Supplementary Information

Modulation of phase behaviors and charge carrier mobilities by linkage length in discotic liquid crystal dimers

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1. Synthesis and characterization

1, 2-dibutoxybenzene (1)

1-Bromobutane (25.7g, 0.187mol) was added to a vigorously stirred solution of catechol (5.5 g, 0.05mol) and potassium carbonate (27.6g) in ethanol (500ml) 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 1:2 dichloromethane: light petroleum to give the product as pale yellow oil. (10.6 g, 95 %); IR (KBr): \( \nu_{\text{max}}/\text{cm}^{-1} \) 1263 (C-O-C); \( \delta_{\text{H}} \) (300MHZ, CDCl\(_3\)) 6.90 (4H, s, ArH), 3.99-4.10 (4H, t, OCH\(_2\)), 1.77-1.86 (4H, m, OCH\(_2\)CH\(_2\)), 1.46-1.58 (m, 4H, OCH\(_2\)CH\(_2\)CH\(_2\)), 0.97-1.07 (t, 6H, CH\(_3\)).

2, 3, 6, 7, 10, 11-hexabutoxytriphenylene (2), (M4)

Compound 1 (7.5g, 0.0337mol) was added to a vigorously stirred suspension of Iron (III) chloride (16.42g, 0.0101mol) in dichloromethane (50ml). 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 black solid which was subjected to a silica gel column chromatography, eluting with 1:1 dichloromethane: light petroleum to give 2 as pale yellow solid which was recrystallized from ethanol. (16.95g, 76%); IR (KBr): \( \nu_{\text{max}}/\text{cm}^{-1} \) 1261 (C-O-C); \( \delta_{\text{H}} \) (300MHZ, CDCl\(_3\)) 7.85 (6H, s, ArH), 4.22-4.26 (12H, t, OCH\(_2\)), 1.89-1.98 (12H, m, OCH\(_2\)CH\(_2\)), 1.62-1.67 (12H, m, OCH\(_2\)CH\(_2\)CH\(_2\)), 1.02-1.07 (18H, t, CH\(_3\)).

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Synthesis scheme for compounds M3-M6
2-hydroxy-3, 6, 7, 10, 11-Pentabutoxytriphenylene (3)

To a cooled suspension of catechol (11g, 0.1mol) in CH\textsubscript{2}Cl\textsubscript{2} (50 mL), a solution (0 °C) of BBr\textsubscript{3} (28.6g, 0.11mol) in CH\textsubscript{2}Cl\textsubscript{2} (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 CH\textsubscript{2}Cl\textsubscript{2} (160 ml) and this was used for next ether cleavage reactions.

A solution of 2 (15g, 0.0227mol) was dissolved in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (150 ml) and cooled to 0°C. To this was added (64ml, 0.032mol) of B-Bromocatecholboronane solution in CH\textsubscript{2}Cl\textsubscript{2} under argon and the mixture was stirred at room temperature for 24h. After that it was poured over ice-water and extracted with CH\textsubscript{2}Cl\textsubscript{2}, the combined extract was dried with anhydrous Na\textsubscript{2}SO\textsubscript{4} 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 3 as white solid which was recrystallized from ethanol. (6.5g, 49%); IR (KBr): \( \nu_{\text{max}}/\text{cm}^{-1} \) 3456 (O-H), 1261 (C-O-C); \( \delta_{\text{H}} \) (300MHZ, CDCl\textsubscript{3}) 7.78-7.97 (6H, m, ArH), 5.91 (1H, s, OH) 4.20-4.38 (10H, t, OCH\textsubscript{2}), 1.89-1.96 (10H, m, OCH\textsubscript{2}CH\textsubscript{2}), 1.57-1.67 (10H, m, OCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 1.05-1.09 (18H, m, CH\textsubscript{3}).

2-propoxy-3, 6, 7, 10, 11-pentabutyloxytriphenylene (M3)

A mixture of 2-hydroxy-3,6,7,10,11-pentabutyloxytriphenylene (500mg), 1-Bromopropane (1.2 eq.) and anhydrous potassium carbonate (0.5g) in ethanol (20ml) was heated under reflux for 24h. The mixture was cooled to 0 °C, filtered, washed with water (50ml), and extracted with dichloromethane (2 \times 50ml), the solvent removed under vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol and n-hexane several times to give pure M3. (0.3g, 56%); IR (KBr): \( \nu_{\text{max}}/\text{cm}^{-1} \) 1261 (C-O-C); \( \delta_{\text{H}} \) (300MHZ, CDCl\textsubscript{3}) 7.85 (6H, m, ArH), 4.18-4.27 (12H, t, OCH\textsubscript{2}), 1.89-2.01 (12H, m, OCH\textsubscript{2}CH\textsubscript{2}), 1.52-1.68 (10H, m, OCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 1.03-1.17 (18H, m, CH\textsubscript{3}); HRMS (ESI): calc. m/z 647.4306 (C\textsubscript{41}H\textsubscript{59}O\textsubscript{6}), found m/z 647.4294 (M)+.

2-pentyloxy-3, 6, 7, 10, 11-pentabutyloxytriphenylene (M5)

A mixture of 2-hydroxy-3,6,7,10,11-pentabutyloxytriphenylene (500mg), 1-Bromopentane (1.2 eq.)
and anhydrous potassium carbonate (0.5g) in ethanol (20ml) was heated under reflux for 24h. The mixture was cooled to 0 °C, filtered, washed with water (50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol and n-hexane several times to give pure M5. (0.53g, 95%); IR (KBr): νmax/cm⁻¹ 1265 (C-O-C); δH (300MHZ, CDCl₃) 7.85 (6H, m, ArH), 4.23-4.27 (12H, t, OCH₂), 1.91-1.96 (12H, m, OCH₂CH₂), 1.56-1.65 (12H, m, OCH₂CH₂CH₂), 1.42-1.50 (2H, m, OCH₂CH₂CH₂CH₂), 0.96-1.11 (18H, m, CH₃); HRMS (ESI): calc. m/z 675.4619 (C₄₃H₆₃O₆), found m/z 675.4603 (M)+.

2-hexyloxy-3, 6, 7, 10, 11-pentabutyloxytriphenylene (M6)

A mixture of 2-hydroxy-3,6,7,10,11-pentabutyloxytriphenylene (500mg), 1-Bromohexane (1.2 eq.) and anhydrous potassium carbonate (0.5g) in ethanol (20ml) was heated under reflux for 24h. The mixture was cooled to 0 °C, filtered, washed with water (50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol and n-hexane several times to give pure M6. (0.54g, 94%); IR (KBr): νmax/cm⁻¹ 1263 (C-O-C); δH (300MHZ, CDCl₃) 7.85 (6H, m, ArH), 4.23-4.27 (12H, t, OCH₂), 1.89-1.98 (12H, m, OCH₂CH₂), 1.60-1.68 (12H, m, OCH₂CH₂CH₂), 1.40-1.41 (4H, m, OCH₂CH₂CH₂CH₂), 0.94-1.08 (18H, m, CH₃); HRMS (ESI): calc. m/z 689.4776 (C₄₄H₆₅O₆), found m/z 689.4759 (M)+.
2. Mesomorphism

Mesomorphism of M3

![Graph showing DSC traces of compound M3 on 2nd heating run (red line) and 1st cooling run (black line) at 10 °C/min under N\textsuperscript{2}.](image)

ESI Fig. 1 DSC traces of compound M3 on 2nd heating run (red line) and 1st cooling run (black line) at 10 °C/min under N\textsuperscript{2}.

Mesomorphism of M4

![Graph showing DSC traces of compound M4 on 2nd heating run (red line) and 1st cooling run (black line) at 10 °C/min under N\textsuperscript{2}.](image)

ESI Fig. 2 DSC traces of compound M4 on 2nd heating run (red line) and 1st cooling run (black line) at 10 °C/min under N\textsuperscript{2}.

Mesomorphism of M5

![Graph showing DSC traces of compound M5 on 2nd heating run (red line) and 1st cooling run (black line) at 10 °C/min under N\textsuperscript{2}.](image)

ESI Fig. 3 DSC traces of compound M5 on 2nd heating run (red line) and 1st cooling run (black line) at 10 °C/min under N\textsuperscript{2}. 
ESI Fig. 4 XRD pattern for Col$_{hp}$ phase of M5 on heating run at 100$^\circ$C

Mesomorphism of M6

ESI Fig. 5 Dendritic texture of compound M6 sandwiched between clean glass slides on cooling from isotropic phase at 120 $^\circ$C (left), this texture which indicated a Col$_h$ phase was observed by POM with 45$^\circ$ angle and did not show any changes when cooled to crystal phase; DSC traces of compound M6 on 2nd heating run (red line) and 1st cooling run (black line) at 10 $^\circ$C/min under N$_2$ (right).

Mesomorphism of D10

ESI Fig. 6 Optical textures of compound D10 sandwiched between clean glass slides on cooling from isotropic phase: (a) dendritic texture which indicated a Col$_h$ phase observed by POM with 90$^\circ$ angle at 146 $^\circ$C; (b) mosaic texture which indicated a Col$_{hp}$ phase observed by POM with 90$^\circ$ angle at 140 $^\circ$C. Phase transition between Col$_h$ and Col$_{hp}$ was clearly observed for the colours and areas of domain were changed while the birefringence increases.
ESI Fig. 7 DSC traces of compound D10 run at 10 °C/min under N₂.