# Electronic Supplementary Information

# Bis(2-oxoindolin-3-ylidene)-benzodifuran-dione and bithiophene-based conjugated polymers for high performance ambipolarorganic thin-film transistors: Impact of substitution positions on bithiophene units

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Table S1. The summarize of the n-type field-effect characteristics of the three BIBDF-based polymers

| Film | Saturated Region | | | | Linear Region | | | |
|---|---|---|---|---|---|---|---|---|
| | mobility, $\mu_e$ [$cm^2V^{-1}s^{-1}$] | | $I_{on}/I_{off}$ | $V_{th}$ [V] | mobility, $\mu_e$ [$cm^2V^{-1}s^{-1}$] | | $I_{on}/I_{off}$ | $V_{th}$ [V] |
| | average | max | | | average | max | | |
| PBIBDF-HH | | | | | | | | |
| TA100 | 0.49 ±0.02 | 0.51 | 9 | 23.6 | 0.43 ±0.04 | 0.47 | $3\times10^6$ | 27.8 |
| TA150 | 0.85 ±0.18 | 1.03 | 8 | 30.3 | 0.51 ±0.07 | 0.58 | $4\times10^5$ | 21.7 |
| TA175 | 0.86 ± 0.23 | 1.23 | 17 | 27.1 | 0.56 ±0.03 | 0.63 | $1\times10^7$ | 18.9 |
| TA200 | 0.64 ±0.27 | 0.93 | 16 | 22.9 | 0.34 ±0.08 | 0.38 | $1\times10^6$ | 15.0 |
| PBIBDF-HT | | | | | | | | |
| TA100 | 0.021 ±0.006 | 0.027 | 40 | 24.1 | | | | |
| TA150 | 0.040 ±0.020 | 0.063 | 72 | 29.0 | 0.020 ±0.004 | 0.021 | 622 | 31.9 |
| TA175 | 0.050 ±0.022 | 0.175 | 220 | 28.0 | 0.046 ±0.031 | 0.105 | $1\times10^5$ | 36.9 |
| TA200 | 0.029 ±0.017 | 0.043 | 642 | 31.5 | | | | |
| PBIBDF-TT | | | | | | | | |
| TA100 | 0.15 ±0.07 | 0.26 | 173 | 11.9 | 0.081 ±0.022 | 0.095 | $2\times10^5$ | 16.5 |
| TA150 | 0.35 ±0.08 | 0.48 | 29 | 29.1 | 0.24 ±0.04 | 0.27 | $5\times10^5$ | 23.5 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| TA175 | 0.50 ±0.24 | 0.64 | 29 | 21.4 | 0.28 ±0.06 | 0.40 | $9\times10^4$ | 18.6 |
| TA200 | 0.50 ±0.16 | 0.70 | 30 | 19.0 | 0.31 ±0.01 | 0.33 | $2\times10^6$ | 16.5 |

Table S2. The summarize of the p-type field-effect characteristics of the three BIBDF-based polymers

| Film | Saturated Region | | | | Linear Region | | | |
|---|---|---|---|---|---|---|---|---|
| | mobility, $\mu_h$ [$cm^2V^{-1}s^{-1}$] | | $I_{on}/I_{off}$ | $V_{th}$ [V] | mobility, $\mu_h$ [$cm^2V^{-1}s^{-1}$] | | $I_{on}/I_{off}$ | $V_{th}$ [V] |
| | average | max | | | average | max | | |
| PBIBDF-HH | | | | | | | | |
| TA100 | 0.20 ±0.01 | 0.21 | 11 | -13.8 | 0.17 ±0.06 | 0.18 | $4\times10^5$ | -29.1 |
| TA150 | 0.30 ±0.05 | 0.34 | 8 | -13.9 | 0.23 ±0.03 | 0.26 | $1\times10^5$ | -25.6 |
| TA175 | 0.32 ±0.04 | 0.37 | 22 | -21.8 | 0.26 ±0.02 | 0.28 | $3\times10^8$ | -24.5 |
| TA200 | 0.16 ±0.03 | 0.19 | 12 | -26.5 | 0.15 ±0.06 | 0.17 | $1\times10^6$ | -26.5 |
| PBIBDF-HT | | | | | | | | |
| TA100 | 0.0025 ±0.0008 | 0.0034 | 7 | -40.1 | | | | |
| TA150 | 0.0006 ±0.0004 | 0.0007 | 6 | -20.5 | 0.00015 ±0.00004 | 0.00017 | 10 | -37.5 |
| TA175 | 0.0007 ±0.0004 | 0.0009 | 6 | -27.3 | 0.0011 ±0.0009 | 0.0017 | $1\times10^7$ | -59.7 |
| TA200 | 0.0010 | 0.0018 | 13 | -17.6 | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | ±0.0008 | | | | | | | |
| PBIBDF-TT | | | | | | | | |
| TA100 | 0.027 ±0.089 | 0.044 | 729 | -36.6 | 0.016 ±0.005 | 0.020 | $7\times10^4$ | -33.3 |
| TA150 | 0.082 ±0.018 | 0.10 | 60 | -37.2 | 0.059 ±0.012 | 0.067 | $8\times10^4$ | -17.4 |
| TA175 | 0.086 ±0.016 | 0.12 | 42 | -37.9 | 0.070 ±0.014 | 0.10 | $7\times10^5$ | -43.2 |
| TA200 | 0.11 ±0.036 | 0.17 | 56 | -37.4 | 0.096 ±0.034 | 0.16 | $5\times10^4$ | -45.6 |

**Experimental details**

The dibromo-monomer **BIBDF,**[1] head-to-head coupled 5,5′-bis(trimethylstannyl)-3,3′-bis(dodecyl)-2,2′-bithiophene (**M1**),[1] and tail-to-tail coupled 5,5′-bis(trimethylstannyl)-4,4′-bis(dodecyl)-2,2′-bithiophene (**M3**),[2] were synthesized according to the literature.

**Synthesis of 5,5′-bis(tributylstannyl)-3,4′-bis(dodecyl)-2,2′-bithiophene.**

A solution of n-butyllithium (6.13 mL, 12.27mmol, 2 M in hexane) was added slowly to 3,4′-bis(dodecyl)-2,2′-bithiophene (2.8 g, 15.58mmol) in tetrahydrofuran (60 mL) at −78 °C. After addition, the mixture was stirred for 30 min at room temperature. The mixture was cooled to −78 °C again, trimethyltin chloride solution (12.27 mL, 12.27 mmol, 1.0 M in hexane) was added to the mixture, stirred for 30 min at −78 °C, then warmed to room temperature and was stirred overnight. The reaction was quenched with addition of water (150 mL) and the mixture was extracted with diethyl ether for three times. The combined organic layer was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by washing with methanol to afford a light yellow liquid (1.87g, 40.4%). 1H NMR (400 MHz, CDCl3, ppm): δ7.07 (s, 1H), δ6.98 (s, 1H) 2.77 (t, 2H), 2.59 (t, 2H), 1.58 (m, 4H), 1.26 (m, 36H), 0.88 (t, 6H), 0.37 (s, 18H).

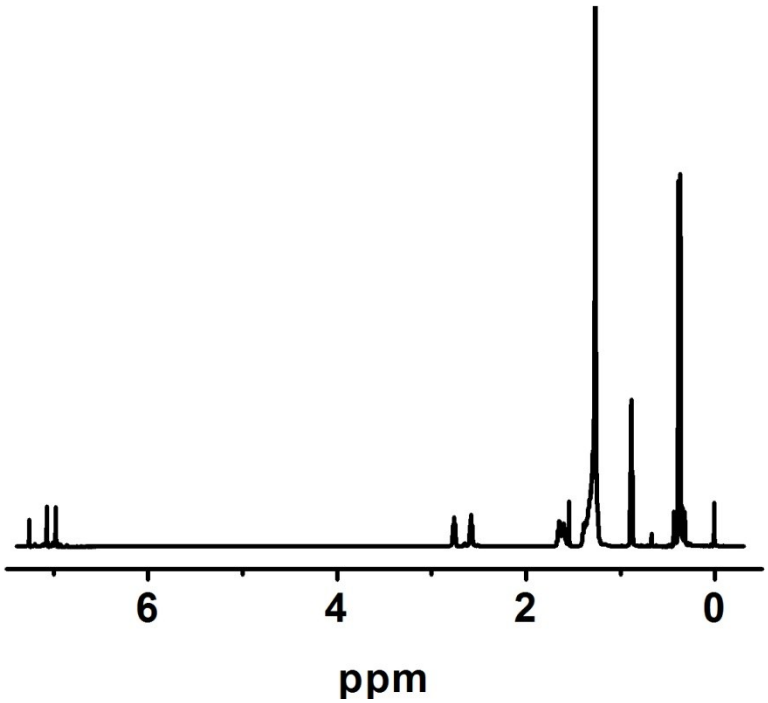



**Figure S1.** $^1$H NMR spectra of 5,5′-bis(tributylstannyl)-3,4′-bis(dodecyl)-2,2′-bithiophene.

**Synthesis of PBIBDF-BT polymers.**

Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$, 0.006 g, 0.0082mmol), tri(o-tolyl)phosphine ($P(o\text{-}tol)_3$, 0.008 g, 0.025 mmol) were added to a solution of **M1** or **M2** or **M3** (0.13 g, 0.157 mmol) and **BIBDF**(0.20 g, 0.157 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 $^oC$ for 48 h. After cooled to room temperature, the mixture was poured into methanol and stirred for 2 h. Ablack 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

PBIBDF-HH yield: 0.21 g, 83%. Elemental Analysis: calcd for $(C_{106}H_{158}N_2O_6S_2)_n$ (%): C 78.62, H 9.77, N 1.73; found (%): C 78.24, H 10.08, N 1.77.

PBIBDF-HT yield: 0.15 g, 59%. Elemental Analysis: calcd for $(C_{106}H_{158}N_2O_6S_2)_n$ (%):

C 78.62, H 9.77, N 1.73; found (%): C 78.21, H 9.63, N 1.74.

PBIBDF-TT yield: 0.22 g, 87%. Elemental Analysis: calcd for $(C_{106}H_{158}N_2O_6S_2)_n$ (%):78.62, H 9.77, N 1.73; found (%): C 78.56, H 10.13, N 1.82.

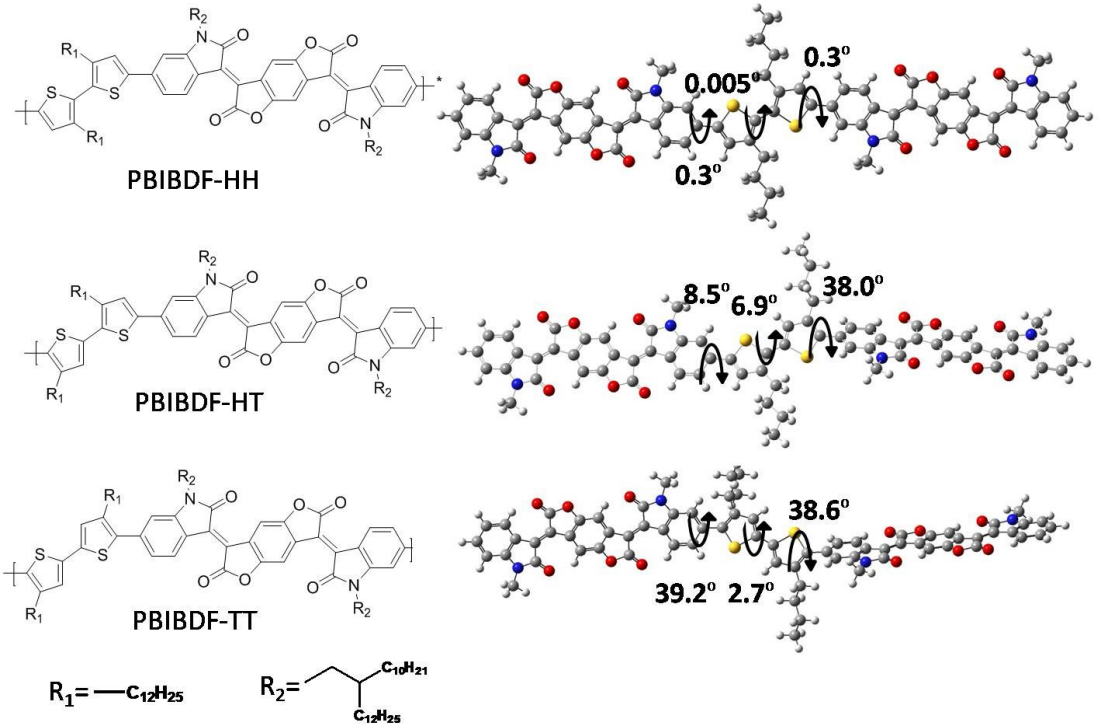



**Figure S2** Density functional theory (DFT) calculations for molecules using Gauussian 09 at B3LYP/6-31g level obtained by replace the dodecyl group on thiophene with lager butyl group.

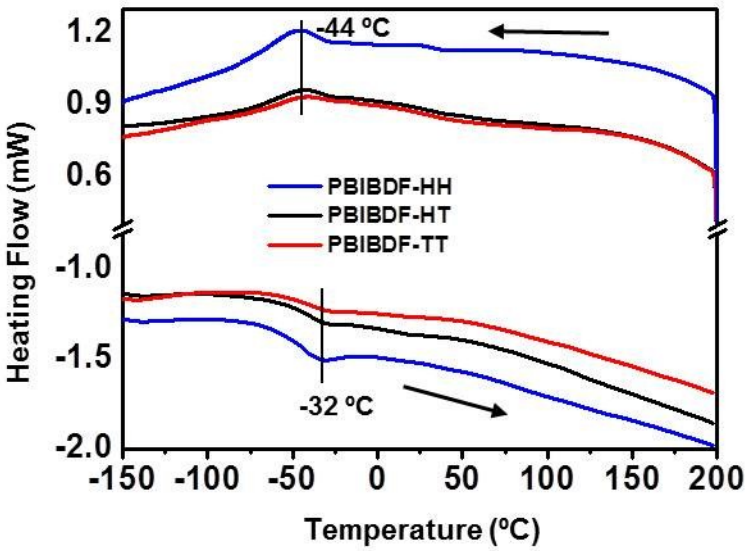
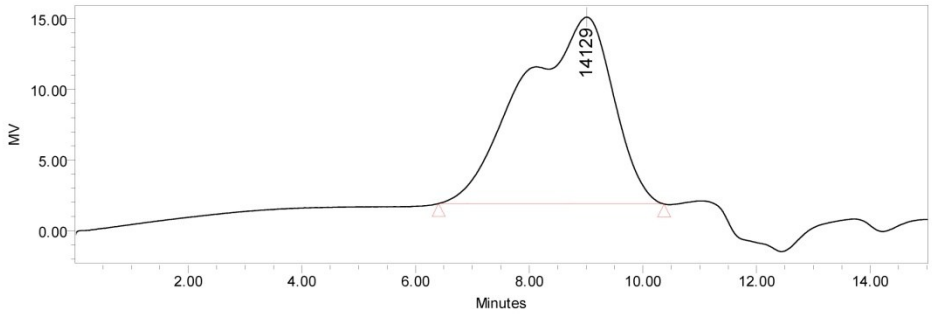


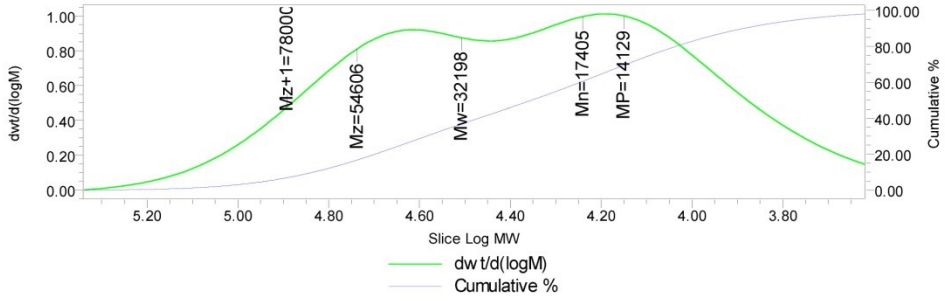

**Figure S3** Differential scanning calorimetry (DSC) traces of **PBIBDF-HH, PBIBDF-HT, and PBIBDF-TT**.

Differential scanning calorimetry (DSC) was performed on a TA instrument Q2000 in a nitrogen atmosphere. All three polymers clearly showed an endothermic peak at -32 ºC during heating up and a correspondingly exothermic peak at -44 ºC when cooled down. Theses phase transition peaks are caused by the melt and crystallization of the long alkyl chains.

## SAMPLE INFORMATION

| | | | |
|---|---|---|---|
| Sample Name: | 0621 | Acquired By: | System |
| Sample Type: | Broad Unknown | Sample Set Name: | |
| Vial: | 6 | Acq. Method Set: | 20150202 |
| Injection #: | 15 | Processing Method: | ljq0319 |
| Injection Volume: | 25.00 ul | Channel Name: | 410 |
| Run Time: | 15.0 Minutes | Proc. Chnl. Descr.: | 410 |
| Date Acquired: | 2015/3/19 21:15:49 HKT | | |
| Date Processed: | 2015/3/20 15:21:57 HKT | | |




### GPC Sample Results

| | Retention Time | Mn | Mw | MP | Mz | Poly-dispersity |
|---|---|---|---|---|---|---|
| 1 | 9.013 | 17405 | 32198 | 14129 | 54606 | 1.850 |



**Figure S3** GPC data for PBIBDF-HH

## SAMPLE INFORMATION

| | | | |
|---|---|---|---|
| Sample Name: | 0619 | Acquired By: | System |
| Sample Type: | Broad Unknown | Sample Set Name: | |
| Vial: | 6 | Acq. Method Set: | 20150202 |
| Injection #: | 17 | Processing Method: | ljq0319 |
| Injection Volume: | 25.00 ul | Channel Name: | 410 |
| Run Time: | 15.0 Minutes | Proc. Chnl. Descr.: | 410 |
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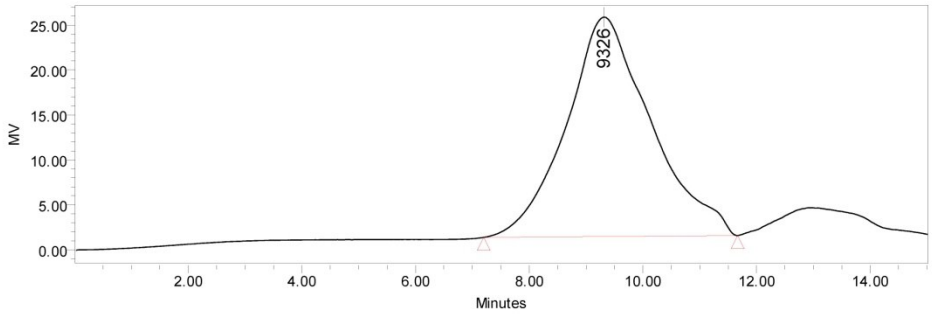
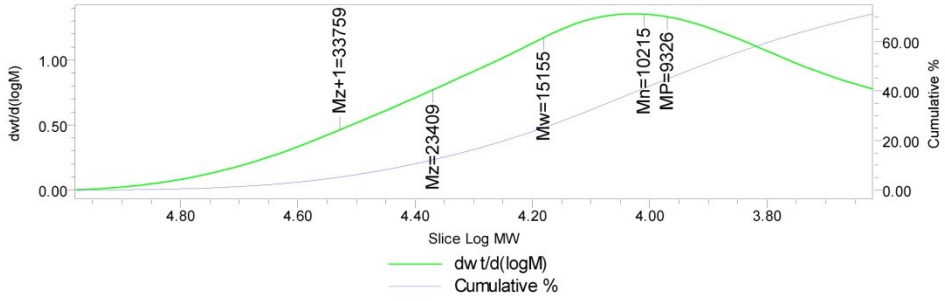
| Date Processed: | 2015/3/20 15:21:10 HKT | | |




GPC Sample Results

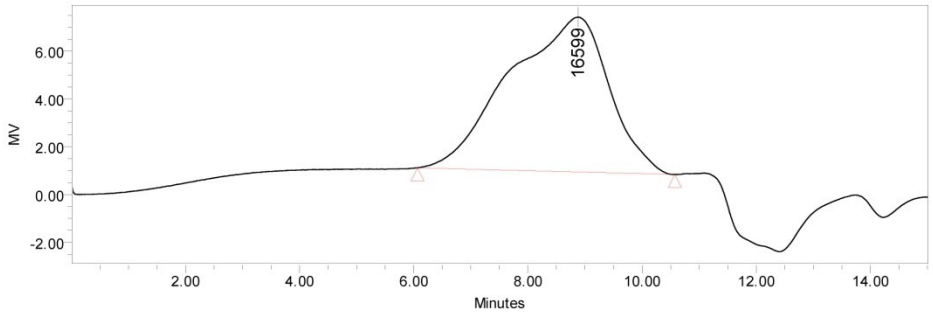
| | Retention Time | Mn | Mw | MP | Mz | Poly-dispersity |
|---|---|---|---|---|---|---|
| 1 | 9.322 | 10215 | 15155 | 9326 | 23409 | 1.484 |

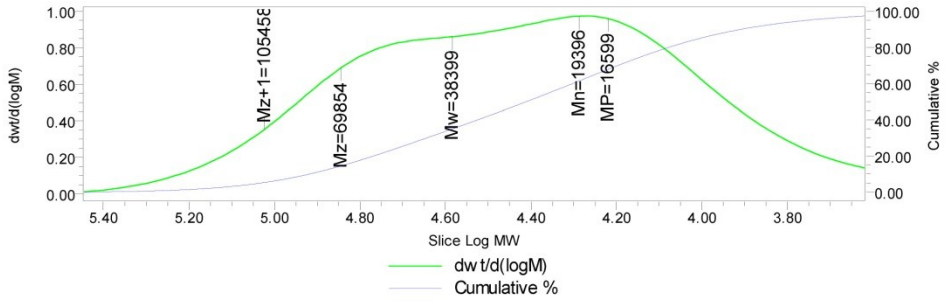


**Figure S4** GPC data for PBIBDF-HT

## SAMPLE INFORMATION

| | | | |
|---|---|---|---|
| Sample Name: | 0620 | Acquired By: | System |
| Sample Type: | Broad Unknow n | Sample Set Name: | |
| Vial: | 6 | Acq. Method Set: | 20150202 |
| Injection #: | 16 | Processing Method: | ljq0319 |
| Injection Volume: | 25.00 ul | Channel Name: | 410 |
| Run Time: | 15.0 Minutes | Proc. Chnl. Descr.: | 410 |
| Date Acquired: | 2015/3/19 21:31:50 HKT | | |
| Date Processed: | 2015/3/20 15:19:45 HKT | | |




### GPC Sample Results

| | Retention Time | Mn | Mw | MP | Mz | Poly-dispersity |
|---|---|---|---|---|---|---|
| 1 | 8.883 | 19396 | 38399 | 16599 | 69854 | 1.980 |



**Figure S5** GPC data for PBIBDF-TT

[1]. Zhang, G. B.; Li, P.; Tang, L. X.; Ma, J. X.; Wang, X. H.; Lu, H. B.; Kang, B.; Cho, K.; Qiu, L. Z. A bis(2-oxoindolin-3-ylidene)-benzodifuran-dione containing copolymer for high-mobility ambipolar transistors, *Chem. Commun.*, **2014**, 50, 3180.

[2]. Osaka, I.; Sauve, G.; Zhang, R.; Kowalewski, T.; McCullough, R. D. Novel thiophene-thiazolothiazole copolymers for organic field-effect transistors, *Adv. Mater.*, **2007**, 19, 4160.