Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Imformations

Bis(2-oxoindolin-3-ylidene)-benzodifuran-dione containing copolymer for high-mobility ambipolar transistors

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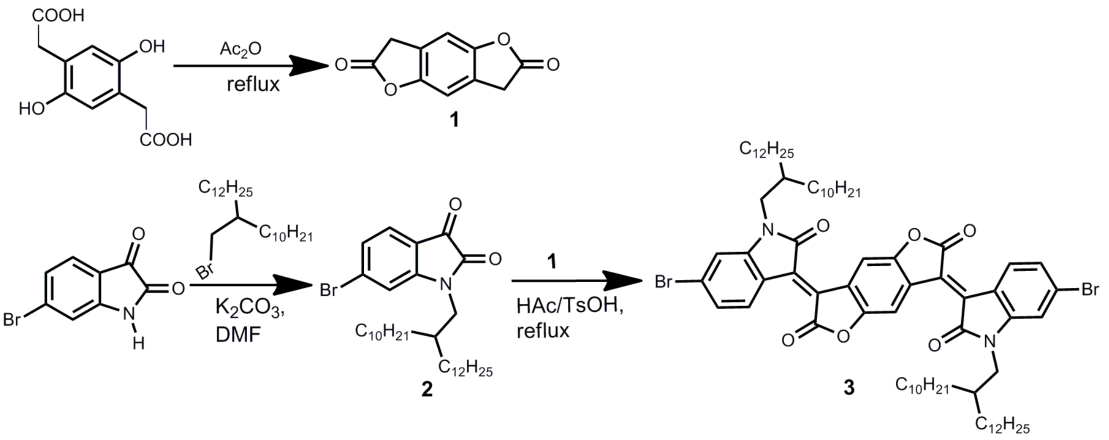


Scheme S1 The synthetic rout to monomer.

EXPERIMENTAL SECTION

Materials. 6-Bromoindoline-2,3-dione were obtained from Darui Chemical Co. Ltd., Shanghai, China. Other chemicals used in this work were purchased from Sigma-Aldrich Chemical Company, Alfa Aeasar Chemical Company and Sinopharm Chemical Reagent Co. Ltd., China. Chemical regents were purchased and used as received. Tetrahydrofuran (THF) and toluene were freshly distilled over sodium wire under nitrogen prior to use. 5,5′-bis(tributylstannyl)-3,3′-bis(dodecyl)-2,2′-bithiophene was synthesized via published procedures.[1]

Synthesis of benzo[1,2-*b*:4,5-*b*']difuran-2,6(3*H*,7*H*)-dione (1). A mixture containing 2,5-dihydroxy-1,4-benzenediacetic acid (2.2 g, 9.73 mmol), acetic anhydride (25 mL) and toluene (60 mL) was reflux for 4 hours. After removing solvent, the crude product was washed with hot alcohol. The white solid was used in next step without further purification.

Synthesis of 6-bromo-1-(2-decyltetradecyl)indoline-2,3-dione (2). Anhydrous potassium carbonate (4.80 g, 34.5 mmol) and 6-bromoindoline-2,3-dione (1.99 g, 8.8 mmol) were dissolved in anhydrous *N*,*N*-dimethylformamide (DMF, 30 mL) and heated to 70 ^{o}C under nitrogen for 1 h. 11-(bromomethyl)tricosane (4.4 g, 10.5 mmol) was added dropwise and the mixture was heated overnight at 70 ^{o}C. After cooled to room temperature, the solution was poured into water (300 mL) and then extracted with dichloromethane. The organic layer was collected and dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by flash chromatography on silica gel with dichloromethane/diethyl ether/hexane (1:1 30) as eluent to give the titled compound (2.4 g, 48.5%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.45 (d, 1H), 7.27 (d, 1H), 7.02 (d, 1H), 3.57 (d, 2H), 1.83 (s, 1H), 1.20-1.35 (m, 40H), 0.87 (t, 6H). ^{13}C (100 MHz, $CDCl_3$): δ= 145.46, 139.92, 139.44, 137.81, 34.59, 33.60, 32.37, 32.34, 32.32, 32.25, 32.24, 32.11, 32.03, 31.40, 25.35, 16.77, -5.58.

Synthesis of (3E, 7E)-3,7-bis(6-bromo-1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)benzo[1,2-b:4,5-b']difuran-2,6(3H,7H)-dione (3). Compound **1** (0.29 g, 1.5 mmol) and compound **2** (1.69 g, 3.0 mmol) was added to a solution of toluenesulfonic acid (TsOH, 0.08 g, 0.42 mmol) in acetic acid (15 mL). The mixture was heated to reflux for 24 h under nitrogen. The reaction mixture was then cooled to room temperature and filtered. The solid was washed with methanol. The residue was purified by flash chromatography on silica gel with dichloromethane /petroleum ether (1:1) as eluent to give the titled compound (0.7 g, 36.4%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.04 (s, 2H), 8.90 (d, 2H), 7.17 (d, 2H), 6.87 (s, 2H), 3.61 (d, 4H), 1.86 (s, 2H), 1.20-1.35 (m, 80H), 0.86 (t, 12H). ^{13}C (100 MHz, $CDCl_3$): δ= 169.72, 169.47, 154.24, 149.81, 137.94, 134.13, 131.52, 129.27, 128.90, 128.08, 122.28, 114.50, 113.50, 47.38, 38.77, 34.57, 34.56, 34.19, 32.66, 32.35, 32.34, 31.32, 31.31, 32.28, 32.01, 31.99, 29.05, 25.33, 16.75. (Eight peaks in ^{13}C NMR spectrum overlap).

Elemental Analysis: calcd for $C_{74}H_{106}Br_2N_2O_6$ (%): C, 69.47, H, 8.35, N, 2.19, found (%) C, 69.93, H, 8.80, N, 2.18.

MS (MALDI-TOF): m/z 1278 ($[M+H]^+$).

Synthesis of polymer PBIBDF-BT. Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$, 0.006 g, 0.0082 mmol), tri(o-tolyl)phosphine ($P(o\text{-}tol)_3$, 0.008 g, 0.025 mmol) were added to a solution of 5,5′-bis(tributylstannyl)-3,3′-bis(dodecyl)-2,2′-bithiophene (0.13 g, 0.16 mmol) and **3** (0.20 g, 0.16 mmol) in toluene (6 mL) under nitrogen. The solution was subjected to three cycles of evacuation and admission of nitrogen. The mixture was then heated to 110 °C for 48 h. After cooled to room temperature, the mixture was poured into methanol and stirred for 2 h. A black precipitate was collected by filtration. The product was purified by washing with methanol and petroleum ether in a Soxhlet extractor for 24 each. It was extracted with hot chloroform in an extractor for 24 h. After removing solvent, a black solid was collected (0.21 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$), σ (ppm): 9.0-9.15 (br, 4H), 6.85-7.20 (br, 6H), 3.65-3.75 (br, 4H), 2.50-2.70 (br, 4H), 0.95-1.95 (br, 72H) 0.65-0.95 (br, 18H). GPC: M_n = 38.6 kDa, PDI = 1.52. Elemental Analysis: calcd for $C_{106}H_{160}N_2O_6S_2$ (%): C, 78.47, H, 9.94, N, 1.73, found (%): C, 78.24, H, 10.08, N, 1.77.

Characterization. Nuclear magnetic resonance (NMR) spectra were recorded on a Mercury plus 400 MHz machine. Gel permeation chromatography (GPC) analyses were performed on a Waters Series 1525 gel coupled with UV-vis detector using tetrahydrofuran as eluent with polystyrene as standards. Thermogravimetric analysis (TGA) analyses were conducted with a TA instrument QS000IR at a heating rate of 20 ^{o}C min^{-1} under nitrogen gas flow. Differential scanning calorimetry (DSC) was performed on a TA instrument Q2000 in a nitrogen atmosphere. The sample (about 10.0 mg in weight) was first heated up to 300 ^{o}C and held for 2 min to remove thermal history, followed by the cooling rate of 20 ^{o}C/min to 0 ^{o}C and then heating rate of 20 ^{o}C/min to 300 ^{o}C in all cases. UV-vis absorption spectra were recorded on a Perkin Elmer model λ 20 UV-vis spectrophotometer. Electrochemical measurements were conducted under nitrogen in a deoxygenated anhydrous acetonitrile solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M), using a CHI 660D electrochemical analyzer. A platinum-disc electrode was used as a working electrode, a platinum-wire was used as an auxiliary electrode, and an Ag/Ag$^+$ electrode was used as a reference electrode. Polymer thin film was coated on the platinum-disc electrode and ferrocene was used as a reference. Tapping atomic force microscopy (AFM) was obtained using a Veeco Multimode V instrument. The grazing-incidence X-ray diffraction (GIXD) studies were performed using 3C beamlines at the Pohang Accelerator Laboratory (PLA) in Korea.

Fabrication and Characterization of Field-Effect Transistors. Top-contact and bottom-gate OTFTs devices were fabricated in this work. A fluoropolymer Cytop was spin-coated onto SiO_2/Si substrate, hence Cytop/SiO_2 and Si work as gate-dielectric and gate-electrode, respectively. A chloroform solution containing semiconductor polymer was dropped onto the Cytop thin film and spin-coated. The polymer films were subsequently annealed (100-200 ^{o}C) in nitrogen. Then Au source-drain electrodes were prepared by thermal evaporation. The OTFTs devices had a channel length (L) of 100 μm and channel width (W) of 1 mm. The evaluations of the OTFTs were performed in glovebox using a Keithley 4200 parameter on probe stage. The mobilities for electron (μ_e) and hole (μ_h) were obtained by the following equation used at saturation regime: $I_d = (W/2L)C_i \mu_{h \text{ or } e}(V_g - V_{th})^2$, where W/L is the channel width/length, I_d is the drain current in the saturated regime, C_i is the capacitance of Cytop/SiO_2 gate-dielectric, and V_{th} is the threshold voltage.

Table S1 Summary of the OTFTs devices performances of PBIBDF-BT.

Annealing temperature [^{o}C]	μ_e (average)[a] [$cm^2V^{-1}s^{-1}$][b]	I_{on}/I_{off}		V_{th} [V]	μ_h (average)[a] [$cm^2V^{-1}s^{-1}$][c]	I_{on}/I_{off}		V_{th} [V]
		80 [V]	10 [V]			-80 [V]	-10 [V]	
N/A	0.28	154	5×10^4		N/A	N/A	N/A	N/A
100	0.38 (0.27±0.08)	32	3×10^5	31.0	0.076 (0.06±0.017)	13	7×10^4	-27.3
150	0.81 (0.59±0.15)	58	2×10^5	24.7	0.33 (0.21±0.071)	60	2×10^5	-46.1
175	1.08 (0.68±0.17)	23	5×10^5	30.6	0.30 (0.24±0.030)	42	9×10^6	-21.8
200	0.65 (0.45±0.19)	18	2×10^6	25.8	0.15 (0.12±0.021)	13	6×10^6	-26.5
175[d]	0.73 (0.47±0.15)	222	1×10^6	19.7	0.035 (0.026±0.01)	58	3×10^3	-29.0

a) Average mobility from more than 12-13 devices; b) Mobility at V_d = 80 V; c) Mobility at V_d = -80 V; d) The annealed devices were exposed in air for three months.

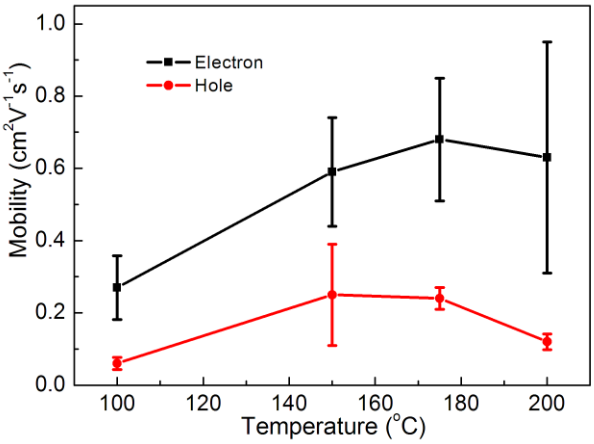


Fig. S1 Effects of the annealing temperature on electron and hole mobilities of PBIBDF-BT.

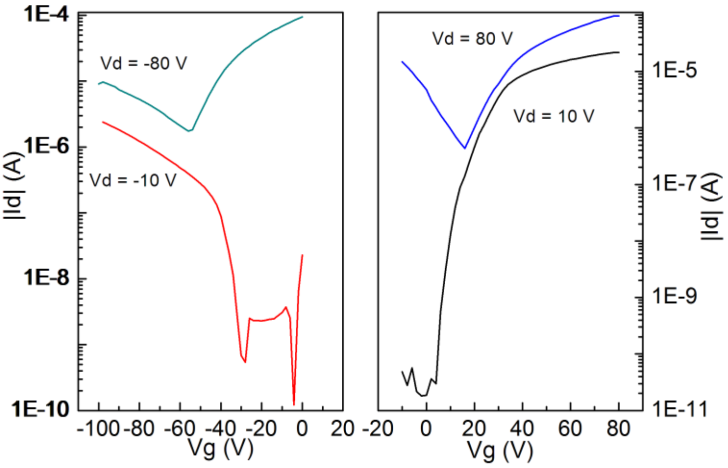


Fig. S2 Typical transfer characteristic of annealing OTFTs devices based on PBTBDF-BT after three months' air exposure.

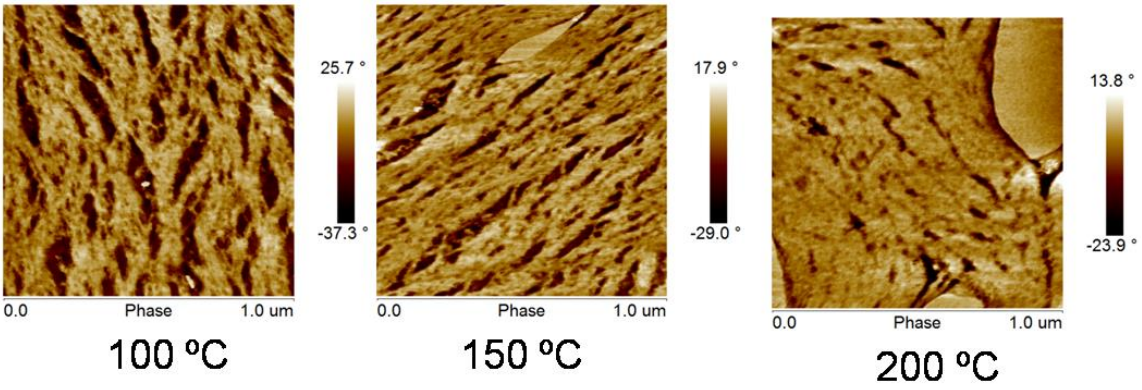


Fig. S3 AFM phase and topography images of PBIBDF-BT at different annealing temperature.

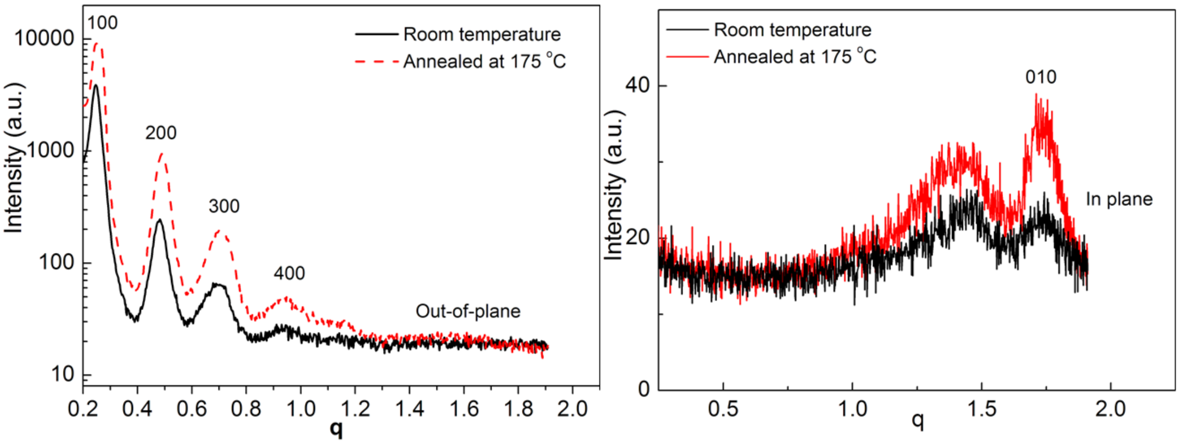


Fig. S4 Out-of-plane and in plane line cuts of GIXD.

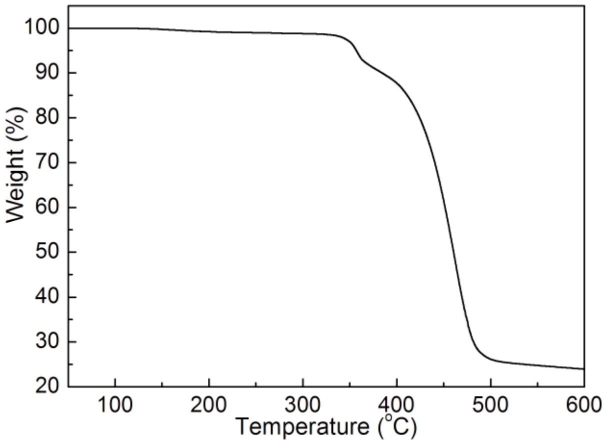


Fig. S5 TGA plot of PBIBDF-BT.

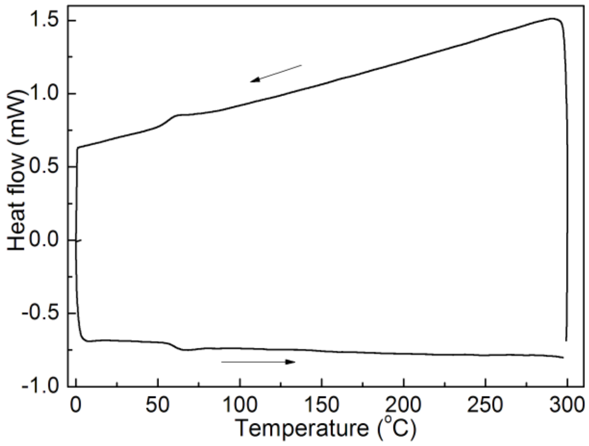


Fig. S6 DSC plot of PBIBDF-BT.

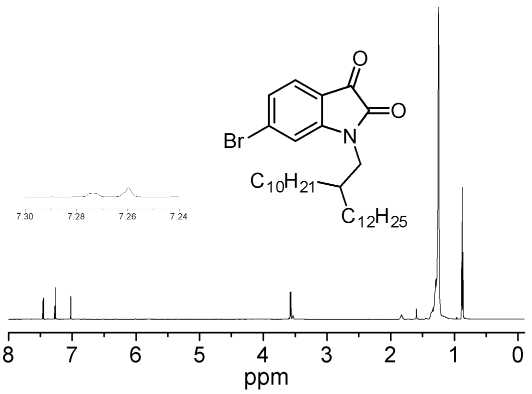


Fig. S7 ^{1}H NMR spectra of compound **2** in $CDCl_3$.

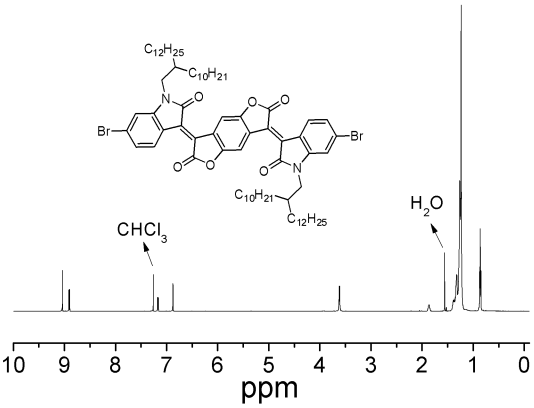


Fig. S8 ^{1}H NMR spectra of compound **3** in $CDCl_3$.

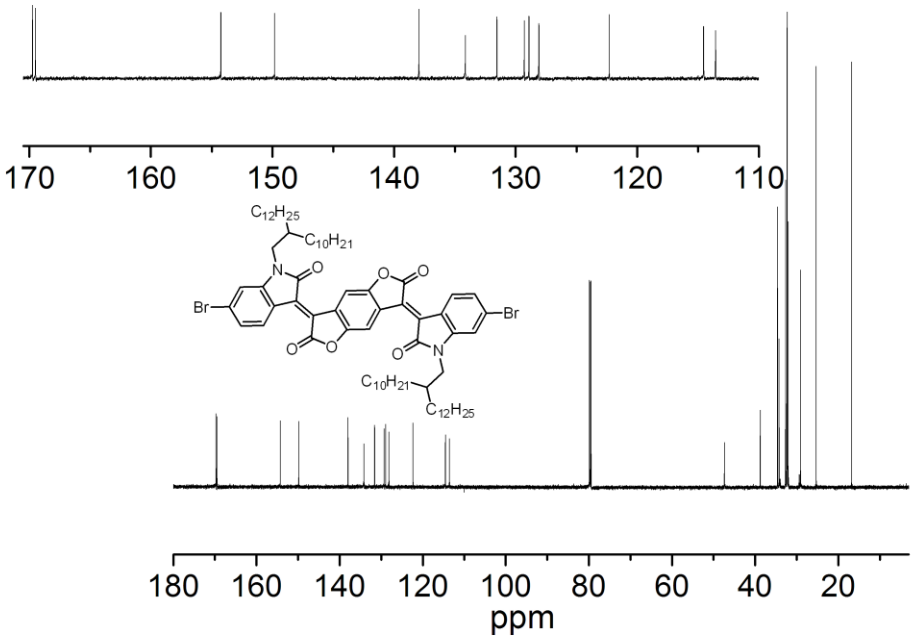


Fig. S9 ^{13}C NMR spectra of compound **3** in $CDCl_3$.

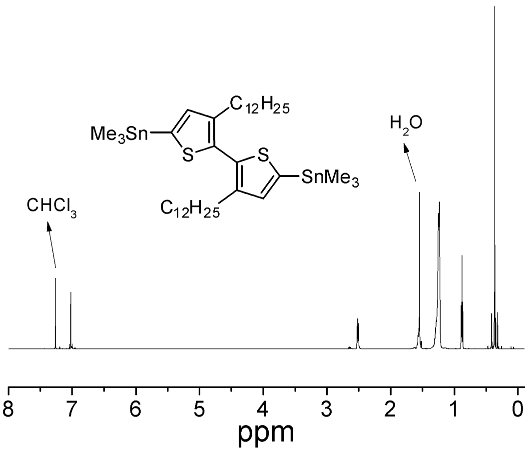


Fig. S10 ^{1}H NMR spectra of momomer in CDCl$_3$.

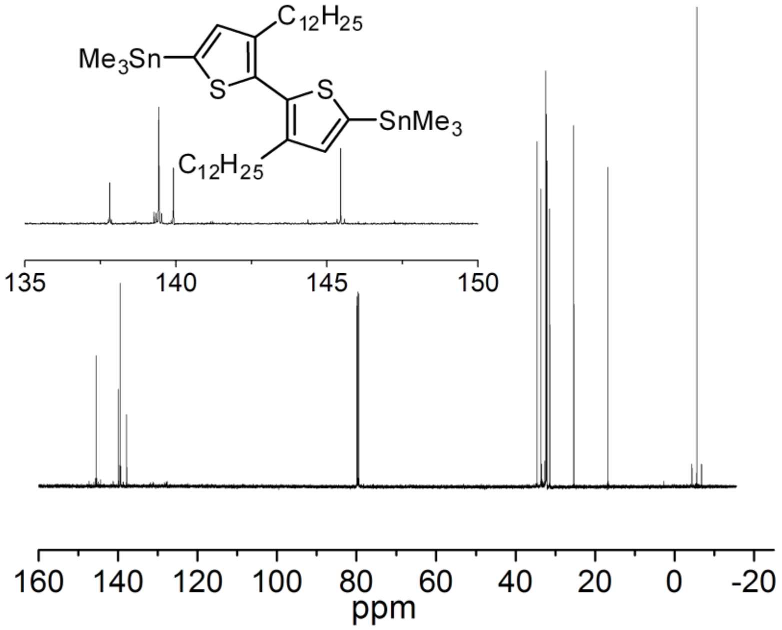


Fig. S11 ^{13}C NMR spectra of monomer in CDCl$_3$.

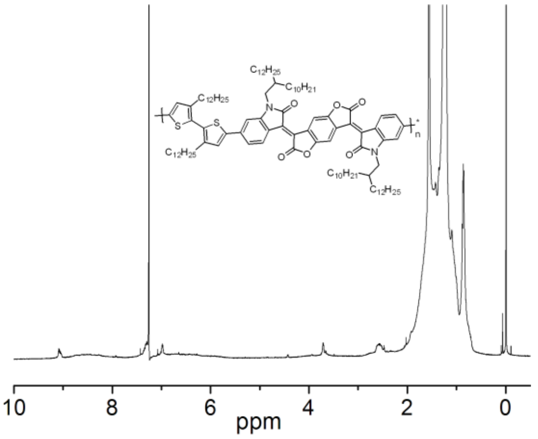


Figure S12 ^{1}H NMR spectra of PBIBDF-BT.

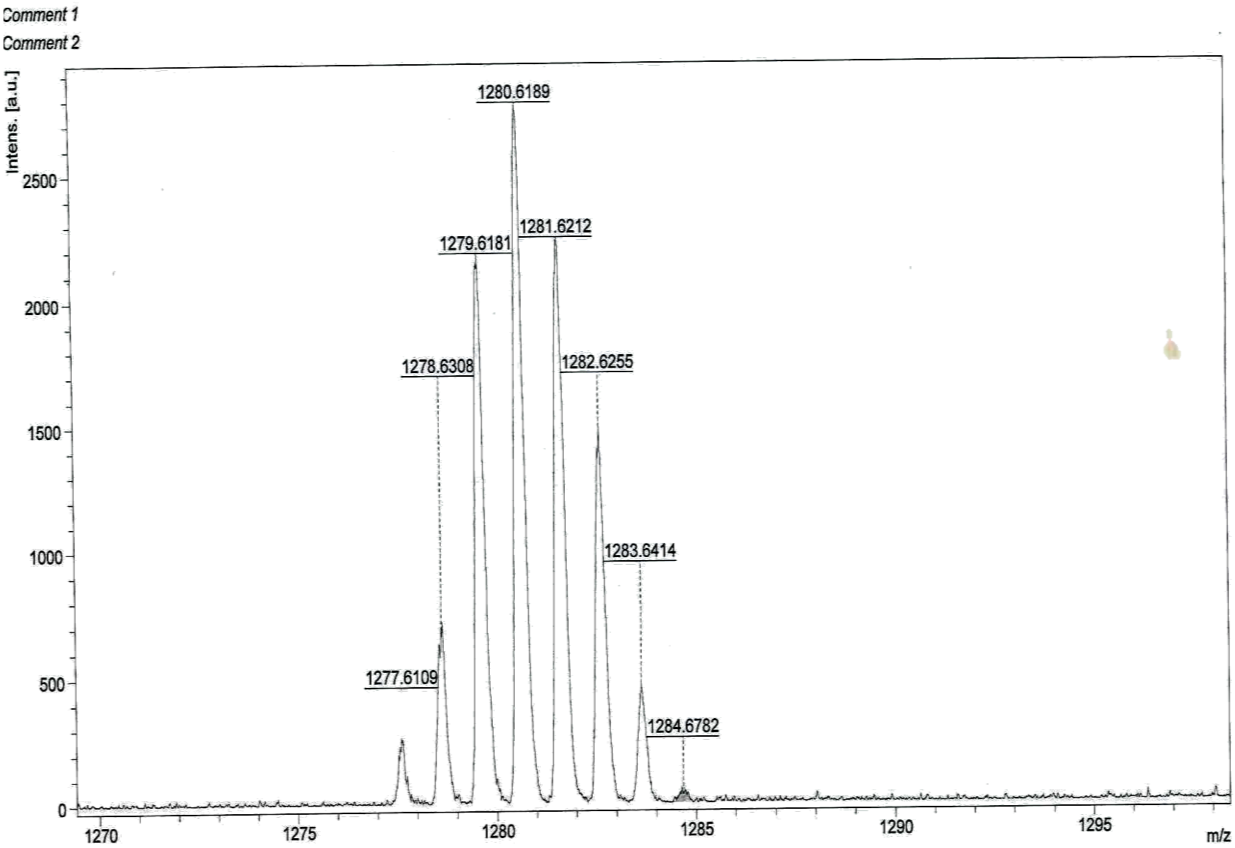
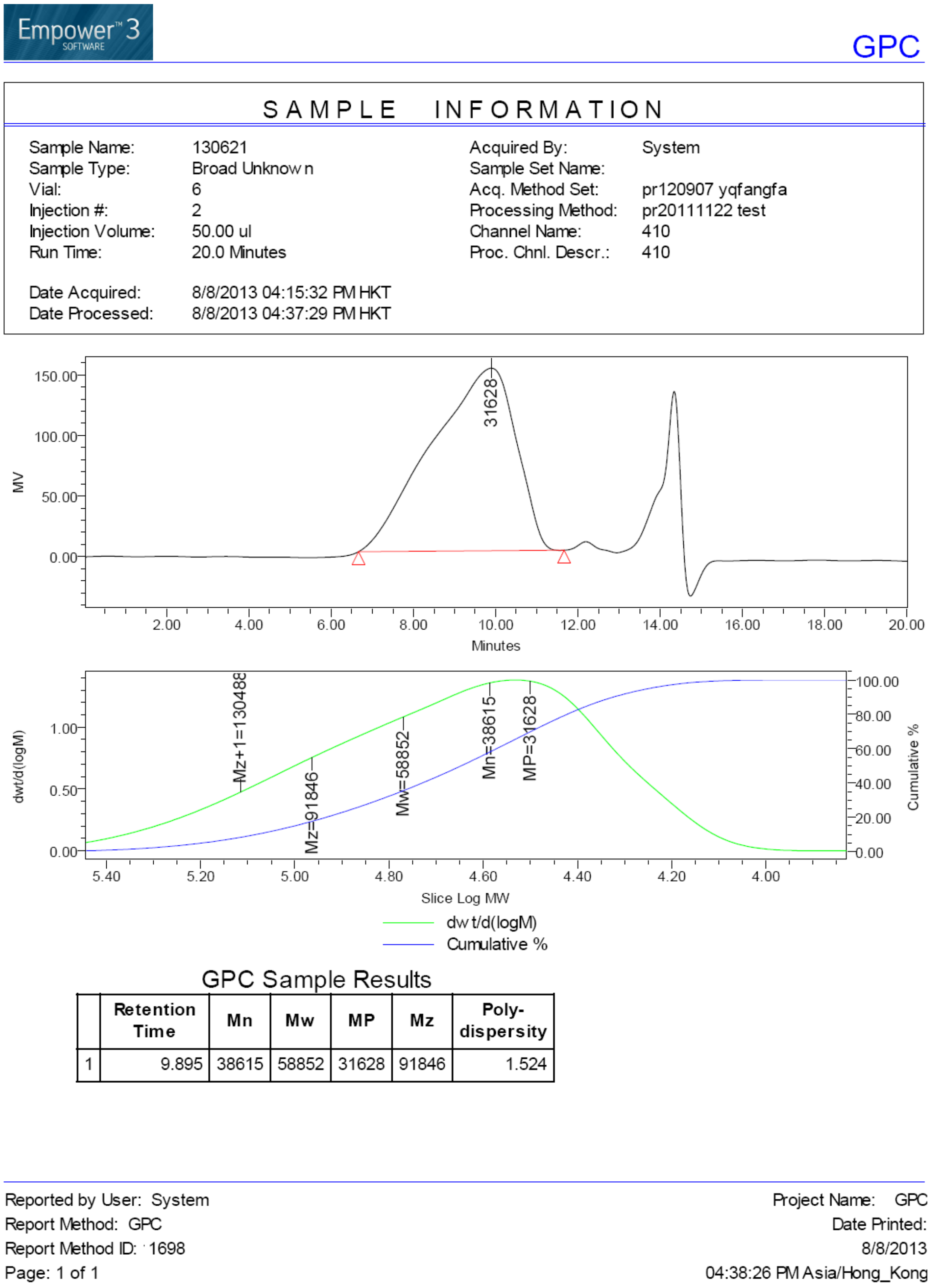


Fig. S13 The mass spectrum (MS (MALDI-TOF): m/z 1278 ($[M+H]^+$)) of compound **3.**



SAMPLE INFORMATION

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Sample Type: Broad Unknown
Vial: 6
Injection #: 2
Injection Volume: 50.00 ul
Run Time: 20.0 Minutes

Date Acquired: 8/8/2013 04:15:32 PM HKT
Date Processed: 8/8/2013 04:37:29 PM HKT

Acquired By: System
Sample Set Name:
Acq. Method Set: pr120907 yqfangfa
Processing Method: pr20111122 test
Channel Name: 410
Proc. Chnl. Descr.: 410

GPC Sample Results

	Retention Time	Mn	Mw	MP	Mz	Poly-dispersity
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Reported by User: System
Report Method: GPC
Report Method ID: 1698
Page: 1 of 1

Project Name: GPC
Date Printed:
8/8/2013
04:38:26 PM Asia/Hong_Kong

Reference

1. X. Guo, M. D. Watson, *Org. Lett.* 2008, **10**, 5333.