

SUPPORTING INFORMATION

Phthalimide-Based Wide Bandgap Donor Polymers for Efficient Non-Fullerene Solar Cells

Jianwei Yu,^{†,‡,+} Jie Yang,^{†,+} Xin Zhou,[†] Simiao Yu,[‡] Yumin Tang,[†] Hang Wang,^{†,‡}
Jianhua Chen,[†] Shiming Zhang,^{*,‡} Xugang Guo^{*,†}

[†] *Department of Materials Science and Engineering and The Shenzhen Key Laboratory for Printed Organic Electronics, South University of Science and Technology of China, No. 1088, Xueyuan Road, Shenzhen, Guangdong 518055, China*

[‡] *Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, China*

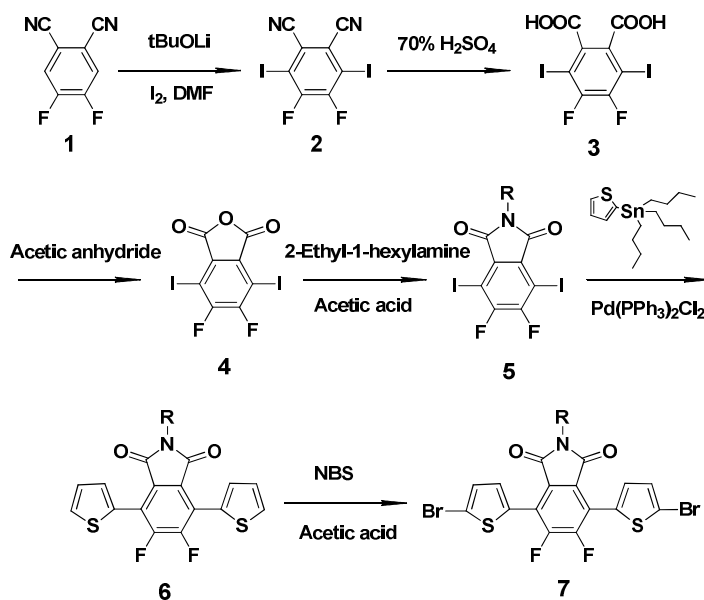
1. Materials and Methods.

All reagents and chemicals are commercially purchased and used without further purification unless otherwise stated. Anhydrous THF and toluene are distilled from Na/benzophenone. The known polymer TPhI-BDT is prepared according to the published procedures.¹ Monomer (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) is purchased from SunaTech Inc. (Suzhou, Jiangsu). All other reagents are used as received unless otherwise stated. All manipulations and reactions are performed under argon using the standard Schlenk line technique, and polymerizations are carried out on Initiator⁺ Microwave Synthesizer (Biotage, Sweden). ¹H and ¹³C spectra are recorded on a Bruker Ascend 500 MHz spectrometer. ¹⁹F spectra are recorded on a Bruker Ascend 400 MHz

spectrometer. Chemical shifts are referenced to residual protio-solvent signals. C, H, and N elemental analyses (EA) of monomers and polymers are performed at the Institute of Chemistry, Chinese Academy of Sciences. Polymer molecular weights are measured on Polymer Laboratories GPC-PL220 high temperature GPC/SEC system at 150 °C vs polystyrene standards using trichlorobenzene as the eluent. DSC curves are recorded on a differential scanning calorimetry (Mettler, STARe, heating rate: 10 °C/min, N₂ purge). TGA curves are recorded on a TA Instrument (Mettler, STARe). UV-Vis spectra are recorded on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. CV measurements of polymer films are carried out under argon atmosphere using a CHI760E voltammetric analyzer with 0.1 M tetra-*n*-butylammonium hexafluorophosphate in acetonitrile as supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and silver wire reference electrode are employed, and Fc/Fc⁺ is used as the internal reference for all measurements. The scan rate is 100 mV/S. Polymer films are drop-coated from chloroform solutions on a Pt working electrode (2 mm diameter). The supporting electrolyte solution is thoroughly purged with argon before all CV measurements. AFM measurements are performed by using a Dimension Icon Scanning Probe Microscope (Asylum Research, MFP-3D-Stand Alone) in tapping mode. TEM specimens are prepared following identical conditions as the actual devices, but are drop-cast onto 40 nm PEDOT:PSS covered substrate. After drying, the substrates are transferred to deionized water and the floated films are transferred to TEM grids. TEM images are obtained on Tecnai Spirit (20 kV) TEM.

2. Monomer and Polymer Synthesis.

Scheme S1. Synthetic Routes of the Related Monomer.



4,5-difluoro-3,6-diiodophthalonitrile (2). 1,2-Difluoro-phthalonitrile **1** (400 mg, 2.44 mmol) and I₂ (1856 mg, 7.32 mmol) were stirred in DMF (2 mL) and a solution of lithium tert-butoxide in DMF (2.28 mL, 3.2 M) was added in one portion.² After the exothermic reaction cooled, the reaction mixture was placed in a 60 °C oil bath for 30 min. The solution was cooled to room temperature and poured into a saturated solution of sodium thiosulfate. The precipitated solid was collected by filtration and washed with water 3x. The crude product was purified via column chromatography on silica gel using ethyl acetate:petroleum ether (1:30) as the eluent to give compound **2** as a white solid (420 mg, 41%). ¹⁹F NMR (400 MHz, CDCl₃) δ -102.6 (s, 2F).

4,5-difluoro-3,6-diiodophthalic acid (3). Compound **2** (458 mg, 1.10 mmol) and aqueous H₂SO₄ (70%, 5 mL) were heated to 150 °C in a sealed screwcap tube 12 h.

The cooled solution was poured into ice water and extracted with dichloromethane 3x. The combined organic layers were washed with water (until the aqueous layer was neutral to litmus), brine and then dried. Evaporation of the solvent yielded a yellow solid compound **3**, which can be used for the next reaction without further purification (425 mg, 85%).

5,6-difluoro-4,7-diiodoisobenzofuran-1,3-dione (4). Compound **3** (400 mg, 0.88 mmol) and acetic anhydride (12 mL) were placed in a screwcap tube and purged with N₂ for 15 minutes. The tube was then sealed and placed in a 150 °C oil bath and the mixture was stirred overnight. After cooled to room temperature, evaporation of the solvent yielded a brown solid compound **4**, which can be used for the next reaction without further purification (340 mg, 89%).

2-(2-ethylhexyl)-5,6-difluoro-4,7-diiodoisoindoline-1,3-dione (5). Compound **4** (340 mg, 0.78 mmol), 2-ethyl-1-hexylamine (129 mg, 1 mmol) and glacial acetic acid (5 ml) were combined and refluxed under N₂ for 6 h. After the acetic acid was removed under reduced pressure, the crude product was purified via column chromatography on silica gel using dichloromethane:petroleum ether (1:1) as the eluent to give compound **5** as a white solid (320 mg, 75%). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 3.61 (m, 2H), 1.83 (m, 1H), 1.32 (m, 8H), 0.92 (m, 6H).

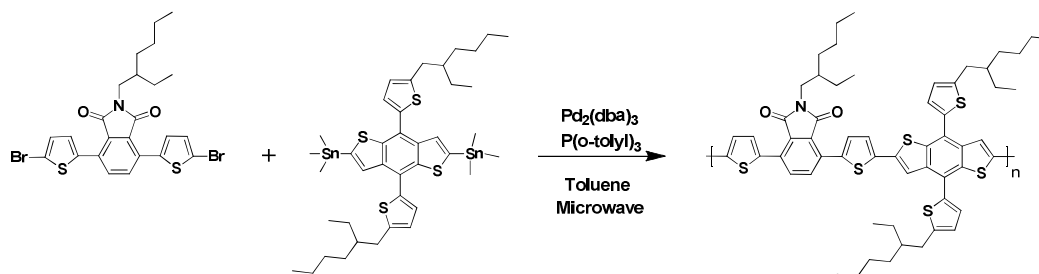
2-(2-ethylhexyl)-5,6-difluoro-4,7-di(thiophen-2-yl)isoindoline-1,3-dione (6). A glass tube was charged with compound **5** (320 mg, 0.58 mmol), 2-(tributylstannyl)thiophene (649 mg, 1.74 mmol), and Pd(PPh₃)₂Cl₂ (35 mg, 0.05 mmol). The reaction tube and its contents were subjected to 3 pump/purge cycles with

argon, followed by the addition of anhydrous toluene (12 mL) via syringe. The tube was sealed under argon flow and then stirred at 130 °C for 3 h under microwave irradiation. After the toluene was removed under reduced pressure, the crude product was purified via column chromatography on silica gel using dichloromethane:petroleum ether (1:1) as the eluent to give compound **6** as a yellow solid (247 mg, 92%). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 7.64 (d, 2H), 7.54 (d, 2H), 7.24 (m, 2H), 3.54 (m, 2H), 1.79 (m, 1H), 1.28 (m, 8H), 0.89 (m, 6H).

4,7-bis(5-bromothiophen-2-yl)-2-(2-ethylhexyl)-5,6-difluoroisoindoline-1,3-dione (7). Compound **6** (247 mg, 0.54 mmol) and NBS (44 mg, 0.25 mmol) were added into a glass bottle, followed by 10 mL chloroform and 0.25 mL acetic acid. The mixture was stirred under room temperature overnight. Then, the mixture was extracted with dichloromethane, washed with water and then dried over anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure. The crude product was purified via column chromatography on silica gel using ethyl dichloromethane:petroleum ether (1:1) as the eluent to give compound **7** as a yellow solid (325 mg, 98%). ¹⁹F NMR (400 MHz, CDCl₃) δ -125.4 (s, 2F). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 7.28 (d, 2H), 7.16 (d, 2H), 3.52 (m, 2H), 1.78 (m, 1H), 1.28 (m, 8H), 0.89 (m, 6H). ¹³C NMR (500 MHz, CDCl₃), δ (ppm): 165.6, 152.4-150.4, 132.4, 130.0, 128.6, 125.3, 122.2, 116.7, 42.6, 38.2, 30.5, 28.5, 23.9, 23.0, 14.1, 10.4.

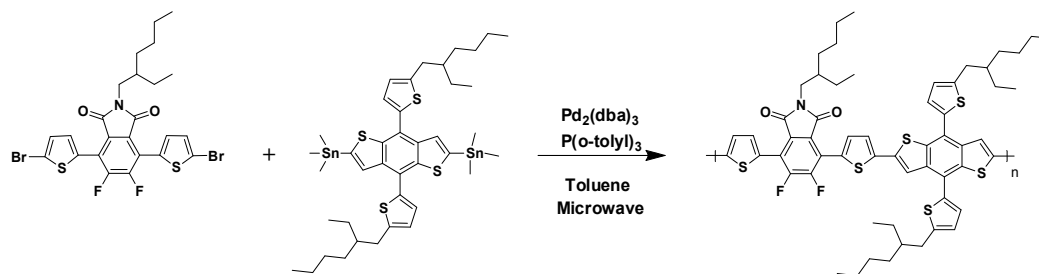
General Procedure for Polymerizations via Stille Coupling for the Synthesis of Polymer TffPhI-BDT and TPhI-BDT. An glass tube was charged with two compounds (1.0 equiv each), Pd₂(dba)₃ (0.015 equiv), and P(*o*-tolyl)₃ (0.12 equiv).

The tube and its contents were subjected to 3 pump/purge cycles with argon, followed by the addition of anhydrous toluene (6-8 mL) via syringe. The tube was sealed under argon flow and then stirred at 80 °C for 10 minutes, 110 °C for 10 minutes, and 140 °C for 1 h under microwave irradiation. Then, 0.1 mL of 2-(tributylstanny)thiophene was added and the reaction mixture was stirred under microwave irradiation at 140 °C for 0.5 h. Finally, 0.2 mL of 2-bromothiophene was added and the reaction mixture was stirred at 140 °C for another 0.5 h. After cooling to room temperature, the reaction mixture was slowly dripped into 100 mL methanol containing 5 mL 12 N hydrochloric acid under vigorous stirring. After stirring for 4 h, the solid precipitate was transferred to a Soxhlet thimble. After drying, the crude product was subjected to sequential Soxhlet extraction with solvents and sequence depending on the solubility of the particular polymer. After final extraction, the polymer solution was concentrated to ~20 mL, and then dripped into 100 mL methanol under vigorous stirring. The polymer was collected by filtration and dried under reduced pressure to afford a dark red solid as the product.



TPhI-BDT. The solvent sequence for Soxhlet extraction was methanol, acetone, hexane, dichloromethane, and chloroform. TPhI-BDT was obtained as a dark red solid with a yield of 82%.¹ $M_n = 40$ kDa, PDI = 1.8. Anal. Calcd for $\text{C}_{58}\text{H}_{63}\text{NO}_2\text{S}_6$ (%): C,

69.77; H, 6.36; N, 1.40. Found (%): C, 69.12; H, 6.42; N, 1.60.



TffPhI-BDT. The solvent sequence for Soxhlet extraction was methanol, acetone, hexane, dichloromethane, and chloroform. TffPhI-BDT was obtained as a dark red solid with a yield of 75%. $M_n = 36$ kDa, PDI = 1.7. ^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) δ 7.20-7.17 (m, 2H), 6.97 (s, 2H), 6.80-6.75 (m, 4H), 6.37 (s, 2H), 2.96(s, 2H), 2.34-2.33 (d, 4H), 1.24 (m, 1H), 1.15-1.14(m, 2H), 0.91-0.72(m, 24H), 0.43-0.31(m, 18H). Anal. Calcd for $\text{C}_{58}\text{H}_{61}\text{F}_2\text{NO}_2\text{S}_6$ (%): C, 67.33; H, 5.94; N, 1.35. Found (%): C, 66.78; H, 5.82; N, 1.34.

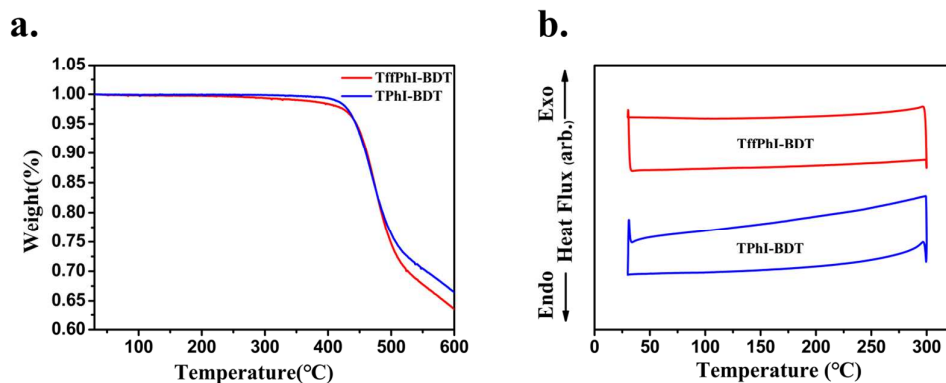


Figure S1. (a) Thermogravimetric analysis of polymers TPhI-BDT and TffPhI-BDT at temperature ramp rate of 10 °C /min. (b) DSC thermograms of TPhI-BDT and TffPhI-BDT from the second heating and cooling scans at a temperature ramp rate of

10 °C /min under N₂.

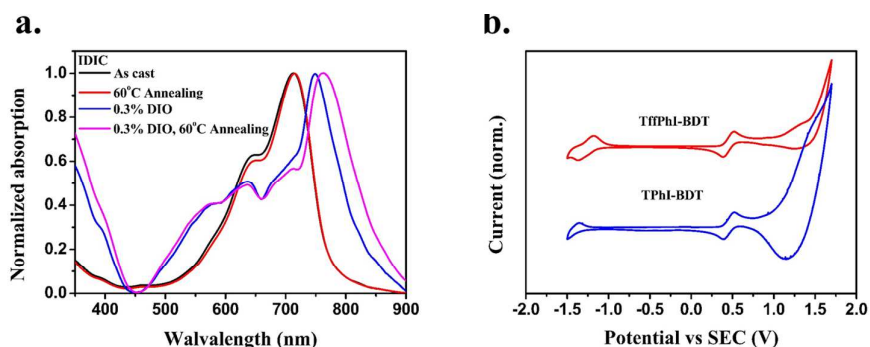


Figure S2. (a) Optical absorption spectra of IDIC film; (b) cyclic voltammograms of TPhI-BDT and TffPhI-BDT film in 0.1 M (n-Bu)₄N⁺PF₆⁻ acetonitrile solution, Fc/Fc⁺ redox couple was used as an external standard having an oxidation potential of +0.45 V vs SCE.

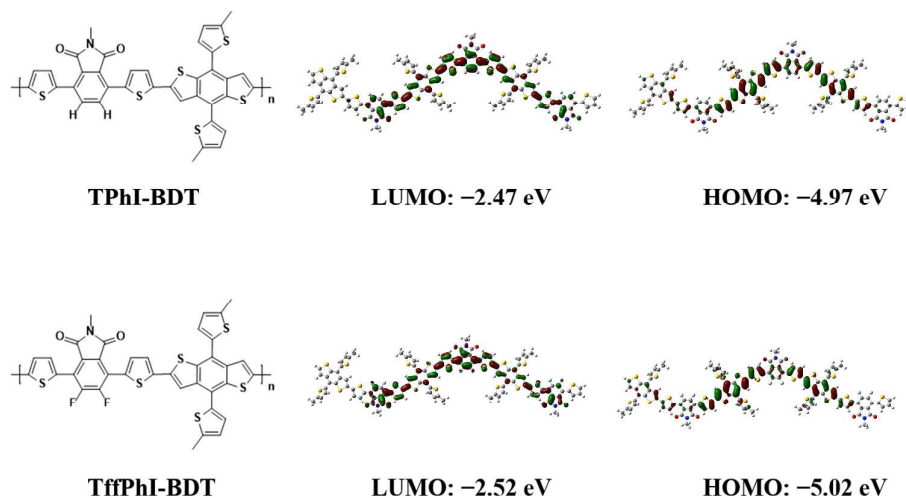


Figure S3. Chemical structures and spatial distribution of frontier molecular orbitals of the repeating units of phthalimide-based polymers. Calculations were carried out at the DFT//B3LYP/6-31G* level.

3. Device Fabrication and Characterization.

Solar Cell Device Fabrication. ITO-coated glass with a sheet resistance of < 10 Ω sq⁻¹ was used as the substrate, which was cleaned by sequential sonication in H₂O

containing detergent, deionized H₂O, acetone, and isopropanol followed by UV/ozone (BZS250GF-TC, HWOTECH, Shenzhen) treatment for 15 min. PEDOT/PSS were then spin-coated (3000) onto ITO glasses. All the films were annealed under 150 °C for 15 min and then were transferred into N₂ glovebox. TPhI-BDT:IDIC and TffPhI-BDT:IDIC blend solution were spin-coated (2000 rpm for 30 s) onto PEDOT:PSS film. Then, PDINO (5nm, 1mg/mL in methanol) were spin-coated (3000 rpm for 30 s) onto the active layers. Finally, Al electrodes were thermally evaporated using a shadow mask under vacuum (pressure $\approx 10^{-4}$ Pa) with the effective device area of 0.045 cm².

Table S1. Device performance parameters of conventional PSCs with a structure of ITO/PEDOT:PSS/TffPhI-BDT:IDIC/PDINO/Al. The TffPhI-BDT:IDIC films were fabricated with different D/A ratios from 1:1.5 to 1.5:1 (w/w) from chloroform solution and 0.3% (v/v) DIO was added as the processing additive.

Condition	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
1:1.5 0.3% DIO	0.94	16.11	48.8	7.41
1:1.5 0.3% DIO+AT ^a	0.95	15.81	51.9	7.81
1:1 0.3% DIO	0.94	14.41	61.4	8.33
1:1 0.3% DIO+AT ^a	0.93	15.92	63.9	9.48
1.5:1 0.3% DIO	0.95	10.50	58.8	5.84
1.5:1 0.3% DIO+AT ^a	0.95	10.50	60.6	6.03

^a Annealed under 60 °C for 10min.

Table S2. Device performance parameters of conventional PSCs with a structure of ITO/PEDOT:PSS/TffPhI-BDT:IDIC(1:1,w/w)/PDINO/Al. Different amount of DIO from 0.1%-0.3% (v/v) was added as the processing additive.

Condition	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
0.1% DIO	0.97	13.63	58.1	7.70
0.1% DIO+AT ^a	0.97	14.08	58.4	7.95
0.3% DIO	0.94	14.41	61.4	8.33

0.3% DIO+AT ^a	0.93	15.92	63.9	9.48
0.5% DIO	0.83	6.29	45.7	2.38
0.5% DIO+AT ^a	0.92	13.39	62.5	7.73

^a Annealed under 60 °C for 10min.

Table S3. Device performance parameters of conventional PSCs with a structure of ITO/PEDOT:PSS/ TffPhI-BDT:IDIC(1:1,w/w)/PDINO/Al. 0.3% (v/v) DIO was added before spin-coating. The film were Annealing at different temperature from 60-80 °C.

Condition	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
Without AT	0.94	14.41	61.4	8.33
60	0.93	15.92	63.9	9.48
80	0.95	15.19	57.7	8.30
100	0.95	16.56	51.0	7.98

Table S4. Device performance parameters of conventional PSCs with a structure of ITO/PEDOT:PSS/TffPhI-BDT:IDIC(1:1,w/w)/PDINO/Al. 0.3% (v/v) of DIO, DPE, CN, PN and OM-A were added as the processing additive before spin-coating.

Condition	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
0.3% DIO	0.94	14.41	61.4	8.33
0.3% DIO AT ^a	0.93	15.92	63.9	9.48
0.3% DPE	0.99	12.46	55.8	6.87
0.3% DPE AT ^a	0.98	12.67	56.1	7.00
0.3% CN	0.98	11.42	60.1	6.76
0.3% CN AT ^a	0.98	12.96	58.9	7.52
0.3% PN	0.60	1.28	31.5	0.24
0.3% PN AT ^a	0.95	2.96	28.5	0.80
0.3% OM-A	0.99	12.07	55.4	6.59
0.3% OM-A AT ^a	0.99	13.40	53.2	7.05

^a Annealed under 60 °C for 10 min.

Table S5. Photovoltaic Performance Parameters of OSCs Incorporating Polymer:IDIC (1:1, w/w) active layer under the Illumination of AM 1.5G, 100 mW/cm².

active layer	V_{oc} (V)	J_{sc} (mA cm ²)	Cal. J_{sc} (mA cm ²) _b	FF (%)	PCE _{max/aver} (%) ^c
TPhI-BDT:IDIC	0.93	12.53	12.41	55.5	6.46/6.44
TPhI-BDT:IDIC AT ^a	0.93	13.02	13.24	54.3	6.59/6.48
TPhI-BDT:IDIC DIO ^a	0.91	12.61	12.42	60.9	6.98/6.81
TPhI-BDT:IDIC	0.90	14.07	14.09	66.0	8.31/8.09

TffPhI-BDT:IDIC	0.99	12.66	12.74	56.3	7.02/6.93
TffPhI-BDT:IDIC AT ^a	0.99	13.04	13.12	56.1	7.21/7.13
TffPhI-BDT:IDIC DIO ^a	0.94	14.41	14.02	61.4	8.33/8.27
TffPhI-BDT:IDIC	0.93	15.92	15.80	63.9	9.48/9.30

^a Annealed under 60 °C for 10 min, 0.3% (v/v) DIO addition. ^b J_{sc} Integrated from EQE curves. ^c The average value of PCE is calculated with 10 devices.

Hole and electron mobility measurements through SCLC method. Hole mobility is characterized from hole-only device structure of ITO/PEDOT:PSS/TPhI-BDT:IDIC or TffPhI-BDT:IDIC/Au³⁻⁵. Electron-only mobility is characterized from electron-only device structure of ITO/ZnO/TPhI-BDT:IDIC and TffPhI-BDT:IDIC/PDINO/Al.⁶⁻⁸ The active films were prepared in the same condition as the optimal solar cell devices. Hole-only and electron-only mobilities were calculated according to the MOTT-Gurney equation:⁶⁻⁷

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{L^3}$$

Where J is the current density, ϵ_r is the relative dielectric constant of active layer material usually 2-4 for organic semiconductor, herein we use a relative dielectric constant of 4, ϵ_0 is the permittivity of empty space, μ is the mobility of hole or electron and d is the thickness of the active layer, V is the internal voltage in the device, and $V = V_{app} - V_{bi}$, where V_{app} is the voltage applied to the device, and V_{bi} is the built-in voltage resulting from the relative work function difference between the two electrodes (the V_{bi} values of hole-only⁷ and electron-only⁶ devices were all selected as 0 V).

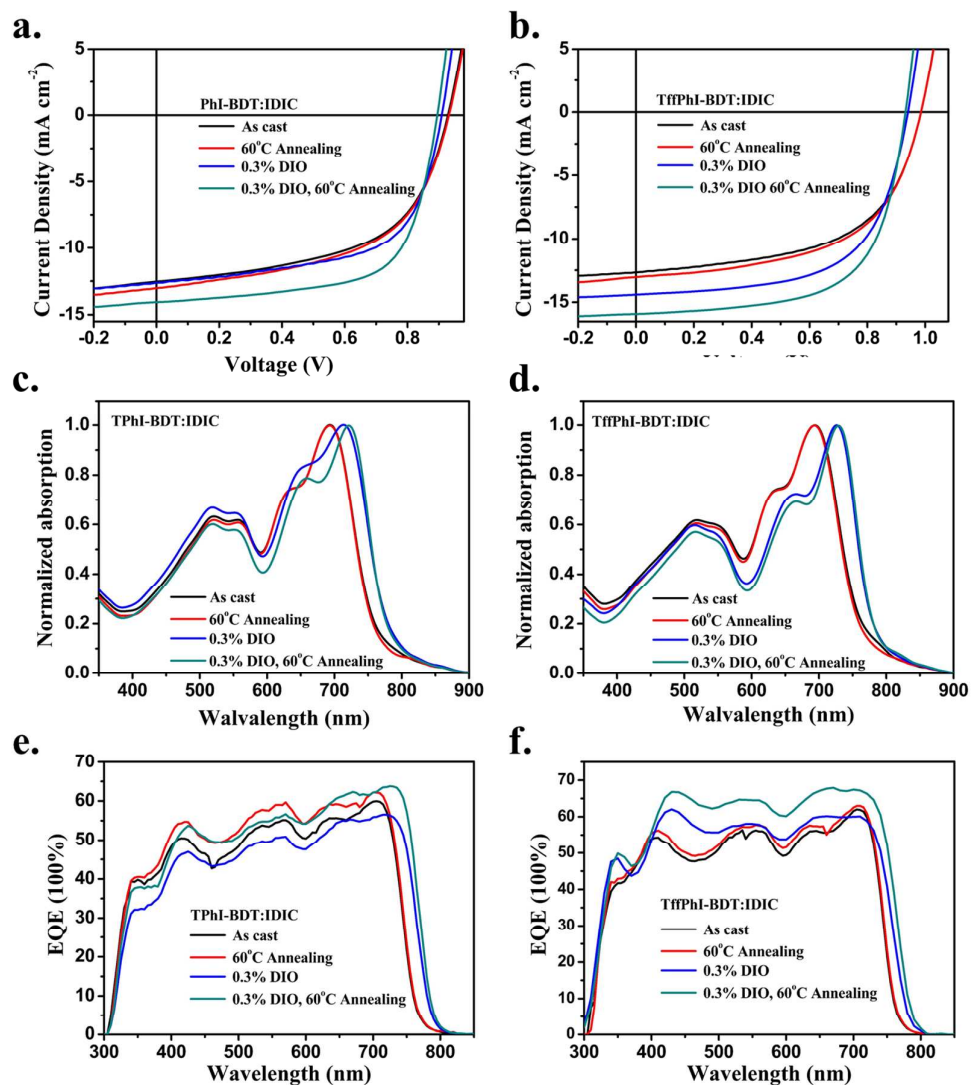


Figure S4. (a, b) Representative $J-V$ characteristics of TPhI-BDT:IDIC and TffPhI-BDT:IDIC OSCs under AM 1.5G radiation (100 mW cm⁻²); (c, d) absorption spectra of TPhI-BDT:IDIC and TffPhI-BDT:IDIC blend films spin-coated from chloroform solutions (5 mg mL⁻¹); (e, f) corresponding EQE spectra of the corresponding OSC devices.

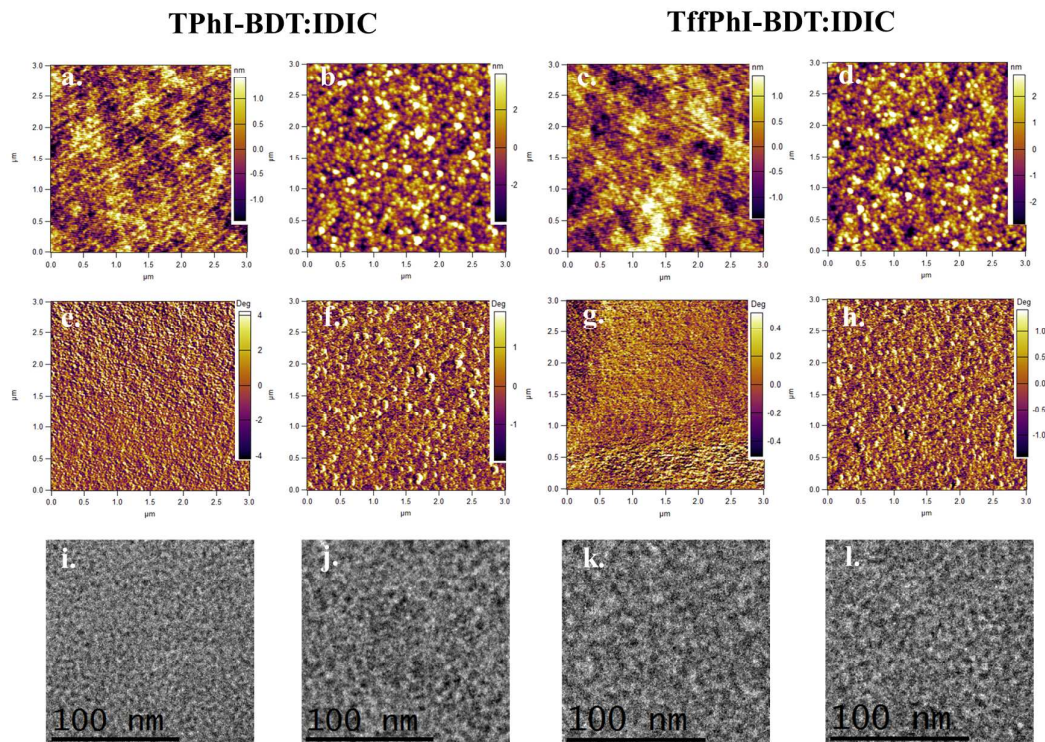


Figure S5. Tapping-mode AFM height (a, b and c, d), phase images (e, f and g, h) and TEM images (i, j and k, l) of TPhI-BDT:IDIC and TffPhI-BDT:IDIC blend films; (a, c, e, g, i, k) are the films after thermal annealing at 60 $^{\circ}\text{C}$, (b, d, f, h, j, l) are the films processed with 0.3% DIO.

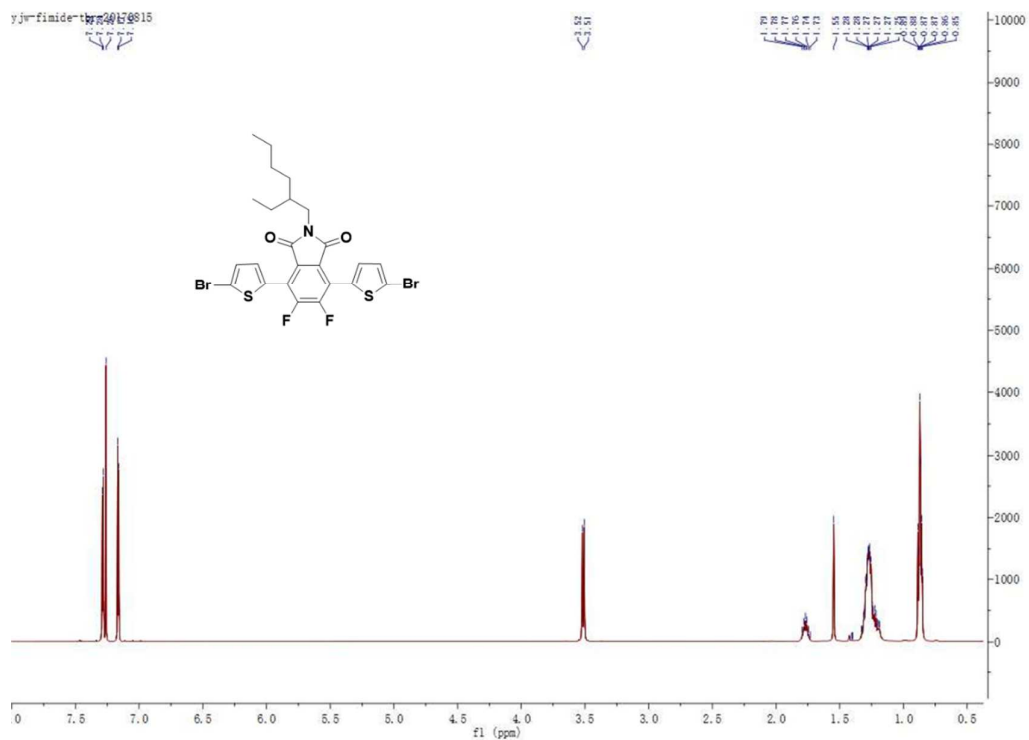


Figure S6. ¹H NMR spectrum of monomer 7.

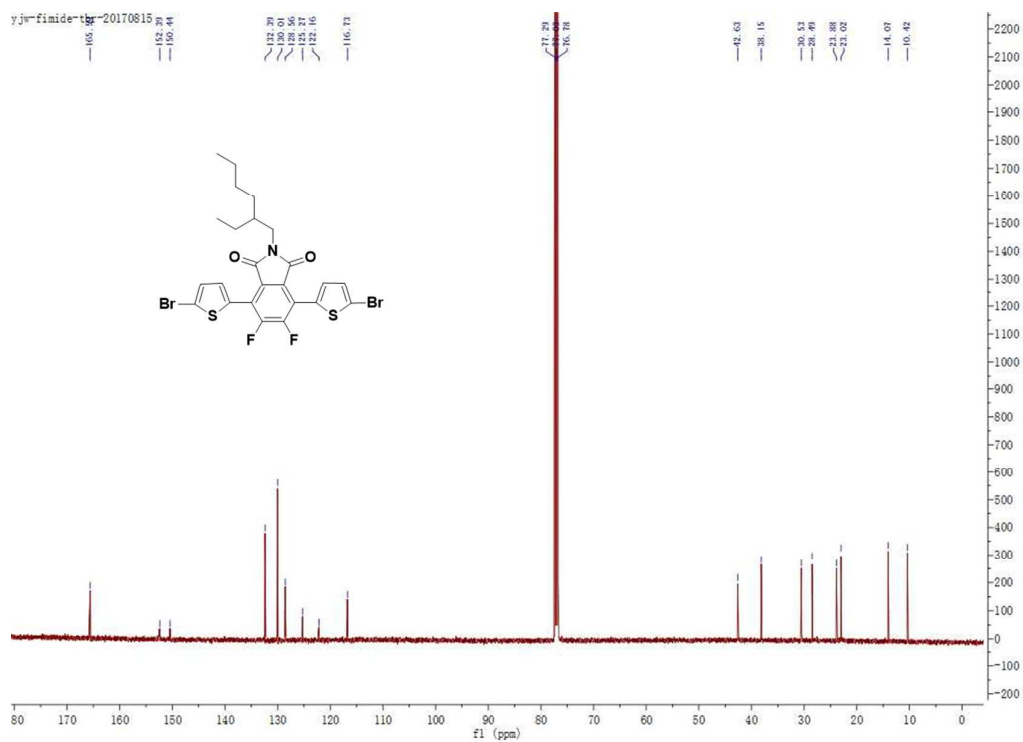


Figure S7. ¹³C NMR spectrum of monomer 7.

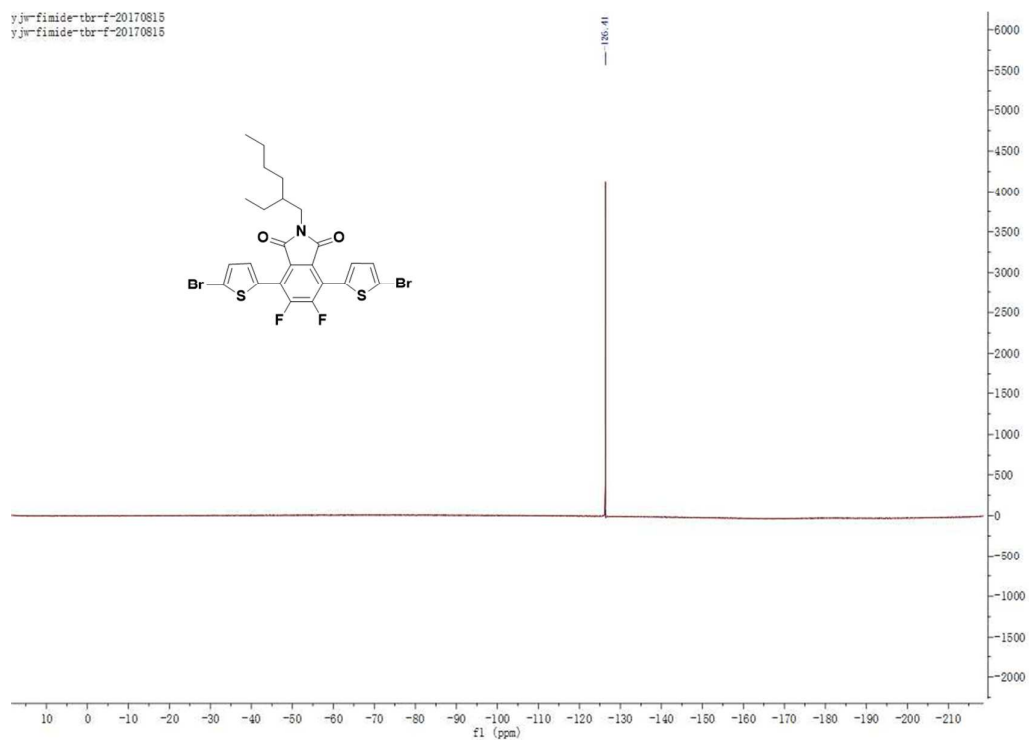


Figure S8. ^{19}F NMR spectrum of monomer 7.

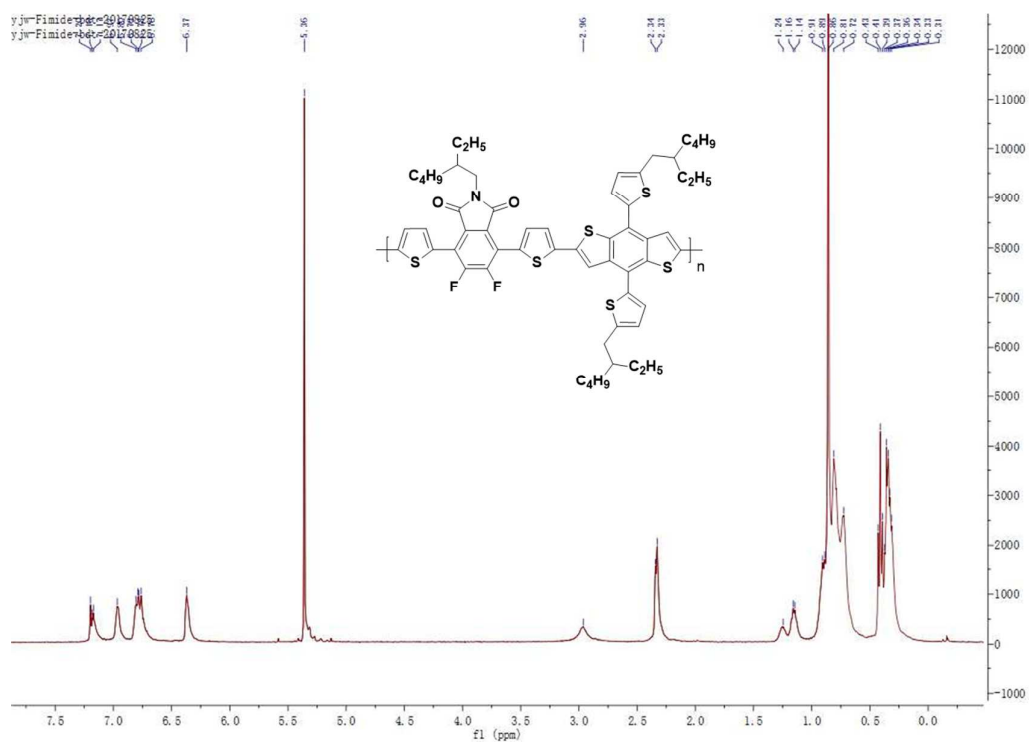


Figure S9. ^1H NMR spectrum of polymer TffPhI-BDT (80 °C, in $\text{C}_2\text{D}_2\text{Cl}_4$).

References:

1. Huang, J.; Wang, X.; Zhan, C.; Zhao, Y.; Sun, Y.; Pei, Q.; Liu, Y.; Yao, J. *Org. Lett.* **2009**, *11* (2), 421-423.
3. Gao, L.; Zhang, Z. G.; Xue, L.; Min, J.; Zhang, J.; Wei, Z.; Li, Y. *Adv. Mater.* **2016**, *28* (9), 1884-1890.
4. Yuan, J.; Qiu, L.; Zhang, Z.-G.; Li, Y.; Chen, Y.; Zou, Y. *Nano Energy* **2016**, *30*, 312-320.
5. Bin, H.; Zhang, Z. G.; Gao, L.; Chen, S.; Zhong, L.; Xue, L.; Yang, C.; Li, Y. *J. Am. Chem. Soc.* **2016**, *138* (13), 4657-4664.
6. Bin, H.; Gao, L.; Zhang, Z. G.; Yang, Y.; Zhang, Y.; Zhang, C.; Chen, S.; Xue, L.; Yang, C.; Xiao, M.; Li, Y. *Nat. Commun.* **2016**, *7*, 13651.
7. Shi, S.; Liao, Q.; Tang, Y.; Guo, H.; Zhou, X.; Wang, Y.; Yang, T.; Liang, Y.; Cheng, X.; Liu, F.; Guo, X. *Adv. Mater.* **2016**, *28* (45), 9969-9977.
8. Zhong, L.; Gao, L.; Bin, H.; Hu, Q.; Zhang, Z.-G.; Liu, F.; Russell, T. P.; Zhang, Z.; Li, Y. *Adv. Energy Mater.* **2017**, *7* (14), 1602215.