gel column (silica, eluting with 1: 30 ethyl acetate: light petroleum to give the product as pale yellow oil.

1, 2-dipentapropyoxiphenylene (5)

1-Bromopentane (181.2g, 1.2mol) was added to a vigorously stirred solution of catechol (44g, 0.4mol) and potassium carbonate (110g) in ethanol (600ml) under nitrogen. The reaction mixture was stirred under reflux for 24 h and filtered with copious washings of ethanol. The filtrate was concentrated in vacuo and subjected to a silica gel column chromatography on silica, eluting with 1:1 dichloromethane: light petroleum to give the product as pale yellow oil. (96g, 96%); TLC Rf: 0.55 (dichloromethane-hexane 1:1); IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} \) 3483 (O-H), 1261 (C-O-C); \(\delta_{\text{H}}(300\text{MHz}, \text{CDCl}_3) \) 7.9 (6H, m, ArH), 5.9 (1H, s, OH) 4.20 (10H, t, OCH₂), 1.8 (10H, m, OCH₂CH₂), 1.0 (10H, t, CH₂).

2, 3, 6, 7, 10, 11-hexapropyoxiphenylene (6)

Compound 5 (15g, 0.06mol) was added to a vigorously stirred suspension of Iron(III) chloride (31.1g, 0.232mol) in dichloromethane (100ml). The reaction occurred with vigorous evolution of gas and was quenched with methanol (150ml) after 70 min. The reaction mixture was filtered and the filtrate concentrated in vacuo to give a pale yellow powder which was subjected to a silica gel column chromatography, eluting with 1: 1 dichloromethane: light petroleum to give 6 as pale yellow powder which was recrystallized from ethanol. (11.6g, 77%); TLC Rf: 0.44 (ethyl acetate - hexane 1:6); IR (KBr): \(\nu_{\text{max}}/\text{cm}^{-1} \) 1253 (C-O-C); \(\delta_{\text{H}}(300\text{MHz}, \text{CDCl}_3) \) 7.85 (6H, s, ArH), 4.25 (12H, t, OCH₂), 1.92-1.99 (12H, m, OCH₂CH₂), 2.0 (12H, m, OCH₂CH₂), 1.42-1.67 (24H, m, OCH₂CH₂, CH₂CH₂), 0.99 (18H, t, CH₃).

2-hydroxy -3, 6, 7, 10, 11-Pentapropyoxiphenylene (7)

To a cooled suspension of catechol (11g, 0.15mol) in CH₂Cl₂ (50mL), a solution (0 °C) of BBr₃(28.6g, 0.11mol) in CH₂Cl₂ (10 ml) was added slowly with stirring 3h under nitrogen. The mixture was brought to room temperature, the solvent removed and the product distilled under vacuum to give B-Bromocatecholboronane as white solid (16g, 80%). The solid was then used to make a 0.5 M solution by mixing with CH₂Cl₂ (160 ml) and this was used for next ether cleavage reactions. A solution of 6 (14.88g, 0.0462mol) was dissolved in anhydrous CH₂Cl₂ (200 ml) and cooled to 0°C. To this was added (48ml, 0.024mol) of B-Bromocatecholboronane solution in CH₂Cl₂ under argon and the mixture was stirred at
room temperature for 24h. After that it was poured over ice-water and extracted with CH₂Cl₂, the combined extract was dried with anhydrous Na₂SO₄ overnight, solvent was removed under vacuum and the crude product was purified by a silica gel column chromatography, eluting with 1: 30 ethyl acetate: light petroleum to give 7 as white powder which was recrystallized from ethanol. (6.2g, 46%); TLC RF: 0.22 (ethyl acetate-hexane 1:6); IR (KBr): νmax/cm⁻¹ 3456 (O-H), 1255 (C-O-C); δH (300MHZ, CDCl₃) 7.96-7.77 (6H, m, ArH), 5.9 (1H, s, OH) 4.31-4.19 (10H, t, OCH₂), 1.97-1.90 (10H, m, OCH₂CH₂), 1.58-1.39(20H, m, OCH₂CH₂CH₂CH₂), 1.0 (10H, t, CH₃).

1, 3-Bis (3, 6, 7, 10, 11-pentapropoxytriphenylene-2'-oxylo)-propane (T3D3)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapropoxytriphenylene (500mg), 1,3-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in THF (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T3D3 (0.19 g, 46%); TLC RF: 0.46 (dichloromethane–ethyl acetate 120:1); (found: C 74.4; H 7.98. C₁₀H₁₈O₂ requires: C, 74.7; H, 7.99%); IR (KBr): νmax/cm⁻¹ 1261 (C–O–C); δH (300 MHZ, CDCl₃) 7.81–7.95 (12H, s, ArH), 4.58 (4H, t, OCH₂), 4.10–4.21 (20H, t, OCH₂), 2.56 (2H, m, OCH₂CH₂), 1.84–1.98 (20H, m, OCH₂CH₂), 1.10–1.20 (30H, m, CH₃); HRMS (ESI): calc. m/z 1108.62703 (C₆₀H₉₈O₁₂), found m/z 1108.62915 (M)+

1, 4-Bis (3, 6, 7, 10, 11-pentapropoxytriphenylene-2'-oxylo)-butane (T3D4)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapropoxytriphenylene (500mg), 1,4-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in THF (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T3D4 (0.21g, 50%); TLC RF: 0.49 (dichloromethane–ethyl acetate 120:1); (found: C, 74.24; H, 8.08. C₁₀H₁₈O₂ requires: C, 74.84; H, 8.07%); IR (KBr): νmax/cm⁻¹ 1263 (C–O–C); δH (300 MHZ, CDCl₃) 7.81–7.89 (12H, s, ArH), 4.41 (4H, t, OCH₂), 4.15–4.21 (20H, t, OCH₂), 2.26 (4H, m, OCH₂CH₂), 1.89–1.99 (20H, m, OCH₂CH₂), 1.10–1.20 (30H, m, CH₃); HRMS (ESI): calc. m/z 1122.64268 (C₆₀H₉₆O₁₂), found m/z 1122.64595 (M)+

1, 5-Bis (3, 6, 7, 10, 11-pentapropoxytriphenylene-2'-oxylo)-pentane (T3D5)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapropoxytriphenylene (500mg), 1,5-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in THF (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T3D5 (0.2 g, 47%); TLC RF: 0.49 (dichloromethane–ethyl acetate 120:1); (found: C, 74.68; H, 8.18. C₁₀H₂₀O₁₂ requires: C, 74.97; H, 8.15%); IR (KBr): νmax/cm⁻¹ 1260 (C–O–C); δH (300 MHZ, CDCl₃) 7.84–7.86 (12H, s, ArH), 4.29–4.33 (4H, t, OCH₂), 4.18–4.22 (20H, t, OCH₂), 2.14–2.09 (4H, m, OCH₂CH₂), 1.92–2.01 (22H, m, OCH₂CH₂), 1.11–1.17 (30H, m, CH₃); HRMS (ESI): calc. m/z 1136.65833 (C₇₁H₉₂O₁₂), found m/z 1136.65912(M)+
1, 6-Bis (3, 6, 7, 10, 11-pentapropytriphenylene-2’-yloxy)-hexane (T3D6)
A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapropytriphenylene (500mg), 1,6-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in THF (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T3D6 (0.19g, 44%); TLC Rf: 0.5 (dichloromethane–ethyl acetate 120:1); (found: C, 74.85; H, 8.24. C_{72}H_{98}O_{12} requires: C, 75.10; H, 8.23%); IR (KBr): ν_{max}/cm\(^{-1}\) 1260 (C–O–C); δ_{H1} (300 MHz, CDCl\(_3\)) 7.83–7.84 (12H, s, ArH), 4.18–4.30 (24H, t, OCH\(_2\)), 1.92–2.01 (24H, m, OCH\(_2\)CH\(_2\)), 1.74 (4H, m, OCH\(_2\)CH\(_2\)CH\(_2\)), 1.03–1.17 (30H, m, CH\(_3\)); HRMS (ESI): calc. m/z 1150.67398 (C_{72}H_{98}O_{12}), found m/z 1150.67558 (M\(^+\)).

1, 7-Bis (3, 6, 7, 10, 11-pentapropytriphenylene-2’-yloxy)-heptane (T3D7)
A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapropytriphenylene (500mg), 1,7-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in THF (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T3D7 (0.2 g, 46%); TLC Rf: 0.49 (dichloromethane–ethyl acetate 120:1); (found: C, 72.88; H, 8.15. C_{73}H_{96}O_{12} requires: C, 75.23; H, 8.30%); IR (KBr): ν_{max}/cm\(^{-1}\) 1262 (C–O–C); δ_{H1} (300 MHz, CDCl\(_3\)) 7.84 (12H, s, ArH), 4.18–4.28 (24H, t, OCH\(_2\)), 1.94–2.01 (24H, m, OCH\(_2\)CH\(_2\)), 1.67 (6H, m, OCH\(_2\)CH\(_2\)), 1.12–1.17 (30H, m, CH\(_3\)); HRMS (ESI): calc. m/z 1164.68963 (C_{73}H_{96}O_{12}), found m/z 1164.69227 (M\(^+\)).

1, 8-Bis (3, 6, 7, 10, 11-pentapropytriphenylene-2’-yloxy)-octane (T3D8)
A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapropytriphenylene (500mg), 1,8-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in THF (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T3D8 (0.23 g, 52%); TLC Rf: 0.51 (dichloromethane–ethyl acetate 120:1); (found: C, 74.75; H, 8.38. C_{74}H_{100}O_{12} requires: C, 75.35; H, 8.37%); IR (KBr): ν_{max}/cm\(^{-1}\) 1262 (C–O–C); δ_{H1} (300 MHz, CDCl\(_3\)) 7.84 (12H, s, ArH), 4.18–4.27 (24H, t, OCH\(_2\)), 1.94–2.01 (24H, m, OCH\(_2\)CH\(_2\)), 1.56–1.63 (8H, m, OCH\(_2\)CH\(_2\)), 1.12–1.17 (30H, m, CH\(_3\)); HRMS (ESI): calc. m/z 1178.70528 (C_{74}H_{100}O_{12}), found m/z 1178.70493 (M\(^+\)).

1, 9-Bis (3, 6, 7, 10, 11-pentapropytriphenylene-2’-yloxy)-nonane (T3D9)
A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapropytriphenylene (500mg), 1,9-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in THF (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T3D9 (0.22 g, 49%); TLC Rf: 0.51 (dichloromethane–ethyl acetate 120:1); (found: C, 75.04; H, 8.45. C_{75}H_{106}O_{12} requires: C,
A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapropyloxytriphenylene (500mg), 1,10-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in THF (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T3D10 (0.23 g. 51%): TLC Rf: 0.51 (dichloromethane–ethyl acetate 120:1); (found: C, 75.30; H, 8.52. C_{76}H_{102}O_{12} requires: C, 75.59; H, 8.51%); IR (KBr): v_{max}/cm^{-1} 1263 (C–O–C); δ_{H} (300 MHz, CDCl₃) 7.84 (12H, s, ArH), 4.18–4.22 (24H, t,OCH₂), 1.94–2.01 (24H, m, OCH₂CH₂), 1.52–1.55 (4H, m, OCH₂CH₂), 1.37 (12H, m, CH₂), 1.12–1.17 (30H, m, CH₃); HRMS (ESI): calc. m/z 1206.73658 (C_{76}H_{102}O_{12}), found m/z 1206.73895 (M^+).

1, 11-Bis (3, 6, 7, 10, 11-pentapropyloxytriphenylene-2’-yloxy)-undecane (T3D11)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapropyloxytriphenylene (500mg), 1,11-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in THF (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T3D11 (0.22 g, 48%): TLC Rf: 0.54 (dichloromethane–ethyl acetate 120:1); (found: C, 75.38; H, 8.59. C_{76}H_{102}O_{12} requires: C, 75.70; H, 8.58%); IR (KBr): v_{max}/cm^{-1} 1257 (C–O–C); δ_{H} (300 MHz, CDCl₃) 7.84 (12H, s, ArH), 4.18–4.26 (24H, t,OCH₂), 1.94–2.03 (24H, m, OCH₂CH₂), 1.52–1.55 (4H, m, OCH₂CH₂), 1.38 (10H, m, OCH₂CH₂), 1.12–1.17 (30H, m, CH₃); HRMS (ESI): calc. m/z 1220.75223 (C_{76}H_{102}O_{12}), found m/z 1220.74980 (M^+).

1, 2-Bis (3, 6, 7, 10, 11-pentapropyloxytriphenylene-2’-yloxy)-dodeane (T3D12)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapropyloxytriphenylene (500mg), 1,3-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in THF (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T3D12 (0.25 g, 54%): TLC Rf: 0.56 (dichloromethane–ethyl acetate 120:1); (found: C, 75.50; H, 8.61. C_{76}H_{102}O_{12} requires: C, 75.82; H, 8.65%); IR (KBr): v_{max}/cm^{-1} 1257 (C–O–C); δ_{H} (300 MHz, CDCl₃) 7.84 (12H, s, ArH), 4.18–4.26 (24H, t,OCH₂), 1.94–2.01 (24H, m, OCH₂CH₂), 1.52–1.55 (4H, m, OCH₂CH₂), 1.37 (12H, m, OCH₂CH₂), 1.12–1.17 (30H, m, CH₃); HRMS (ESI): calc. m/z 1234.76787 (C_{76}H_{102}O_{12}), found m/z 1234.76785 (M^+).

1, 3-Bis (3, 6, 7, 10, 11-pentapentyloxytriphenylene-2’-yloxy)-propane (T5D3)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapentyloxytriphenylene (500mg), 1,3-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in acetone (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered,
washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure TSD3 (0.19 g, 46%); TLC Rf: 0.54 (dichloromethane–hexane 4:1); (found: C, 76.86; H, 9.33. C₂₅H₁₂O₁₂ requires: C, 76.91; H, 9.28%); IR (KBr): νmax/cm⁻¹ 1261 (C–O–C); δH (300 MHz, CDCl₃) 7.80–7.97 (12H, s, ArH), 4.58 (4H, t, OCH₂), 4.10–4.26 (20H, t, OCH₂), 2.56 (2H, m, OCH₂CH₂), 1.78–1.95 (20H, m, OCH₂CH₂), 1.27–1.56 (40H, m, OCH₂CH₂CH₂CH₂), 1.10–1.20 (30H, m, CH₃); HRMS (ESI): calc. m/z 1388.93894 (C₉₀H₁₂O₁₂), found m/z 1388.94003 (M⁺)

1, 4-Bis (3, 6, 7, 10, 11-pentapentyloxytriphenylen-2'-yloxy)-butane (TSD4)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapentyloxytriphenylene (500mg), 1,4-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in acetone (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure TSD4 (0.21 g, 50%); TLC Rf: 0.58 (dichloromethane–hexane 4:1); (found: C, 75.94; H, 9.46. C₂₅H₁₃O₁₂ requires: C, 76.99; H, 9.33%); IR (KBr): νmax/cm⁻¹ 1261 (C–O–C); δH (300 MHz, CDCl₃) 7.81–7.89 (12H, s, ArH), 4.41 (4H, t, OCH₂), 4.16–4.24 (20H, t, OCH₂), 2.26 (2H, m, OCH₂CH₂), 1.87–1.95 (20H, m, OCH₂CH₂), 1.40–1.56 (40H, m, OCH₂CH₂CH₂CH₂), 0.91–1.00 (30H, m, CH₃); HRMS (ESI): calc. m/z 1402.95473 (C₉₀H₁₃O₁₂), found m/z 1402.95568 (M⁺)

1, 5-Bis (3, 6, 7, 10, 11-pentapentyloxytriphenylen-2'-yloxy)-pentane (TSD5)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapentyloxytriphenylene (500mg), 1,5-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in acetone (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure TSD5 (0.2 g, 48%); TLC Rf: 0.58 (dichloromethane–hexane 4:1); (found: C, 77.03; H, 9.43. C₂₅H₁₃O₁₂ requires: C, 77.08; H, 9.38%); IR (KBr): νmax/cm⁻¹ 1261 (C–O–C); δH (300 MHz, CDCl₃) 7.83–7.86 (12H, s, ArH), 4.22–4.33 (24H, t, OCH₂), 1.88–2.13 (24H, m, OCH₂CH₂), 1.37–1.62 (42H, m, OCH₂CH₂CH₂CH₂), 0.92–1.00 (30H, m, CH₃); HRMS (ESI): calc. m/z 1416.97127 (C₉₀H₁₃₂O₁₂), found m/z 1416.97133 (M⁺)

1, 6-Bis (3, 6, 7, 10, 11-pentapentyloxytriphenylen-2'-yloxy)-hexane (TSD6)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapentyloxytriphenylene (500mg), 1,6-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in acetone (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure TSD6 (0.21 g, 49%); TLC Rf: 0.58 (dichloromethane–hexane 4:1); (found: C, 77.19; H, 9.47. C₂₅H₁₃₄O₁₂ requires: C, 77.16; H, 9.43%); IR (KBr): νmax/cm⁻¹ 1263 (C–O–C); δH (300 MHz, CDCl₃) 7.82–7.83 (12H, s, ArH), 4.23–4.27 (24H, t, OCH₂), 1.91–1.98 (24H, m, OCH₂CH₂),
1.40–1.74 (44H, m, OCH₂CH₂CH₂CH₂), 0.93–1.00 (30H, m, CH₃); HRMS (ESI): calc. m/z 1430.98653 (C₉₂H₁₃₅O₁₂), found m/z 1430.98698 (M)+

1, 7-Bis (3, 6, 7, 10, 11-pentapentylxoytriphenylene-2'-yloxy)-heptane (T5D7)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapentylxoytriphenylene (500mg), 1,3-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in acetone (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T5D7 (0.21 g, 49%): TLC Rf: 0.59 (dichloromethane–hexane 4:1); (found: C, 77.23; H, 9.48. C₉₂H₁₃₅O₁₂ requires: C, 77.24; H, 9.48%); IR (KBr): νₘₛₐₓ/cm⁻¹ 1263 (C–O–C); δₒ (300 MHz, CDCl₃) 7.83 (12H, s, ArH), 4.21–4.25 (24H, t, OCH₂), 1.92–1.98 (24H, m, OCH₂CH₂CH₂CH₂), 0.93–1.00 (30H, m, CH₃); HRMS (ESI): calc. m/z 1445.00501 (C₉₂H₁₃₅O₁₂), found m/z 1445.00263 (M)+

1, 8-Bis (3, 6, 7, 10, 11-pentapentylxoytriphenylene-2'-yloxy)-octane (T5D8)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapentylxoytriphenylene (500mg), 1,8-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in acetone (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T5D8 (0.21 g, 48%): TLC Rf: 0.59 (dichloromethane–hexane 4:1); (found: C, 77.35; H, 9.54. C₉₄H₁₃₈O₁₂ requires: C, 77.32; H, 9.53%); IR (KBr): νₘₛₐₓ/cm⁻¹ 1263 (C–O–C); δₒ (300 MHz, CDCl₃) 7.83 (12H, s, ArH), 4.21–4.26 (24H, t, OCH₂), 1.93–1.98 (24H, m, OCH₂CH₂CH₂CH₂), 0.93–1.00 (30H, m, CH₃); HRMS (ESI): calc. m/z 1459.01841 (C₉₄H₁₃₈O₁₂), found m/z 1459.01828 (M)+

1, 9-Bis (3, 6, 7, 10, 11-pentapentylxoytriphenylene-2'-yloxy)-nonane (T5D9)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapentylxoytriphenylene (500mg), 1,9-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in acetone (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T5D9 (0.21 g, 47%): TLC Rf: 0.64 (dichloromethane–hexane 4:1); (found: C, 77.41; H, 9.60. C₉₅H₁₄₀O₁₂ requires: C, 77.40; H, 9.57%); IR (KBr): νₘₛₐₓ/cm⁻¹ 1263 (C–O–C); δₒ (300 MHz, CDCl₃) 7.83 (12H, s, ArH), 4.21–4.26 (24H, t, OCH₂), 1.93–1.98 (24H, m, OCH₂CH₂CH₂CH₂), 1.42–1.56 (50H, m, OCH₂CH₂CH₂CH₂CH₂), 0.93–1.00 (30H, m, CH₃); HRMS (ESI): calc. m/z 1473.03319 (C₉₅H₁₄₀O₁₂), found m/z 1473.03393 (M)+

1, 10-Bis (3, 6, 7, 10, 11-pentapentylxoytriphenylene-2'-yloxy)-decan (T5D10)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapentylxoytriphenylene (500mg), 1,10-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in acetone (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally
recrystallized from a mixture of ethanol and dichloromethane to give pure T5D10 (0.2 g, 45%). TLC Rf: 0.66 (dichloromethane–hexane 4:1); (found: C, 77.42; H, 9.41. C₉₀H₁₄₂O₁₂ requires: C, 77.48; H, 9.62%). IR (KBr): νmax/cm⁻¹ 1263 (C–O–C); δH (300 MHz, CDCl₃) 7.83 (12H, s, ArH), 4.21–4.26 (24H, t, OCH₂), 1.91–1.98 (24H, m, OCH₂CH₂), 1.44–1.56 (52H, m, OCH₃CH₂CH₂CH₃), 0.95–1.00 (30H, m, CH₃); HRMS (ESI): calc. m/z 1487.0497 (C₉₀H₁₄₂O₁₂), found m/z 1487.04958 (M)+

1, 11-Bis (3, 6, 7, 10, 11-pentapentyloxytriphenylene-2’-yloxy)-undecane (T5D11)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapentyloxytriphenylene (500mg), 1,11-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in acetone (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T5D11 (0.21 g, 47%). TLC Rf: 0.68 (dichloromethane–hexane 4:1); (found: C, 77.43; H, 9.63. C₉₀H₁₄₂O₁₂ requires: C, 77.56; H, 9.66%). IR (KBr): νmax/cm⁻¹ 1263 (C–O–C); δH (300 MHz, CDCl₃) 7.83 (12H, s, ArH), 4.21–4.26 (24H, t, OCH₂), 1.91–1.98 (24H, m, OCH₂CH₂), 1.42–1.59 (54H, m, OCH₃CH₂CH₂CH₃), 0.95–1.00 (30H, m, CH₃); HRMS (ESI): calc. m/z 1501.06436(C₉₀H₁₄₂O₁₂), found m/z 1501.06523 (M)+

1, 12-Bis (3, 6, 7, 10, 11-pentapentyloxytriphenylene-2’-yloxy)-dodeane (T5D12)

A mixture of 2-hydroxy-3, 6, 7, 10, 11-pentapentyloxytriphenylene (500mg), 1,12-dibromoalkane (0.4 eq.) and anhydrous potassium carbonate (1.0 g) in acetone (50ml) was heated under reflux for 72 h. The mixture was cooled to room temperature, filtered, washed with dichloromethane. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from a mixture of ethanol and dichloromethane to give pure T5D12 (0.23 g, 51%). TLC Rf: 0.73 (dichloromethane–hexane 4:1); (found: C, 77.64; H, 9.70. C₉₀H₁₄₆O₁₂ requires: C, 77.63; H, 9.71%). IR (KBr): νmax/cm⁻¹ 1268 (C–O–C); δH (300 MHz, CDCl₃) 7.83 (12H, s, ArH), 4.21–4.26 (24H, t, OCH₂), 1.91–1.98 (24H, m, OCH₂CH₂), 1.42–1.59 (56H, m, OCH₃CH₂CH₂CH₃), 0.86–1.00 (30H, m, CH₃); HRMS (ESI): calc. m/z 1515.08437(C₉₀H₁₄₆O₁₂), found m/z 1515.08088 (M)+
2. $^1$H-NMR and FT-IR spectra

Fig. 1S $^1$HNMR spectra of 1

Fig. 2S $^1$HNMR spectra of 2
Fig. 3S $^1$HNMR spectra of 3

Fig. 4S $^1$HNMR spectra of 5
Fig. 5S $^1$HNMR spectra of 6

Fig. 6S $^1$HNMR spectra of 7
Fig. 7S $^1$HNMR spectra of T3D3

Fig. 8S HRSM spectra of T3D3
Fig. 9S $^1$HNMR spectra of T3D4

Fig. 10S HRSM spectra of T3D4
Fig. 11S $^1$HNMR spectra of T3D5

Fig. 12S HRMS spectra of T3D5
Fig. 13S $^1$HNMR spectra of T3D6

Fig. 14S HRMS spectra of T3D6
Fig. 15S $^1$HNMR spectra of T3D7

Fig. 16S HRMS spectra of T3D7
Fig. 17S ¹HNMR spectra of T3D8

Fig. 18S HRMS spectra of T3D8
Fig. 19S $^1$HNMR spectra of T3D9

Fig. 20S HRMS spectra of T3D9
Fig. 21S $^1$HNMR spectra of T3D10

Fig. 22S HRMS spectra of T3D10
Fig. 23S $^1$HNMR spectra of T3D11

Fig. 24S HRMS spectra of T3D11
Fig. 25S $^1$HNMR spectra of T3D12

Fig. 26S HRMS spectra of T3D12
Fig. 27S $^1$HNMR spectra of T5D3

Fig. 28S HRMS spectra of T5D3
Fig. 29S $^1$HNMR spectra of T5D4

Fig. 30S HRMS spectra of T5D4
Fig. 31S $^1$HNMR spectra of T5D5

Fig. 32S HRMS spectra of T5D5
Fig. 33S $^1$HNMR spectra of T5D6

Fig. 34S HRMS spectra of T5D6
Fig. 35S $^1$HNMR spectra of T5D7

Fig. 36S HRMS spectra of T5D7
Fig. 37S $^1$HNMR spectra of T5D8

Fig. 38S HRMS spectra of T5D8
Fig. 39S $^1$HNMR spectra of T5D9

Fig. 40S HRMS spectra of T5D9
Fig. 41S $^1$HNMR spectra of T5D10

Fig. 42S HRMS spectra of T5D10
Fig. 43S $^1$HNMR spectra of T5D11

Fig. 44S HRMS spectra of T5D11
Fig. 4S $^1$HNMR spectra of T5D12

Fig. 46S HRMS spectra of T5D12
3. Mesomorphism

Mesomorphism of T3D3

Fig. 47S Crystalline texture observed by POM with 90° angle of compound T3D3 sandwiched between clean glass slides on cooling from isotropic phase at 175°C (left); DSC trace of compound T3D3 run at 10°C min⁻¹ under N² (right).

Mesomorphism of T3D4

Fig. 48S Crystalline texture observed by POM with 90° angle of compound T3D4 sandwiched between clean glass slides on cooling from isotropic phase at 120°C (left); DSC trace of compound T3D4 run at 10°C min⁻¹ under N² (right).

Mesomorphism of T3D5

Fig. 49S DSC trace of compound T3D5 run at 10°C min⁻¹ under N² (right).
Mesomorphism of T3D6

Fig. 50 S DSC trace of compound T3D6 run at 10°Cmin⁻¹ under N² (right).

Mesomorphism of T3D7

Fig. 51 S Dendritic texture observed by POM with 90° angle of compound T3D7 sandwiched between clean glass slides on cooling from isotropic phase at 179°C (left); DSC trace of compound T3D7 run at 10°Cmin⁻¹ under N² (right).

Mesomorphism of T3D8

Fig. 52 S Dendritic texture observed by POM with 90° angle of compound T3D8 sandwiched between clean glass slides on cooling from isotropic phase at 178°C (left); DSC trace of compound T3D8 run at 10°Cmin⁻¹ under N² (right).
Mesomorphism of T3D9

Fig. 53S Dendritic texture observed by POM with 90° angle of compound T3D9 sandwiched between clean glass slides on cooling from isotropic phase at 172°C (left); DSC trace of compound T3D9 run at 10°C min⁻¹ under N² (right).

Mesomorphism of T3D10

Fig. 54S Dendritic texture observed by POM with 90° angle of compound T3D10 sandwiched between clean glass slides on cooling from isotropic phase at 140°C (left); DSC trace of compound T3D10 run at 10°C min⁻¹ under N² (right).

Mesomorphism of T3D11

Fig. 55S Dendritic texture observed by POM with 90° angle of compound T3D11 sandwiched between clean glass slides on cooling from isotropic phase at 118°C (left); DSC trace of compound T3D11 run at 10°C min⁻¹ under N² (right).
Mesomorphism of T3D12

Fig. 56S Mosaic texture observed by POM with 90° angle of compound T3D12 sandwiched between clean glass slides on cooling from isotropic phase at 80°C(left); DSC trace of compound T3D12 run at 10°Cmin⁻¹ under N² (right).

Mesomorphism of T5D3

Fig. 57S Crystalline texture observed by POM with 90° angle of compound T5D3 sandwiched between clean glass slides on cooling from isotropic phase at 107°C(left); DSC trace of compound T5D3 run at 10°Cmin⁻¹ under N² (right).

Mesomorphism of T5D4

Fig. 58S Crystalline texture observed by POM with 90° angle of compound T5D4 sandwiched between clean glass slides on cooling from isotropic phase at 102°C(left); DSC trace of compound T5D4 run at 10°Cmin⁻¹ under N² (right).
Mesomorphism of T5D5

Fig. 59S Crystalline texture observed by POM with 90° angle of compound T5D5 sandwiched between clean glass slides on cooling from isotropic phase at 40°C (left); DSC trace of compound T5D5 run at 10°C min⁻¹ under N₂ (right).

Mesomorphism of T5D6

Fig. 60S Fan-shaped texture observed by POM with 90° angle of compound T5D6 sandwiched between clean glass slides on cooling from isotropic phase at 85°C (left); DSC trace of compound T5D6 run at 10°C min⁻¹ under N₂ (right).

Mesomorphism of T5D7

Fig. 61S Fan-shaped texture observed by POM with 90° angle of compound T5D7 sandwiched between clean glass slides on cooling from isotropic phase at 85°C (left);
DSC trace of compound T5D7 run at 10°Cmin⁻¹ under N² (right).

**Mesomorphism of T5D8**

Fig. 62S Fan-shaped texture observed by POM with 90° angle of compound T5D8 sandwiched between clean glass slides on cooling from isotropic phase at 114°C(left); DSC trace of compound T5D8 run at 10°Cmin⁻¹ under N² (right).

**Mesomorphism of T5D9**

Fig. 63S Fan-shaped texture observed by POM with 90° angle of compound T5D9 sandwiched between clean glass slides on cooling from isotropic phase at 116°C(left); DSC trace of compound T5D9 run at 10°Cmin⁻¹ under N² (right).

**Mesomorphism of T5D10**

Fig. 64S Fan-shaped texture observed by POM with 90° angle of compound T5D10
sandwiched between clean glass slides on cooling from isotropic phase at 126°C (left); DSC trace of compound T5D10 run at 10°C/min under N₂ (right).

**Moesomorphism of T5D11**

**Fig. 65** Fan-shaped texture observed by POM with 90° angle of compound T5D11 sandwiched between clean glass slides on cooling from isotropic phase at 124°C (left); DSC trace of compound T5D11 run at 10°C/min under N₂ (right).

**Mesomorphism of T5D12**

**Fig. 66** Fan-shaped texture observed by POM with 90° angle of compound T5D12 sandwiched between clean glass slides on cooling from isotropic phase at 115°C (left); DSC trace of compound T5D12 run at 10°C/min under N₂ (right).