Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Systematical studies on structure-properties relationship of main chain discotic liquid crystalline polyethers: effects of the spacer lengths and substitution positions

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1. Materials and Measuments

Materials

All solvents employed were purchased from Aldrich and used without further purification unless stated otherwise. Anhydrous tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon and used immediately. Dichloromethane (CH_2Cl_2) were dried over CaH_2. Column and thin layer chromatography were performed on silica gel 60 (200–300 mesh ASTM) and Silica Gel 60 glass backed sheets, respectively.

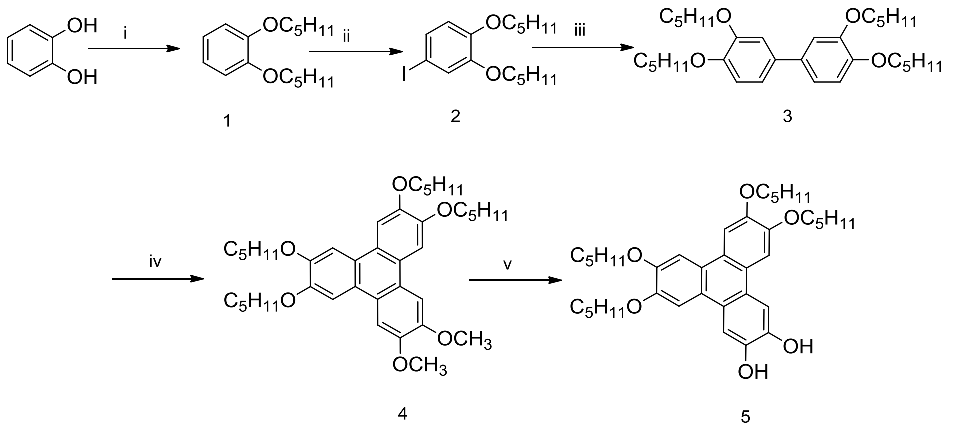
Measuments

^{1}H-NMR spectra were obtained from 300MHz (Bruker AMX300) instruments with TMS as internal standards. Multiplicities of the peaks are given as s=singlet, d=doublet, t=triplet, m=multiplet. Fourier transform infrared spectra (FT-IR) were recorded on a Shimadzu-8400 infrared spectrometer with pressed potassium bromide pellets. High resolution mass spectrum was recorded on a Bruker Apex IV FTMS mass spectrometer. Elemental analysis (C,H) were carried out at the Elementar Vario EL CUBE elements analyzer. Gel-permeation chromatography (GPC) measurements were performed at 25 ℃ on a Waters 515 equiped with Wyatt Technology Optilab rEX differential refractive index and UV detectors. THF was used as the eluent at a flow rate 1.0 ml min^{-1}, the solvent THF and sample solution were filtered over a filter with pore size of 0.45 μm(Nylon, Millex-HN 13 mm syringes Filters, Millipore, US). The differential scanning calorimetry (DSC) thermograms were recorded on a Netzsch DSC 200. Typically, about 5mg of the powder sample was encapsulated in a sealed aluminum pan with an identical empty pan as the reference, the heating and cooling rate was 10 ℃ min^{-1}. The phase transition and liquid crystalline textures were also investigated and photographed using melt-pressed preparations sandwiched between two glass plates with a polarized optical microscope (POM) equipped with a Linkam TMS94 hot stage. 1D wide angle X-Ray diffraction (1D WAXD) studies were performed on a Bruker D8 Advance diffractometer equipped with variable temperature controller. Typically, the powder sample was encapsulated with aluminum foil during the measument and the obtained

X-ray analysis data were processed with the associated software and the aluminum foil background signal was subtracted. 2D WAXD was carried out using a BRUKER AXS D8 Discover diffractometer with a 40KV FL tube as the X-ray source (Cu Kα) and a VANTEC 500 detector. The point-focused X-ray beam was aligned either perpendicular or in parallel to the mechanical shearing direction. For both the 1D and 2D experiments, the background scattering was recorded and subtracted from the sample patterns. Charge carrier mobility was measured using a time-of-flight device (TOF-401). The LC cells with a thickness 15 μm were purchased from E.H.C. company with semi-transparent indium tin oxide (ITO) electrodes. The purified polymers were capillary-filled into the cell at the temperature 30-50 ℃ higher than their clear point, and then slowly cooled to their mesophases at a rate of 0.1 ℃ min^{-1} in order to obtain a higher order. 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 using a NF low-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 at room temperature.

2. Synthesis of Intermediate Dihydroxytetrapentyloxytriphenylene

In general, The two hydroxyl groups in a dihydroxytetraalkoxytriphenylene may give rise to four different isomers, in structures 2,3-, 2,6-, 2,7- and 3,6-dihydroxy tetrapentyloxy triphenylene dirivatives. These intermediates was prepared according to the previous reports.[1-5] The synthesis routes were outlined in scheme S1−4.



Scheme S1 Synthesis of triphenylene intermediate **5**

Reagents: (i) $C_5H_{11}Br$, K_2CO_3, ethanol, reflux; (ii) I_2/HIO_3, acetic acid, 98% H_2SO_4, $CHCl_3/H_2O$, 40 ℃; (iii) Cu, 270 ℃; (iv) veratrole, $FeCl_3$, MeOH; (v) $LiPPh_2$, THF.

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 ℃ at (1.6 mmHg) afforded as a colorless oil (180g, 90%). TLC R_f: 0.65 (dichloromethane-hexane 1:1). ^1H 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.

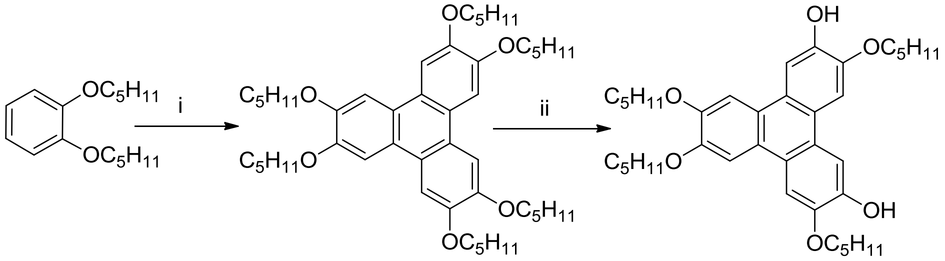
Preparation of 1-iodo-3,4-dipentoxybenzene (2). 1,2-dipentoxybenzene (30g, 0.12mol), 60ml acetic acid, 20ml water, 20ml chloroform, 1ml sulfuric acid, iodine (10.2g), and iodic acid (4.2g, 0.02mol) were mixed and vigorously stirred at 40 ℃. After 24 hours 600 ml water was added and the organic phase 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 R_f: 0.71 (dichloromethane-hexane 1:1). ^1H 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 ℃ under argon and vigorous stirring. After four hours the temperature was lowered to 180 ℃ 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 R_f: 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 ℃. 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 R_f: 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 ℃ 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 ℃. TLC R_f: 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. Anal. Calcd (%) for $C_{38}H_{52}O_6$ (603.3691):

C, 75.46; H, 8.67. Found: C, 75.20; H, 8.84. m/z (ESI) 603.3702 $(M)^+$.



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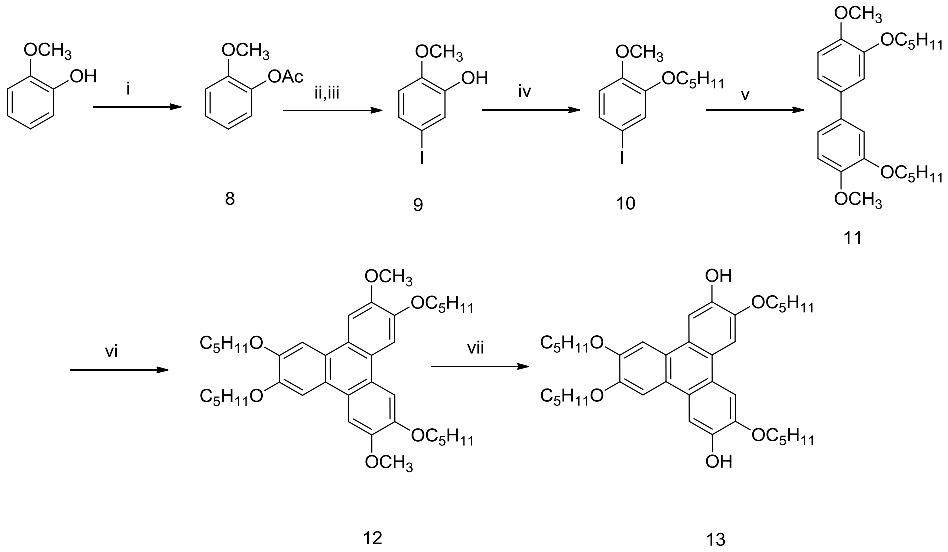
Scheme S2 Synthesis of triphenylene intermediate **7**

Reagents: (i) $FeCl_3$, MeOH; (ii) B-bromocatecholborane, CH_2Cl_2.

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 R_f: 0.62 (dichloromethane-hexane 4:1). ^1H 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 ℃. 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 ℃ 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 R_f: 0.36 (ethyl acetate-hexane 1:8). ^1H 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. Anal. Calcd (%) for $C_{38}H_{52}O_6$ (603.3691): C, 75.46; H, 8.67. Found: C, 75.28; H, 8.82. m/z (ESI) 603.3698 $(M)^+$.



Scheme S3 Synthesis of triphenylene intermediate **13**

Reagents: (i) AcCl, RT; (ii) ICl, $CHCl_3$; (iii) ethanol/H_2O, NaOH; (iv) $C_5H_{11}Br$, K_2CO_3, ethanol, Reflux; (v) Cu, 270 ℃; (vi) 1,2-bis(pentyloxy)benzene, $FeCl_3$, MeOH; (vii) $LiPPh_2$, THF.

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 ($MgSO_4$) and the solvent removed in vacuo. Distillation of the residue at 90-96 ℃ at 0.8mmHg afforded 2-(methoxy)-phenyl Acetate as a colorless oil (98.9g, 85%). TLC R_f: 0.33 (dichloromethane-hexane 2:1). ^1H 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.

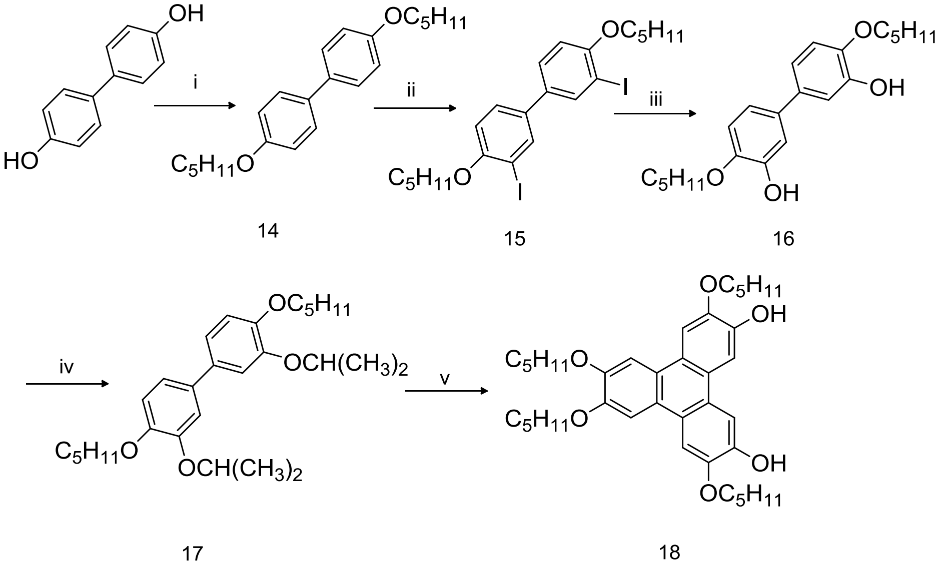
Preparation of 2-(methoxy)-5-iodophenol (9). 2-(methoxy)phenyl Acetate (23g, 0.14mmol) was dissolved in chloroform (200ml) and cooled to 8-13 ℃. Iodine monochloride (27.7g, 0.17mmol) in chloroform (70ml) was added dropwise, maintaining the reaction temperature between 8 and 13 ℃. The mixture was stirred 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 ℃ at (1.2mmHg) gave a yellow oil which crystallized overnight and recrystallization from light petroleum affored 2-(methoxy)-5-iodophenol(20.5g, 58.3%). TLC R_f: 0.39 (dichloromethane-hexane 2:1). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.36-7.15 (m, 2H, Ar-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. Anal. Calcd (%) for $C_7H_7IO_2$ (248.9418): C, 33.60; H, 2.80. Found: C, 33.58; H, 2.82. m/z (ESI) 248.9417 $(M)^+$.

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 R_f: 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. Anal. Calcd (%) for $C_{12}H_{17}IO_2$ (320.0268): C, 44.97; H, 5.31. Found: C, 44.93; H, 5.35. m/z (ESI) 320.0268 $(M)^+$.

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℃ 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 R_f: 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. Anal. Calcd (%) for $C_{24}H_{34}O_4$ (387.2530): C, 74.51; H, 8.79. Found: C, 74.23; H, 8.82. m/z (ESI) 387.2527 $(M)^+$.

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 R_f: 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. Anal. Calcd (%) for $C_{40}H_{56}O_6$ (632.4071): C, 75.84; H, 8.85. Found: C, 75.78; H, 8.86. m/z (ESI) 632.4070 $(M)^+$.

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℃. TLC R_f: 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. Anal. Calcd (%) for $C_{38}H_{52}O_6$ (603.3691): C, 75.46; H, 8.67. Found: C, 75.35; H, 8.83. m/z (ESI) 603.3699 $(M)^+$.



Scheme S4 Synthesis of triphenylene intermediate **18**

Reagents: (i) $C_5H_{11}Br$, K_2CO_3, ethanol, reflux; (ii) I_2/HIO_3, acetic acid, 98% H_2SO_4, $CHCl_3/H_2O$, 85 ℃;; (iii) PEG400, H_2O, CuI, KOH, 140 ℃, Reflux; (iv) 2-bromopropane, K_2CO_3, ethanol, reflux; (v) 1,2-bis(pentyloxy)benzene, $FeCl_3$, MeOH.

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 R_f: 0.61 (dichloromethane-hexane 1:1). ^1H 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. Anal. Calcd (%) for $C_{22}H_{30}O_2$ (326.2240): C, 80.94; H, 9.26. Found: C, 80.36; H, 9.37. m/z (ESI) 326.2241 $(M)^+$.

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 ℃ 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 R_f: 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. Anal. Calcd (%) for $C_{22}H_{28}I_2O_2$ (578.0173): C, 45.69; H, 4.88. Found: C, 45.60; H, 4.95. m/z (ESI) 578.0184 (M)$^+$.

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 ℃ 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 R_f: 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. Anal. Calcd (%) for $C_{22}H_{31}O_4$ (359.2217): C, 73.71; H, 8.44. Found: C, 73.48; H, 8.56. m/z (ESI) 359.2218 (M)$^+$.

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 R_f: 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. Anal. Calcd (%) for $C_{28}H_{43}O_4$ (443.3156): C, 75.98; H, 9.56. Found: C, 75.81; H, 9.75. m/z (ESI) 443.3163 (M)$^+$.

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 ℃. TLC R_f: 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. Anal. Calcd (%) for $C_{38}H_{53}O_6$ (605.3836): C, 75.46; H, 8.67. Found: C, 75.20; H, 8.84. m/z (ESI) 605.3832 (M)$^+$.

3. Synthesis of main chain polymers

The synthesis method are similar in series $P_{2,3}$-n, $P_{2,6}$-n, $P_{2,7}$-n, and $P_{3,6}$-n, respectively.[6] Herein, the synthesis process of the representative polymers $P_{a,b}$-10 was shown in detail , while the experimental data was provided for other polymers.

Synthesis of $P_{2,3}$-10. 5 (1.2g, 1.98×10^{-3} mol) was stirred in degassed N-methylpyrrolidone (NMP) (4.5 mL) with cesium carbonate (1.3 g) under argon. 1,10-Dibromodecane (0.595g, 1.98×10^{-3} mol) in NMP was added and the flask immediately submerged in an oil bath at 110 ℃. The mixture was stirred at 110 ℃ for 24 h and cooled and water (15 mL) was added. The solid was filtered off, washed with water and ethanol, and reprecipitated from dichloromethane with ethanol to give the polymer $P_{2,3}$-10 (1.06g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.80 (d, J=5.4Hz, 6H, Ar-H), 4.21 (d, J=4.8Hz, 12H, OCH_2), 1.94 (s, 12H, OCH_2CH_2), 1.56-1.30 (m, 24H, CH_2), 0.97 (s, 12H, CH_3). FT-IR (cm^{-1}): 3110, 2926, 2864, 1620, 1523, 1432, 1385, 1258, 1166.

$P_{2,3}$-08. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.83 (d, J=10.8Hz, 6H, Ar-H), 4.23 (d, J=3.9Hz, 12H, OCH_2), 1.96 (s, 12H, OCH_2CH_2), 1.55-1.46 (m, 24H, CH_2), 0.95 (s, 12H, CH_3). FT-IR (cm^{-1}): 3104, 2925, 2855, 1618, 1525, 1430, 1388, 1260, 1174, 1063.

$P_{2,3}$-09. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.83 (d, J=9.3Hz, 6H, Ar-H), 4.22 (s, 12H, OCH_2), 1.95 (s, 12H, OCH_2CH_2), 1.46-1.27 (m, 26H, CH_2), 0.98 (s, 12H, CH_3). FT-IR (cm^{-1}): 3095, 2925, 2855, 1618, 1516, 1430, 1388, 1260, 1174, 1047.

$P_{2,3}$-11. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.82 (s, 6H, Ar-H), 4.22 (s, 12H, OCH_2), 1.94 (s, 12H, OCH_2CH_2), 1.45-1.31 (m, 30H, CH_2), 0.98 (s, 12H, CH_3). FT-IR (cm^{-1}): 3086, 2925, 2855, 1618, 1516, 1435, 1387, 1251, 1166, 1047.

$P_{2,3}$-12. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.82 (s, 6H, Ar-H), 4.22 (s, 12H, OCH_2), 1.94 (s, 12H, OCH_2CH_2), 1.46-1.35 (m, 32H, CH_2), 0.98 (s, 12H, CH_3). FT-IR (cm^{-1}): 3104, 2916, 2855, 1618, 1516, 1439, 1380, 1260, 1174, 1038.

Synthesis of $P_{2,6}$-10. 7 (400mg, 6.61×10^{-4} mol) and cesium carbonate (430 mg, 1.32×10^{-3} mol) were dissolved in NMP (1.5 mL). 1,10-Dibromodecane (198.3 mg, 6.61×10^{-4} mol) in NMP (1 mL) was added and the mixture immediately submerged in an oil bath at 110 ℃. The mixture was stirred for 1 h at 110 ℃ and cooled. Water was added and the resulting solid repeatedly washed with water and ethanol. Reprecipitation from dichloromethane with ethanol afforded the polymer $P_{2,6}$-10 0.35g. yield 71%. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.83 (s, 6H, Ar-H), 4.23 (t, J=6.3Hz, 12H, OCH_2), 1.94 (q, J=6.9Hz, 12H, OCH_2CH_2), 1.56-1.27 (m, 24H, CH_2), 0.97 (t, J=7.2Hz, 12H, CH_3). FT-IR (cm^{-1}): 3101, 2919, 2856, 1620, 1516, 1425, 1385, 1258, 1163.

$P_{2,6}$-08. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.84 (s, 6H, Ar-H), 4.24 (s, 12H, OCH_2), 1.96 (s, 12H, OCH_2CH_2), 1.57-1.43 (m, 24H, CH_2), 0.99 (d, J=6.3Hz, 12H, CH_3). FT-IR (cm^{-1}): 3085, 2925, 2864, 1618, 1516, 1430, 1388, 1260, 1166, 1038.

$P_{2,6}$-09. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.84 (s, 6H, Ar-H), 4.24 (s, 12H, OCH_2), 1.96 (s, 12H, OCH_2CH_2), 1.59-1.37 (m, 26H, CH_2), 0.99 (d, J=6.3Hz, 12H, CH_3). FT-IR (cm^{-1}): 3095, 2932, 2855, 1627, 1525, 1430, 1388, 1260, 1166, 1038.

$P_{2,6}$-11. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.84 (s, 6H, Ar-H), 4.23 (s, 12H, OCH_2), 1.95 (s, 12H, OCH_2CH_2), 1.47-1.32 (m, 30H, CH_2), 1.00-0.95 (m, 12H, CH_3). FT-IR (cm^{-1}): 3104, 2925, 2839, 1618, 1516, 1430, 1380, 1260, 1174, 1055.

$P_{2,6}$-12. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.83 (s, 6H, Ar-H), 4.23 (t, J=6.3Hz, 12H, OCH_2), 1.95 (t, J=7.2Hz, 12H, OCH_2CH_2), 1.55-1.34 (m, 32H, CH_2), 0.97 (t, J=6.9Hz, 12H, CH_3). FT-IR (cm^{-1}): 3086, 2925, 2839, 1609, 1516, 1430, 1380, 1260, 1174, 1055.

Synthesis of $P_{2,7}$-10. 13 (600mg, 1.0×10^{-3} mol) and cesium carbonate (650 mg, 1.98×10^{-3} mol) were dissolved in NMP (2.5 mL). 1,10-Dibromodecane (297.5 mg, 1.0×10^{-3} mol) in NMP (1.5 mL) was added and the mixture immediately submerged in an oil bath at 110 ℃. The mixture was stirred for 1 h at 110 ℃ and cooled. Water was added and the resulting solid repeatedly washed with water and ethanol. Reprecipitation from dichloromethane with ethanol afforded the polymer $P_{2,7}$-10 0.64g. yield 87%. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.84 (s, 6H, Ar-H), 4.23 (t, J=6.3Hz, 12H, OCH_2), 1.96 (t, J=6.9Hz, 12H, OCH_2CH_2), 1.54-1.27 (m, 24H, CH_2), 0.98 (t, J=6.9Hz, 12H, CH_3). FT-IR (cm^{-1}): 3108, 2924, 2849, 1619, 1512, 1436, 1388, 1253, 1162.

$P_{2,7}$-08. The polymer was prepared by elongating the reaction time for 24 hours due to the strong steric hindrance. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.84 (s, 6H, Ar-H), 4.23 (s, 12H, OCH_2), 1.96 (d, J=6.0Hz, 12H, OCH_2CH_2), 1.56-1.44 (m, 24H, CH_2), 0.97 (t, J=6.9Hz, 12H, CH_3). FT-IR (cm^{-1}): 3095, 2916, 2839, 1609, 1516, 1422, 1388, 1251, 1166, 1047.

$P_{2,7}$-09. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.84 (s, 6H, Ar-H), 4.25 (d, J=6.3Hz, 12H, OCH_2), 1.96 (s, 12H, OCH_2CH_2), 1.60-1.47 (m, 26H, CH_2), 0.98 (t, J=6.6Hz, 12H, CH_3). FT-IR (cm^{-1}): 3086, 2932, 2848, 1618, 1525, 1439, 1388, 1260, 1174, 1047.

$P_{2,7}$-11. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.84 (s, 6H, Ar-H), 4.24 (s, 12H, OCH_2), 1.96 (s, 12H, OCH_2CH_2), 1.60-1.33 (m, 30H, CH_2), 1.00-0.96 (m, 12H, CH_3). FT-IR (cm^{-1}): 3086, 2916, 2848, 1627, 1507, 1439, 1380, 1251, 1166, 1038.

$P_{2,7}$-12. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.84 (s, 6H, Ar-H), 4.24 (t, J=5.7Hz, 12H, OCH_2), 1.96 (t, J=6.3Hz, 12H, OCH_2CH_2), 1.52-1.43 (m, 32H, CH_2), 1.00-0.96 (m, 12H, CH_3). FT-IR (cm^{-1}): 3095, 2925, 2839, 1618, 1525, 1430, 1388, 1269, 1166, 1055.

Synthesis of $P_{3,6}$-10. 18 (1.0 g, 1.65×10^{-3} mol) was stirred in NMP (3.5 mL) and degassed with argon. Cesium carbonate (1.075g) was added and the mixture stirred for 5 min. 1,10-Dibromodecane (0.496g, 1.65×10^{-3} mol) in NMP (1 mL) was added and the flask immediately immersed in an oil bath at 85 ℃. A two phase mixture was immediately formed which was stirred at 85 ℃ for 2 days and poured onto water. The solid was filtered, reprecipitated from dichloromethane with ethanol, and separated by column chromatography (silica, benzene, then dichloromethane) to remove low molecular weight monomers and obtain the final polymer $P_{3,6}$-10 0.39g. yield 32%. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.82 (s, 6H, Ar-H), 4.21 (t, J=5.7Hz, 12H, OCH_2), 1.94 (S, 12H, OCH_2CH_2), 1.53-1.26 (m, 24H, CH_2), 0.96 (t, J=4.4Hz, 12H, CH_3). FT-IR (cm^{-1}): 3116, 2940, 2849, 1619, 1520, 1436, 1381, 1251, 1170.

$P_{3,6}$-08. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.82 (s, 6H, Ar-H), 4.22 (s, 12H, OCH_2), 1.94 (s, 12H, OCH_2CH_2), 1.56-1.44 (m, 24H, CH_2), 0.97 (d, J=6.6Hz, 12H, CH_3). FT-IR (cm^{-1}): 3086, 2950, 2855, 1609, 1507, 1448, 1388, 1269, 1166, 1029.

$P_{3,6}$-09. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.82 (s, 6H, Ar-H), 4.21 (d, J=5.7Hz, 12H, OCH_2), 1.94-1.84 (m, 12H, OCH_2CH_2), 1.56-1.44 (m, 26H, CH_2), 0.97 (t, J=6.6Hz, 12H, CH_3). FT-IR (cm^{-1}): 3086, 2925, 2848, 1618, 1516, 1430, 1380, 1260, 1166, 1038.

$P_{3,6}$-11. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.83 (s, 6H, Ar-H), 4.23 (s, 12H, OCH_2), 1.95 (s, 12H, OCH_2CH_2), 1.47-1.38 (m, 30H, CH_2), 0.99 (d, J=4.4Hz, 12H, CH_3). FT-IR (cm^{-1}): 3104, 2925, 2855, 1609, 1516, 1430, 1380, 1260, 1166, 1047.

$P_{3,6}$-12. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.82 (s, 6H, Ar-H), 4.22 (s, 12H, OCH_2), 1.94 (s, 12H, OCH_2CH_2), 1.55-1.41 (m, 32H, CH_2), 0.97 (t, J=6.6Hz, 12H, CH_3). FT-IR (cm^{-1}): 3095, 2932, 2848, 1618, 1516, 1430, 1388, 1269, 1158, 1047.

4. GPC, DSC, POM and X-Ray Diffraction Analyses

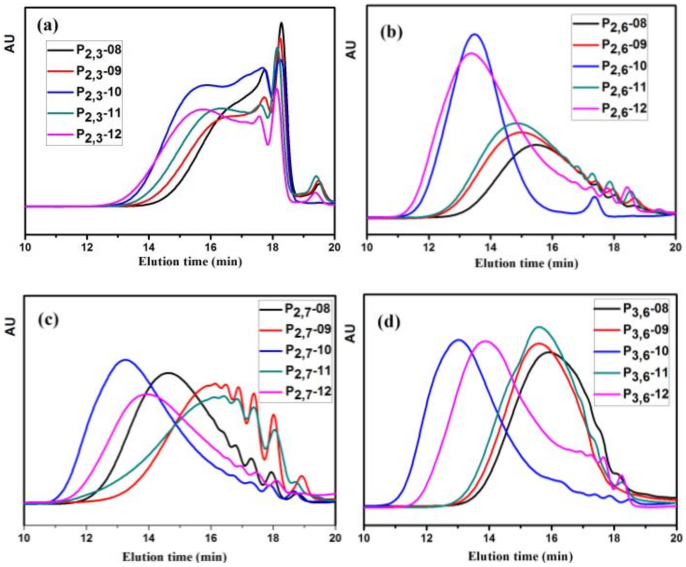


Fig. S1 Normalized GPC traces of the series polymers (a) $P_{2,3}$-n (b) $P_{2,6}$-n (c) $P_{2,7}$-n (d) $P_{3,6}$-n.

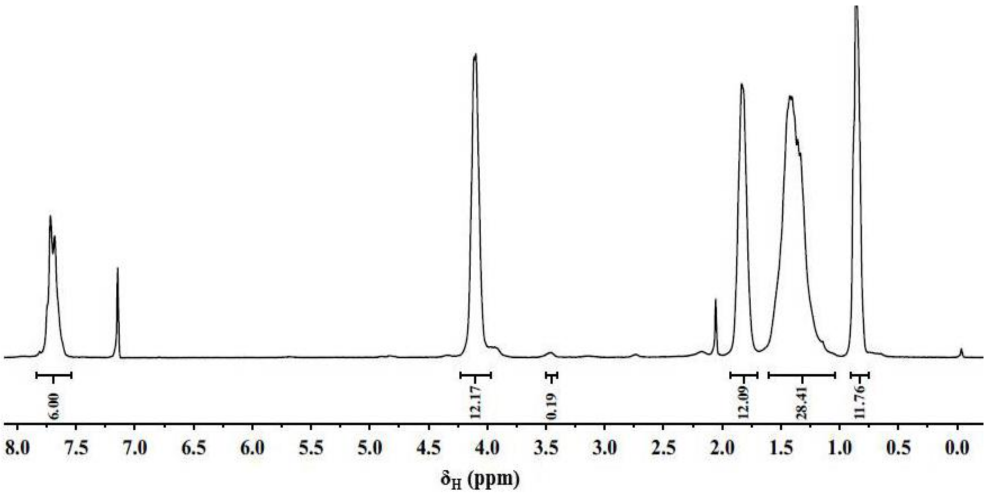


Fig. S2 ^{1}H NMR spectra of $P_{2,3}$-08

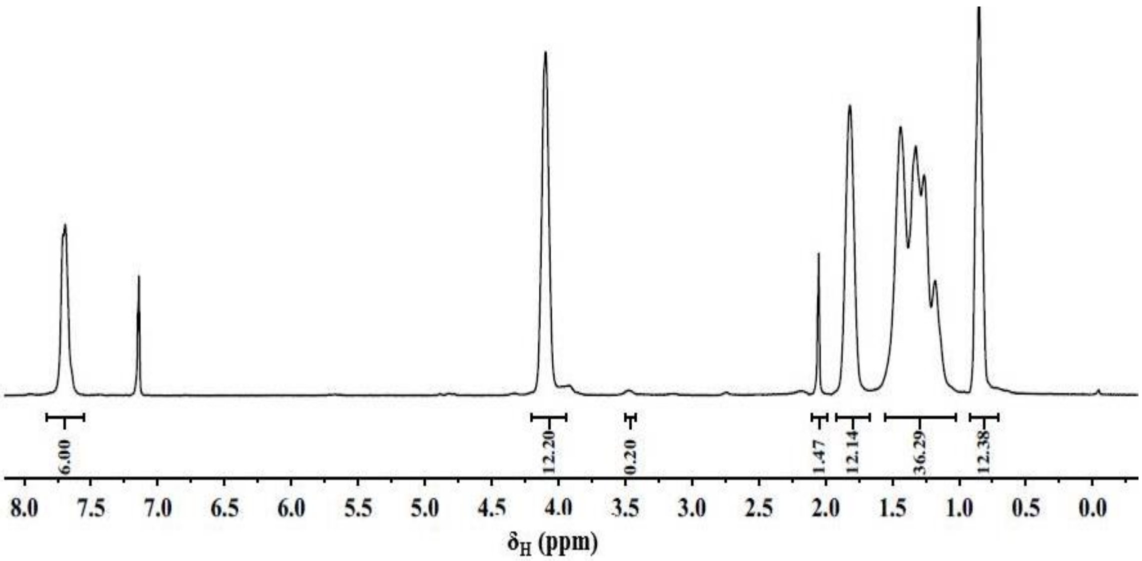


Fig. S3 ^{1}H NMR spectra of $P_{2,3}$-10

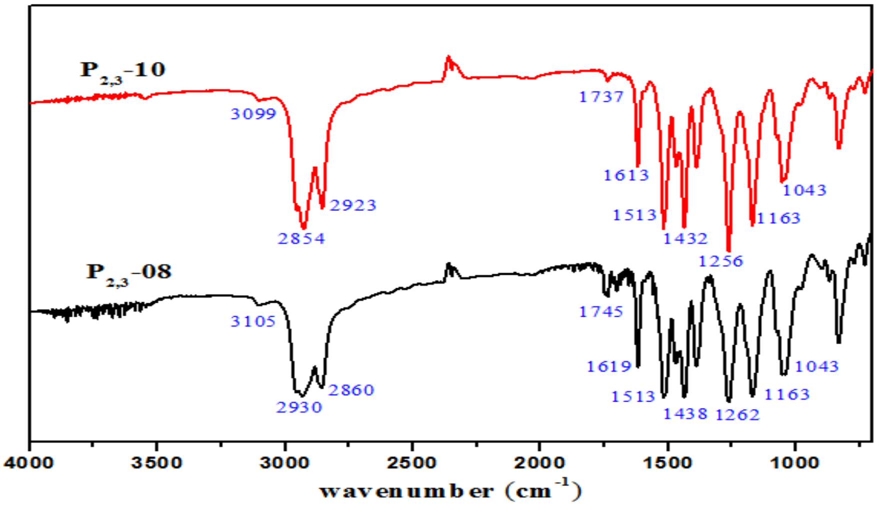


Fig. S4 FT-IR spectra of $P_{2,3}$-08 and $P_{2,3}$-10

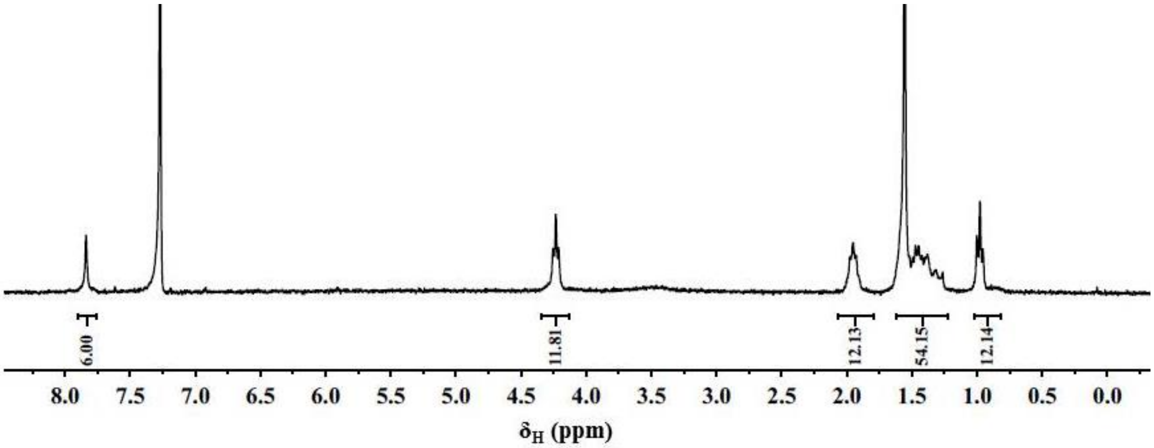


Fig. S5 ^{1}H NMR spectrum of $P_{3,6}$-09

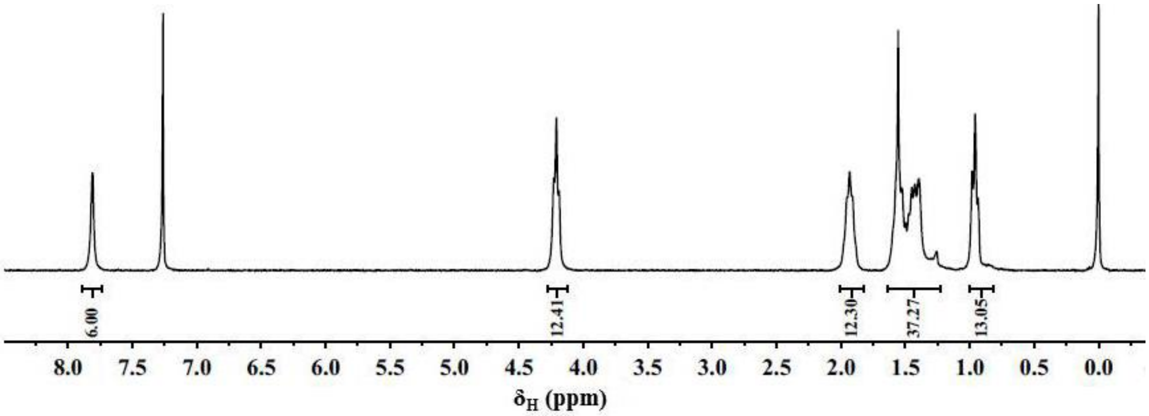


Fig. S6 ^{1}H NMR spectrum of $P_{3,6}$-10

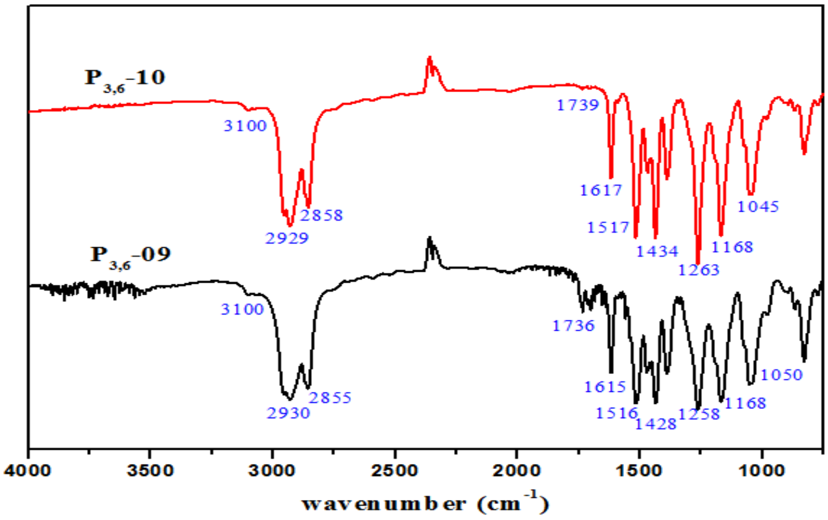


Fig. S7 FT-IR spectra of $P_{3,6}$-09 and $P_{3,6}$-10

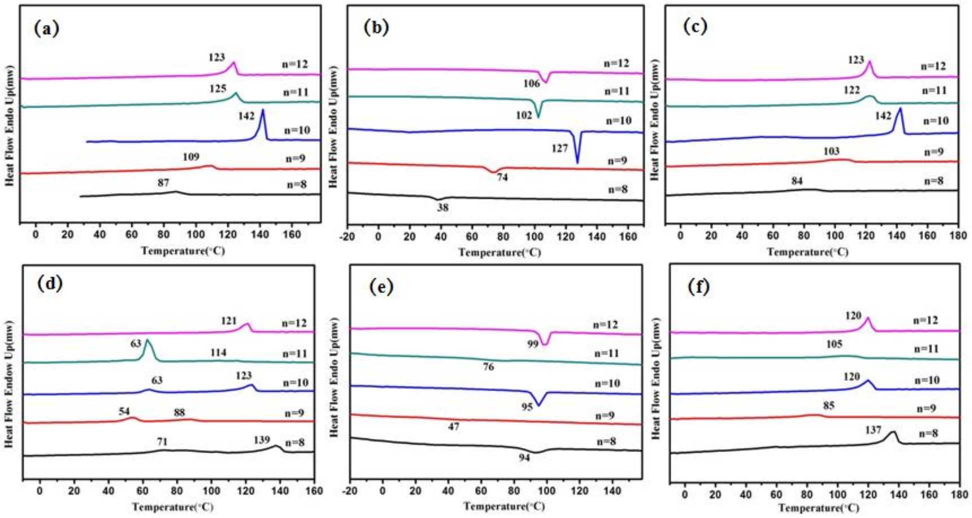


Fig. S8 DSC traces during first heating (a) and (d), first cooling (b) and (e), and second heating (c) and (f) of the series DLC polymers $P_{2,6}$-n and $P_{2,7}$-n, respectively, at a rate of 10 ℃ min^{-1}.

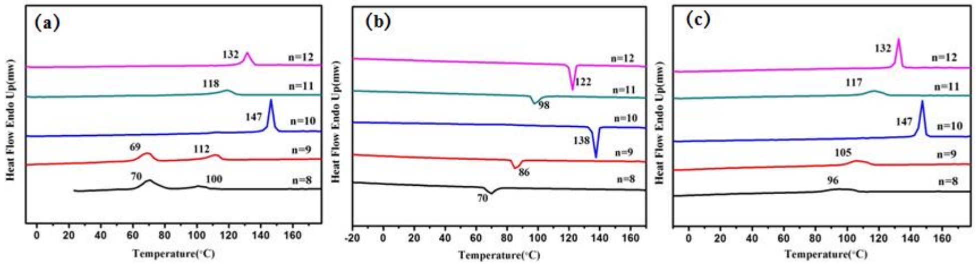


Fig. S9 DSC traces during first heating (a), first cooling (b), and second heating (c) of the series polymers $P_{3,6}$-n at a rate of 10 ℃ min^{-1}.

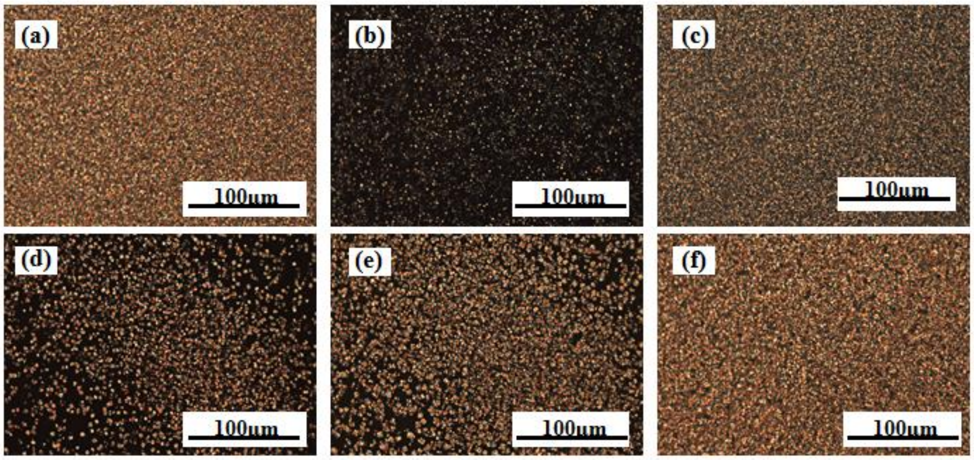


Fig. S10 Representative POM images: (a) $P_{2,3}$-10, 75 ℃; (b) $P_{2,3}$-11, 95 ℃; (c) $P_{2,3}$-11, 60 ℃; (d) $P_{2,3}$-12, 115 ℃; (e) $P_{2,3}$-12, 110 ℃; (f) $P_{2,3}$-12, 95 ℃ cooled from the isotropic melt state.

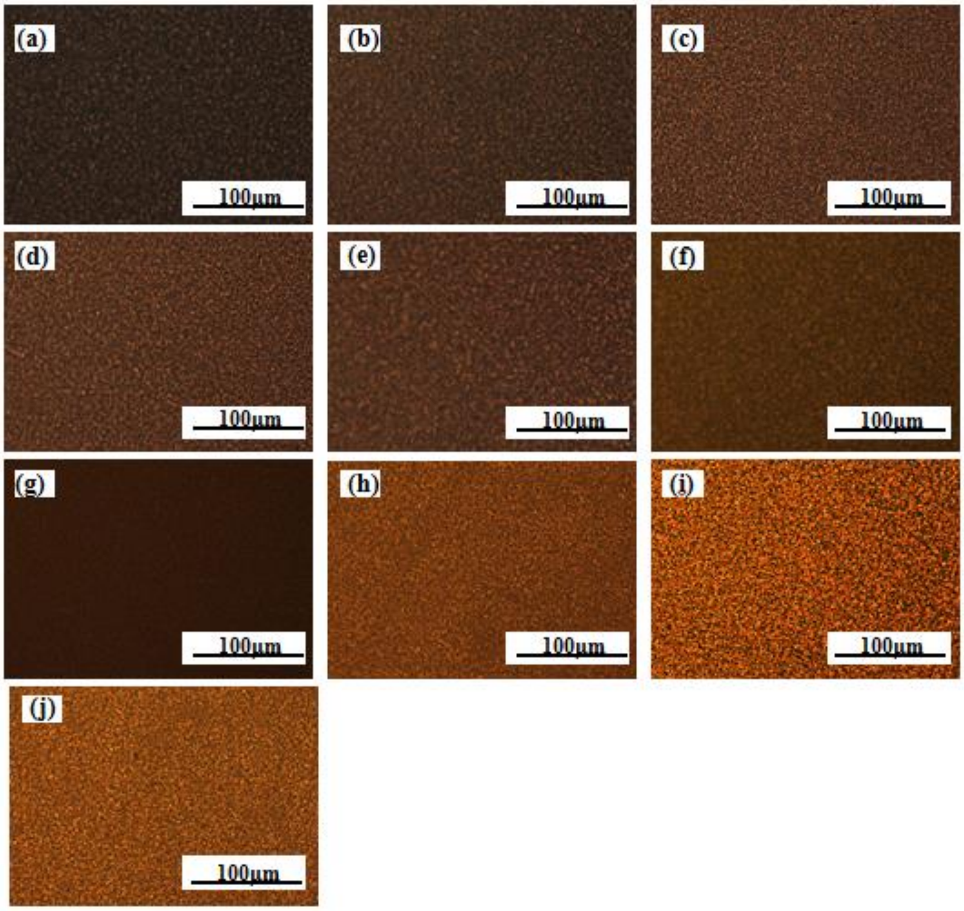


Fig. S11 Representative POM images: (a) $P_{2,6}$-08, 30 ℃; (b) $P_{2,6}$-09, 55 ℃; (c) $P_{2,6}$-10, 129 ℃; (d) $P_{2,6}$-11, 90 ℃; (e) $P_{2,6}$-12, 95 ℃; (f) $P_{2,7}$-08, 60 ℃; (g) $P_{2,7}$-09, 30 ℃; (h) $P_{2,7}$-10, 80 ℃; (i) $P_{2,7}$-11, 40 ℃; (j) $P_{2,7}$-12, 90 ℃ cooled from the isotropic melt state.

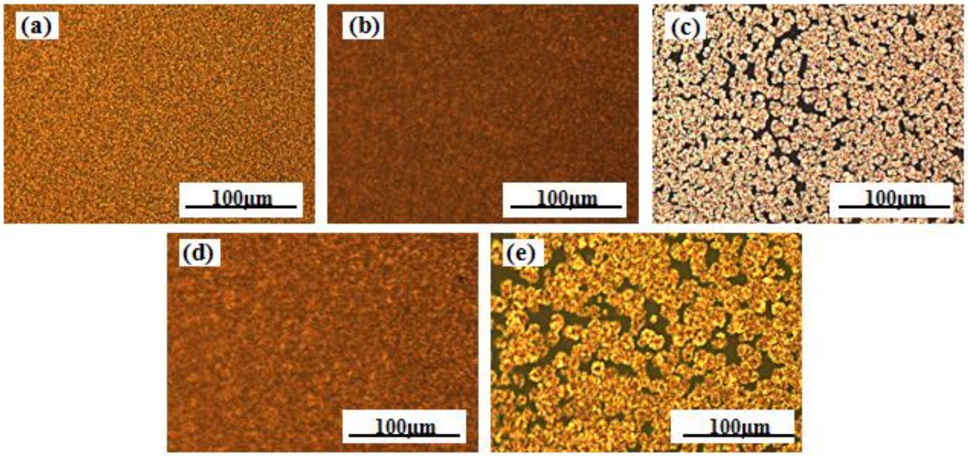


Fig. S12 Representative POM images: (a) $P_{3,6}$-08, 60 ℃; (b) $P_{3,6}$-09, 75 ℃; (c) $P_{3,6}$-10, 130 ℃; (d) $P_{3,6}$-11, 90 ℃; (e) $P_{3,6}$-12,115 ℃ cooled from the isotropic melt state.

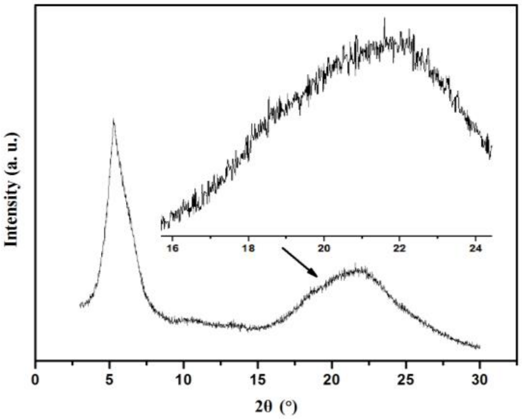


Fig. S13 1D WAXD powder patterns of $P_{2,3}$-08 obtained at 40 ℃ during the first heating.

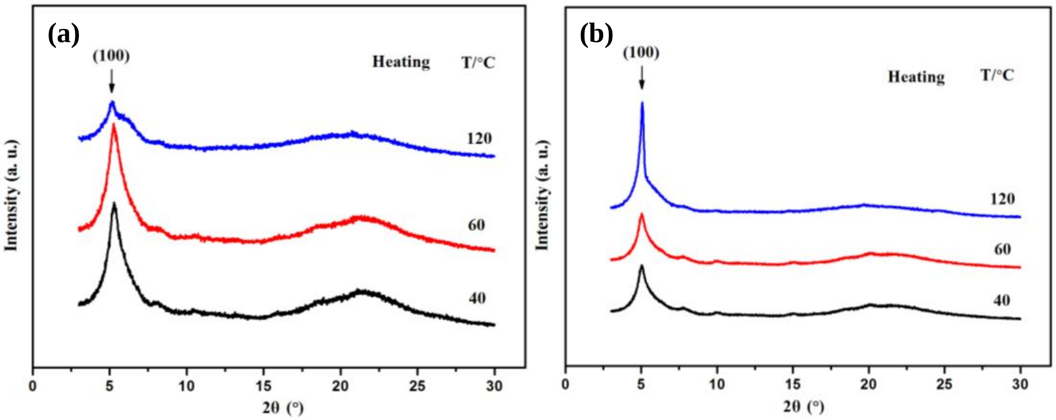


Fig. S14 1D WAXD powder patterns of $P_{2,3}$-09 (a) and $P_{2,3}$-11 (b) obtained during heating.

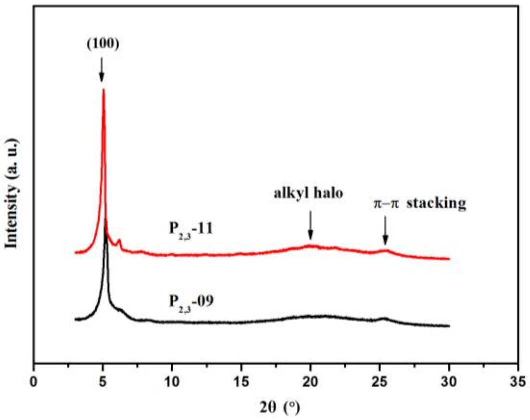


Fig. S15 1D WAXD powder patterns of $P_{2,3}$-09 and $P_{2,3}$-11obtained at 40 ℃ during cooling from the isotropic state.

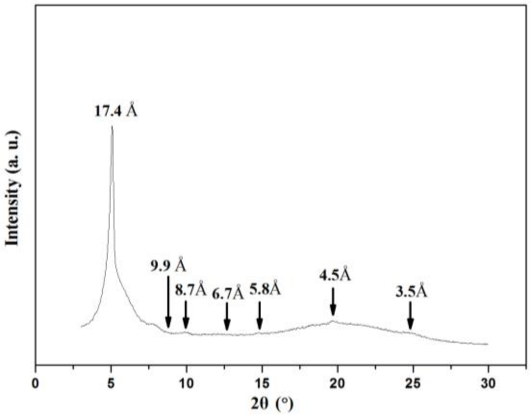


Fig. S16 1D WAXD powder pattern of $P_{2,3-}$11 at 90 ℃ during heating runs.

The assignments of crystalline phases of $P_{2,3}$-09 and $P_{2,3}$-11 were completely wrong. They should be specified as columnar phases **(Fig. S8)**. The diffractogram appeared reflections at 17.4, 9.9, 8.7, 6.7, 5.8 which were just corresponding to the characteristic ratio of $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}:1/\sqrt{9}$ for （10），（11），（20），(21), （30）, respectively as shown in **Fig. S9**. The diffractogram did not show any crystalline diffraction peaks demonstrate that the LC columnar phases of the two compounds can be preserved at room temperature.

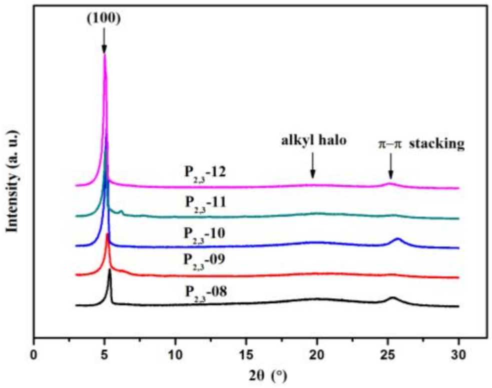


Fig. S17 1D WAXD powder patterns of $P_{2,3}$-n at 40 ℃ cooled from the isotropic state.

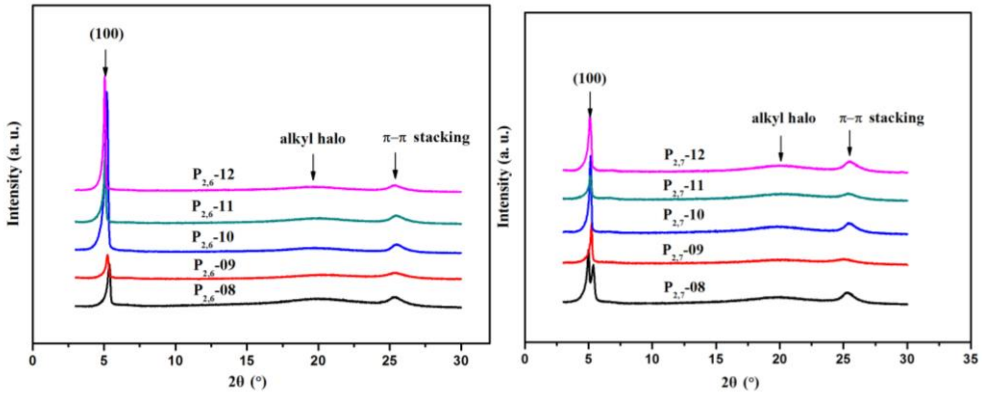
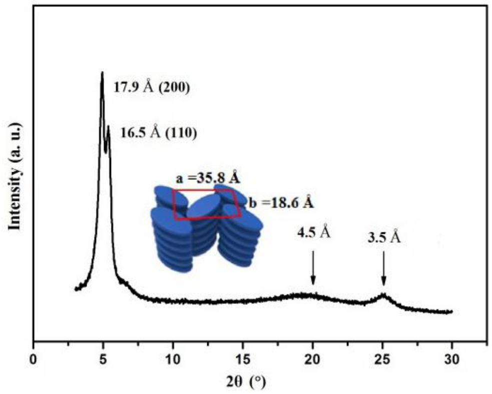


Fig. S18 1D WAXD powder patterns of $P_{2,6}$-n and $P_{2,7}$-n at 40°C cooled from the isotropic state.



$$1/d_{hkl}^{2}=h^{2}/a^{2}+k^{2}/b^{2}$$

Fig. S19 XRD pattern of $P_{2,7}$-08 at 80 ℃ on heating process and the supposed structure of Colr phase.

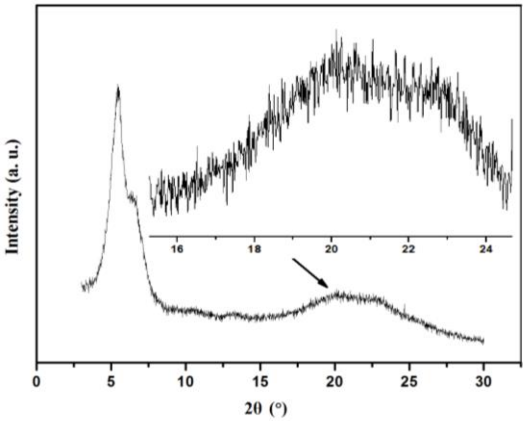


Fig. S20 1D WAXD powder patterns of $P_{2,7}$-08 obtained at 40 ℃ during the first heating.

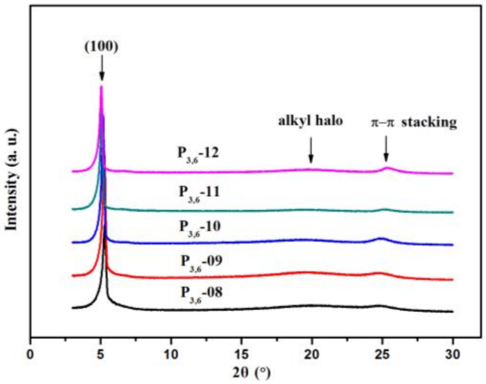


Fig. S21 1D WAXD powder patterns of $P_{3,6}$-n at 40 ℃ cooled from the isotropic state.

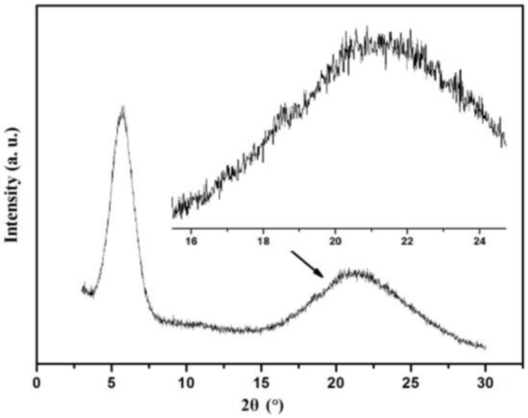


Fig. S22 1D WAXD powder patterns of $P_{2,7}$-08 obtained at 40 ℃ during the first heating.

Table S1 1D WAXD data of $P_{2,3}$-n at 40 ℃ cooled from the isotropic state.

Temperature/ ℃	d-spacing/Å	Miller Index (hkl)	Phase (lattice constants)
$P_{2,3}$-08	16.8	100	Col_h
	4.6		(a=19.4 Å)
	3.6	π-π	
$P_{2,3}$-09	17.0	100	
	4.5		(a=19.6 Å)
	3.5	π-π	
$P_{2,3}$-10	17.2	100	Col_h
	4.5		(a=19.9 Å)
	3.6	π-π	
$P_{2,3}$-11	17.5	100	
	4.4		(a=20.2 Å)
	3.5	π-π	
$P_{2,3}$-12	17.6	100	Col_h
	4.4		(a=20.3 Å)
	3.5	π-π	

Table S2 1D WAXD data of $P_{2,6}$-n at 40 ℃ cooled from the isotropic state.

Temperature/ ℃	d-spacing/Å	Miller Index (hkl)	Phase (lattice constants)
$P_{2,6}$-08	16.5	100	Col_h
	4.4		(a=19.0 Å)
	3.5	π-π	
$P_{2,6}$-09	16.8	100	Col_h
	4.5		(a=19.4 Å)
	3.5	π-π	
$P_{2,6}$-10	17.0	100	Col_h
	4.4		(a=19.6 Å)
	3.5	π-π	
$P_{2,6}$-11	17.4	100	Col_h
	4.5		(a=20.1 Å)
	3.5	π-π	
$P_{2,6}$-12	17.5	100	Col_h
	4.4		(a=20.2 Å)
	3.5	π-π	

Table S3 1D WAXD data of $P_{2,7}$-n at 40 ℃ cooled from the isotropic state.

Temperature/ ℃	d-spacing/Å	Miller Index (hkl)	Phase (lattice constants)
$P_{2,7}$-08	17.7	200	Col_r
	16.4	110	(a=35.4Å)
	4.5		(b=18.5Å)
	3.5	π-π	
$P_{2,7}$-09	16.8	100	Col_h
	4.4		(a=19.4 Å)
	3.5	π-π	
$P_{2,7}$-10	17.1	100	Col_h
	4.5		(a=19.7 Å)
	3.5	π-π	
$P_{2,7}$-11	17.2	100	Col_h
	4.4		(a=19.9 Å)
	3.5	π-π	
$P_{2,7}$-12	17.3	100	Col_h
	4.5		(a=20.0 Å)
	3.5	π-π	

Table S4 1D WAXD data of $P_{3,6}$-n at 40 ℃ cooled from the isotropic state.

Temperature/ ℃	d-spacing/Å	Miller Index (hkl)	Phase (lattice constants)
$P_{3,6}$-08	16.4	100	Col_h
	4.4		(a=18.9 Å)
	3.6	π-π	
$P_{3,6}$-09	16.7	100	Col_h
	4.5		(a=19.3Å)
	3.5	π-π	
$P_{3,6}$-10	17.1	100	Col_h
	4.6		(a=19.7 Å)
	3.6	π-π	
$P_{3,6}$-11	17.3	100	Col_h
	4.5		(a=20.0 Å)
	3.5	π-π	
$P_{3,6}$-12	17.6	100	Col_h
	4.5		(a=20.3 Å)
	3.5	π-π	

5. Some ^{1}H NMR and HRMS spectra

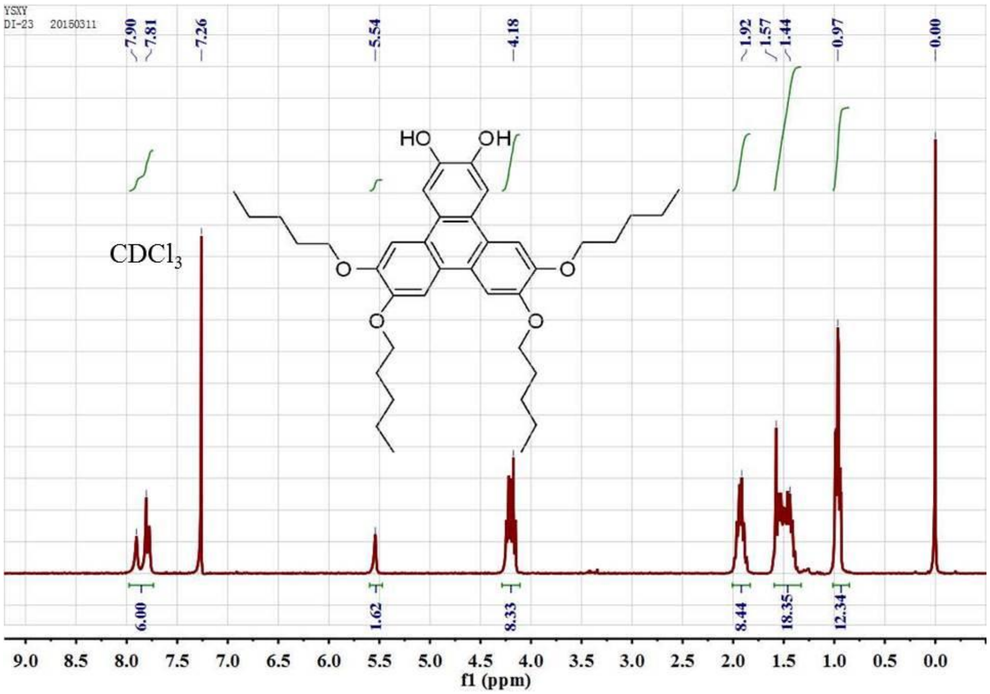


Fig. S23 ^{1}H NMR spectrum of compound **5**.

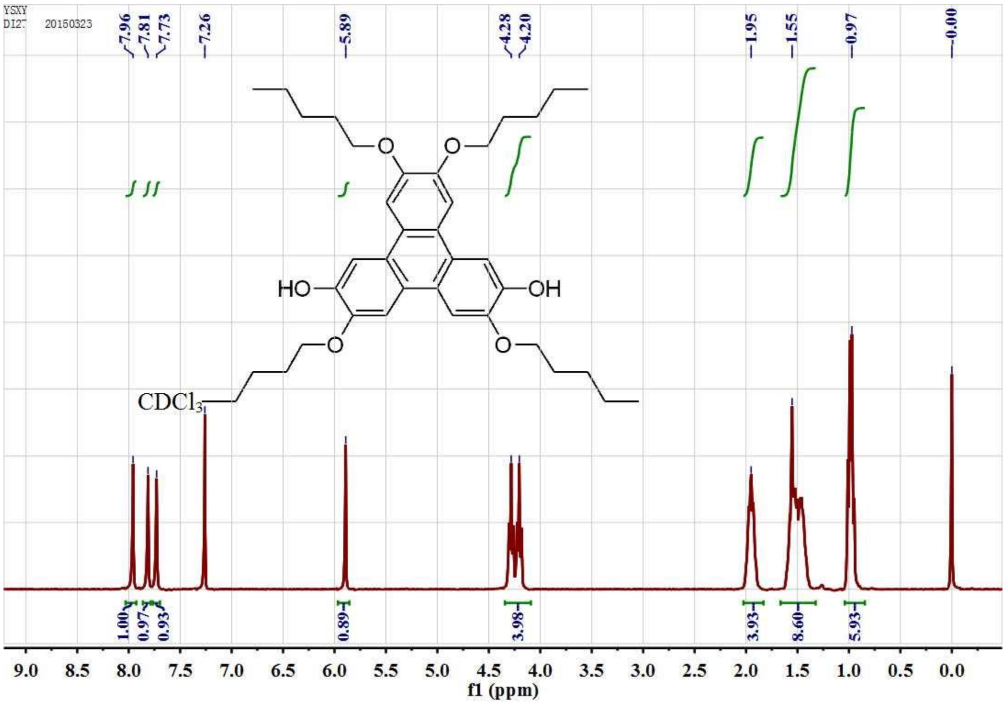


Fig. S24 ^{1}H NMR spectrum of compound **13**.

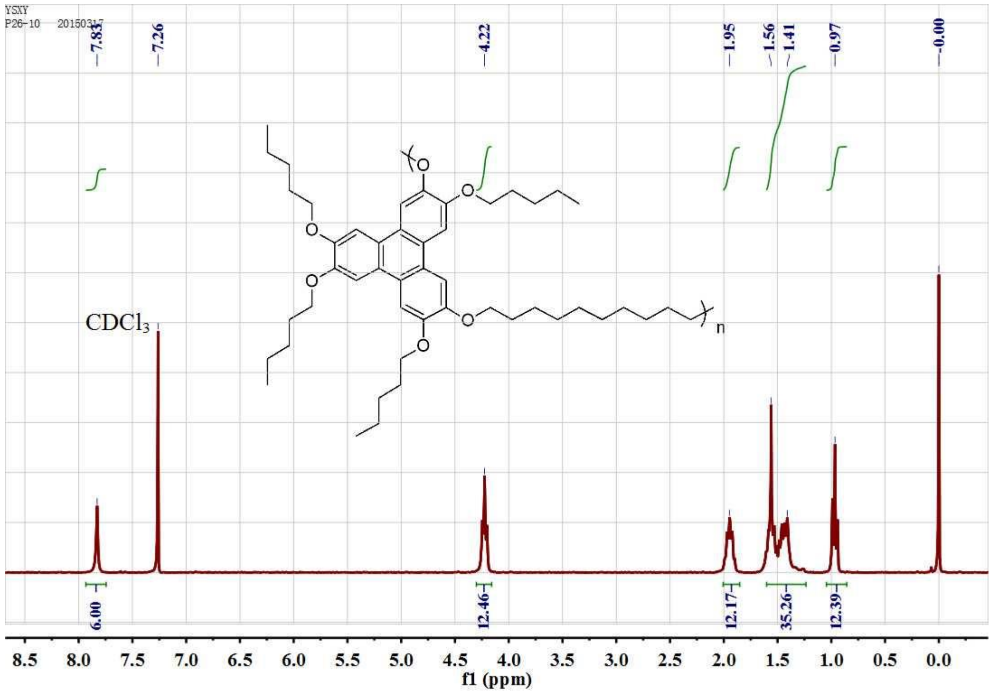


Fig. S25 ^{1}H NMR spectrum of polymer **$P_{2,6}$-10**.

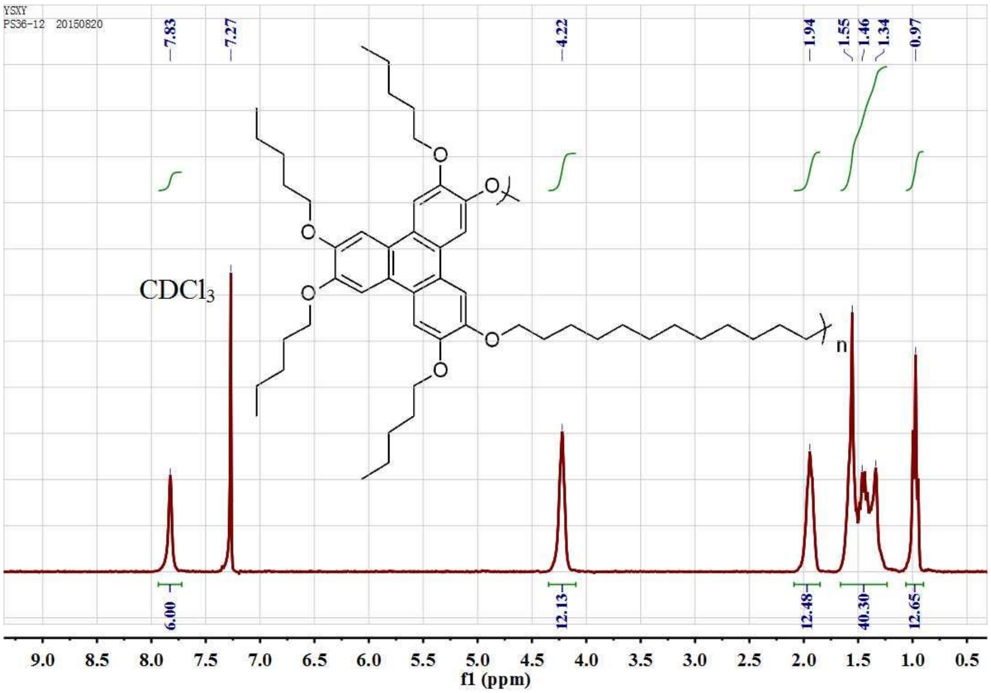


Fig. S26 ^{1}H NMR spectrum of polymer **$P_{3,6}$-12**.

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
1	C38H52O6	C38H51O6-	603.3702	603.3691	1.82

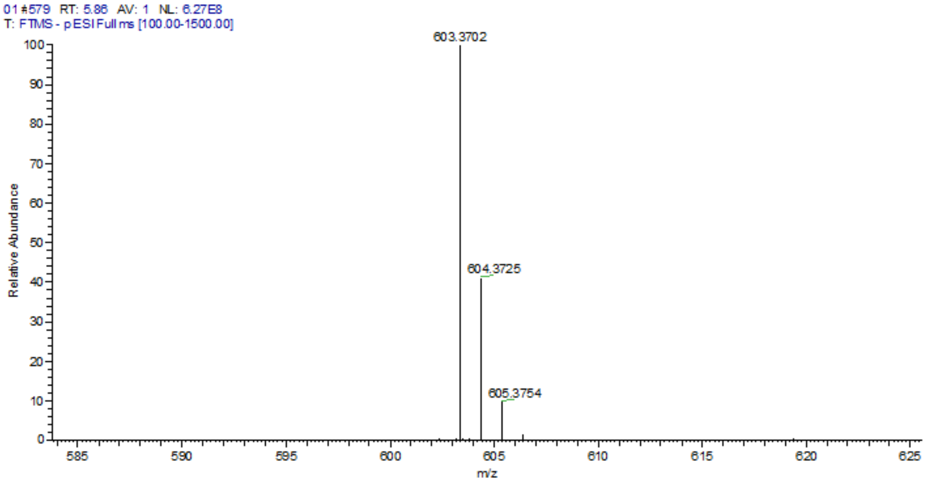


Fig. S27 HRMS spectrum of **5**.

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
2	C38H52O6	C38H51O6-	603.3698	603.3691	1. 16

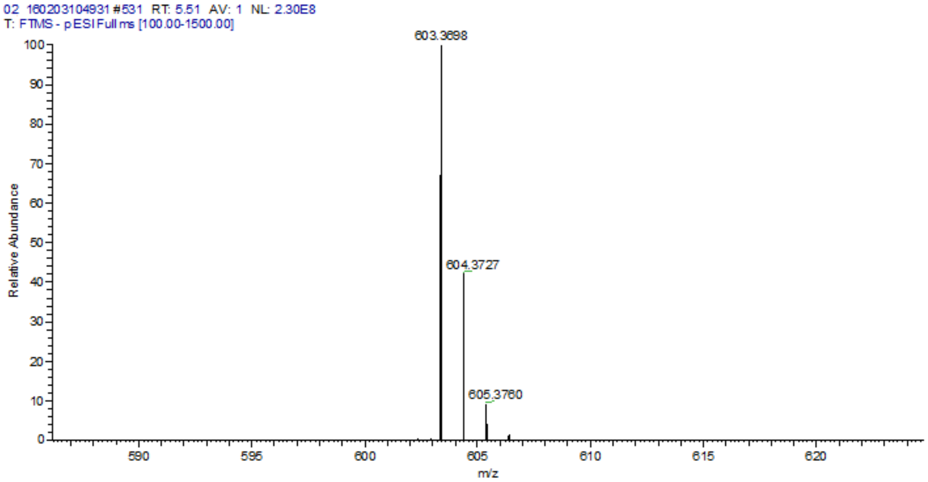


Fig. S28 HRMS spectrum of **7**.

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
3	C7H7IO2	C7H6IO2-	248.9417	248.9418	−0. 40

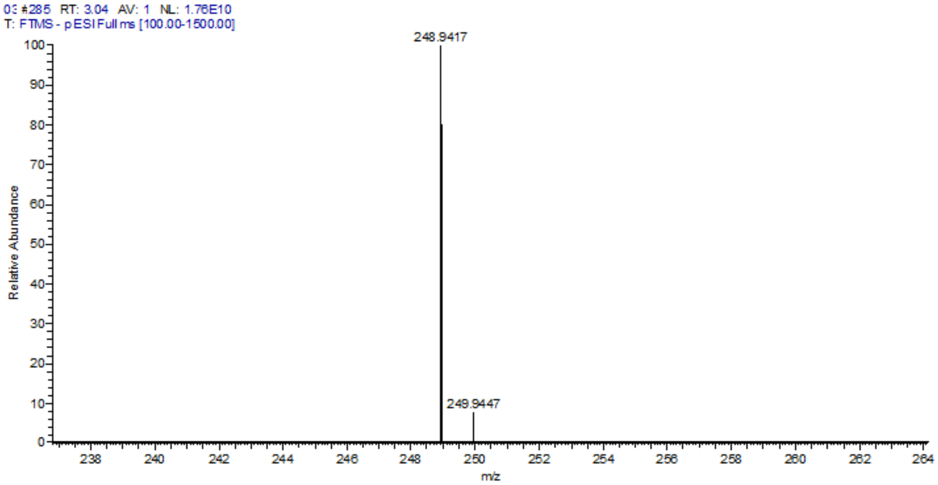


Fig. S29 HRMS spectrum of **9**.

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
4	C12H17IO2	[C12H17IO2]+.	320.0268	320.0268	0

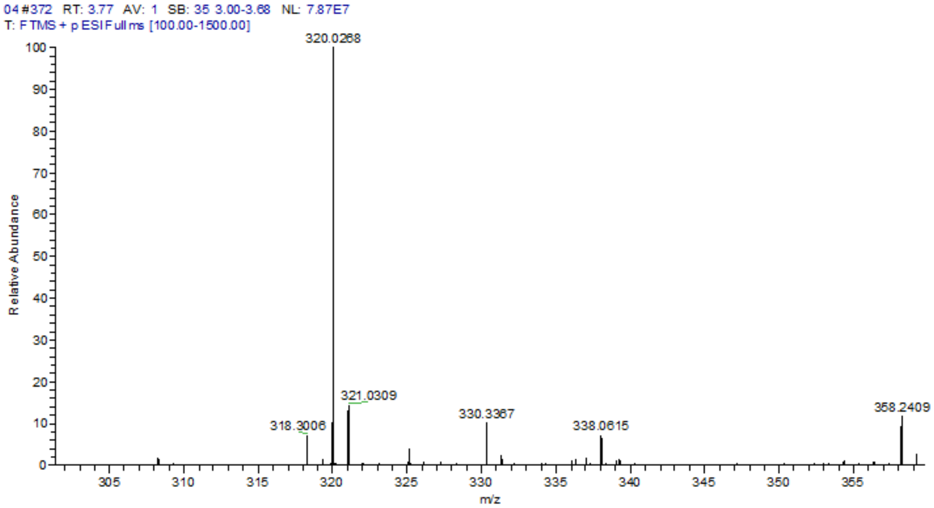


Fig. S30 HRMS spectrum of **10**.

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
5	C24H34O4	C24H35O4+	387.2527	387.2530	−0. 77

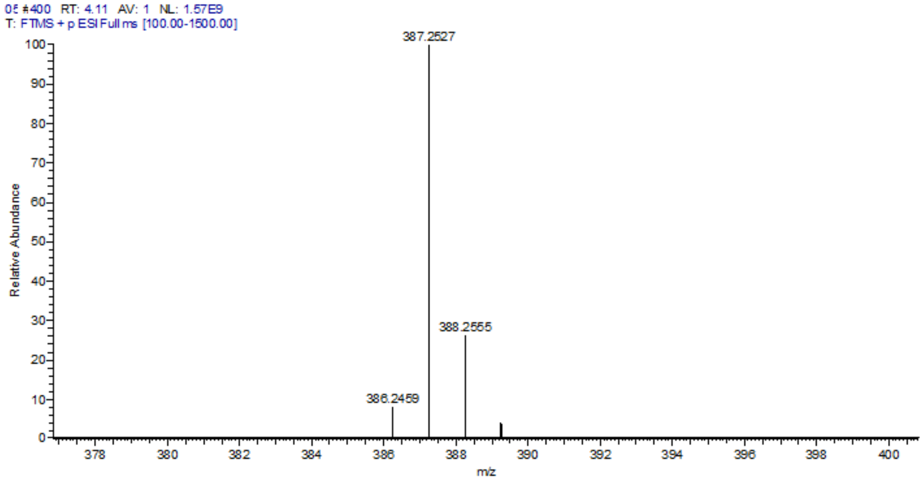


Fig. S31 HRMS spectrum of **11**.

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
6	C40H56O6	[C40H56O6]+.	632.4070	632.4071	−0. 16

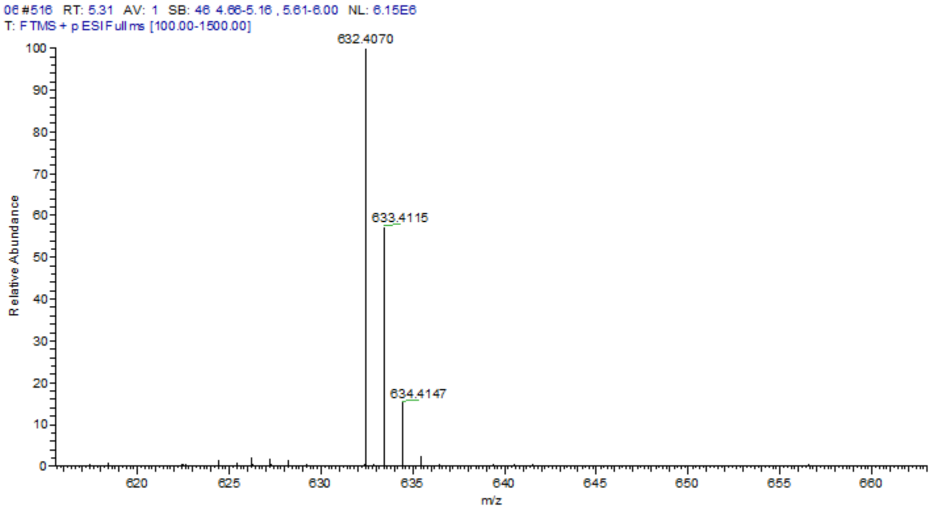


Fig. S32 HRMS spectrum of **12**.

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
7	C38H52O6	C38H51O6-	603.3699	603.3691	1. 33

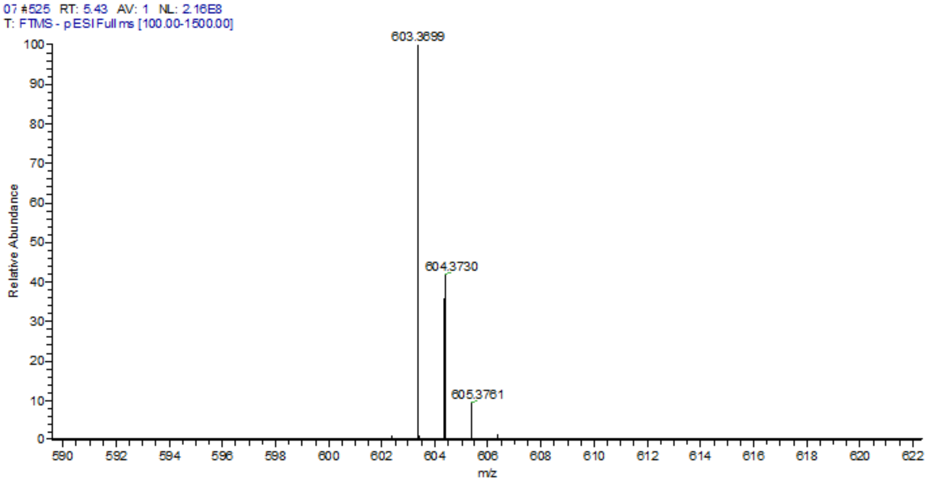
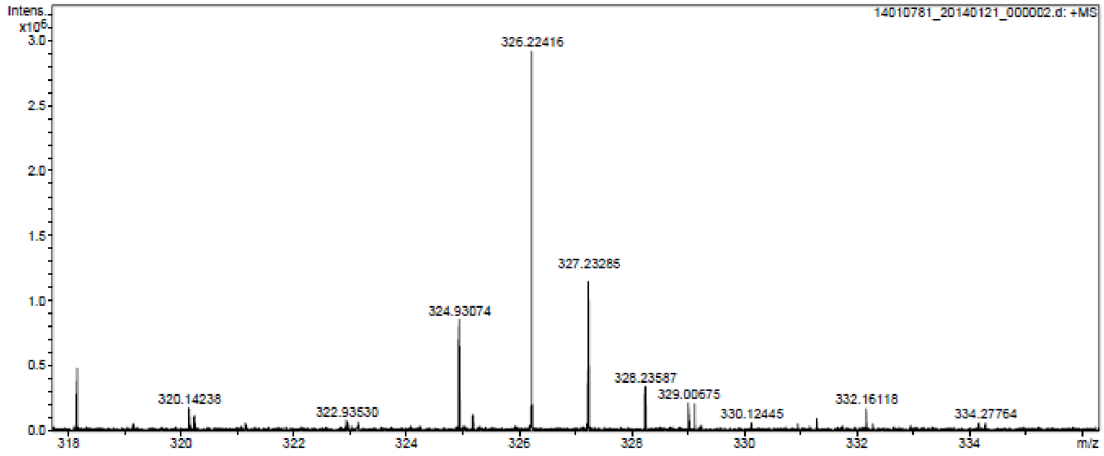
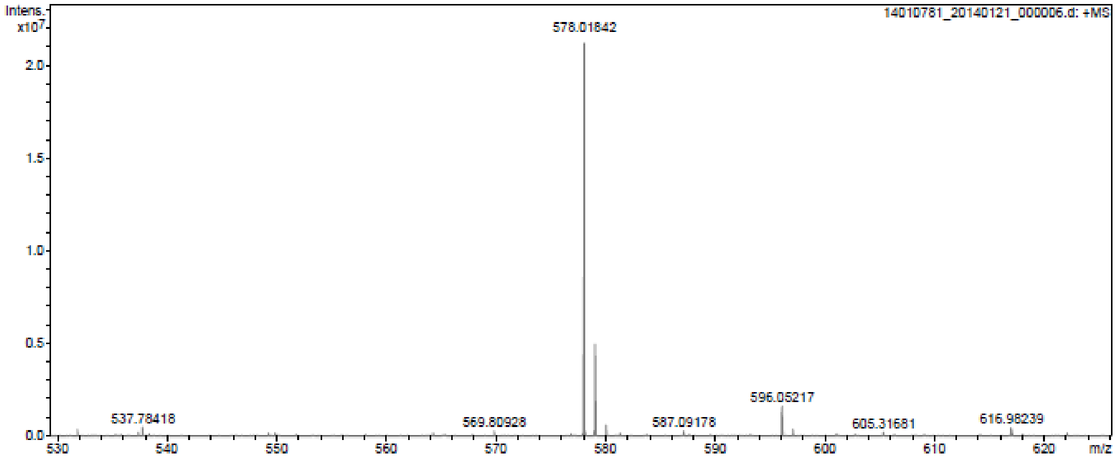


Fig. S33 HRMS spectrum of **13**.



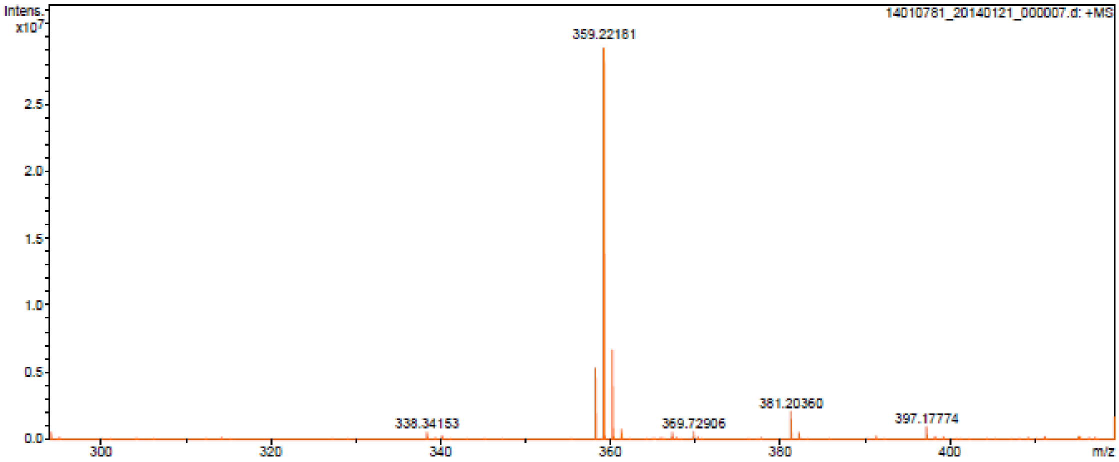
Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
326.22416	2927073	C 22 H 30 O 2	326.22403	-0.1	-0.4	34.4	8.0	odd	ok

Fig. S34 HRMS spectrum of **14**.



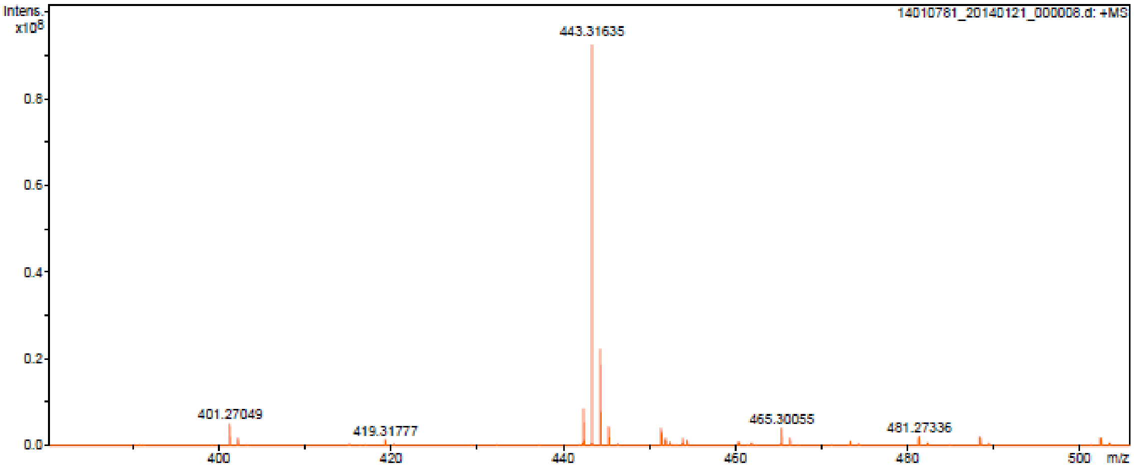
Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
578.01842	21571742	C 22 H 28 I 2 O 2	578.01732	-1.1	-1.9	4.0	8.0	odd	ok

Fig. S35 HRMS spectrum of **15**.



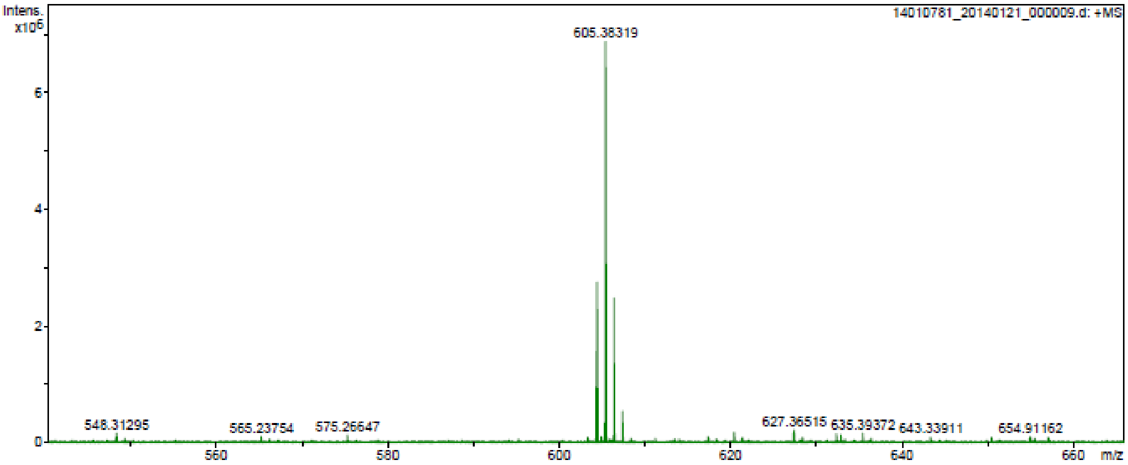
Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
359.22181	29613424	C 22 H 31 O 4	359.22169	-0.1	-0.3	9.8	7.5	even	ok

Fig. S36 HRMS spectrum of **16**.



Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
443.31635	93714856	C 28 H 43 O 4	443.31559	-0.8	-1.7	32.2	7.5	even	ok

Fig. S37 HRMS spectrum of **17**.



Meas. m/z	I	Formula	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
605.38319	6898699	C 38 H 53 O 6	605.38367	0.5	0.8	25.5	12.5	even	ok

Fig. S38 HRMS spectrum of **18**.

6. References for Supporting Information

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