Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

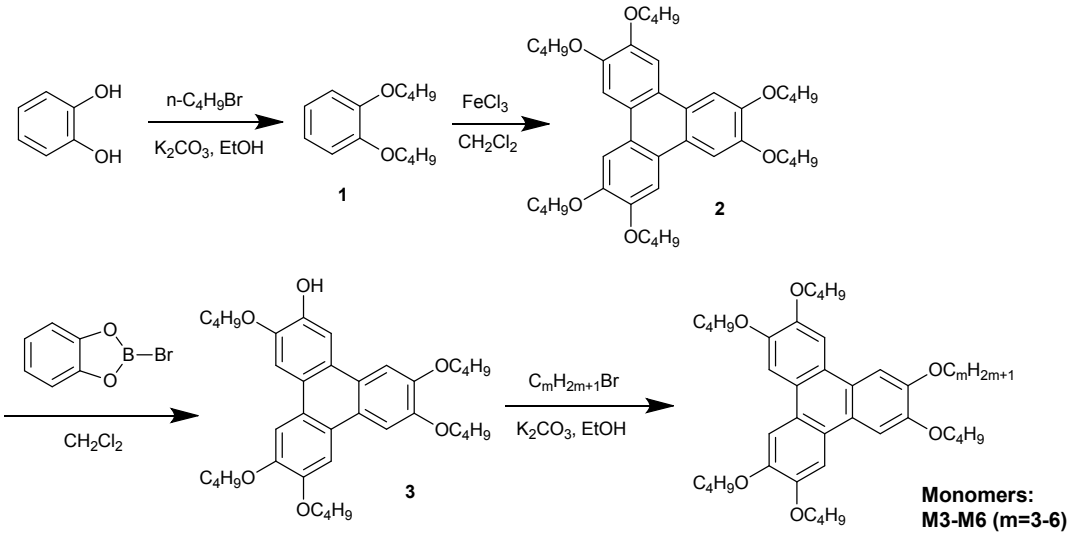
Modulation of phase behaviors and charge carrier mobilities by linkage length in discotic liquid crystal dimers

Yi-Fei Wang, Chun-Xiu Zhang*, Hao Wu, Ao Zhang, Jian-Chuang Wang, Shuai-Feng Zhang and Jia-Ling Pu

Information Recording Materials Lab, Lab of Printing & Packaging Material and Technology, Beijing Institute of Graphic Communication, 102600 Beijing, China .
E-mail: zhangchunxiu@bigc.edu.cn

Table of Contents

1. Synthesis and characterization



Synthesis scheme for compounds M3-M6

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): ν_{max}/cm^{-1} 1263 (C-O-C); δ_H (300MHZ, $CDCl_3$) 6.90 (4H, s, ArH), 3.99-4.10 (4H, t, OCH_2), 1.77-1.86 (4H, m, OCH_2CH_2), 1.46-1.58 (m, 4H, $OCH_2CH_2CH_2$), 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): ν_{max}/cm^{-1} 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.85 (6H, s, ArH), 4.22-4.26 (12H, t, OCH_2), 1.89-1.98 (12H, m, OCH_2CH_2), 1.62-1.67 (12H, m, $OCH_2CH_2CH_2$), 1.02-1.07 (18H, t, CH_3).

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

To a cooled suspension of catechol (11g, 0.1mol) in CH_2Cl_2 (50 mL), a solution (0 °C) of BBr_3 (28.6g, 0.11mol) in CH_2Cl_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_2Cl_2 (160 ml) and this was used for next ether cleavage reactions.

A solution of **2** (15g, 0.0227mol) was dissolved in anhydrous CH_2Cl_2 (150 ml) and cooled to 0°C. To this was added (64ml, 0.032mol) of B-Bromocatecholboronane solution in CH_2Cl_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_2Cl_2, the combined extract was dried with anhydrous Na_2SO_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): ν_{max}/cm^{-1} 3456 (O-H), 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.78-7.97 (6H, m, ArH), 5.91 (1H, s, OH) 4.20-4.38 (10H, t, OCH_2), 1.89-1.96 (10H, m, OCH_2CH_2), 1.57-1.67 (10H, m, $OCH_2CH_2CH_2$), 1.05-1.09 (18H, t, CH_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 (2×50ml), 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 **M3**. (0.3g, 56%); IR (KBr): ν_{max}/cm^{-1} 1261 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.85 (6H, m, ArH), 4.18-4.27 (12H, t, OCH_2), 1.89-2.01 (12H, m, OCH_2CH_2), 1.52-1.68 (10H, m, $OCH_2CH_2CH_2$), 1.03-1.17 (18H, m, CH_3); HRMS (ESI): calc. m/z 647.4306 ($C_{41}H_{59}O_6$), 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.)

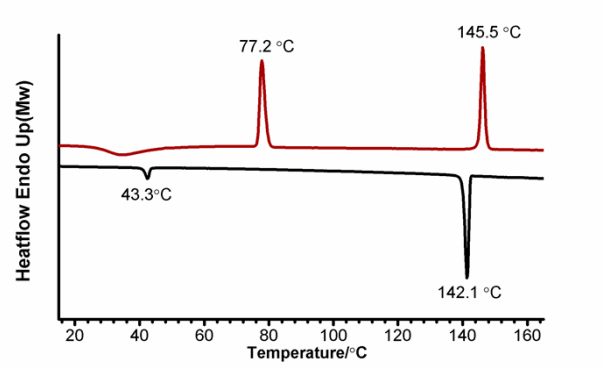
and anhydrous potassium carbonate (0.5g) in ethanol (20ml) was heated under reflux for 24h. The mixture was cooled to 0 °C, filtered, washed with water (50ml), and extracted with dichloromethane (2×50ml), the solvent removed in vacuo, and the residue purified by column chromatography on silica eluting with dichloromethane and finally recrystallized from ethanol and n-hexane several times to give pure **M5**. (0.53g, 95%); IR (KBr): ν_{max}/cm^{-1} 1265 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.85 (6H, m, ArH), 4.23-4.27 (12H, t, OCH_2), 1.91-1.96 (12H, m, OCH_2CH_2), 1.56-1.65 (12H, m, $OCH_2CH_2CH_2$), 1.42-1.50 (2H, m, $OCH_2CH_2CH_2CH_2$), 0.96-1.11 (18H, m, CH_3); HRMS (ESI): calc. m/z 675.4619 ($C_{43}H_{63}O_6$), 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): ν_{max}/cm^{-1} 1263 (C-O-C); δ_H (300MHZ, $CDCl_3$) 7.85 (6H, m, ArH), 4.23-4.27 (12H, t, OCH_2), 1.89-1.98 (12H, m, OCH_2CH_2), 1.60-1.68 (12H, m, $OCH_2CH_2CH_2$), 1.40-1.41 (4H, m, $OCH_2CH_2CH_2CH_2CH_2$), 0.94-1.08 (18H, m, CH_3); HRMS (ESI): calc. m/z 689.4776 ($C_{44}H_{65}O_6$), found m/z 689.4759 $(M)^+$.

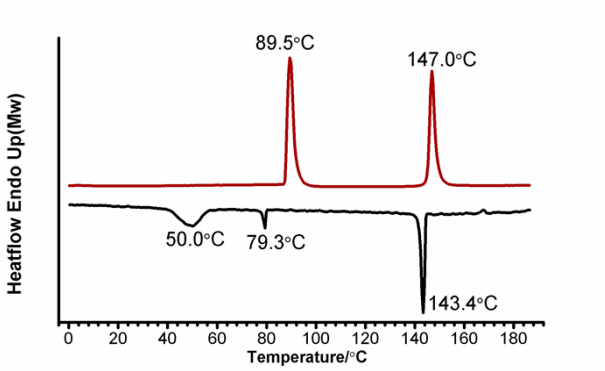
2. Mesomorphism

Mesomorphism of M3



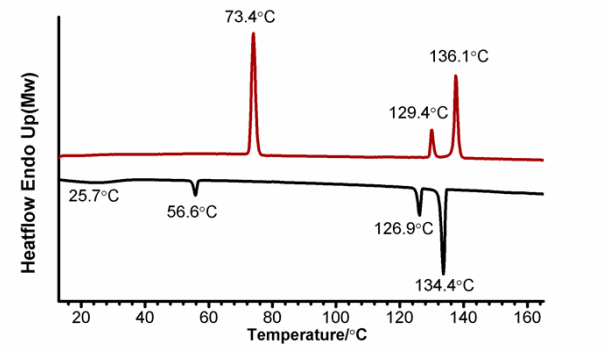
ESI Fig. 1 DSC traces of compound **M3** on 2nd heating run (red line) and 1st cooling run (black line) at 10 ºC/min under N^2.

Mesomorphism of M4

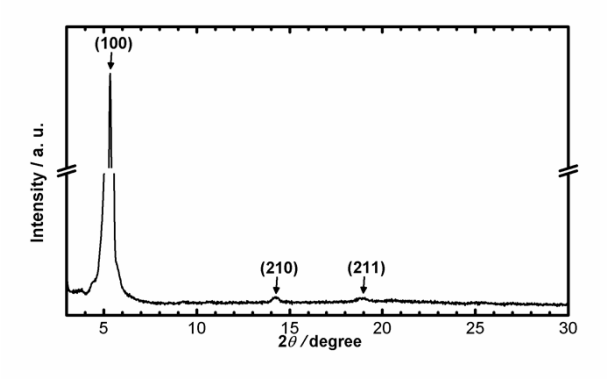


ESI Fig. 2 DSC traces of compound **M4** on 2nd heating run (red line) and 1st cooling run (black line) at 10 ºC/min under N^2.

Mesomorphism of M5

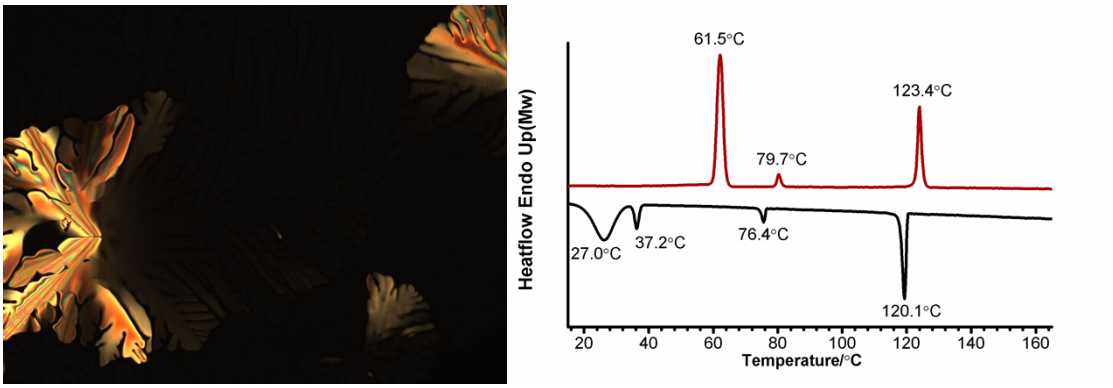


ESI Fig. 3 DSC traces of compound **M5** on 2nd heating run (red line) and 1st cooling run (black line) at 10 ºC/min under N^2.



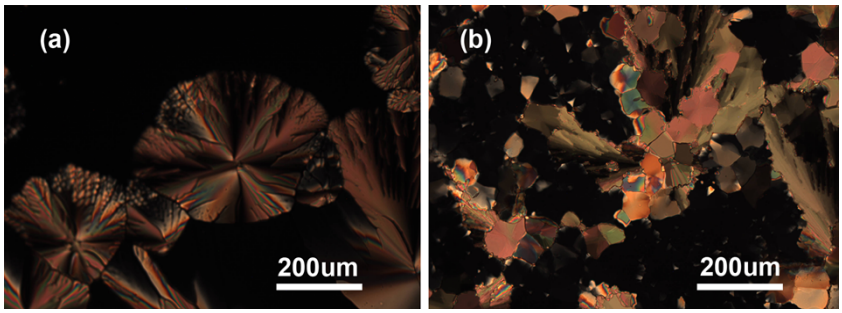
ESI Fig. 4 XRD pattern for Col_{hp} phase of **M5** on heating run at 100°C

Mesomorphism of M6

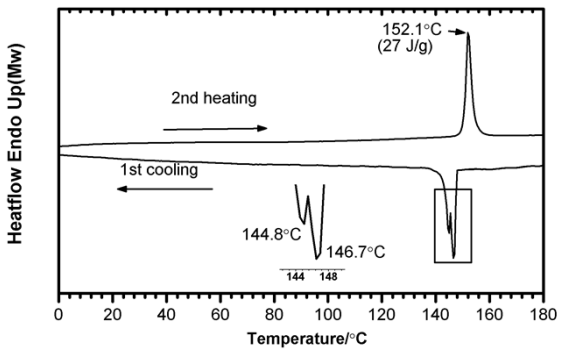


ESI Fig. 5 Dendritic texture of compound **M6** sandwiched between clean glass slides on cooling from isotropic phase at 120 ºC (left), this texture which indicated a Col_h phase was observed by POM with 45° angle and did not show any changes when cooled to crystal phase; DSC traces of compound **M6** on 2nd heating run (red line) and 1st cooling run (black line) at 10 ºC/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° angle at 146 ºC; (b) mosaic texture which indicated a Col_{hp} phase observed by POM with 90° angle at 140 ºC. 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 ºC/min under N^2.