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Electronic Supplementary Information

Highly Ordered Columnar Superlattice Nanostructures with Improved Charge Carrier Mobility by Thermotropic Self-assembly of Tripheylene-based Discotics

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S1. Materials

All chemicals were purchased from Aladdin, and all solvents from Aldrich. All chemicals and solvents were used without further purification. Silica gel 60 (200-300 mesh ASTM) and silica gel 60 glass thin-layer chromatography was used for the purification and identification of the reaction, respectively.

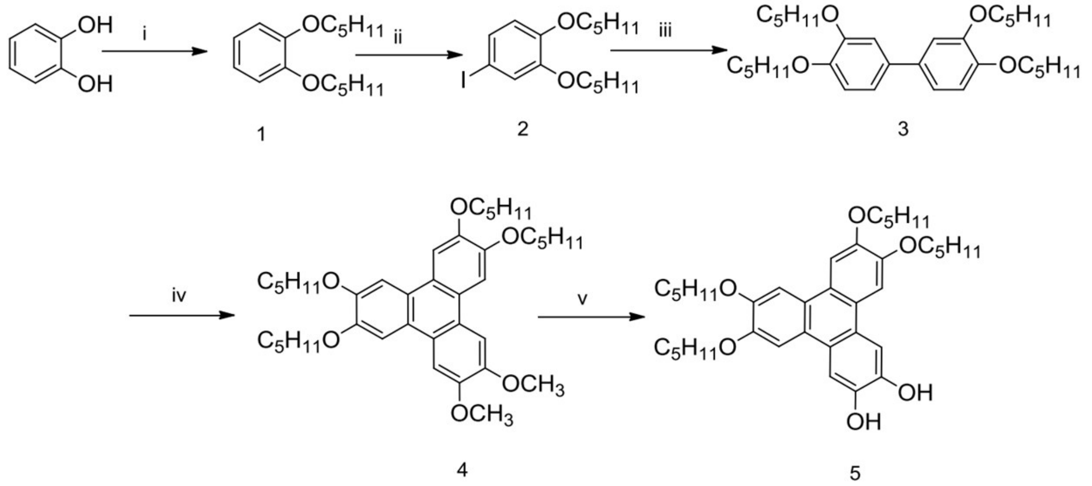
S2. Instrumentations

S2.1. Chemical structure characterizations : The ^{1}H-NMR spectra were recorded by a Bruker NMR spectrometer (DMX 300 MHz) in $CDCl_3$, Chemical shifts are given as units of measurement and expressed in parts per million (δ) with tetra-methylsilane (TMS) as a reference. Multiplicities of peaks are expressed as s = singlet, d = doublet, t = triplet, m = multiplet; The KBr pellets were used to make the test samples and the infrared spectrum (FT-IR) was recorded on a Shimadzu FTIR-8400 spectrometer by Fourier transform; The high resolution mass spectrum was recorded on a Bruker Apex IV FTMS mass spectrometer. Elemental analysis (C, H) was performed on an Elementar Vario EL CUBE elements analyzer.

S2.2. Mesophase characterizations of samples: The thermal properties of discotic liquid crystals were characterized by using differential scanning calorimeter (DSC) on a Netzsch DSC 200. Its optical properties were characterized by a Polarizing Microscope (POM) on a Leica DM4500P with a Linkam TMS94 hot stage.

S2.3. Self-assembly properties of samples: The structural characterizations of samples were characterized by 1D wide angle X-ray diffraction (1DWAXD) through a Bruker D8 Advance diffractometer equipped with a variable temperature controller; two-dimensional wide-angle X-ray diffraction (2DWAXD) using a 40KV FL tube as the X-ray source (Cu Ka) and the small-angle X-ray scattering (SAXS) (SAXSess, Anton Paar) equipped with Kratky block-collimation system; at last, the structure and morphology were investigated by Transmission Electron Microscope (FEI Tecnai G2 20 STWIN).

S3. Syntheses



Preparation of 1,2-dipentoxybenzene (1).1-bromopentane (362g, 2.4mol) was added dropwise under argon to a mixture of catechol (88g, 0.8mol) and potassium carbonate (662g) in 200ml ethanol and 200ml acetone component solvent and the mixture was stirred under reflux for 24 hours. Then the mixture was filtered and the solvent removed in vacuo. Distillation of the residue at 210-215°C at (1.6 mmHg) afforded as a colorless oil (180g, 90%). TLC Rf: 0.65 (dichloromethane-hexane 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 6.99-6.81(m, 4H, Ar-H), 4.11-3.99 (m, 4H, OCH_2), 1.89-1.80 (m, 4H, OCH_2CH_2), 1.71-1.35 (m, 8H, CH_2), 1.28-0.72 (m, 12H, CH_3). FT-IR (cm^{-1}): 3062, 2963, 2864, 1588, 1497, 1467, 1381, 1260, 1222, 1122.

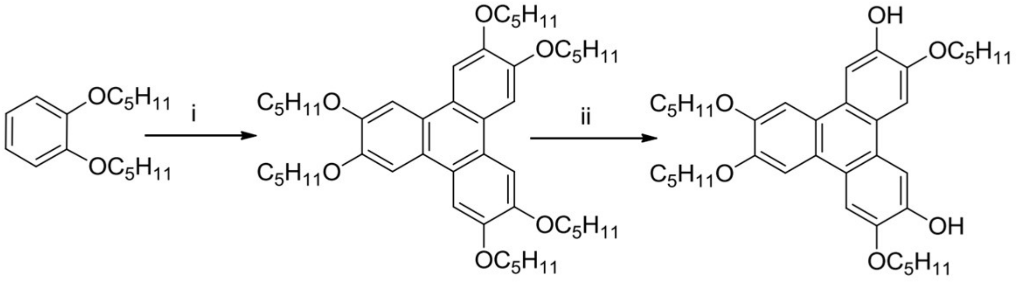
Preparation of 1-iodo-3,4-dipentoxybenzene (2). 1,2-dipentoxybenzene (30g, 0.12mol), 60ml acetic acid, 20ml water, 20ml chloroform, 1ml sulfuric acid, iodine (10.2g), and iodic acid (4.2g, 0.02mol) were mixed and vigorously stirred at 40°C. After 24 hours 600 ml water was added and the organic phase was separated. The aqueous layer was extracted with dichloromethane several times. The combined organic phase was washed with $NaHSO_3$, $Na_2S_2O_3$ and water, dried over magnesium sulfate in sequence and the solvent was removed in vacuo. Final purification was achieved by column chromatography to obtain a colorless liquid (24.2g, 44.5%). TLC Rf: 0.71 (dichloromethane-hexane 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.21-7.13 (m, 2H, Ar-H), 6.62 (d, J=8.4Hz, 1H, Ar-H), 3.95 (t, J=4.4Hz, 4H, OCH_2), 1.84-1.58 (m, 4H, OCH_2CH_2), 1.50-1.33 (m, 8H, CH_2), 0.96-0.91 (m, 6H, CH_3). FT-IR (cm^{-1}): 3078, 2956, 2872, 1582, 1505, 1461, 1387, 1246, 1222, 1135.

Preparation of 3,3’,4,4’-tetrapentyloxybiphenyl (3). 1-iodo-3,4-dipentoxybenzene (20g, 0.054mol) was mixed with fine powdered copper (20g) and heated to 250°C under argon and vigorous stirring. After four hours the temperature was lowered to 180°C and the hot solution was carefully poured into 400ml of dichloromethane. The resulting mixture was filtered over celithe and the solvent was removed in vacuo to a brown solid. Final purification was achieved by column chromatography (silica gel, hexane: dichloromethane 2:1) to obtain a white crystalline solid (9.16g, 68%). TLC Rf: 0.30 (dichloromethane-hexane 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.08-6.91 (m, 6H, Ar-H), 4.09-4.01 (m, 8H, OCH_2), 1.84 (q, J=6.6Hz, 8H, OCH_2CH_2), 1.53-

1.37 (m, 16H, CH_2), 1.02-0.92 (m, 12H, CH_3). FT-IR (cm^{-1}): 3086, 2956, 2857, 1597, 1505, 1467, 1394, 1254, 1222, 1119.

Preparation of 2,3-dimethoxy-6,7,10,11–tetrakis(pentyloxy)triphenylene (4). Iron (III) chloride (3.14g, 19.3mmol) was added to a solution of **1** (1g, 2mmol) and veratrole (0.83g, 6mmol) in 10ml of dichloromethane and three drops of concentrated sulphuric acid. The mixture was heated for 1.5h at 50°C. Work-up was performed by addition of 2ml methanol before the mixture was subjected to a short flash chromatography on silica gel (dichloromethane: Hexane=4:1). Recrystallization from ethanol afforded the white solid (1.16g, 91.5%). TLC Rf: 0.65 (acetone-hexane 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.94-7.81 (m, 6H, Ar-H), 4.33-4.13 (m, 14H, OCH_3/OCH_2), 2.01-1.92 (m, 8H, OCH_2CH_2), 1.65-1.40 (m, 16H, CH_2), 1.09-0.96 (m, 12H, CH_3). FT-IR (cm^{-1}): 3117, 2972, 2865, 1620, 1521, 1467, 1437, 1387, 1262, 1169, 1056.

Preparation of 2,3-dihydroxy-6,7,10,11–tetrakis(pentyloxy)triphenylene (5) the whole reaction process was in anhydrous and low temperature atomosphere. Diphenylphosphine (4.28g, 23.0mmol) was dissolved in dry THF (60ml) and cooled in an ice bath under argon. Butyllithium (2.4M in hexanes, 32ml, 76.8mmol) was added over 10min. **4** (1.6g, 2.35mmol) was added and the solution was magnetically stirred at 50-60°C for 4h and overnight at room temperature. The mixture was poured onto dilute sulfuric acid and extracted with ethyl acetate (3×70ml). The solvent was removed in vacuo and the residue precipitated from dichloromethane with methanol. The precipitate was filtered off, dried, and purified by column chromatography (silica, ethyl acetate: dichloromethane=1:60) to give the target compound **5** (0.45g, 26.7%), mp=124°C. TLC Rf: 0.12 (dichloromethane-hexane 4:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.91 (s, 2H, Ar-H), 7.80 (d, J=6.4Hz, 4H, Ar-H), 5.5 (s, 2H, OH), 4.25-4.16 (m, 8H, OCH_2), 1.97-1.87 (m, 8H, OCH_2CH_2), 1.58-1.37 (m, 16H, CH_2), 0.99-0.94 (m, 12H, CH_3). FT-IR (cm^{-1}): 3535, 3429, 3080, 2965, 2865, 1607, 1516, 1447, 1381, 1258, 1168, 1029.



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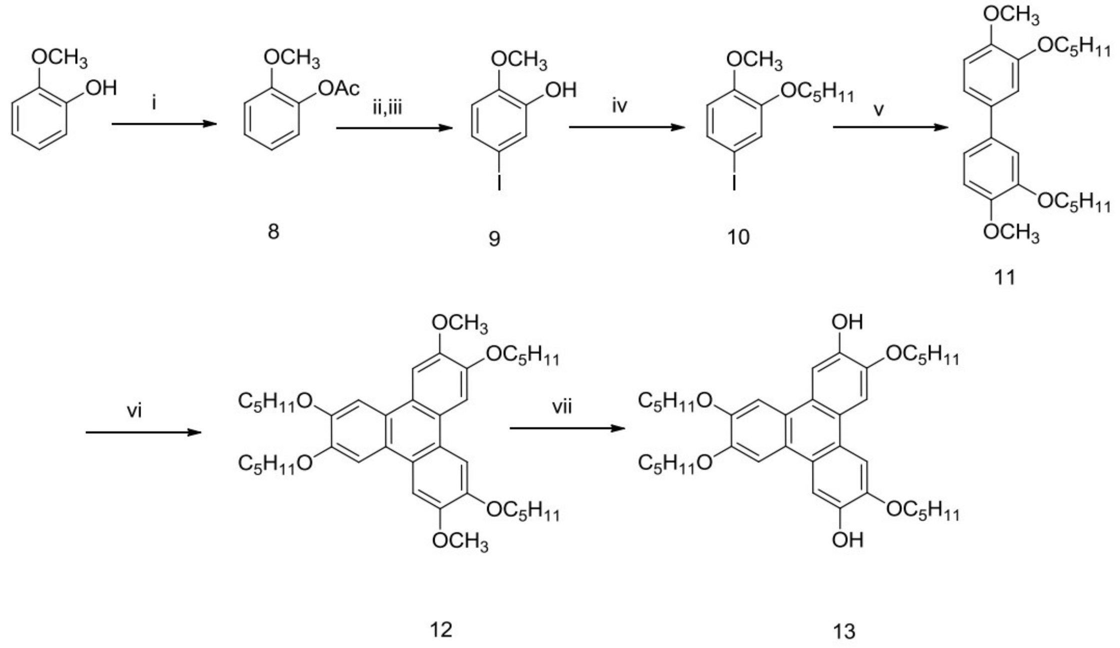
Preparation of 2,3,6,7,10,11–hexakis(pentyloxy)triphenylene (6). The colorless grease 1,2-dipentyloxybenzene (17g, 67.9mmol) was added to a vigorously stirred suspension of iron III chloride (33.0g, 203.7mmol) in dichloromethane (100ml) with concentrated sulphuric acid (0.5ml). The reaction occurred with vigorous evolution of gas and was quenched with methanol (500ml) after 2-3h. The reaction mixture was filtered and the filtrate concentrated in vacuo to black solid which was subjected to column chromatography, eluting with 2:1 dichloromethane: hexanes to give the product as a pale yellow solid which was recrystallized from ethanol to obtain white solid (12.4g, 73%). TLC Rf: 0.62 (dichloromethane-hexane 4:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.85 (s, 6H, Ar-H), 4.25 (t, J=6.0Hz, 12H, OCH_2), 1.99-1.92 (m, 12H, OCH_2CH_2), 1.67-1.42 (m, 24H, CH_2), 0.99 (t, J=5.4Hz, 18H, CH_3). FT-IR (cm^{-1}): 3062, 2931, 2870, 1593, 1504, 1454, 1386, 1329, 1254, 1223, 1124.

Preparation of 2,6-dihydroxy-3,7,10,11–hexakis(pentyloxy)triphenylene (7). A solution of 2,3,6,7,10,11-hexakis(pentyloxy)triphenylene (15g, 20.13mmol) was dissolved in anhydrous CH_2Cl_2 (150ml) and cooled to 0°C. To this was added the desired amount (0.5M, 100.6ml) of B-bromocatecholborane solution in CH_2Cl_2 dichloromethane under argon and the mixture was stirred at 40°C for 24 hours. After that it was poured over ice-water and extracted with CH_2Cl_2, the combined extract was dried (anhydrous Na_2SO_4), solvent was removed under vacuum and the crude product was purified by column chromatography to obtain the final product (silica gel, hexane/CH_2Cl_2) (3.6g, 29.5%).TLC Rf: 0.36 (ethyl acetate-hexane 1:8). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.94 (d, J=3.6Hz, 2H, Ar-H), 7.83-7.60 (m, 4H, Ar-H), 5.92 (s, 2H, OH), 4.30-4.19 (m, 8H, OCH_2), 2.24-1.93 (m, 8H, OCH_2CH_2), 1.59-1.40 (m, 16H, CH_2), 1.01-0.87 (m, 12H, CH_3). FT-IR (cm^{-1}): 3534, 3463, 3093, 2958, 2927, 2871, 1614, 1509, 1446, 1380, 1265, 1167, 1027.



Preparation of 2-(methoxy)phenyl Acetate (8). Acetyl chloride (71.43g, 0.91mol) was added to guaiacol (86.9g, 0.7mol) with stirring over 1h and the mixture stirred for an another 24h. Dichloromethane (400ml) was added and the solution washed with dilute potassium carbonate until the aqueous layer was basic. The organic solution was dried (Mg_2SO_4) and the solvent removed in vacuo. Distillation of the residue at 90-96°C at 0.8mmHg afforded 2-(methoxy)-phenyl Acetate as a colorless oil (98.9g, 85%). TLC Rf: 0.33 (dichloromethane-hexane 2:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.24-7.18 (m, 1H, Ar-H), 7.06-6.86 (m, 3H, Ar-H), 3.84 (s, 3H, OCH_3), 2.32 (d, J=3.9Hz, 3H, $OOCCH_3$). FT-IR (cm^{-1}): 3086, 2941, 2834, 1765, 1605, 1498, 1454, 1368, 1275, 1262, 1208, 1169, 1109, 1042.

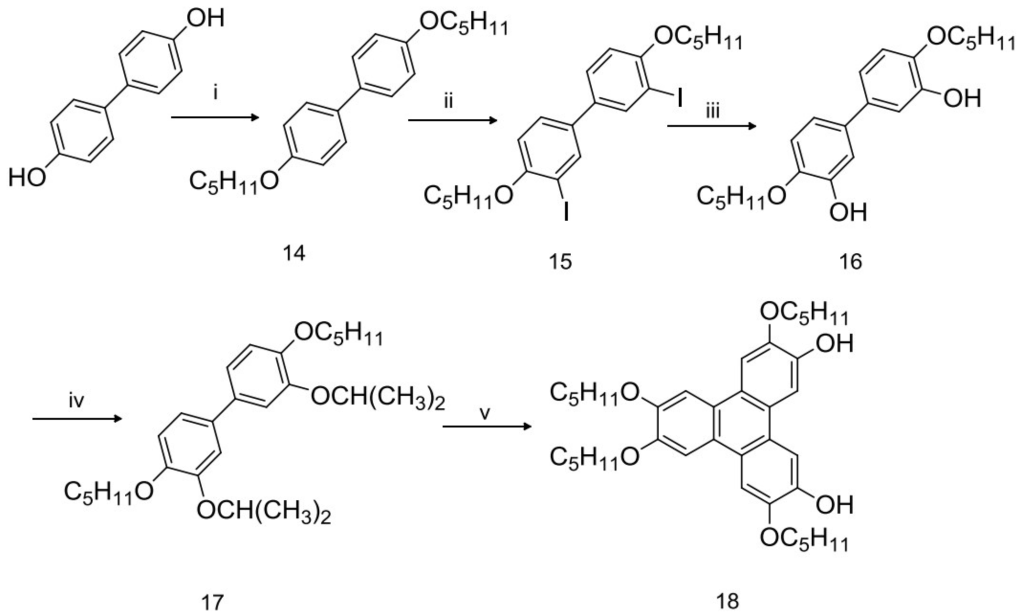
Preparation of 2-(methoxy)-5-iodophenol (9). 2-(methoxy)phenyl Acetate (23g, 0.14mmol) was dissolved in chloroform (200ml) and cooled to 8-13°C. Iodine monochloride (27.7g, 0.17mmol) in chloroform (70ml) was added dropwise, maintaining the reaction temperature between 8 and 13°C. The mixture was stirred at room temperature overnight and washed with sodium metabisulfite until the iodine color disappear and then with water. The organic solution was separated and the solvent removed in vacuo. The residual red/brown oil was dissolved in ethanol (20ml) and a solution of sodium hydroxide (35g, 0.86mol) in ethanol (50ml) and water (40ml) was added. The solution was refluxed for 1h, allowed to cool, and carefully acidified with 40% sulfuric acid. The mixture was extracted with dichloromethane (2×150ml) and the organic solutions were dried (Mg_2SO_4). Removal of solvent in vacuo followed by distillation of the residue at 130-135°C at (1.2mmHg) gave a yellow oil which crystallized overnight and recrystallization from light petroleum afforded 2-(methoxy)-5-iodophenol(20.5g, 58.3%). TLC Rf: 0.39 (dichloromethane-hexane 2:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.36-7.15 (m, 2H,vAr-H), 6.60 (d, J=8.4Hz, 1H, Ar-H), 5.59 (s, 1H, OH), 3.87 (s, 3H, OCH_3). FT-IR (cm^{-1}): 3478, 3399, 3020, 2921, 2834, 1582, 1490, 1440, 1328, 1294, 1238, 1222, 1129, 1023.

Preparation of 4-Iodo-2-(pentyloxy)anisole (10). 2-(methoxy)-5-iodophenol (50g, 0.2mol) pentylbromide (38g, 0.23mol), and potassium carbonate (42g) were stirred in refluxing ethanol (150ml) for 12h. The solid was filtered off, concentrated, dried and purified by column chromatography (silica gel, Hexanes: dichloromethane=2:1) to give 4-Iodo-2-(pentyloxy)-anisole (24g,91.5%). TLC Rf: 0.80 (dichloromethane-hexane 2:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.27-7.12 (m, 2H, Ar-H), 6.61 (d, J=8.4Hz, 1H, Ar-H), 3.97 (t, J=6.9Hz, 2H, OCH_2), 3.84 (s, 3H, OCH_3), 1.89-1.80 (m, 2H, OCH_2CH_2), 1.48-1.32 (m, 4H, CH_2), 0.93 (t, J=6.9Hz, 3H, CH_3). FT-IR (cm^{-1}): 3033, 2956, 2921, 2865, 1627, 1597, 1505, 1474, 1394, 1322, 1238, 1215, 1135, 1016.

Preparation of 3,3'-Bis(pentyloxy)-4,4'-dimethoxyphenyl (11). 10 (24g, 0.075mol) and copper powder (24g) were thoroughly mixed together and heated to 270°C for 10min. The mixture was cooled and extracted repeatedly with chloroform. The solvent was removed in vacuo and the residue crystallized from ethanol to afford 3,3'-Bis(pentyloxy)-4,4'-dimethoxyphenyl (8.1g, 56.2%). TLC Rf: 0.38 (dichloromethane-hexane 2:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.10-6.92 (m, 6H, Ar-H), 4.08 (t, J=6.9Hz, 4H, OCH_2), 3.91 (s, 6H, OCH_3), 1.94-1.84 (m, 4H, OCH_2CH_2), 1.54-1.26 (m, 8H, CH_2), 0.93 (q, J=9.3Hz, 6H, CH_3). FT-IR (cm^{-1}): 3086, 2934, 2861, 1613, 1567, 1507, 1467, 1434, 1394, 1288, 1262, 1215, 1175, 1135, 1063.

Preparation of 2,7-Dimethoxy-3,6,10,11-tetrakis(pentyloxy)triphenylene (12). A mixture of iron (III) chloride (32g, 0.206mol), concentrated sulfuric acid (0.5ml), **11** (7.7g,0.020mol),and 1,2-bis(pentyloxy) benzene (15.5g, 0.062mol) was stirred in dichloromethane (150ml) for 1.5h. The reaction mixture was carefully poured onto methanol (500ml), and after cooling in ice the resulting solid was filtered off and washed with methanol. Separation on silica (benzene eluant) afforded 2,7-Dimethoxy-3,6,10,11-tetrakis(pentyloxy) triphenylene (8.2g, 65%). TLC Rf: 0.41 (ethyl acetate-hexane 1:8). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.86 (s, 2H, Ar-H), 7.83 (d, J=2.1Hz, 4H, Ar-H), 4.26 (q, J=6.6Hz, 8H, OCH_2), 4.11 (s, 6H, OCH_3), 2.04-1.91 (m, 8H, OCH_2CH_2), 1.60-1.40 (m, 16H, CH_2), 1.00-0.86 (m, 12H, CH_3). FT-IR (cm^{-1}): 3125, 2949, 2927, 2865, 1631, 1521, 1474, 1427, 1381, 1262, 1162, 1049.

Preparation of 2,7-Dihydroxy-3,6,10,11-tetrakis(pentyloxy)triphenylene (13). By use of a similar procedure to that used in the preparation of intermediate **5**. 2,7-Dihydroxy-3,6,10,11-tetrakis(pentyloxy)triphenylene was obtained in 65% yield, mp=186°C. TLC Rf: 0.23 (ethyl acetate-hexane 1:8). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.96 (s, 2H, Ar-H), 7.82 (s, 2H, Ar-H), 7.73 (s, 2H, Ar-H), 5.90 (s, 2H, OH), 4.31-4.19 (m, 8H, OCH_2), 1.96 (t, J=6.0Hz, 8H, OCH_2CH_2), 1.56-1.47 (m, 16H, CH_2), 1.02-0.96 (m, 12H, CH_3). FT-IR (cm^{-1}): 3531, 3392, 3071, 2956, 2865, 1620, 1514, 1474, 1445, 1400, 1334, 1262, 1181, 1029.



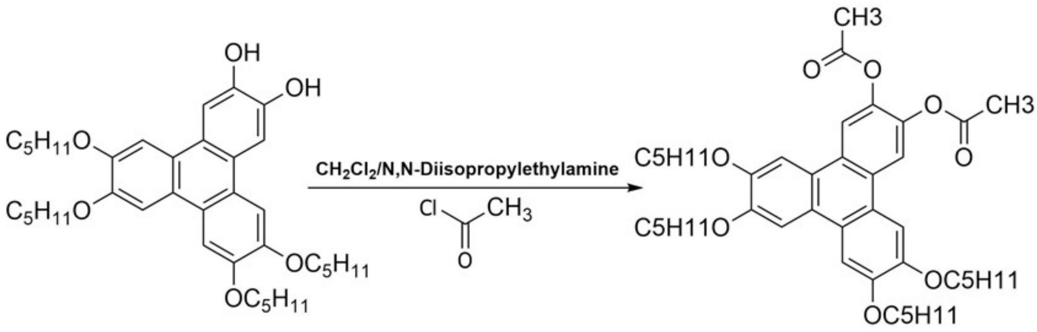
Preparation of 4,4’-dipentyloxyphenyl (14). A mixture of 4,4’-dihydroxybiphenylene (32.6 g ,0.175 mol), K_2CO_3 (80 g, 0.56 mol), hexadecyl trimethyl ammonium bromide (catalytic amount) and KI catalytic amount in ethanol/acetone (150/50 ml) was refluxed under argon for 1 h, then 1-bromopentane (72.5 g, 0.48 mol) was added, and the mixture was refluxed for another 24 h. Once the reaction was complete, the reaction mixture was poured into 1:1 ice-water to precipitate the product. The white precipitate was filtered and washed several times by water resulting in the crude product. After recrystallisation from ethanol, white scaly solid was obtained (54.8 g, 97%). TLC Rf: 0.61 (dichloromethane-hexane 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.57-7.38 (m, 4H, Ar-H), 6.95 (d, J=6.3Hz, 4H, Ar-H), 4.08-3.97 (m, 4H, OCH_2), 1.86-1.77 (m, 4H, OCH_2CH_2), 1.49-1.28 (m, 8H, CH_2), 0.97-0.85 (m, 6H, CH_3). FT-IR (cm^{-1}): 3056, 2960, 2941, 2865, 1613, 1498, 1474, 1394, 1262, 1181, 1035.

Preparation of 3,3’-diiodo-4,4’-dipentyloxyphenyl (15). A mixture of glacial acetic acid 100 g , iodine (21 g, 84 mmol), iodic acid (8.87 g, 50.4 mmol), deionized water 30 ml, chloroform 70 ml and 4,4’-dipentyloxybiphenyl (32.6 g, 100 mmol) was stirred for a while, and then concentrated sulphuric acid (3.8 g) was added and the mixture was heated with stirring at 85°C for 20 h. After the reaction was complete, 140 ml of chloroform and 60 ml deionized water were added and the mixture was stirred for 10 min. the organic layer was separated and washed by saturated Na_2SO_3 solution three times and deionized water once. The organic layer was dried over anhydrous sodium sulphate and passed through a short silica column (chloroform) to get the crude product, 3,3'-diiodo-4,4'-dipentyloxybiphenyl. The crude product was recrystallised by ethanol to obtain the white solid (54.7g, 94.6%). TLC Rf: 0.71 (dichloromethane-hexane 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.93 (s, 2H, Ar-H), 7.42 (dd, J=1.5Hz, J=8.4Hz, 2H, Ar-H), 6.82 (d, J=8.4Hz, 2H, Ar-H), 4.04 (t, J=6.6Hz, 4H, OCH_2), 1.91-1.82 (m, 4H, OCH_2CH_2), 1.57-1.36 (m, 8H, CH_2), 0.99-0.89 (m, 6H, CH_3). FT-IR (cm^{-1}): 3086, 2956, 2927, 2872, 1597, 1460, 1387, 1281, 1248, 1056.

Preparation of 3,3'-dihydroxy-4,4'-dipentyloxyphenyl (16). A mixture of PEG-400 240 ml, deionized water 60 ml, KOH (33.6 g ,600 mmol) and **15** (28.9 g ,50 mmol) was stirred under nitrogen protection for 30 min and then CuI (3.9 g ,10 mmol) was added carefully. The mixture was heated to 140°C under nitrogen protection for 36 h. After the reaction was complete, the reaction mixture was cooled to room temperature. hydrochloric acid (1 M) was added to acidify the solution (pH = 2) and the solution was extracted with ethyl acetate (3×200ml). The organic layer was concentrated and recrystallised by ethanol (very small amount) to give white needle crystal (9g, 50%). TLC Rf: 0.28 (dichloromethane-hexane 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.15 (s, 2H, Ar-H), 7.02 (dd, J=2.1Hz, J=6.3Hz, 2H, Ar-H), 6.88 (d, J=8.4Hz, 2H, Ar-H), 5.68 (s, 2H, OH), 4.07 (t, 4H, OCH_2), 1.89-1.80 (m, 4H, OCH_2CH_2), 1.51-1.32 (m, 8H, CH_2), 0.98-0.89 (m, 6H, CH_3). FT-IR (cm^{-1}): 3414, 3078, 2956, 2865, 1633, 1574, 1505, 1461, 1381, 1262, 1135, 1063.

Preparation of 3,3'-diisopropyl-4,4'-dipentyloxyphenyl (17). A mixture of **16** (8 g ,22 mmol), K_2CO_3 (18 g ,132 mmol), hexadecyl trimethyl ammonium bromide (catalytic amount) and KI catalytic amount ,ethanol/acetone (100/50 ml) was refluxed under argon for 1 h, then 2-bromopropane (5.3 g, 88 mmol) was added and the mixture was refluxed for another 24 h. Once the reaction was complete, the reaction mixture was filtered and the filtrate was concentrated to give the crude product. After recrystallisation from ethanol (small amount), white scaly solid was obtained(8.8g, 90%). TLC Rf: 0.52 (dichloromethane-hexane 1:1). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.12-7.08 (m, 4H, Ar-H), 6.94-6.85 (m, 2H, Ar-H), 4.56-4.46 (m, 2H, OCH), 4.01 (d, J=6.6Hz, 4H, OCH_2), 1.88-1.79 (m, 4H, OCH_2 CH_2), 1.56-1.50 (m, 20H, $OCH(CH_3)2/CH_3$), 0.94 (t, J=6.9Hz, 6H, CH_3). FT-IR (cm^{-1}): 3040, 2967, 2925, 2872, 1605, 1498, 1467, 1387, 1254, 1142, 1109, 1049.

Preparation of 3,6-dihydroxy-2,7,10,11-tetrakis(pentyloxy)triphenylene (18). A mixture of **17** (6.65 g, 15 mmol), 1,2-dipentyloxybenzene (5.65 g, 22.5 mmol) and anhydrous dichloromethane (80 ml) was stirred under nitrogen protection for 30 min and then anhydrous ferric chloride (9.25 g ,57 mmol) was added slowly. The mixture was stirred vigorously for another 12 h at room temperature. After the reaction was complete, the reaction mixture was poured into 150 ml cool methanol carefully. The mixture was concentrated and filtered. The filter cake was purified by columnar chromatography (silica, CH_2Cl_2: EtOAc = 80:1) to give the final white product (5.4g, 60%) mp 142°C. TLC Rf: 0.27 (ethyl acetate-hexane 1:4). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.94 (s, 2H, Ar-H), 7.81 (s, 2H, Ar-H), 7.75 (s, 2H, Ar-H), 5.88 (s, 2H, OH), 4.30-4.21 (m, 8H, OCH_2), 2.00-1.91 (m, 8H, OCH_2CH_2), 1.62-1.40 (m, 16H, CH_2), 0.99 (dd, J=6.0Hz, J=7.2Hz, 12H, CH_3). FT-IR (cm^{-1}): 3535, 3422, 3102, 2955, 2922, 2865, 1622, 1510, 1435, 1387, 1308, 1259, 1157, 1035.



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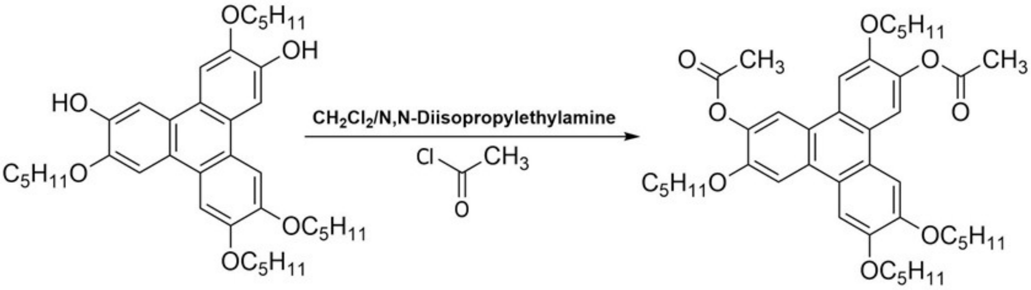

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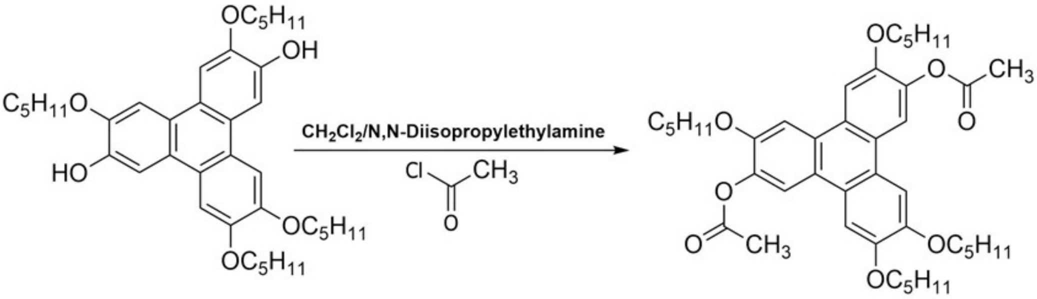

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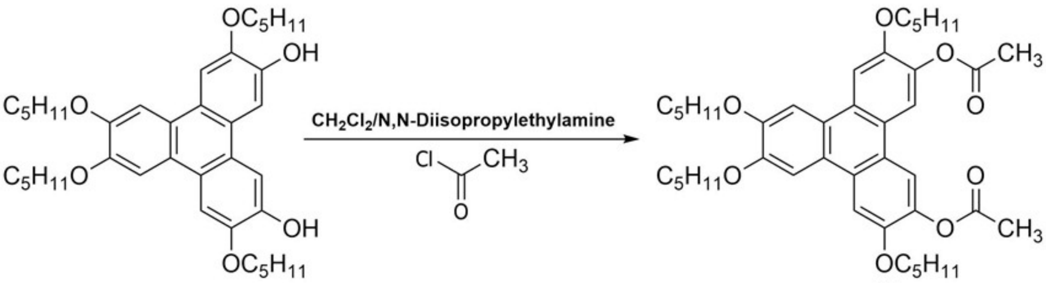

22

Preparation of 2,3-diethoxycarbonyl-6,7,10,11-tetrakis(pentyloxy)triphenylene(19). A magnetically stirred solution of 2,3-diethoxycarbonyl-6,7,10,11-tetrapentaloxytriphenylene 0.5g (0.83mmol) and N,N-diisopropylethylamine 0.58ml (3.32mmol) in dichloromethane (30ml, after CaH_2 dried) was cooled to 0°C by ice-water bath under nitrogen protection. Then, acetyl chloride (3.32mmol) was injected slowly. The result solution was stirred for another 3 hours at room temperature and then washed with K_2CO_3 solution. The organic phase was dried over anhydrous Na_2SO_4, and then filtered. The filtrate was evaporated to dryness under a reduced pressure. The residue crude product was purified by column chromatography on silica eluting with ethyl acetate/petroleum ether (1:18) to give a white solid. The solid was recrystallized by absolute alcohol for several times (0.52g, 91.2%).According to the same method, 2,3-diethoxycarbonyl-6,7,10,11-tetrapentaloxytriphenylene, TLC Rf: 0.67(ethyl acetate- petroleum ether 1:4). FT-IR (cm^{-1}): 3103, 2957, 2853, 1747, 1622, 1510, 1435, 1387, 1308, 1259, 1157, 1035. Anal. calcd for C42H56O8 (688.9): C, 73.23; H, 8.19. Found: C, 73.1; H, 8.0.

Preparation of 2,7-diethoxycarbonyl-3,6,10,11tetrapentaloxy-triphenylene(20). The synthesis of 2,7-diethoxycarbonyl-3,6,10,11-tetrapentaloxytriphenylene was similar to **19**, TLC Rf: 0.51 (ethyl acetate- petroleum ether 1:8). FT-IR (cm^{-1}): 3101, 2954, 2863, 1749, 1633, 1574, 1505, 1461, 1381, 1262, 1135, 1063. Anal. calcd for C42H56O8 (688.9): C, 73.23; H, 8.19. Found: C, 73.0; H, 8.0.

Preparation of 2,6-diethoxycarbonyl-3,7,10,11-tetrapentaloxy-triphenylene(21). The synthesis of 2,6-diethoxycarbonyl-3,7,10,11-tetrapentaloxy-triphenyleneh was similar to **19**, TLC Rf: 0.56 (ethyl acetate- petroleum ether 1:8). FT-IR (cm^{-1}): 3108, 2954, 2858, 1739, 1618, 1566, 1512, 1438, 1391, 1239, 1144, 1051. Anal. calcd for C42H56O8 (688.8): C, 73.23; H, 8.19. Found: C, 73.0; H, 8.1.

Preparation of 3,6-diethoxycarbonyl-2,7,10,11-tetrapentaloxy-triphenylene(22). The synthesis of 3,6-diethoxycarbonyl-2,7,10,11-tetrapentaloxy-triphenyleneh was similar to **19**, TLC Rf: 0.53 (ethyl acetate- petroleum ether 1:8). FT-IR (cm^{-1}): 3110, 2958, 2856, 1738, 1645, 1523, 1541, 1421, 1361, 1255, 1152, 1033. Anal. calcd for C42H56O8 (689.0): C, 73.23; H, 8.19. Found: C, 72.9; H, 8.0.

^{1}H-NMR results for these samples are in S4 and HRMS results for these samples are in S5.

S4. Supplementary ^{1}HNMR results

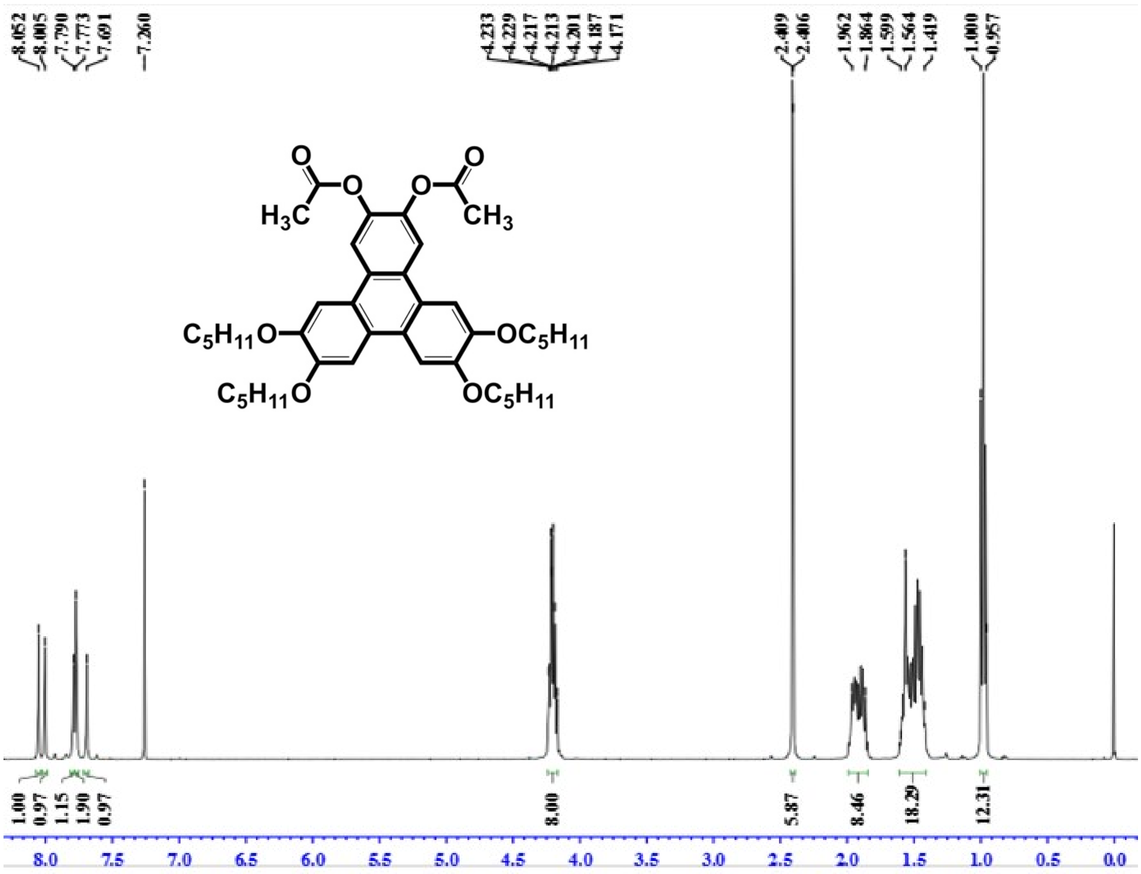

Figure S1. ^{1}H NMR spectrum for T5E23

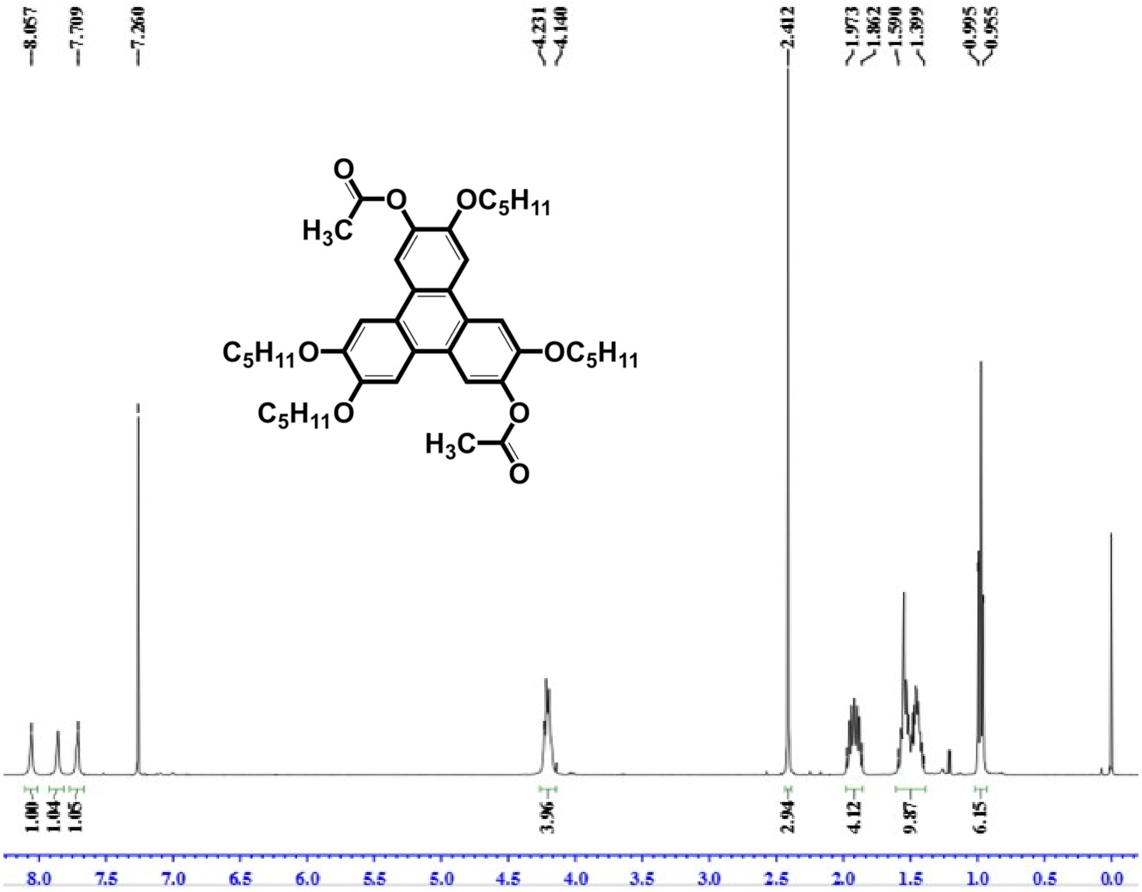

Figure S2. ^{1}H NMR spectrum for T5E27

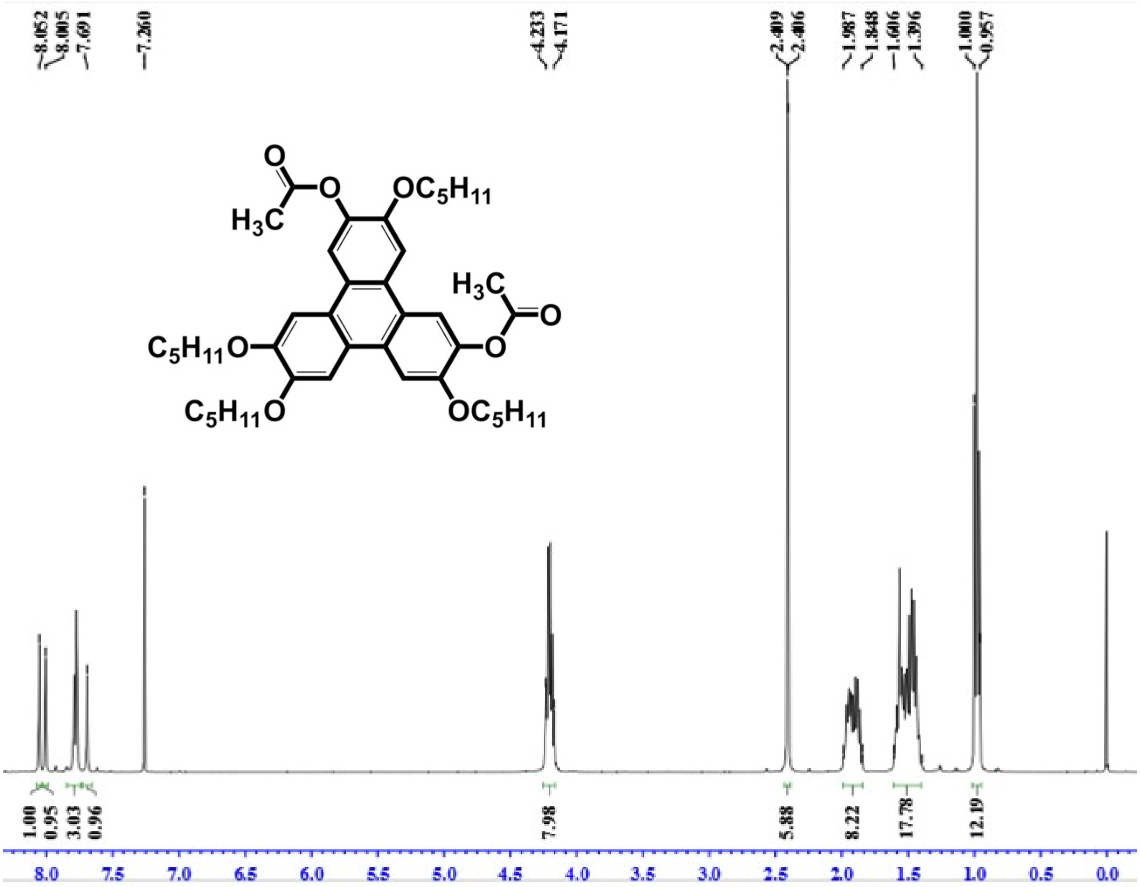

Figure S3. ^{1}H NMR spectrum for T5E26

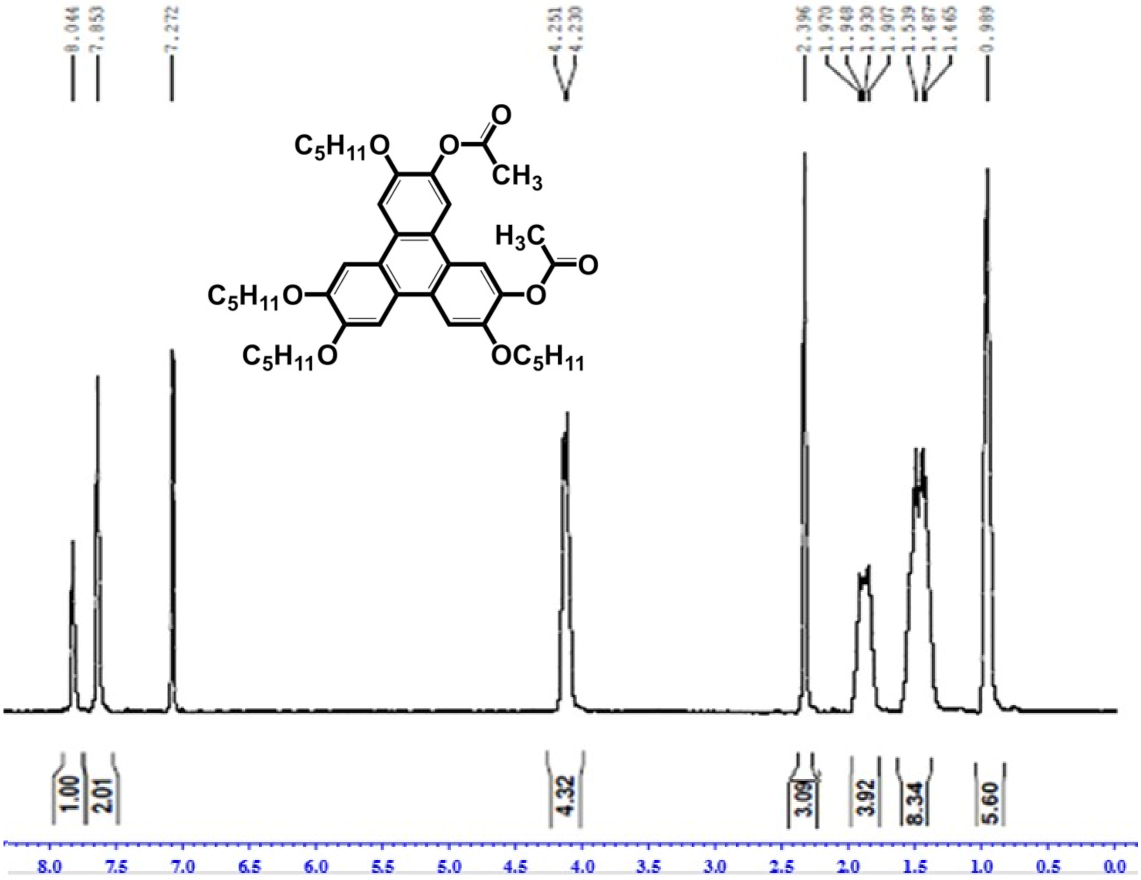

Figure S4. ^1H NMR spectrum for T5E36

S4. Supplementary HRMS results

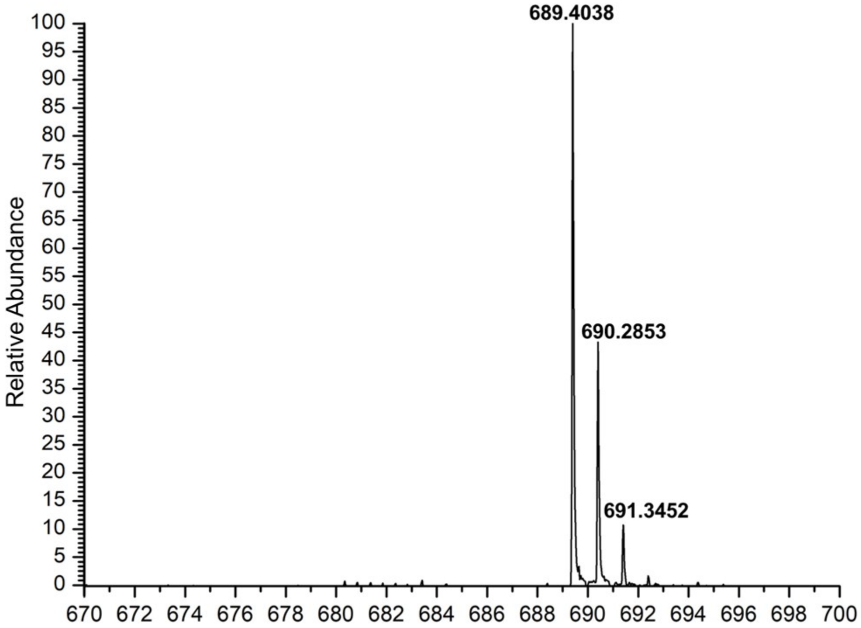

Figure S5. HRMS spectrum for T5E23

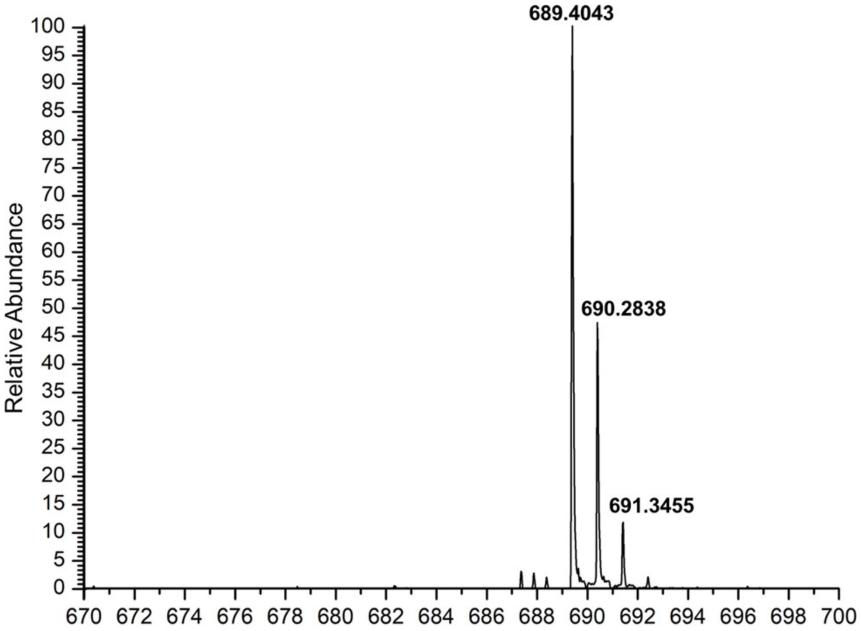

Figure S6. HRMS spectrum for T5E27

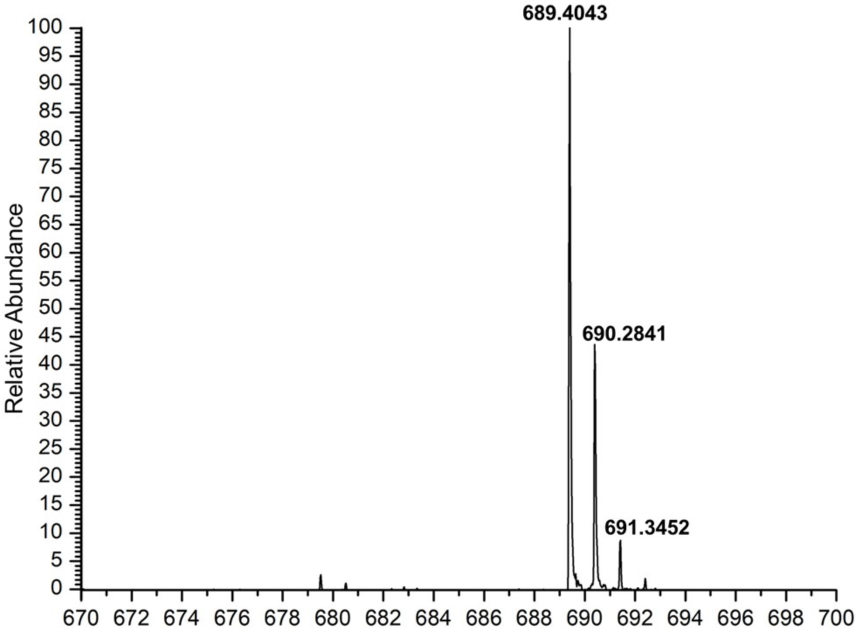

Figure S7. HRMS spectrum for T5E26

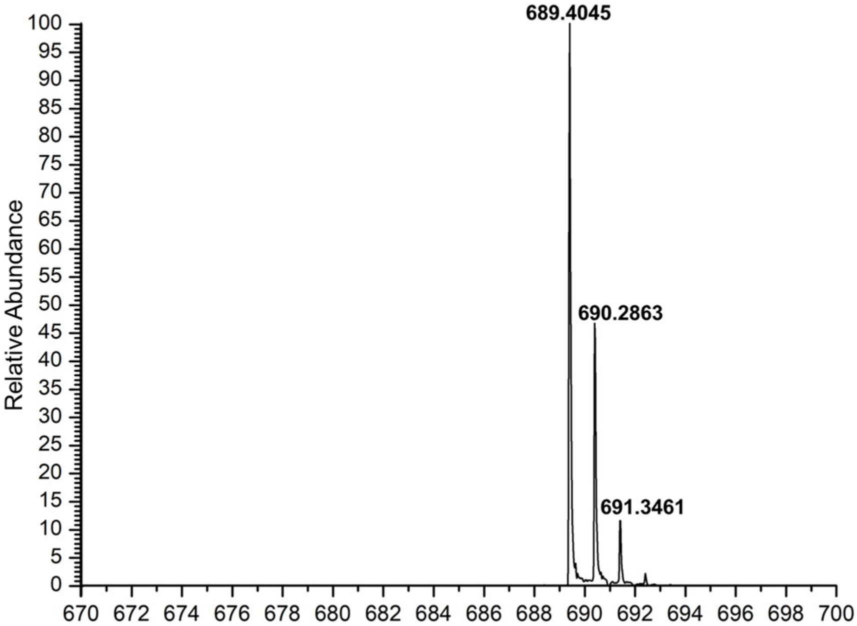

Figure S8. HRMS spectrum for T5E36

S6. Full citations for Gaussian 09 program

Ref Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

S7. Cartesian coordinates for the optimized structure

S7.1. Cartesian coordinates for the optimized structure of T5E23

Atom	X/Å	Y/Å	Z/Å	Atom	X/Å	Y/Å	Z/Å
C	-3.56682	0.39102	0.00022	H	-2.85614	6.64306	-0.87772
C	-2.85746	-0.79322	0.00018	H	-5.23329	7.45498	-0.87786
C	-1.43998	-0.82560	0.00023	H	-5.23423	7.45506	0.87650
C	-0.73052	0.39831	0.00034	H	-4.81397	9.76280	-0.00053
C	-1.47329	1.60664	0.00040	H	-3.39413	9.18987	0.88406
C	-2.85438	1.62450	0.00033	H	-3.39322	9.18982	-0.88363
C	-0.70910	-2.08948	0.00016	H	2.34571	4.11492	-0.88783
C	0.70910	-2.08948	0.00017	H	2.34622	4.11516	0.88876
C	1.43998	-0.82560	0.00025	H	4.71258	4.93142	0.87885
C	0.73052	0.39831	0.00034	H	4.71188	4.93130	-0.87973
C	2.85746	-0.79322	0.00021	H	2.85601	6.64297	-0.87798
C	3.56682	0.39102	0.00024	H	2.85715	6.64327	0.87863
C	2.85438	1.62450	0.00031	H	5.23437	7.45515	0.87579
C	1.47329	1.60664	0.00039	H	5.23315	7.45489	-0.87858
C	-1.39241	-3.32777	0.00006	H	4.81397	9.76280	-0.00139
C	-0.70783	-4.52619	-0.00003	H	3.39309	9.18974	-0.88422
C	0.70783	-4.52619	-0.00001	H	3.39426	9.18996	0.88346
C	1.39241	-3.32777	0.00009	H	-5.45680	-1.30345	-0.88753
C	-2.98798	4.01685	0.00041	H	-5.45692	-1.30357	0.88753
C	-4.07456	5.08290	0.00009	H	-7.36398	0.31921	0.87956
C	-3.50359	6.50582	0.00028	H	-7.36386	0.31934	-0.87957
C	-4.58722	7.59123	-0.00034	H	-7.88343	-2.15097	-0.87794
C	-4.01696	9.01240	-0.00010	H	-7.88355	-2.15110	0.87746

C	2.98798	4.01685	0.00029	H	-9.80149	-0.52714	0.87702
C	4.07456	5.08290	-0.00020	H	-9.80136	-0.52699	-0.87751
C	3.50359	6.50582	-0.00007	H	-11.56520	-2.07498	-0.00051
C	4.58722	7.59123	-0.00097	H	-10.34184	-2.99724	-0.88420
C	4.01697	9.01240	-0.00077	H	-10.34197	-2.99740	0.88320
C	-5.69787	-0.70030	0.00003	H	5.45689	-1.30355	0.88762
C	-7.16796	-0.30593	-0.00004	H	5.45683	-1.30348	-0.88744
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C	-9.58585	-1.15164	-0.00028	H	7.36395	0.31923	0.87966
C	-10.51144	-2.37183	-0.00046	H	7.88352	-2.15108	0.87766
C	5.69787	-0.70030	0.00010	H	7.88346	-2.15099	-0.87775
C	7.16796	-0.30593	0.00007	H	9.80140	-0.52702	-0.87729
C	8.09821	-1.52513	-0.00002	H	9.80146	-0.52711	0.87724
C	9.58585	-1.15164	-0.00005	H	11.56520	-2.07498	-0.00017
C	10.51144	-2.37183	-0.00015	H	10.34193	-2.99737	0.88352
C	-2.60972	-6.07307	-0.00015	H	10.34187	-2.99727	-0.88388
C	-2.80224	-7.57084	-0.00042	H	-2.32699	-8.01036	-0.88208
C	2.60972	-6.07307	-0.00016	H	-2.32628	-8.01082	0.88061
C	2.80223	-7.57084	-0.00031	H	-3.86806	-7.79571	-0.00008
H	-3.41010	-1.72102	0.00010	H	2.32648	-8.01071	0.88089
H	-0.95067	2.55167	0.00050	H	2.32678	-8.01047	-0.88180
H	3.41010	-1.72102	0.00014	H	3.86806	-7.79571	-0.00018
H	0.95067	2.55167	0.00047	O	1.27603	-5.79647	-0.00010
H	-2.46742	-3.36797	0.00006	O	-1.27603	-5.79647	-0.00016
H	2.46742	-3.36798	0.00010	O	-4.92354	0.49785	0.00016
H	-2.34616	4.11509	0.88884	O	-3.62841	2.74433	0.00034
H	-2.34577	4.11499	-0.88775	O	3.62841	2.74433	0.00028
H	-4.71195	4.93137	-0.87940	O	4.92354	0.49785	0.00018
H	-4.71250	4.93135	0.87918	O	-3.50246	-5.25759	0.00003
H	-2.85701	6.64318	0.87889	O	3.50246	-5.25759	-0.00011

S7.2. Cartesian coordinates for the optimized structure of T5E27

Atom	X/Å	Y/Å	Z/Å	Atom	X/Å	Y/Å	Z/Å
C	2.17831	-2.85346	-0.34555	H	-6.46969	-5.04418	0.89143
C	2.15936	-1.46898	-0.34574	H	-8.92433	-4.53587	1.03592
C	0.95072	-0.73182	-0.30699	H	-9.03201	-4.54895	-0.71507
C	-0.28264	-1.43341	-0.27005	H	-9.78961	-6.74206	0.22848
C	-0.24050	-2.84730	-0.26549	H	-8.33422	-6.97900	-0.74731
C	0.94468	-3.53848	-0.29750	H	-8.22283	-6.96624	1.01680
C	0.95072	0.73183	-0.30700	H	-4.75728	3.11261	0.79463
C	-0.28266	1.43341	-0.27007	H	-4.85026	3.13625	-0.97956
C	-1.54791	0.70649	-0.23035	H	-7.30341	2.64521	-0.84463

C	-1.54790	-0.70650	-0.23034	H	-7.20725	2.62734	0.91109
C	-2.79170	1.38577	-0.18770	H	-6.46974	5.04413	0.89138
C	-3.99625	0.71224	-0.14242	H	-6.57607	5.06087	-0.86189
C	-3.99624	-0.71228	-0.14241	H	-9.03205	4.54886	-0.71514
C	-2.79169	-1.38579	-0.18769	H	-8.92438	4.53580	1.03585
C	2.15934	1.46901	-0.34576	H	-9.78967	6.74197	0.22839
C	2.17828	2.85349	-0.34559	H	-8.22290	6.96618	1.01672
C	0.94464	3.53850	-0.29756	H	-8.33428	6.97892	-0.74739
C	-0.24054	2.84731	-0.26554	H	2.20784	7.28735	-0.36934
C	-5.30862	-2.71721	-0.07129	H	0.47678	7.42815	-0.06365
C	-6.78214	-3.08963	0.01196	H	1.64015	7.68170	1.27633
C	-7.00972	-4.60575	0.04008	H	4.59224	2.38636	0.62584
C	-8.49181	-4.98888	0.13386	H	4.76151	2.36921	-1.14459
C	-8.72370	-6.50235	0.15947	H	5.52935	4.75501	-1.07795
C	-5.30865	2.71716	-0.07132	H	5.36648	4.75674	0.67528
C	-6.78217	3.08958	0.01193	H	7.10454	2.92678	0.82780
C	-7.00976	4.60569	0.04003	H	7.27547	2.94734	-0.92073
C	-8.49186	4.98881	0.13380	H	8.02982	5.34303	-0.81508
C	-8.72376	6.50227	0.15939	H	7.85879	5.31832	0.93100
C	1.38633	5.63962	0.71170	H	10.25011	4.96197	0.27452
C	1.42555	7.10874	0.37497	H	9.62812	3.52017	1.08715
C	4.57104	3.01560	-0.27500	H	9.79781	3.53889	-0.67245
C	5.61135	4.12273	-0.18521	H	4.76150	-2.36905	-1.14445
C	7.03952	3.58062	-0.05359	H	4.59231	-2.38644	0.62599
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H	3.10334	-0.94560	-0.38263	H	2.20795	-7.28729	-0.36927
H	-1.14674	-3.43817	-0.23482	H	1.64029	-7.68166	1.27640
H	-2.80827	2.46560	-0.18750	H	0.47689	-7.42815	-0.06356
H	-2.80824	-2.46562	-0.18747	O	0.92111	4.93001	-0.36963
H	3.10333	0.94565	-0.38264	O	3.29038	3.63381	-0.39983
H	-1.14679	3.43817	-0.23489	O	3.29042	-3.63377	-0.39979
H	-4.85023	-3.13630	-0.97954	O	0.92115	-4.93000	-0.36954
H	-4.75725	-3.11265	0.79465	O	-5.22514	-1.29433	-0.09453
H	-7.20722	-2.62739	0.91112	O	-5.22516	1.29429	-0.09454
H	-7.30339	-2.64528	-0.84460	O	1.70692	5.13854	1.75865

H	-6.57603	-5.06094	-0.86184	O	1.70699	-5.13851	1.75874

S7.3. Cartesian coordinates for the optimized structure of T5E26

Atom	X/Å	Y/Å	Z/Å	Atom	X/Å	Y/Å	Z/Å
C	1.26225	-3.59227	-0.16686	H	5.45509	-6.12741	2.01558
C	0.01983	-3.01070	-0.02871	H	7.10072	-7.01315	0.34004
C	-0.14064	-1.60867	0.02792	H	8.10080	-5.58854	0.56483
C	1.01553	-0.78675	-0.07403	H	8.98200	-7.50094	1.92076
C	2.27699	-1.41357	-0.19014	H	8.44061	-6.20424	2.99463
C	2.41850	-2.78739	-0.22742	H	7.43476	-7.63967	2.76568
C	-1.45993	-0.99786	0.18582	H	4.51219	2.61664	0.44510
C	-1.58212	0.41817	0.21627	H	4.32140	2.59285	-1.32133
C	-0.39518	1.26048	0.07895	H	4.92489	5.01878	-1.41251
C	0.88124	0.66878	-0.05587	H	5.11337	5.04535	0.33612
C	-0.49045	2.67442	0.07639	H	6.96897	3.34562	0.16379
C	0.61939	3.48769	-0.04722	H	6.77650	3.30773	-1.58152
C	1.90687	2.89094	-0.17706	H	7.37883	5.74307	-1.70086
C	2.01212	1.51385	-0.18061	H	7.57168	5.78231	0.04247
C	-2.62643	-1.78369	0.31187	H	9.79553	5.53502	-1.08215
C	-3.87872	-1.22287	0.47589	H	9.44654	4.09360	-0.11950
C	-3.98615	0.17926	0.52170	H	9.25138	4.05165	-1.87590
C	-2.86940	0.97347	0.39290	H	-1.30537	5.20503	-0.79680
C	4.21565	-4.00336	0.76255	H	-1.15339	5.24899	0.97329
C	5.44947	-4.77627	0.32579	H	0.28272	7.28448	0.79917
C	6.15887	-5.45712	1.50295	H	0.16445	7.23147	-0.95481
C	7.39707	-6.25707	1.07893	H	-2.33061	7.56159	-0.79952
C	8.10384	-6.93869	2.25412	H	-2.21917	7.61032	0.95284
C	4.26377	3.23514	-0.43007	H	-0.75727	9.64469	0.80578
C	5.22387	4.40984	-0.55079	H	-0.85594	9.59304	-0.94511
C	6.68190	3.96000	-0.70152	H	-2.47986	11.26168	-0.02344
C	7.66476	5.12973	-0.83592	H	-3.35557	9.94984	-0.82269
C	9.12030	4.67876	-0.98674	H	-3.25814	10.00101	0.94165
C	-0.65241	5.51747	0.03156	H	-7.84180	0.61646	1.38197
C	-0.38276	7.01418	-0.02952	H	-7.54963	1.58980	2.84651
C	-1.66888	7.84662	0.03086	H	-7.23662	2.26508	1.21542
C	-1.41197	9.35773	-0.02779	H	-6.18186	-1.15584	-0.82424
C	-2.69668	10.18961	0.01957	H	-5.25393	-2.58010	-1.34063
C	-5.78387	0.84070	1.91492	H	-6.60408	-4.01028	0.20758
C	-7.19361	1.36982	1.84078	H	-7.52089	-2.60189	0.72192
C	-5.83116	-2.14784	-0.51051	H	-8.35778	-2.28656	-1.64135
C	-6.99952	-3.04634	-0.13521	H	-7.44886	-3.70002	-2.15056
C	-7.97982	-3.25920	-1.29505	H	-8.78986	-5.12992	-0.58165

C	-9.16700	-4.15659	-0.92260	H	-9.69398	-3.71853	-0.06443
C	-10.15121	-4.36409	-2.07718	H	-10.98497	-5.00839	-1.78056
C	1.79892	-5.68071	-1.26538	H	-10.57222	-3.41063	-2.41603
C	1.82115	-4.94644	-2.58503	H	-9.66000	-4.83172	-2.93799
H	-0.82963	-3.67866	0.03519	H	0.91611	-4.35264	-2.73447
H	3.19022	-0.83635	-0.25880	H	2.67837	-4.26778	-2.60761
H	-1.45939	3.14160	0.17116	H	1.92553	-5.68497	-3.37914
H	2.99293	1.07531	-0.28776	O	-5.24626	0.76635	0.64680
H	-2.58119	-2.86538	0.30392	O	-4.98149	-2.02245	0.64498
H	-3.01915	2.04422	0.44304	O	1.37624	-4.97571	-0.15163
H	4.46860	-3.23382	1.50529	O	3.65782	-3.35380	-0.40446
H	3.47060	-4.67576	1.20247	O	2.94447	3.76094	-0.29428
H	5.14571	-5.52819	-0.41256	O	0.60314	4.84630	-0.06129
H	6.13693	-4.08853	-0.18277	O	-5.18942	0.52525	2.91157
H	6.45383	-4.69981	2.24326	O	2.09970	-6.83595	-1.11590

S7.1. Cartesian coordinates for the optimized structure of T5E36

Atom	X/Å	Y/Å	Z/Å	Atom	X/Å	Y/Å	Z/Å
C	-0.03117	0.70695	0.18292	H	0.01494	-11.62784	-0.07848
C	0.03117	-0.70695	0.18292	H	-0.93480	-10.42763	0.80684
C	-0.06897	1.44160	-1.08093	H	0.82550	-10.45476	0.96711
C	-0.05601	1.38305	1.42930	H	0.26372	-6.72640	8.45136
C	0.06897	-1.44160	-1.08093	H	1.15708	-6.92610	6.93879
C	0.03490	-0.72841	-2.30638	H	-0.60926	-6.99714	6.93794
C	-0.03490	0.72841	-2.30638	H	-0.26372	6.72640	8.45136
C	0.05601	-1.38305	1.42930	H	-1.15708	6.92610	6.93879
C	-0.14746	2.85542	-1.11349	H	0.60926	6.99714	6.93794
C	0.14746	-2.85542	-1.11349	H	1.32428	5.56152	-6.76969
C	-0.06495	1.46882	-3.51058	H	-0.33478	5.78073	-6.14642
C	0.06495	-1.46882	-3.51058	H	0.03848	4.36690	-7.13170
C	-0.02768	0.71144	2.63518	H	-1.32428	-5.56152	-6.76969
C	0.02768	-0.71144	2.63518	H	0.33478	-5.78073	-6.14642
C	-0.13386	2.83947	-3.51524	H	-0.03848	-4.36690	-7.13170
C	-0.18680	3.56263	-2.30353	H	0.69816	9.79623	-1.62957
C	0.18680	-3.56263	-2.30353	H	-1.04908	9.82191	-1.47208
C	0.13386	-2.83947	-3.51524	H	-0.92846	7.96124	0.20852
C	0.00033	-10.58627	0.25790	H	0.82210	7.94005	0.06083
C	0.25474	-6.49024	7.38251	H	0.61553	7.33772	-2.37845
C	-0.25474	6.49024	7.38251	H	-1.13917	7.36361	-2.23634
C	0.44490	5.04945	-6.38085	H	0.73394	5.47968	-0.70734
C	-0.44490	-5.04945	-6.38085	H	-1.03961	5.49768	-0.57543
C	-0.12148	9.61680	-0.92111	H	-0.69816	-9.79623	-1.62957

C	0.81558	4.29685	-5.12799	H	1.04908	-9.82191	-1.47208
C	-0.81558	-4.29685	-5.12799	H	0.92846	-7.96124	0.20852
C	-0.10388	2.71481	3.95075	H	-0.82210	-7.94005	0.06083
C	-0.11843	3.08496	5.42713	H	-0.61553	-7.33772	-2.37845
C	-0.17910	4.59950	5.65914	H	1.13917	-7.36361	-2.23634
C	-0.19390	4.97865	7.14516	H	-0.73394	-5.47968	-0.70734
C	0.10388	-2.71481	3.95075	H	1.03961	-5.49768	-0.57543
C	0.11843	-3.08496	5.42713	H	1.05205	-4.49575	7.63131
C	0.17910	-4.59950	5.65914	H	-0.70085	-4.56659	7.63055
C	0.19390	-4.97865	7.14516	H	-0.68041	-5.08241	5.17254
C	0.19491	-5.71601	-1.24547	H	1.07494	-5.01177	5.17303
C	0.21327	-7.17463	-1.67919	H	0.97873	-2.59593	5.89991
C	0.10388	-8.14326	-0.49563	H	-0.77819	-2.66625	5.89989
C	0.12148	-9.61680	-0.92111	H	1.00768	-3.08771	3.44605
C	-0.19491	5.71601	-1.24547	H	-0.76804	-3.15688	3.44592
C	-0.21327	7.17463	-1.67919	H	-1.05205	4.49575	7.63131
C	-0.10388	8.14326	-0.49563	H	0.70085	4.56659	7.63055
C	-0.00033	10.58627	0.25790	H	0.68041	5.08241	5.17254
H	-1.00768	3.08771	3.44605	H	-1.07494	5.01177	5.17303
H	0.03505	-0.97774	-4.47473	H	-0.97873	2.59593	5.89991
H	0.77819	2.66625	5.89989	H	-0.09542	2.46195	1.44818
H	-0.03505	0.97774	-4.47473	O	-1.86849	-4.35389	-4.54619
H	0.18845	-3.41011	-0.18773	O	-0.28683	4.91342	-2.42201
H	-0.18845	3.41011	-0.18773	O	-0.24105	3.51368	-4.73019
H	0.09542	-2.46195	1.44818	O	0.24105	-3.51368	-4.73019
H	0.76804	3.15688	3.44592	O	0.28683	-4.91342	-2.42201
H	-0.01494	11.62784	-0.07848	O	0.04842	-1.29311	3.86483
H	0.93480	10.42763	0.80684	O	-0.04842	1.29311	3.86483
H	-0.82550	10.45476	0.96711	O	1.86849	4.35389	-4.54619

S8. Table of dipople moments

Sample	Dipomoment(Total)	Dipomoment(x)	Dipomoment(y)	Dipomoment(z)
T5E23	1.34 D	0 D	1.34 D	0 D
T5E27	1.28 D	1.28 D	0 D	0 D
T5E26	5.91 D	-0.83 D	5.19 D	-2.69 D
T5E36	2.65 D	0 D	2.65 D	0 D

S9. Table of DSC results

Sample	Second Heating	First Cooling
T5E23	**Cr**126.2(48.8)**Colh**158.9(21.1)**Iso**	**Iso**155.5(20.4)**Colh**56.1(48.2)**Cr**
T5E27	**Cr**174.2(60.5)**Iso**	**Iso**165.2(17.0)**Colh**128.4(43.2)**Cr**
T5E26	**Colh**168.1(15.8)**Iso**	**Iso**164.2(15.7)**Colh**
T5E36	**Colh$_2$**134.9(6.1)**Colh$_1$**173.1(24.8)**Iso**	**Iso**167.4(24.7)**Colh$_1$**121.1(4.3)**Colh$_2$**
Phase transition temperature ,°C (enthalpy change, J g^{-1})		

S10. Table of 1DXRD results

Sample	D-Spacing （Å）	Miller index (hkl)	Lattice parameter （Å）	Sample	D-Spacing （Å）	Miller index (hkl)	Lattice parameter （Å）
T5E23	16.38	(100)	a=b=18.9 Å	T5E26	16.42	(100)	a=b=18.9 Å
	9.63	(110)			9.48	(110)	
	8.23	(200)			8.19	(200)	
	6.23	(210)			6.19	(210)	
	3.52	π - π			3.53	π - π	
T5E27	16.36	(100)	a=b=18.9 Å	T5E36	16.32	(100)	a=b=18.8 Å
	9.52	(110)			9.43	(110)	
	8.23	(200)			8.18	(200)	
	6.97	(210)			6.17	(210)	
	3.59	π - π			3.44	π - π	

S11. Mesophase of T5E23 and T5E27

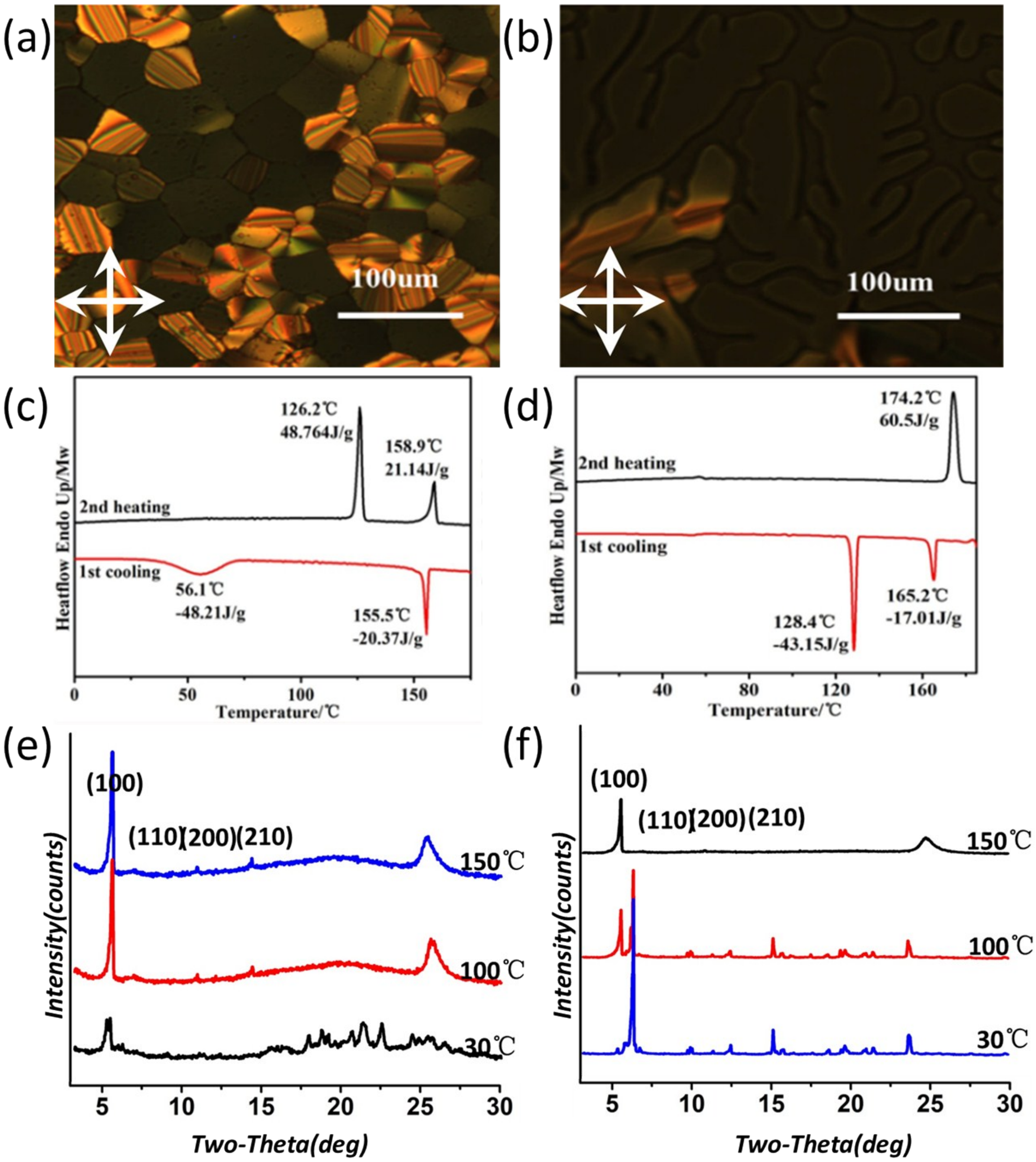

Figure S9. Pseudo focal conic textures of a) T5E23 at 155°C and b) T5E27 at 165°C. DSC thermograms of c) T5E23 and d) T5E27. 1DXRD patterns of e) T5E23 and f) T5E27

S12. Mesophase of T5E26 and T5E36

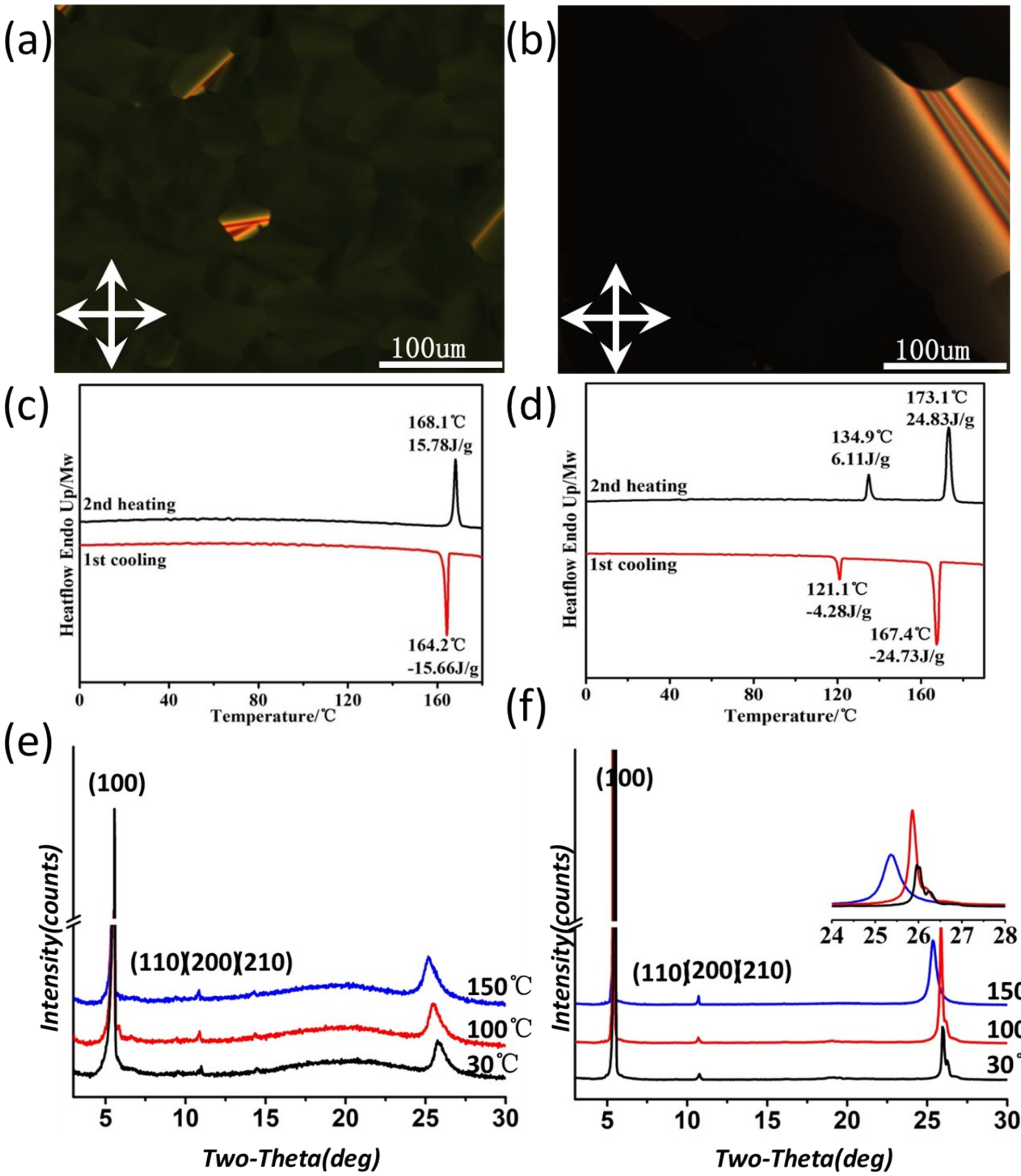

Figure S10. Pseudo focal conic textures of a) T5E26 at 164°C and b) T5E36 at 167°C. DSC thermograms of c) T5E26 and d) T5E36. 1DXRD patterns of e) T5E26 and f) T5E36

S13. SAXS patterns of T5E26 and T5E36

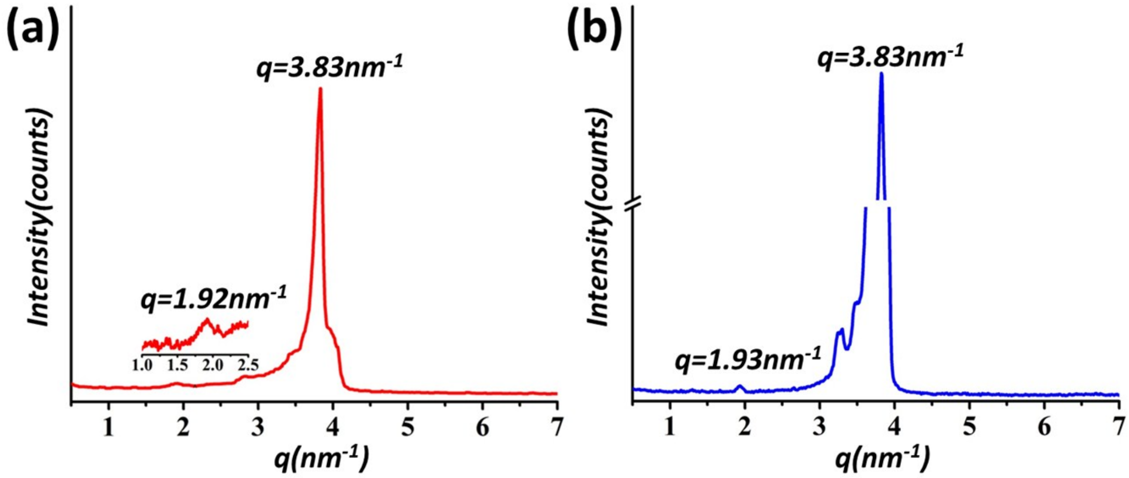

Figure S11. SAXS patterns of oriented samples at 30°C a) T5E26, b) T5E36.

S14. 2DXRD patterns of T5E36

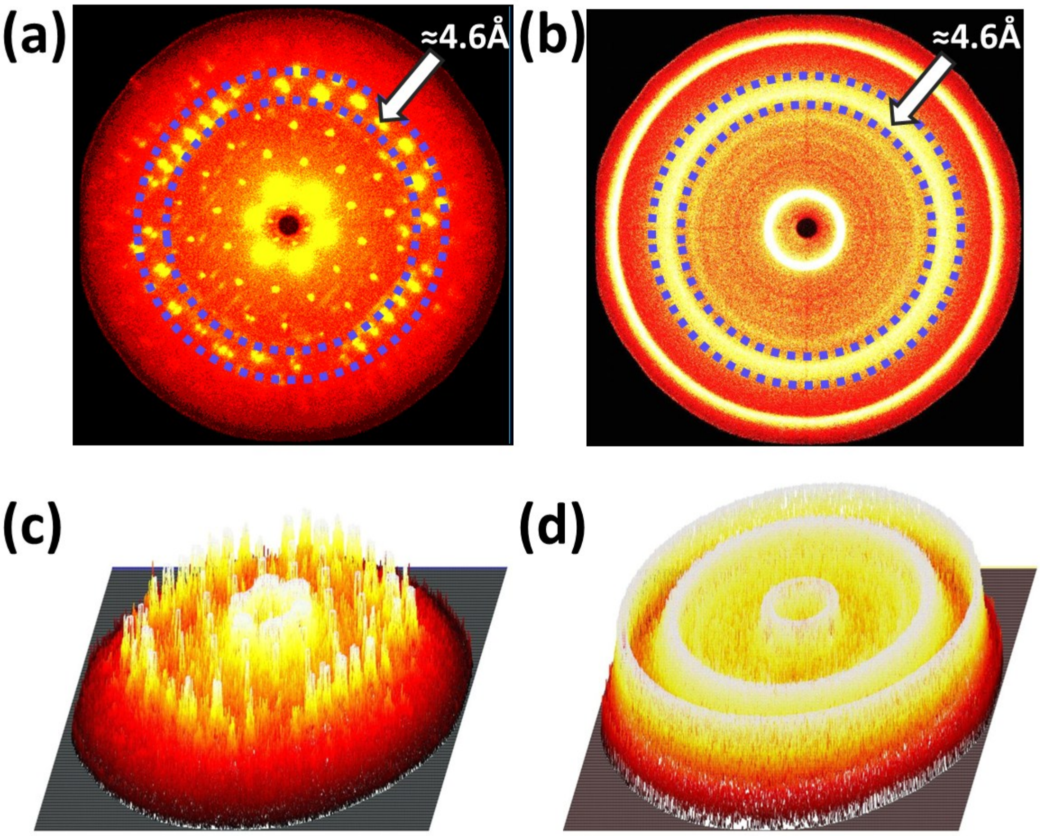

Figure S12. 2DXRD patterns of T5E36 at 30°C a) oriented sample, b) powder sample. 3D reconstructed intensity maps of T5E36 at 30°C c) oriented sample, d) powder sample.