Electronic Supplementary Information (ESI)

Synthesis and application of dithienobenzodithiophene in conjugated polymer

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Experimental

Materials:

4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene and the TT monomers were purchased from Solarmer Materials Inc.. Tetrahydrofuran (THF) was dried over Na/benzophenone and freshly distilled prior to use. [$Pd(PPh_3)_4$] was purchased from Frontiers Scientific Inc. All of these chemicals were used as received. The other materials are common commercial level and used as received.

Instruments:

^{1}H and ^{13}C NMR spectra were measured on a Bruker arx-400 and a Bruker arx-300 spectrometer using tetramethylsilane as an internal standard. Absorption spectra were taken on a Hitachi U-3010 UV-Vis spectrophotometer. The molecular weight of polymers was measured by the GPC method, and polystyrene was used as a standard by using THF as eluent. TGA measurements were performed on PE Inc., Pyris 1. DSC measurements were performed on METTLER Inc., DSC-822e. The electrochemical cyclic voltammetry experiments were conducted on a CHI650D Electrochemical Workstation with glassy carbon disk, Pt wire, and a Ag/Ag^+ electrode as the working electrode, counter electrode, and reference electrode, respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. AFM measurements were performed on Bruker veeco MultiMode 8 Atomic Force Microscope, and TEM measurements were performed on Transmission Electron Microscopes (TEM): JEM-2200FS.

Synthesis

2,3,6,7-tetrabromo-4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene

To a solution of 4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene (4 mmol, 2.7 g) in 30 mL of $CHCl_3$ was added dropwise a solution of Br_2 (24 mmol, 3.8 g) in 20 mL of $CHCl_3$. The reaction mixture was stirred at room temperature for 24 h and then was poured into a saturated sodium thiosulphate solution. The organic phase was extracted with CH_2Cl_2 (3×50 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel with Hex as eluent to give 2,3,6,7-tetrabromo-4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene as white solid (3.52 g, 89%).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (d, J = 6.4 Hz, 2H), 2.17 – 1.94 (m, 1H), 1.66 – 1.18 (m, 24H), 0.90 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.27, 132.35, 128.14, 116.72, 107.13, 79.72, 77.42, 77.10, 76.78, 38.97, 32.01, 31.10, 30.18, 29.86, 29.74, 29.46, 26.93, 26.89, 22.79, 14.24. Melting point: 53 ^{0}C

3,7-dibromo-4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-dicarbaldehyde

2,3,6,7-tetrabromo-4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene (3.52 g, 3.56 mmol) and 150 ml THF were added into a flask under an inert atmosphere. The solution was cooled down to -78 ^{0}C by a nitrogen-acetone bath, and 2.8 ml of n-BuLi (2.5 M in hexanes, 7.1 mmol) was added dropwise. After being stirred at -78 ^{0}C for 30min, *N*-Formylpiperidine (11 mmol, 1.1g) was added in one portion. The cooling bath was removed, and the reactant was allowed to warm to room temperature and stirred at this temperature for another 1 h. 200 ml water was added and the mixture was extracted by CH_2Cl_2 (3×50 mL), and the organic phases were combined and dried over $MgSO_4$. After removing solvent under vacuum, the residue was purified by flash chromatography on silica gel with Hex/DCM =5:1 as eluent to give 3,7-dibromo-4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-dicarbaldehyde as red solid (2.83 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 2H), 4.08 (d, J = 6.6 Hz, 4H), 2.36 – 1.97 (m, 2H), 1.84 – 1.07 (m, 48H), 1.03 – 0.71 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.43, 147.82, 138.95, 133.15, 131.46, 114.16, 80.07, 77.42, 77.10, 76.78, 39.09, 32.00, 31.10, 30.16, 29.84, 29.73, 29.44, 26.98, 26.94, 22.78, 14.22. Melting point: 58 ^{0}C

5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-dicarboxylic acid ester

To a solution of 3,7-dibromo-4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-dicarbaldehyde (2.83 g, 3.2 mmol), K_2CO_3 (12.8 mmol,1.77 g) and DMF (150 ml) in a 250 ml round-bottom flask under an argon atmosphere, at 60 ^{0}C, was added ethyl mercaptoacetate (0.77 g, 6.4mmol) dropwise. The mixture was kept at 60 ^{0}C overnight and then was cooled to room temperature. Water (500 mL) was added and the organic phase was extracted with CH_2Cl_2 (3×50 mL). The organic phases were combined and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel with Hex/DCM =5:1 as eluent to give 5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-dicarboxylic acid ester as red solid (2.5 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 2H), 4.42 (q, *J* = 7.1 Hz, 4H), 4.25 (d, *J* = 6.0 Hz, 4H), 2.09 (s, 2H), 1.75 – 1.20 (m, 54H), 0.89 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.42, 144.62, 137.26, 137.20, 132.02, 125.95, 125.78, 77.42, 77.11, 76.79, 76.53, 61.56, 39.43, 32.02, 31.99, 31.24, 30.17, 29.83, 29.74, 29.45, 27.01, 26.98, 22.79, 14.46, 14.23. Melting point: 97 ^{0}C

5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-dicarboxylic acid

5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-dicarboxylic acid ester (2.5 g, 2.7 mmol) was mixed with NaOH (10%, 30 mL water solution), THF (30 mL), MeOH (30 mL) in a 250 ml round-bottom flask. The mixture was refluxed overnight and then poured into 300 mL HCl (1M solution).The solid formed was filtered and washed with water several times. The solid then was vacuum dried and was not further purified to give 5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-dicarboxylic acid as yellow solid (2.2 g, 98%).

5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene

A solution of 5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-dicarboxylic acid (2.2 g, 2.5 mmol), copper powder (1.2 g) and quinoline (50 mL) were heated at 180 ^{0}C. After the reaction was completed (about 1 h), the mixture was cooled to room temperature and poured into 100 mL HCl (1M solution). The organic phase was extracted with CH_2Cl_2 (3×50 mL) and the organic phases were combined and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel with Hex/DCM =5:1 as eluent to give 5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-b:4,5-b']dithiophene as yellow oil (1.37 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 5.1 Hz, 1H), 7.32 (d, *J* = 5.1 Hz, 1H), 4.22 (d, *J* = 5.9 Hz, 2H), 2.08 (m, 1H), 1.75 – 1.20 (m, 24H), 0.99 – 0.82 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.86, 137.31, 132.02, 131.94, 129.45, 125.34, 119.97, 77.42, 77.10, 76.79, 76.52, 39.44, 32.02, 31.31, 30.20, 29.87, 29.74, 29.47, 27.03, 22.81, 14.25.

(5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-diyl)bis(trimethylstannane)

5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene (0.4 g, 0.5 mmol) and 10 ml THF were added into a flask under an inert atmosphere. The solution was cooled down to -78 ^{0}C by a nitrogen-acetone bath, and 0.75 ml of LDA (2.0 M in hexanes, 1.5 mmol) was added dropwise. After being stirred at -78 ^{0}C for 1h, 1.75 ml of trimethylchlorostannane (1.0 M in THF, 1.75 mmol) was added in one portion. The mixture was stirred at this temperature for 10 min and then the cooling bath was removed. The reactant was allowed to warm to room temperature and 1 h later, 50 ml water was added and the mixture was extracted by ether (3×50 mL), and the organic phases were combined. After removing solvent under vacuum, the residue was pure enough for the next step. (0.44 g, 80%). ^{1}H NMR (400 MHz, Acetone) δ 7.50 (s, 1H), 4.22 (d, *J* = 5.8 Hz, 2H), 2.06 – 2.02 (m, 1H), 1.77 – 1.18 (m, 24H), 0.87 (m, 6H), 0.56 – 0.36 (m, 9H). ^{13}C NMR (101 MHz, Acetone) δ 145.03, 139.40, 127.34, 78.39, 76.18, 39.39, 31.87, 31.32, 31.27, 30.02, 29.78, 29.72, 29.61, 29.41, 29.22, 29.03, 28.84, 28.65, 28.45, 26.98, 22.59, 22.56, 13.63, 13.60, -8.87.

2,7-dibromo-5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene

5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene (0.17 g, 0.2 mmol) and 10 ml $CHCl_3$ were added into a flask under an inert atmosphere. The solution was cooled by ice-water bath, and a solution of NBS (0.09g, 0.5 mmol) in 2 mL DMF was added dropwise. After being stirred at 0 ^{0}C for 1h, the reaction mixture was poured into a saturated sodium sulfite solution (50mL). The organic phase was extracted with ether (3×50 mL), the organic phases were combined and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel with Hex as eluent to give 2,7-dibromo-5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene as white oil (0.13g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (s, 2H), 4.14 (s, 4H), 2.14 – 1.86 (m, 2H), 1.74 – 1.14 (m, 48H), 1.01 – 0.75 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.54, 135.94, 132.13, 130.13, 125.24, 122.60, 115.75, 77.58, 77.15, 76.73, 76.25, 39.45, 32.10, 31.26, 30.25, 29.92, 29.84, 29.56, 27.08, 22.89, 22.87, 14.32, 14.30.

Synthesis of the Polymer Using Stille Coupling Reaction.

A mixture of (5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-diyl)bis(trimethylstannane) (0.22 g, 0.2 mmol), TT-C (0.088 g, 0.2 mmol), in toluene (10 ml) and DMF (2 ml) were purged by argon for 30 minutes, and then 20 mg of $Pd(PPh_3)_4$ was added. After being purged for another 20 minutes, the mixture was allowed to reflux for 10 h. After cooled to room temperature the polymer was precipitated in methanol. The crude product was collected by filtration and then purified by washing extracted on a soxhlet's extractor with methanol, hexane in succession. The final product was obtained by precipitating the chloroform solution in methanol as dark blue powder. Anal. Caled for $C_{61}H_{86}O_3S_6$ (%): C, 69.14 %; H, 8.18 %. Found: C, 68.23 %; H, 8.25 %.

Device fabrications

OSCs with device structures of glass/ITO/PEDOT:PSS/PDTT:$PC_{71}BM$/Ca/Al was fabricated as follows: A 30 nm layer of PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) was spin-coated onto a pre-cleaned ITO (indium-tin oxide) glass substrates, and then the substrates were transferred into a nitrogen filled glovebox. A mixture of polymer/$PC_{71}BM$ in dichlorobenzene was spin-coated as a film on the top of the PEDOT:PSS layer. The thickness of the active layer was 70~75 nm. The devices were completed by evaporating and 19 nm thick of Ca layer and 75 nm thick of Al layer with an area of 4 mm^2 as defined by masks were used as metal electrodes.

Hole mobility measurement

The device was fabricated in a structure of glass/ITO/PEDOT:PSS/PDTT:$PC_{71}BM$/Au for the hole mobility measurement based on the space-charge-limited current (SCLC) model.

According to the equation:

$$\ln\frac{JL^3}{V^2} = 0.89\left(\frac{1}{E_0}\right)^{0.5}\left(\frac{V}{L}\right)^{0.5} + \ln\left(\frac{9\varepsilon\varepsilon_0\mu_0}{8}\right)$$

Where μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, ε is the dielectric constant of the polymer, ε_0 is the permittivity of the vacuum, L is the thickness of the polymer layer, $V = V_{appl} - V_{bi}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential (in this device structure, $V_{bi} = 0.2$ V).

The hole mobility can be calculated as $1.57\times10^{-3} cm^2V^{-1}s^{-1}$.

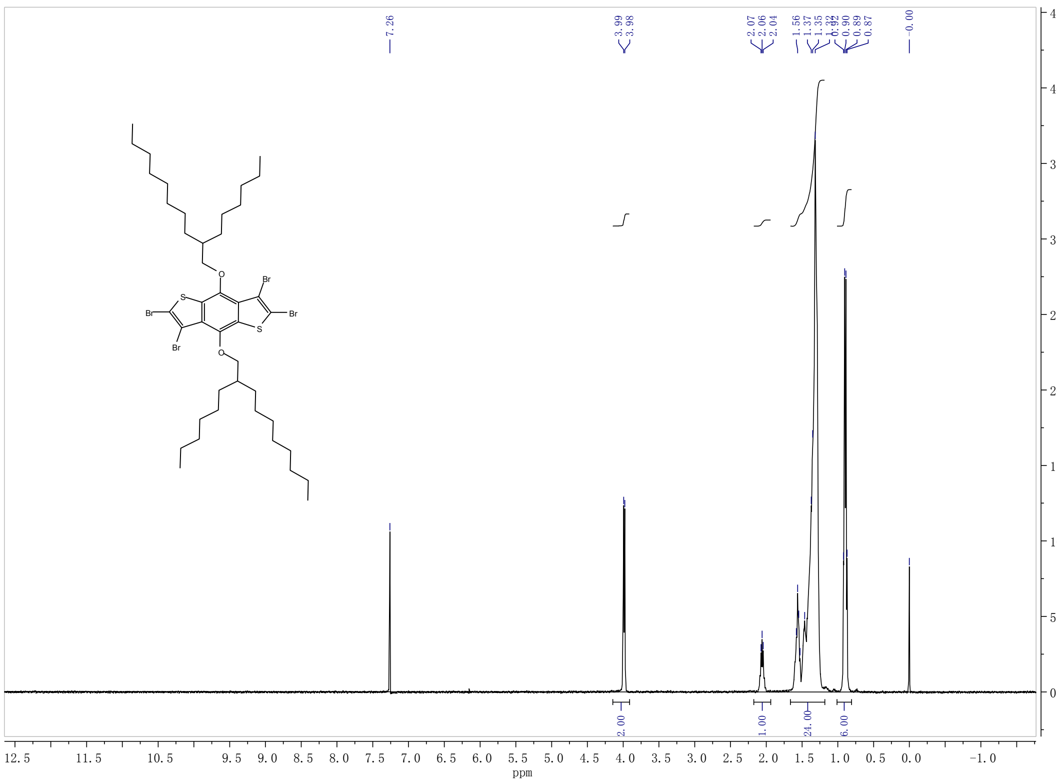

Fig. S1 ^{1}H spectra of 2,3,6,7-tetrabromo-4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene

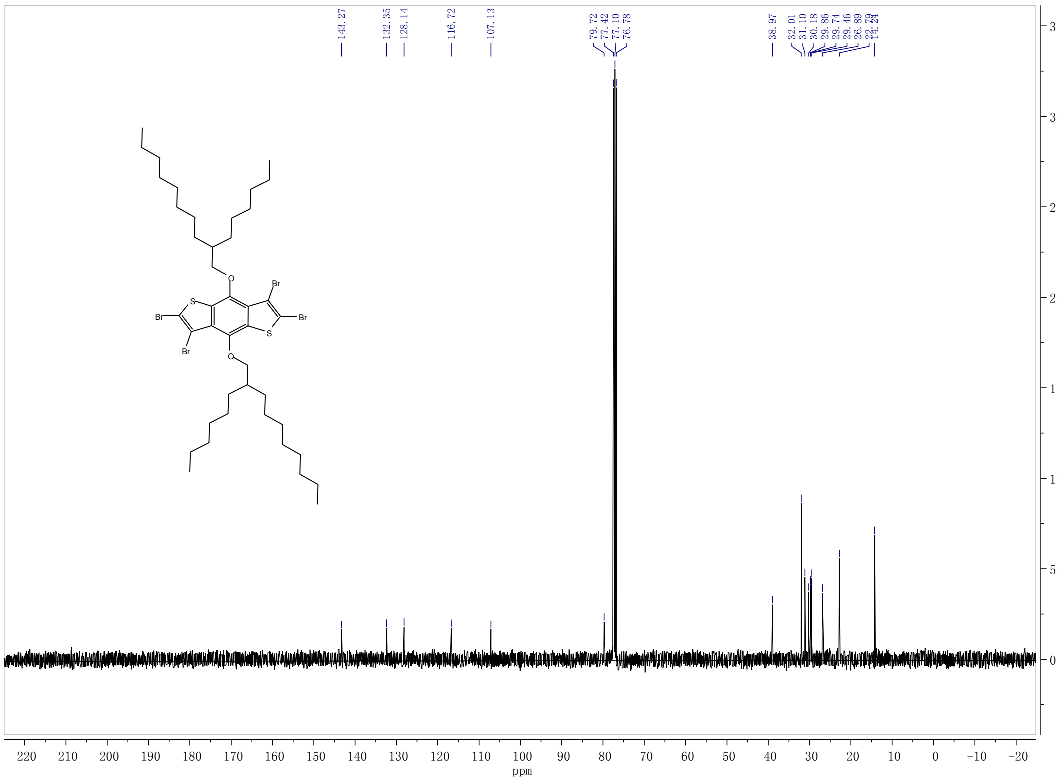

Fig. S2 ^{13}C spectra of 2,3,6,7-tetrabromo-4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene

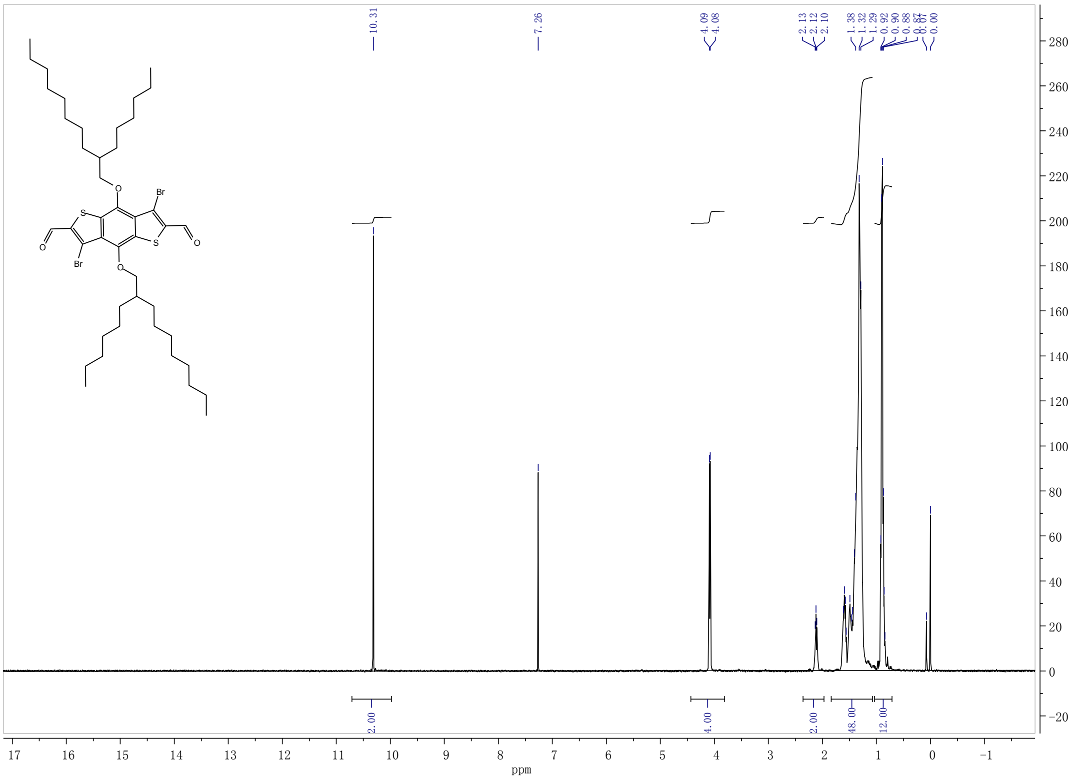

Fig. **S3** ^{1}H spectra of 3,7-dibromo-4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-dicarbaldehyde

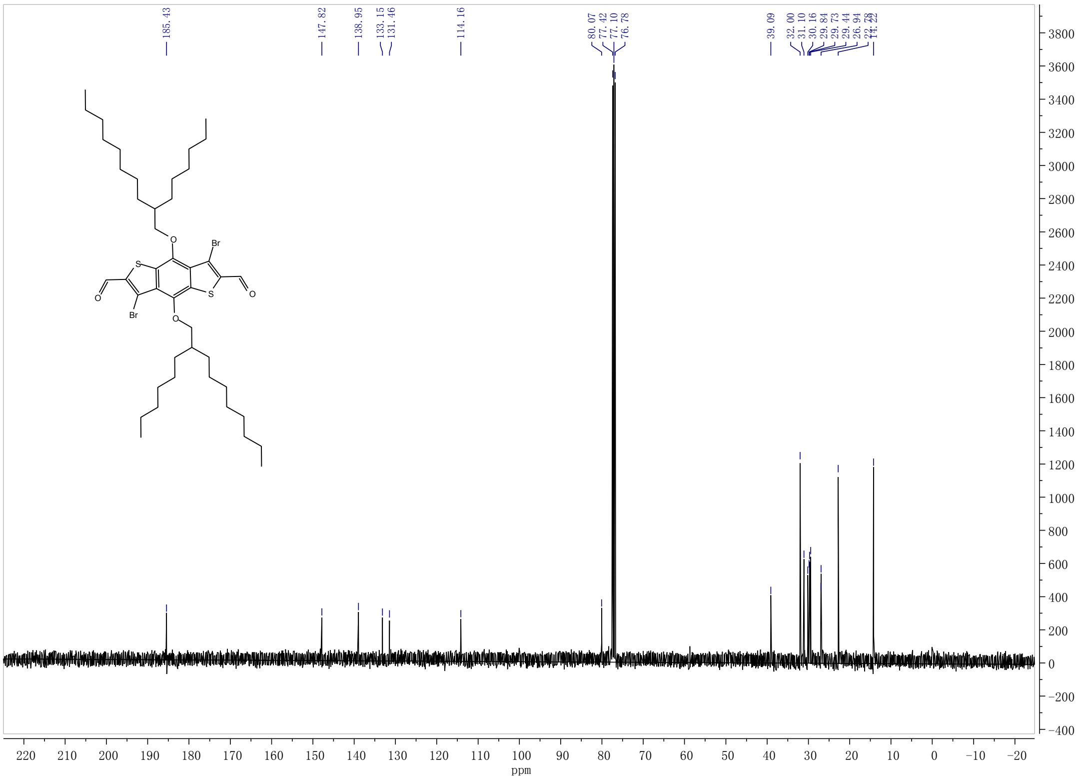

Fig. **S4** ^{13}C spectra of 3,7-dibromo-4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-dicarbaldehyde

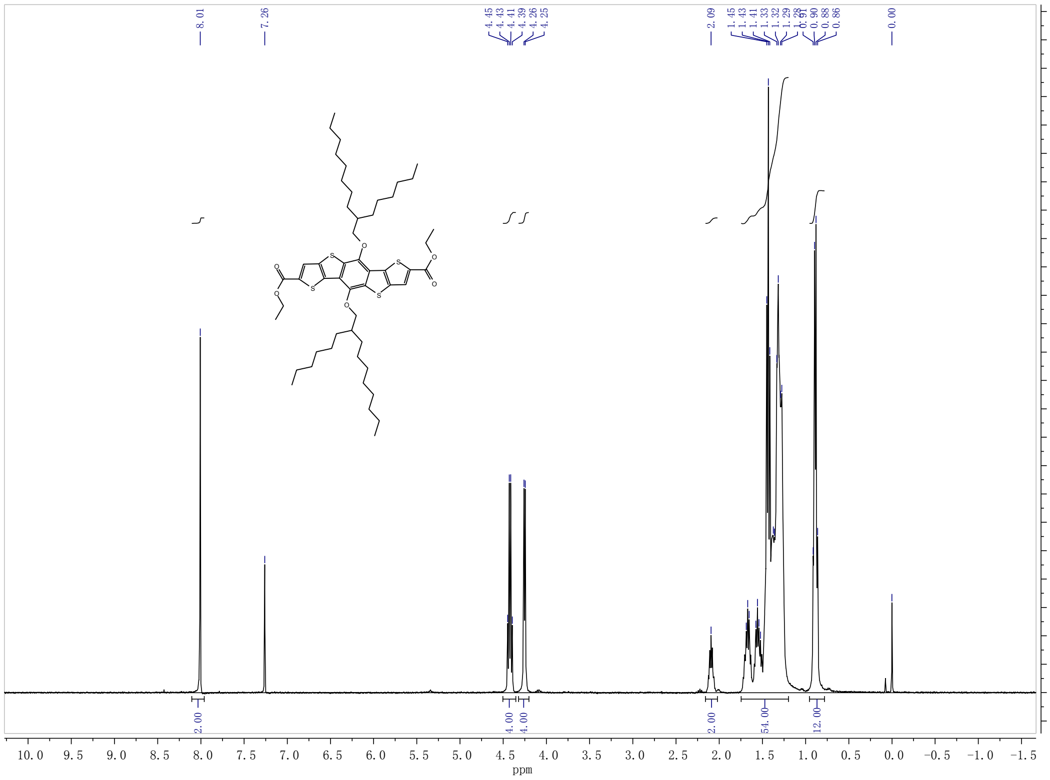

Fig. S5 ^{1}H spectra of 5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-dicarboxylic acid ester

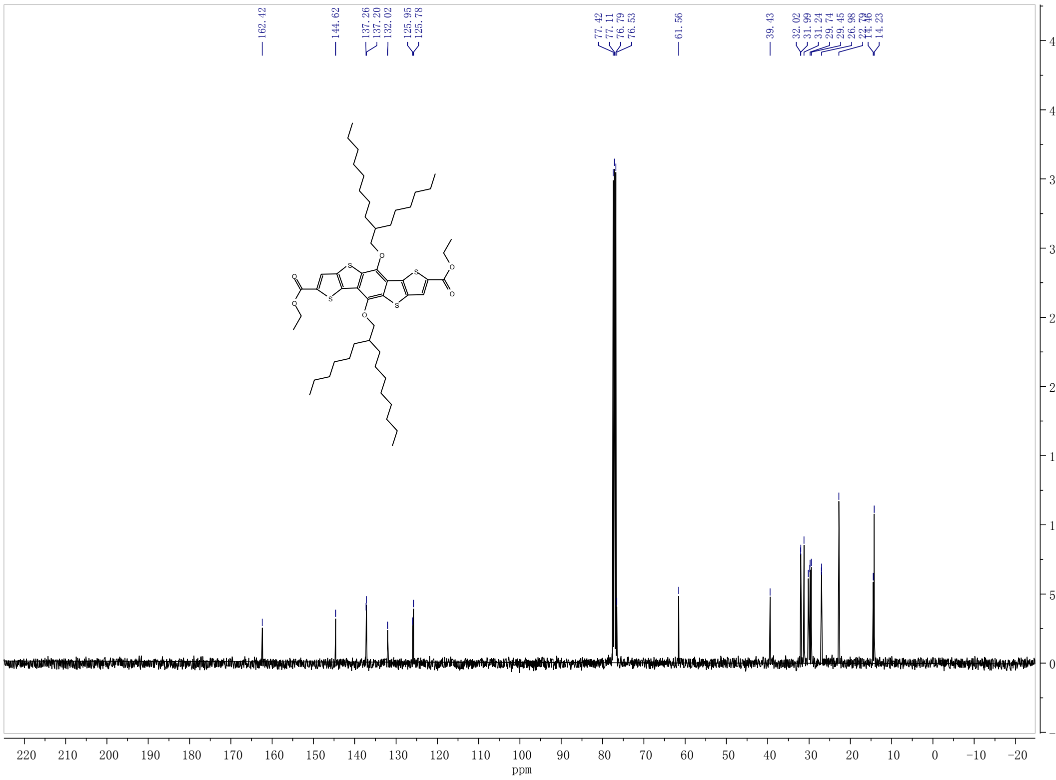

Fig. S6 ^{13}C spectra of 5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-dicarboxylic acid ester

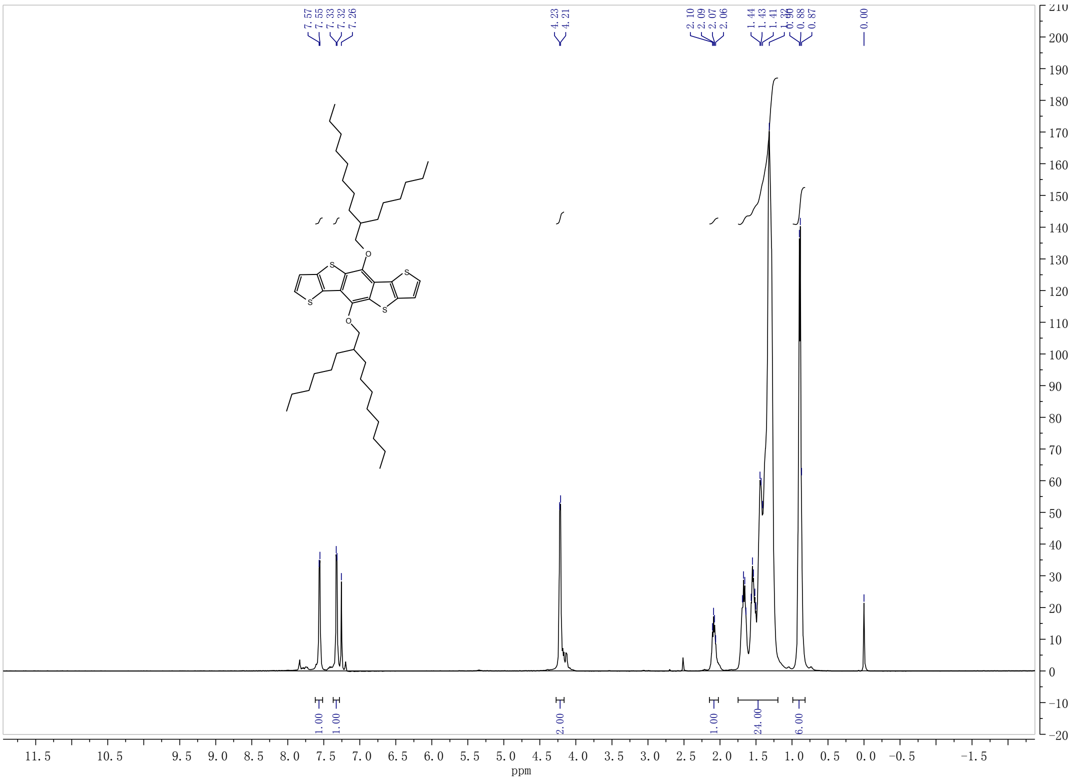

Fig. S7 ^{1}H spectra of 5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene

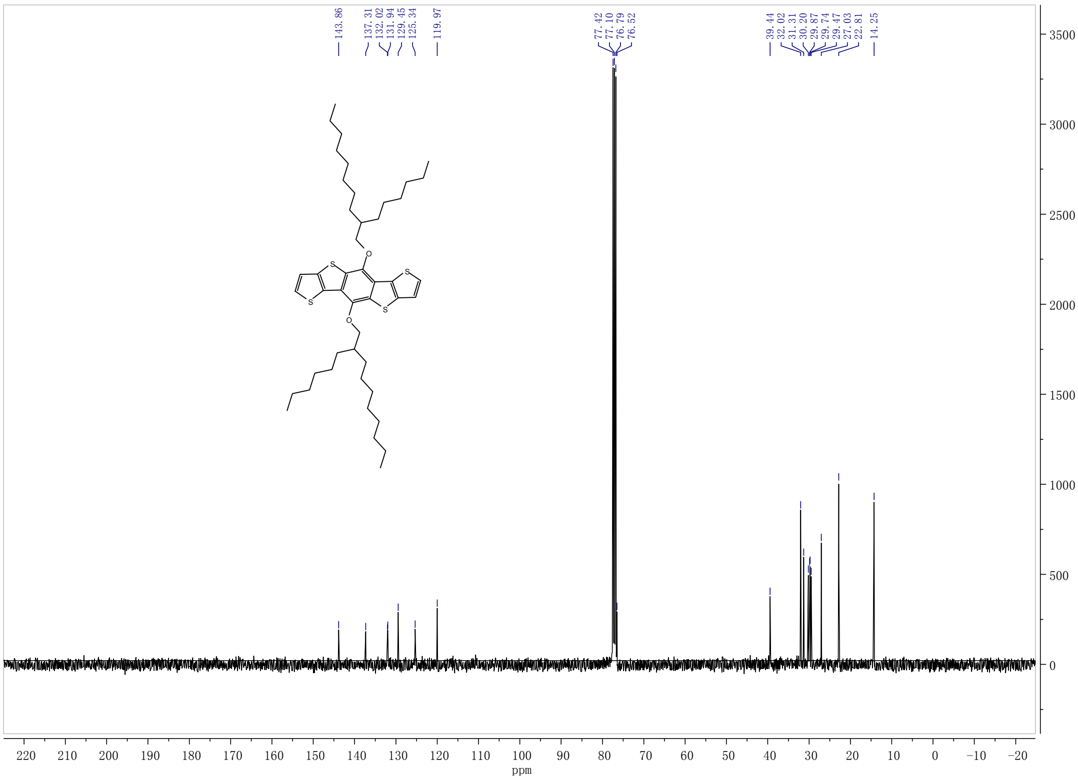

Fig. S8 ^{13}C spectra of 5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene

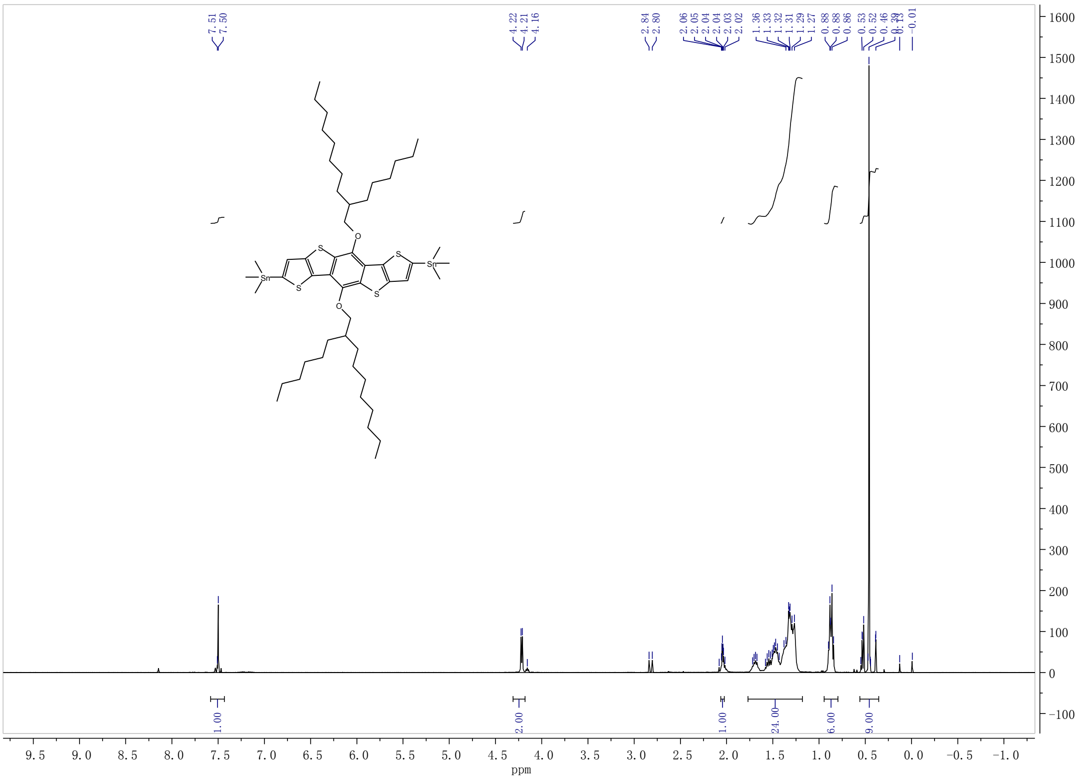

Fig. S9 ^1H spectra of (5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-diyl)bis(trimethylstannane)

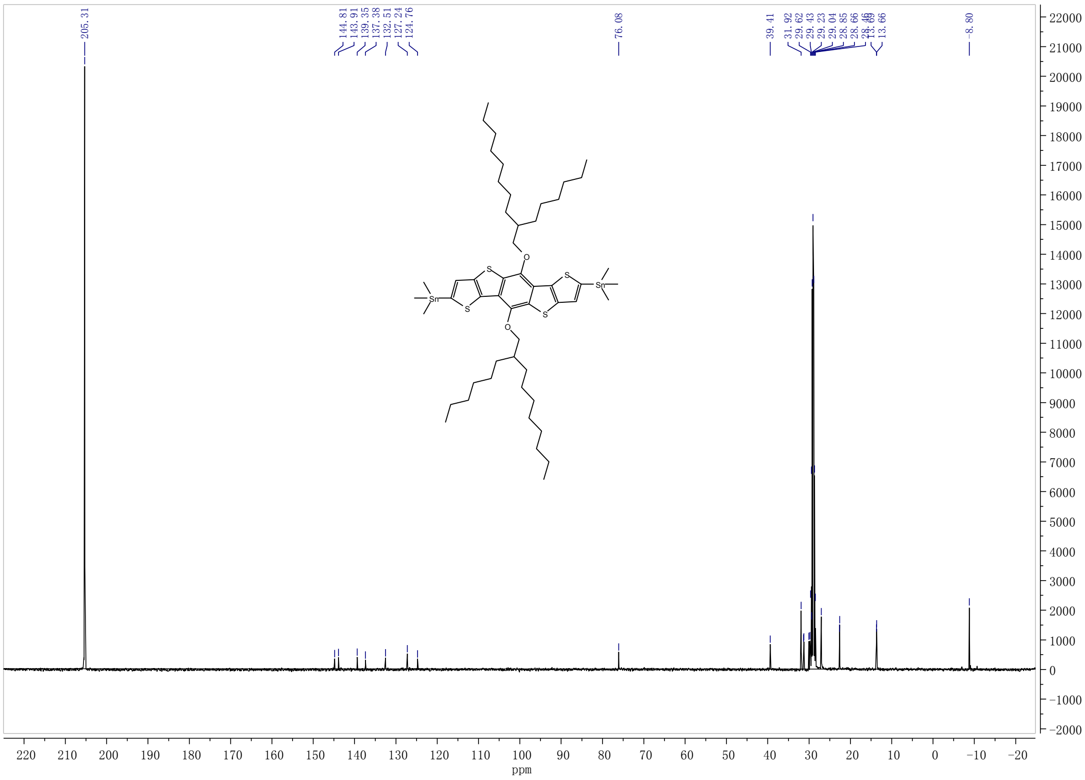

Fig. S10 ^{13}C spectra of (5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene-2,7-diyl)bis(trimethylstannane)

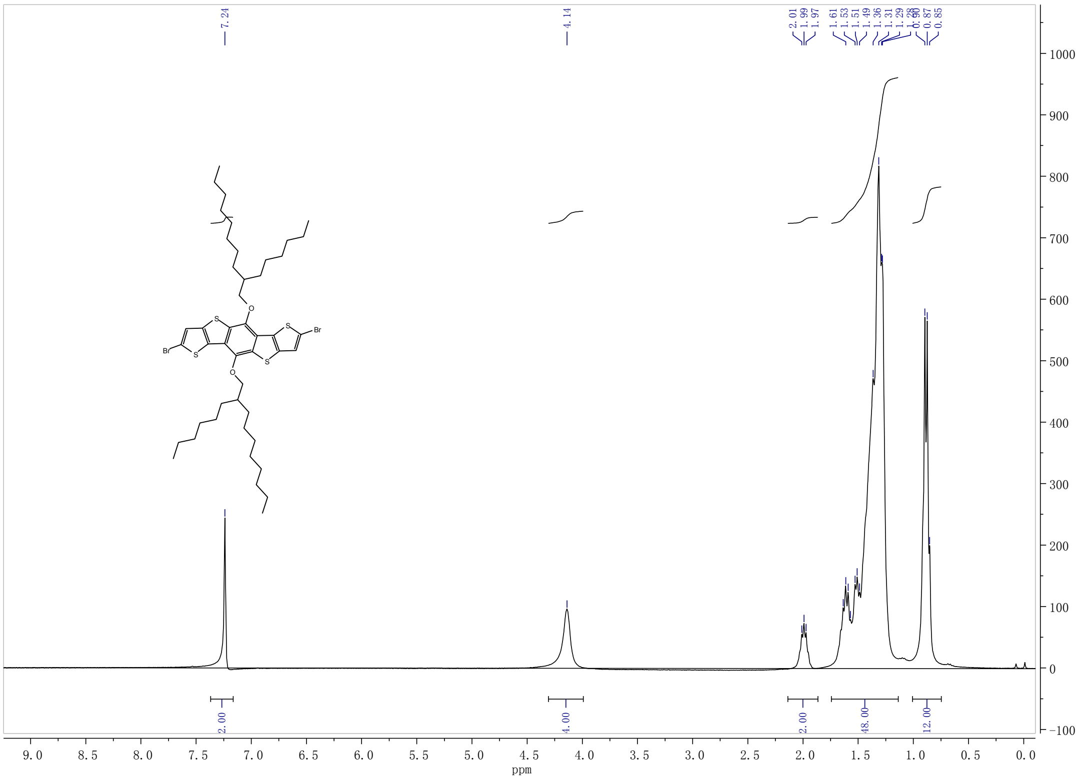

Fig. S11 ^{1}H spectra of 2,7-dibromo-5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene

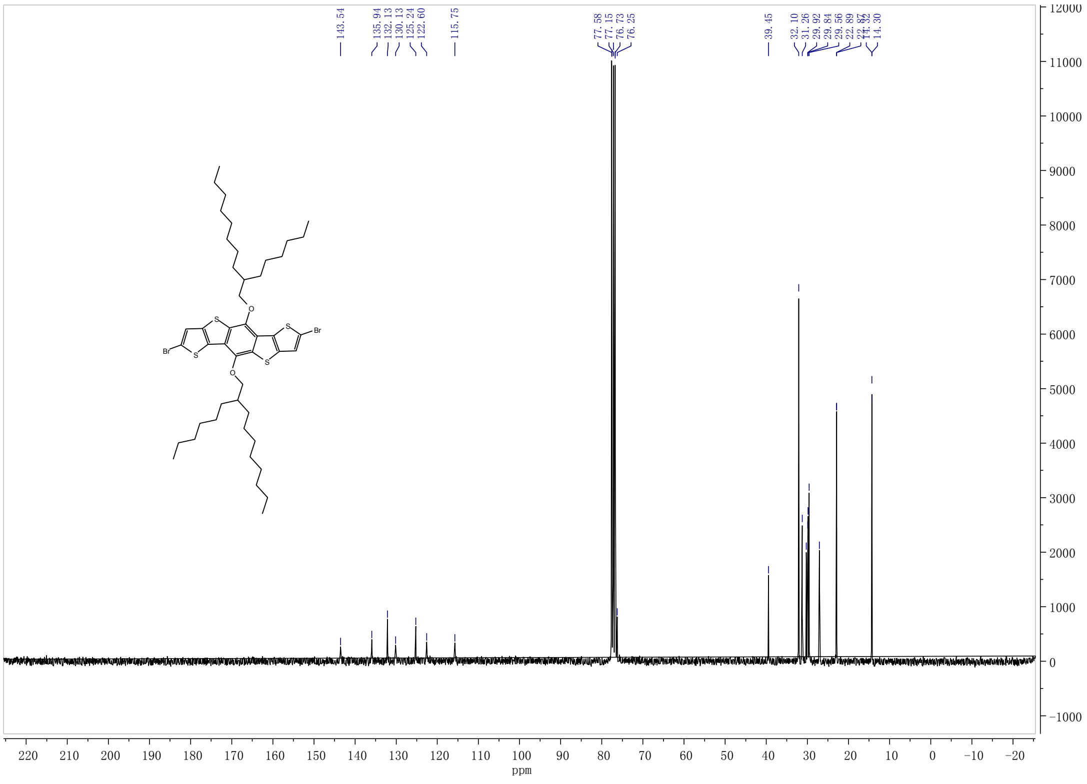

Fig. S12 ^{13}C spectra of 2,7-dibromo-5,10-bis((2-hexyldecyl)oxy)dithieno[2,3-*d*:2',3'-*d*']benzo[1,2-*b*:4,5-*b*']dithiophene

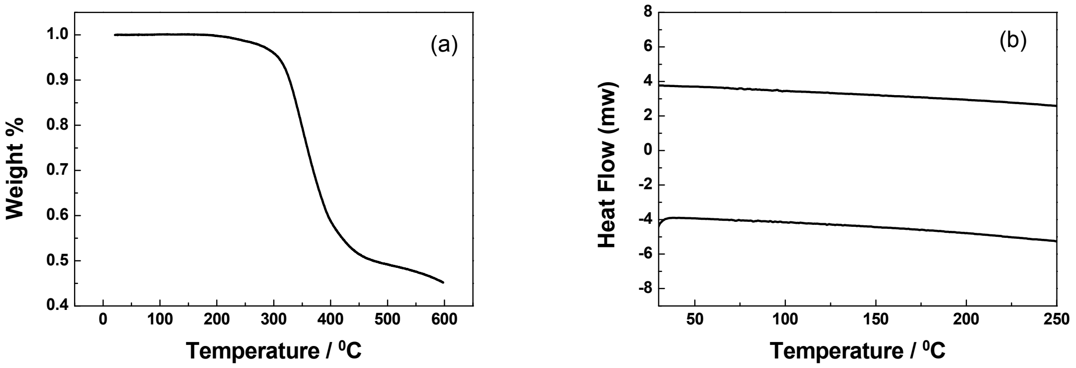

Fig. S13 (a) TGA plot of PDTT with a heating rate of 10 ^{o}C/min under the protection of nitrogen and (b) DSC thermograms of PDTT under the protection of nitrogen (heating and cooling rate: 10 ^{o}C/min).

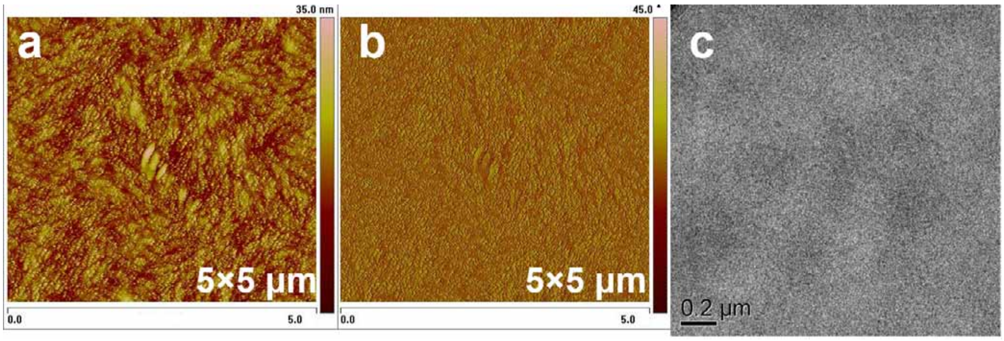

Fig. S14 Tapping mode AFM topography (a), phase (b) and TEM (c) images of pure polymer film.