Electron acceptors based on alpha-substituted PDI for organic solar cells

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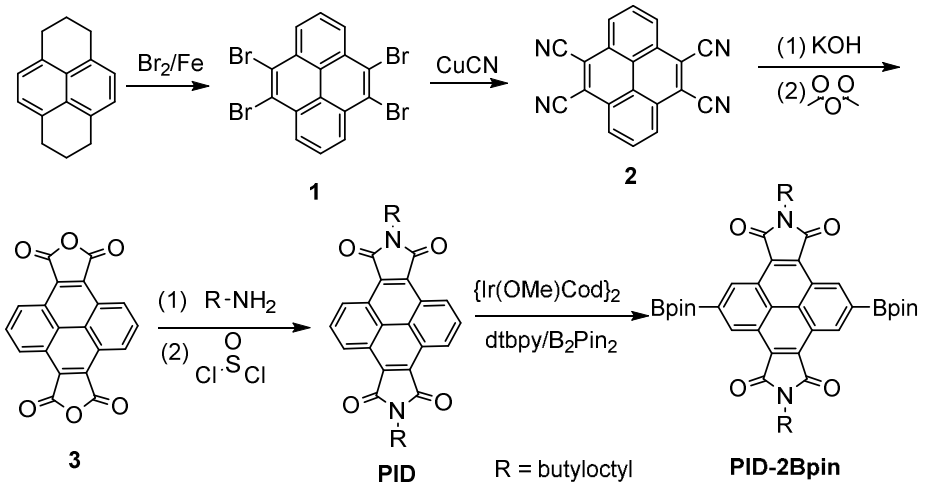
1. The synthesis and characterization



Scheme 1. The synthesis of PID-2Bpin.

Compound **4**, **5**, **7**, **8** and 1,2,3,6,7,8-hexahydropyrene was synthesized according to the literature.[1-3]

Compound **1**

1,2,3,6,7,8-hexahydropyrene (3.12 g), Bromine (27.17 g), iron powder (0.59 g) and 100 ml dichloromethane were added to a 250 mL round bottom flask and refluxed overnight. The precipitate was filtered and washed with acetone (3×200 ml) and boiling chloroform (3×200 ml). 6.52g 4,5,9,10-tetrabromopyrene was obtained in the yield of 84%. MS (MALDI-TOF) m/z : $C_{16}H_6Br_4$ m/z: 517.84; Found: 518.15 $(M+H)^+$

Compound **2** and **3**

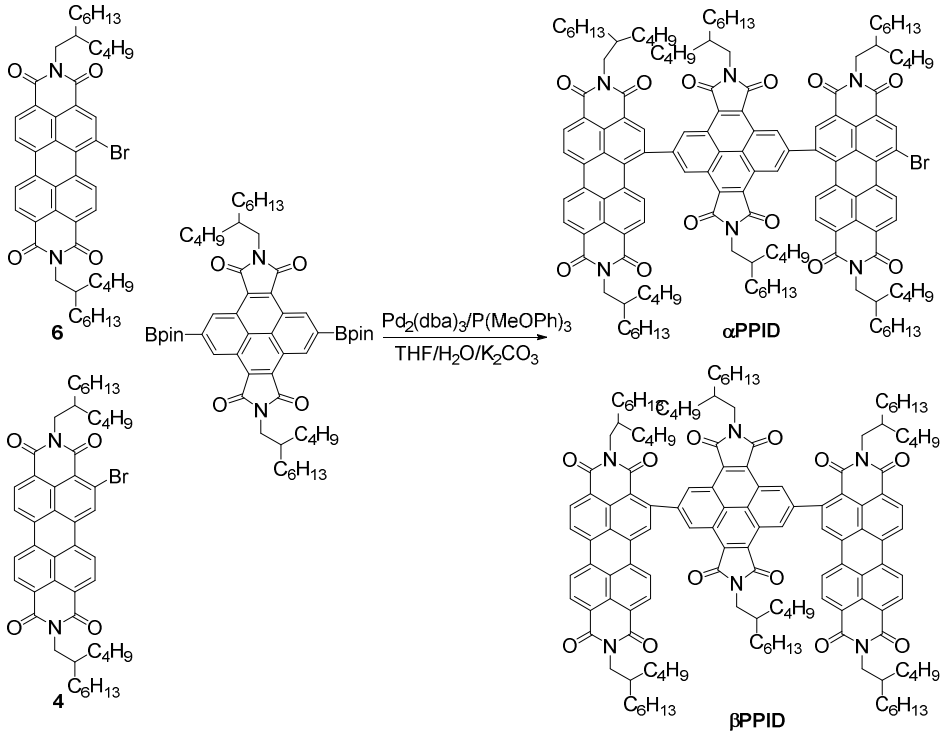
4,5,9,10-tetrabromopyrene (6.20 g), CuCN (8.60 g) and anhydrous NMP were added to a 250 mL round bottom flask under nitrogen atmosphere and reacted at 200 °C for 2 hours. After cooling down, the solution was poured into saturated ammonium. The precipitate was filtered and washed with ammonium, acetone and boiling chloroform. Without further purification, the insoluble solid was added to the KOH (13.5 g) solution in $HOCH_2CH_2OH$ (60 mL) and water (15 mL) and heated to 160 for 48 hours. After cooling down to 0, concentrated hydrochloric acid were added dropwise to pH = 1. The precipitate was filtered and washed with water and acetone. The obtained crude product was refluxed in acetic anhydrate (60 ml) overnight. 0.65 g yellow product was obtained by filtration. The yield for three-step reactions is 15.8 %. The solubility of compound **2**, **3** are very low in common solvent such as chloroform, chlorobenzene, DMF, DMSO.

Compound PID

0.34 g compound **3** and 0.56 g 2-butyloctylamine in 20 ml anhydrous toluene was heated to reflux for 5 hours. After removing the solvent under reduced pressure, the reaction mixture was added thionyl chloride (5 ml) and refluxed for 2 hours. The thionyl chloride was removed under reduced pressure. The crude product was purified by column chromatography, using dichloromethane as the eluent. 0.51 g compound **3** was obtained (yield: 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.49 (d, J = 80 Hz, 4H), 8.28 (T, J = 80 Hz, 2H), 3.74 (d, J = 72 Hz, 4H), 2.0 (m, 2H), 1.35 (br, 32H), 0.90 (br, 12H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.096, 14.127, 22.663, 23.072, 26.391, 28.607, 29.707,31.276, 31.618, 31.861, 37.328, 42.367, 124.484, 126.721, 128.244, 128.715, 128.810, 169.792. MS (MALDI-TOF) $C_{44}H_{56}N_2O_4$ m/z: 676.42; Found: 677.13 $(M + H)^+$

Compound PID-2Bpin

{Ir(OMe)Cod} (33 mg), 4,4'-di-tert-butyl-2,2'-dipyridyl (66 mg) and $(BPin)_2$ (64 mg) were mixed in20 ml anhydrous hexane under N_2 atmosphere. Then the mixture were transfer to sealed tube which contains compound 3 (0.338 g) and $(BPin)_2$ (0.254 g). After reacting at 120 °C for 24 hours, the solvent was removed under reduced pressure. 0.288 g of pure compound 4 (62 %) was obtained by column chromatography, using dichloromethane as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.86 (s, 4H), 3.76 (d, J = 72 Hz, 4H), 2.0 (m, 2H), 1.50 (s, 24H)1.35 (br, 32H), 0.88 (br, 12H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.102, 14.179, 22.660, 23.122, 25.133, 26.605, 28.872, 29.776, 31.420, 31.756, 31.918, 37.388, 42.662, 84.636, 123.678, 128.034, 129.296, 132.428, 169.447. MS (MALDI-TOF) $C_{56}H_{78}B_2N_2O_8$ m/z: 928.59; Found: 929.97 $(M + H)^+$.



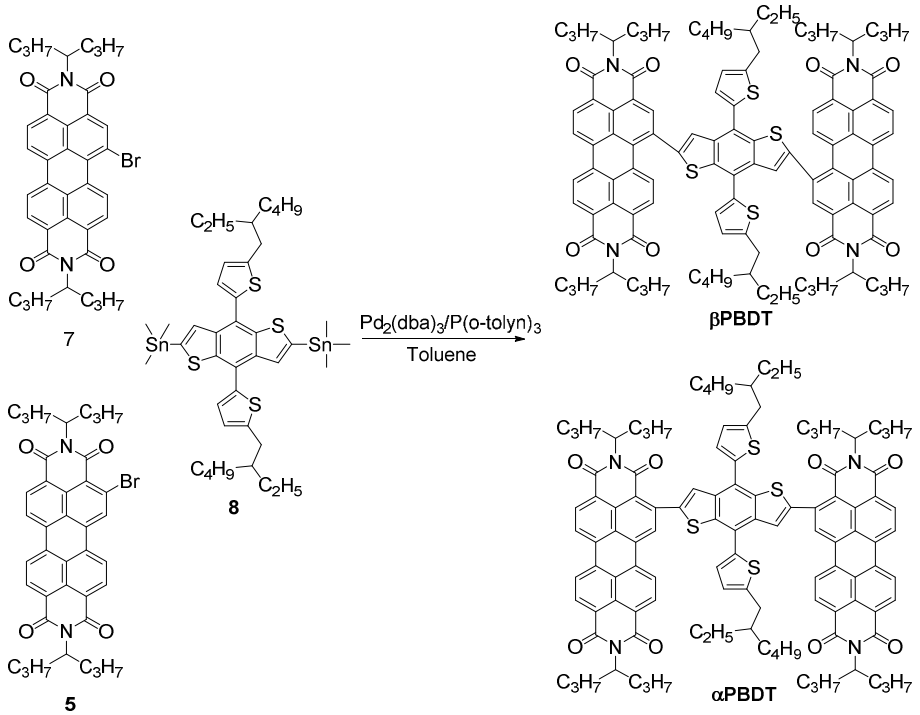
Scheme 2. The synthesis of βPPID and αPPID.

Compound βPPID

$Pd_2(dba)_3$ (9 mg)and $P(MeOPh)_3$ was added to the mixture of compound **4** (104 mg), compound **3** (60 mg), THF (8 mL) and 2M K_2CO_3 aqueous solution (2 mL) under nitrogen. After refluxing overnight, the mixture was poured into methanol. The red precipitate was filtered and purified by column chromatography, using chloroform as the eluent. 96 mg of pure βPPID (70%) was obtained. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ (ppm): 9.79 (s, 4H), 8.78 (br, 10H), 7.90 (d, J = 84 Hz 2H), 7.63 (d, J = 84 Hz 2H), 4.1 (br, 8H), 3.59 (br, 4H) 2.1 (br, 6H), 1.26 (br, 96H), 0.90 (br, 36H). MS (MALDI-TOF) $C_{140}H_{168}N_6O_{12}$ m/z: 2125.27; Found: 2125.68 (M^+). Anal. Calcd for $C_{140}H_{168}N_6O_{12}$: C, 79.06; H, 7.96; N, 3.95. Found: C, 79.12; H, 8.06; N, 4.04.

Compound αPPID

αPPID was synthesized according to the same procedure as βPPID in the yield of 76%. (Due to the self-assembly of αPPID, the multiple and broad peaks was observed in ^{1}H NMR) ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ (ppm): 9.37-9.72 (br, 4H), 8.98-7.73 (br, 14H), 4.36-3.71 (br, 12H), 2.20-1.98 (br, 6H), 1.33 (br, 96H), 0.90 (br, 36H). MS (MALDI-TOF) $C_{140}H_{168}N_6O_{12}$ m/z: 2125.27; Found: 2125.82 (M^+) Anal. Calcd for $C_{140}H_{168}N_6O_{12}$: C, 79.06; H, 7.96; N, 3.95. Found: C, 79.49; H, 8.14; N, 4.05.



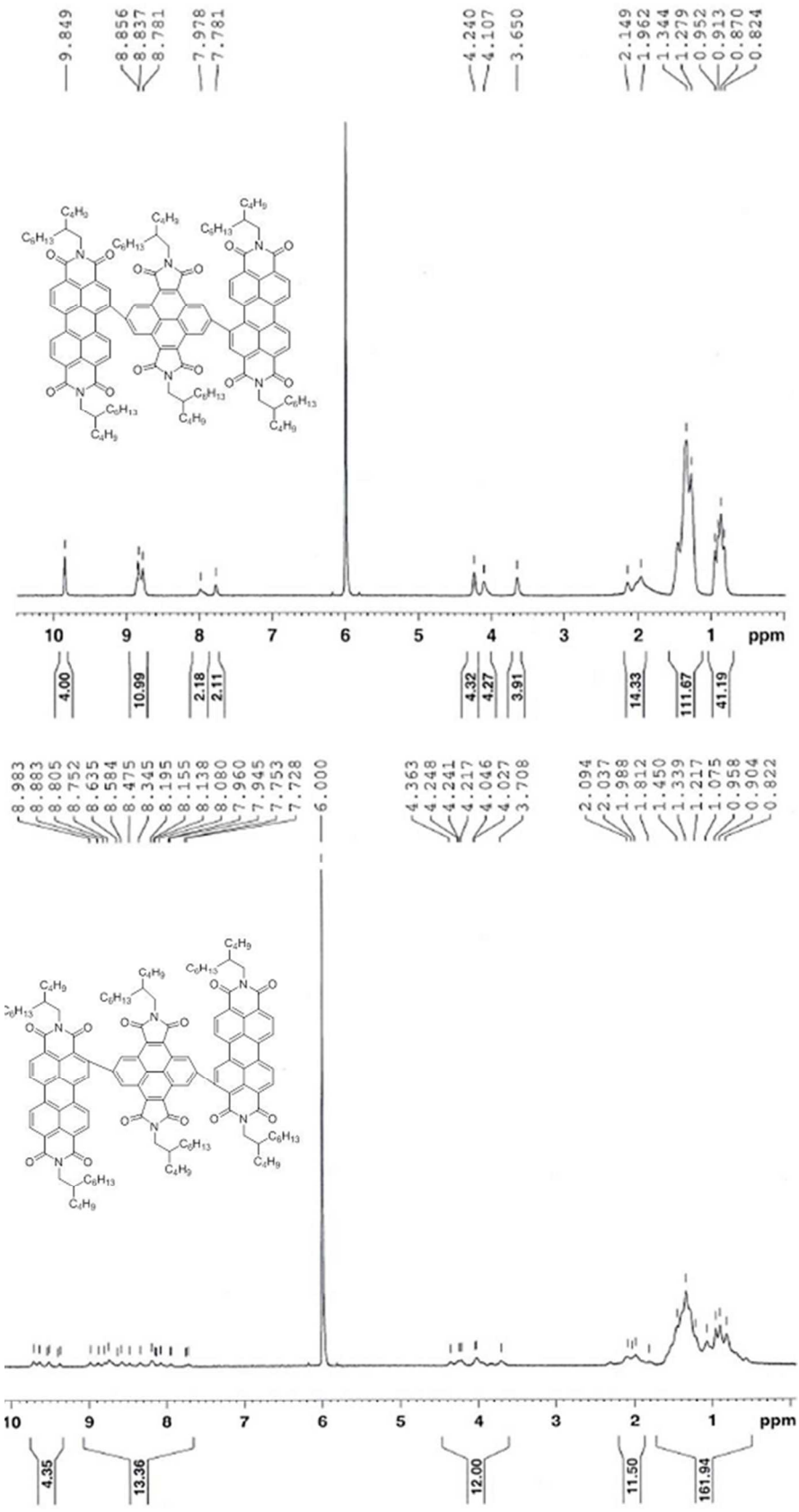
Scheme 3. The synthesis of βPBDT and αPBDT.

Compound βPBDT

$Pd_2(dba)_3$ (9 mg)and P(o-tolyn)$_3$ (24 mg)was added to the mixture of compound **4** (133 mg), compound **6** (90.5 mg) and dry toluene (6 mL) under nitrogen. After refluxing overnight, the mixture was poured into methanol. The dark red precipitate was filtered and purified by column chromatography, using chloroform as the eluent. 120 mg of pure β-PPBDT (69%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.70-8.35 (br, 14H), 7.95 (s, 2H), 7.34 (d, 2H), 6.80 (d, 2H), 5.25 (br, 4H), 2.74 (br, 4H), 2.26 (br, 8H), 1.82 (br, 8H), 1.56 (br, 2H), 1.32 (br, 32H), 0.96-0.81 (br, 36H). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 164.49 (br), 146.39, 146.17, 140.27, 137.70, 136.25, 134.98, 134.09, 133.82, 133.77, 133.50, 131.44-130.89 (br), 130.19, 129.17, 129.09, 129.04, 128.29, 128.23, 127.92, 127.37, 125.51, 125.24, 123.67, 123.32, 122.94, 54.30, 54.16, 41.24, 34.49, 34.18, 32.39, 29.72, 28.78, 25.61, 22.88, 20.15, 20.12, 14.13, 14.02. MS (MALDI-TOF) $C_{110}H_{114}N_4O_8S_4$ m/z: 1746.75; Found: 1746.60 (M^+) Anal. Calcd for $C_{110}H_{114}N_4O_8S_4$: C, 75.57; H, 6.57; N, 3.20. Found: C, 75.48; H, 6.64; N, 3.20.

Compound αPBDT

αPBDT was synthesized according to the same procedure as βPBDT in the yield of 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.63-8.67 (br, 14H), 7.80 (s, 2H), 7.43 (d, 2H), 6.86 (d, 2H), 5.25-5.14 (br, 4H), 2.81 (d, 4H), 2.25 (br, 8H), 1.80 (br, 8H), 1.63 (br, 2), 1.33 (br, 32H), 0.90 (br, 36H). ^{13}C NMR (500 MHz, $CDCl_3$) δ (ppm): 164 (br), 145.86, 144.10, 140.14, 137.18, 137.04, 134.46, 134.30, 133.93, 133.22, 131-132 (br), 130.38, 129.55, 128.05, 127.91, 126.44, 126.29, 125.36, 124.36, 124 (br), 123.46, 123.12, 122.79, 54.24, 41.39, 34.54, 34.37, 34.24, 32.44, 28.85, 25.60, 22.97, 20.16, 14.09, 14.02, 14.01, 10.80. MS (MALDI-TOF) $C_{110}H_{114}N_4O_8S_4$ m/z: 1746.75; Found: 1746.58 (M^+). Anal. Calcd for $C_{110}H_{114}N_4O_8S_4$: C, 75.57; H, 6.57; N, 3.20. Found: C, 75.86; H, 6.54; N, 3.34.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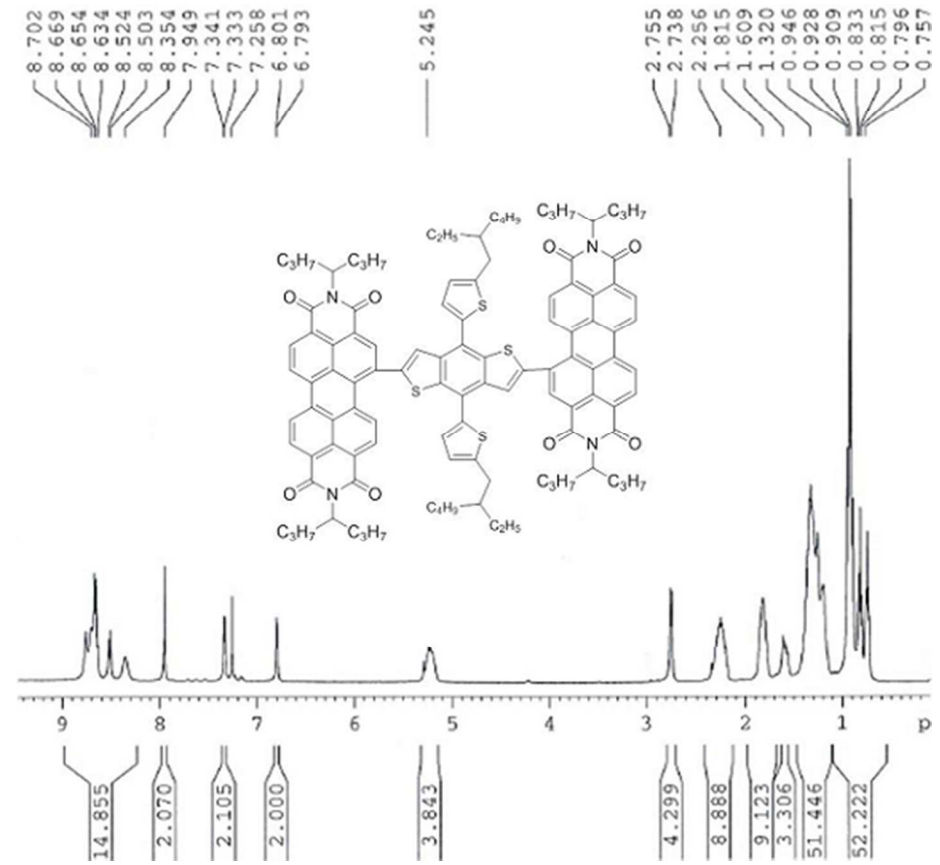
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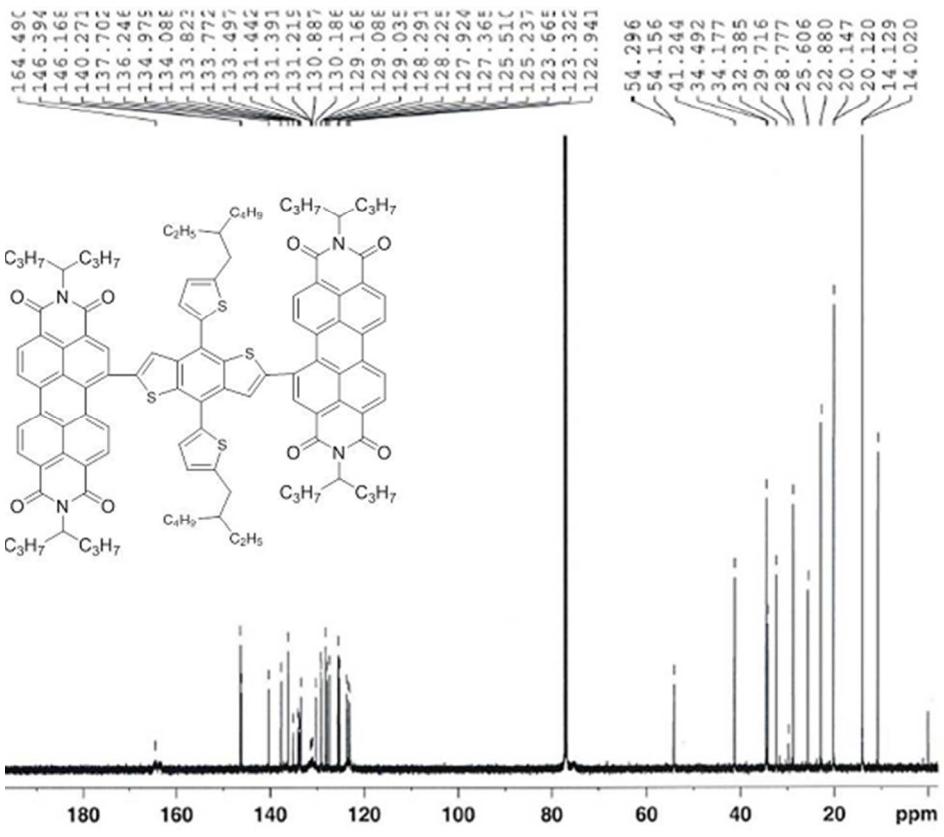
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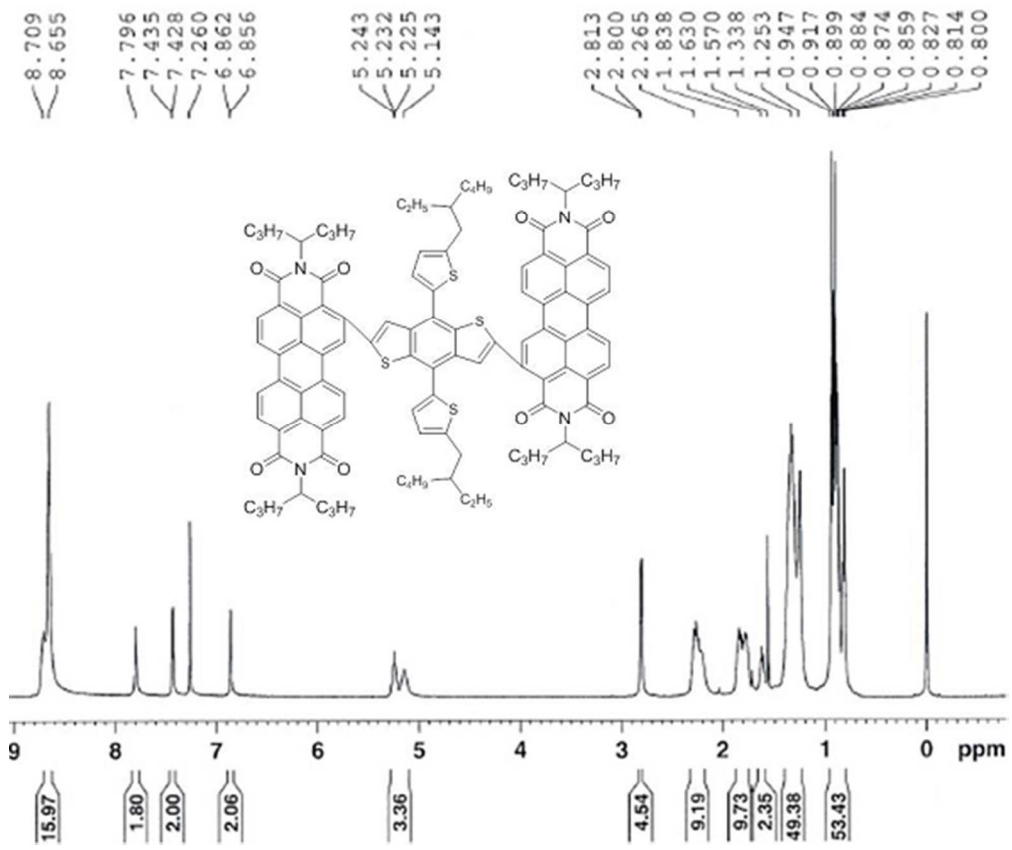
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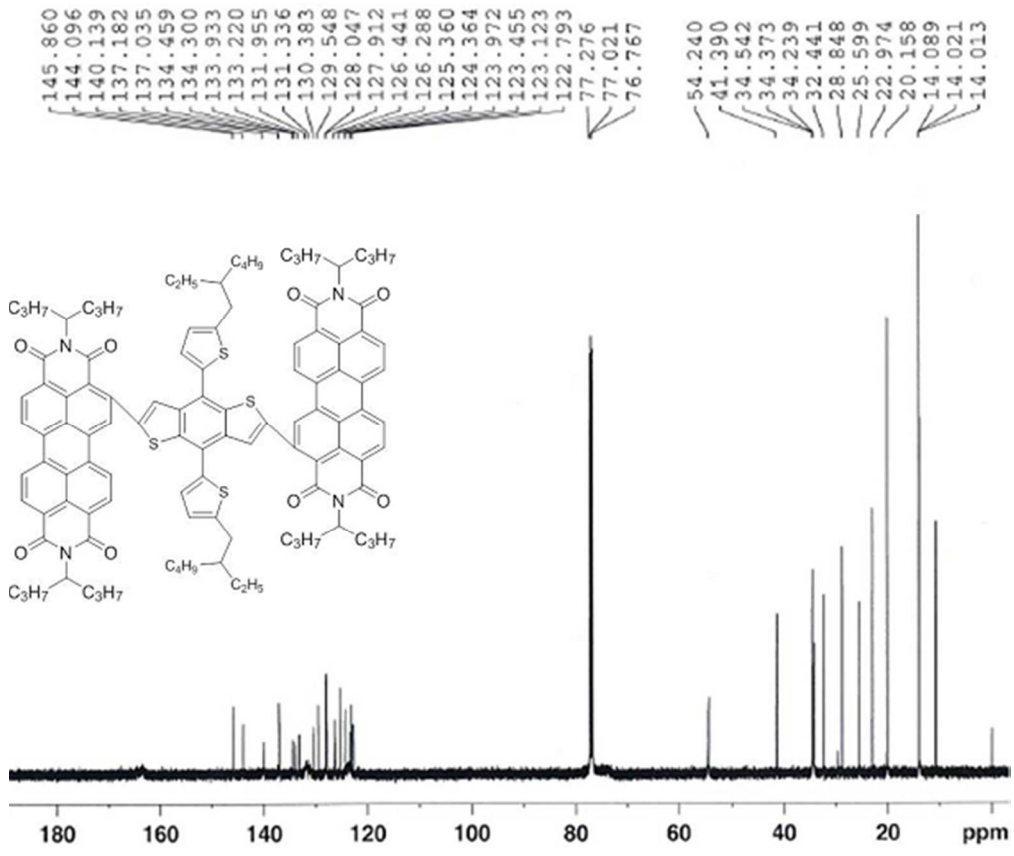
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34.373
34.239
32.441
28.848
25.599
22.974
20.158
14.089
14.021
14.013
180 160 140 120 100 80 60 40 20 ppm

2. Device fabrication

Polymer PTB7-TH was obtained from 1-material. $ZnAc_2$• $2H_2O$, 2-methoyethanol and ethanolamine were purchased from Sigma-Aldrich. Zinc Oxide Sol-Gel stock solution was prepared by stirring 0.46 g $ZnAc_2$•$2H_2O$ in 5ml 2-methoxyethanol and 0.15 ml ethanol amine at 60 °C under ambient condition. Then the solution was cooled to room temperature and subsequently filtered from 0.45μm PTFE film before use. The PTB7-TH and small molecule acceptors were co-dissolved in chlorobenzene and chloronaphthalene (95:5 vol/vol). The overall material concentration was 15 mg ml^{-1} and the solution was stirred at 110 °C for 12 h under a N_2 atmosphere. ITO glass substrate (Thin Film Devices) was cleaned in water, acetone and isopropylalcohol for 15 min under sonication. Glasses were then exposed to ultraviolet ozone irradiation for 30 min. Athin layer (~40 nm) of ZnO sol-gel was spin-coated at 4,000 rpm. for 40 sec onto ITO glasses and annealed at 200 °C in ambient condition for 30 min. After treated ZnO surface with 1 % ethanolamine solution in methoxyethanol (3000 rpm for 40 s), the substrates were dried in 90 °C oven then transferred into glovebox immediately. Active layers were spin-coated using the as-prepared solutions at 1,000 rpm in a glove box. MoO_3 (7.5 nm) and Al (80 nm) anodes were thermal evaporated in a glove box at a chamber pressure of ~2.0 × 10−6 torr.

3. Solar cell characterization.

J–V characteristics of the solar cells were measured under 1 sun, AM 1.5G irradiation (100 mWcm−2) from a solar simulator with a xenon arc lamp (Oriel model 69920). Masks with a well-defined area of 3.14 mm^2 were used to determine the effective area of the *J–V* measurement. Light intensity was calibrated using an NREL-certified monocrystaline silicon reference cell (Newport, 91150V) with a fused silica window. AFM images were obtained using an Asylum Cypher AFM. UV–vis spectra were taken using a UV-2401PC model UV–Vis spectrophotometer. The EQE measurement system was composed of a 250WQuartz Tungsten Halogen lamp as the light source, a filter wheel, a chopper, a monochromator, a lock-in amplifier and a calibrated silicon photodetector. GIWAXS measurements were performed at the 8ID-E beamline at the Advanced Source (APS), Argonne National Laboratory, using X-rays with awavelength of λ = 1.6868 Å and a beam size of 200 μm (horizontal) and 20 μm (vertical).

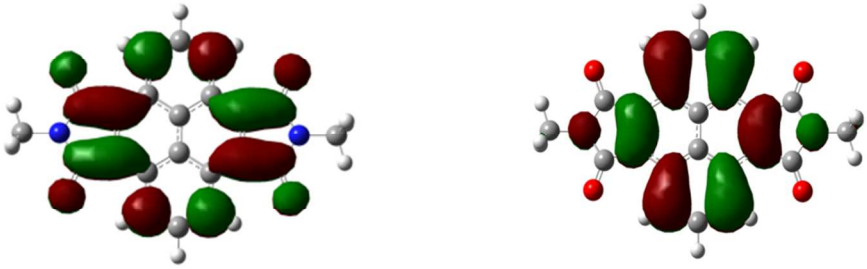

Figure S1. LUMO (left, -3.00eV) and HOMO (right, -6.05eV) orbitals of PID monomer which is simulated with Gaussian b3lyp/6-31gd.

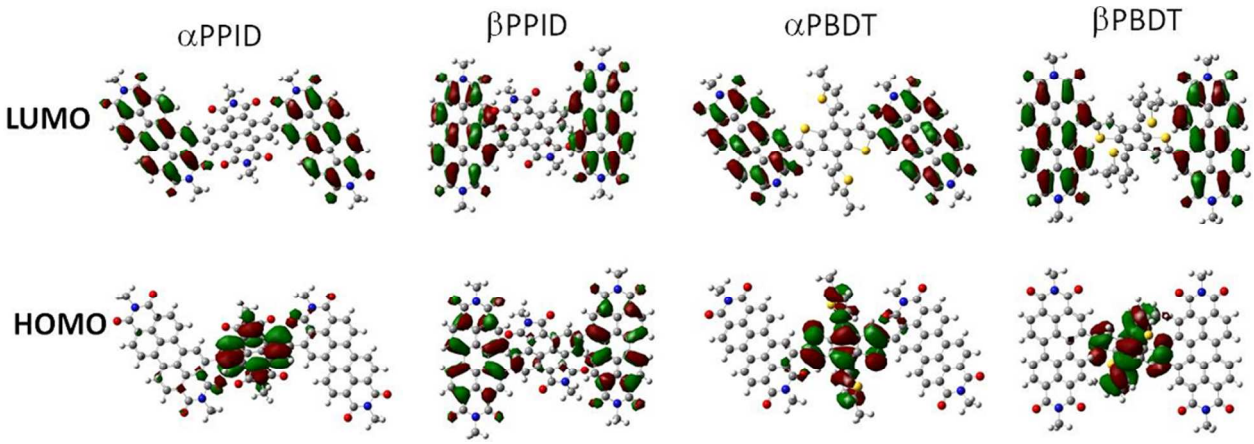

Figure S2. Calculated LUMO and HOMO of four compounds αPPID, βPPID, αPBDT and βPBDT.

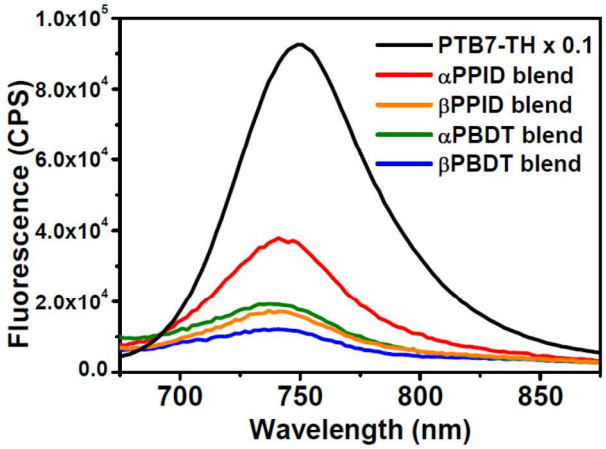

Figure S3. Film photoluminescence spectra of pure PTB7-TH, PTB7-TH:αPPPID, PTB7-TH:βPPID, PTB7-TH:αPBDT and PTB7-TH:βPBDT (donor:acceptor=1:1.5) excited at 642 nm.

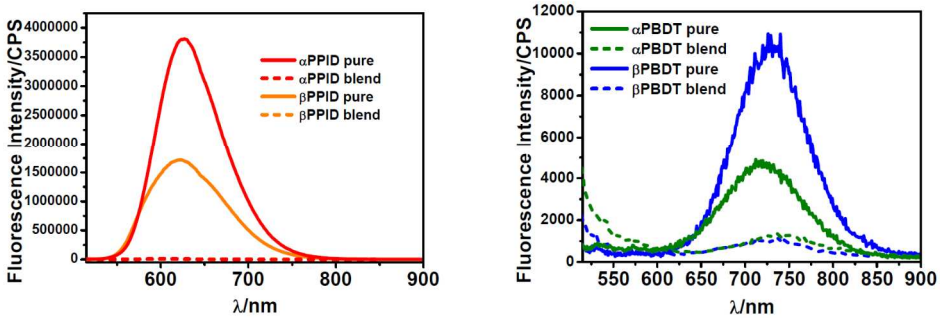

Figure S4. Film photoluminescence spectra of pure acceptors and blends (donor:acceptor=1:1.5). Left, αPPPID, PTB7-TH:αPPPID, βPPID and PTB7-TH:βPPID; right, αPBDT, PTB7-TH: αPBDT, βPBDT and PTB7-TH: βPBDT. Excited at 495 nm.

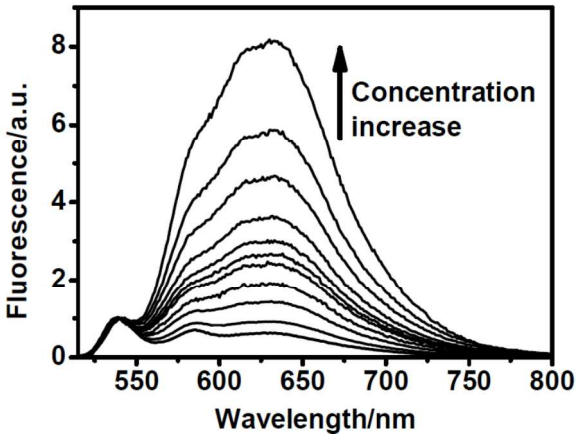

Figure S5. Concentration dependence fluorescence study of αPPID dissolved in chlorobenzene. Spectra were normalized at 0-0 transition emission peak (535 nm). Concentration was gradually increased from 2.1×10^{-9} M to 1.0×10^{-6} M. (Concentration from low to high: 2.1×10^{-9} M, 6.3×10^{-9} M, 1.9×10^{-8} M, 5.6×10^{-8} M, 1.1×10^{-7} M, 1.7×10^{-7} M, 2.5×10^{-7} M, 3.8×10^{-7} M, 5.7×10^{-7} M, 8.0×10^{-7} M, 1.0×10^{-6} M.)

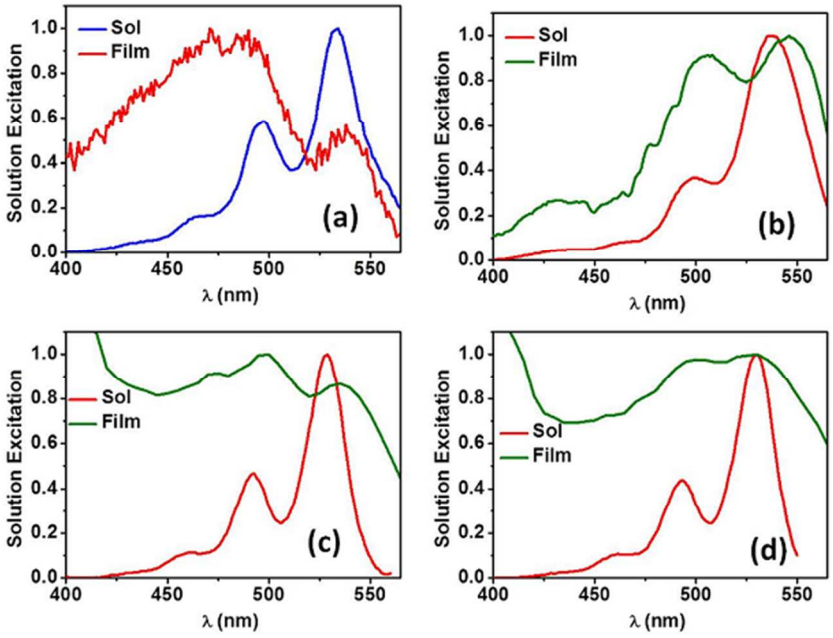

Figure S6. The solution and film excitation spectrum of (a), αPPID; (b), βPPID; (c) αPBDT; (d), βPBDT.

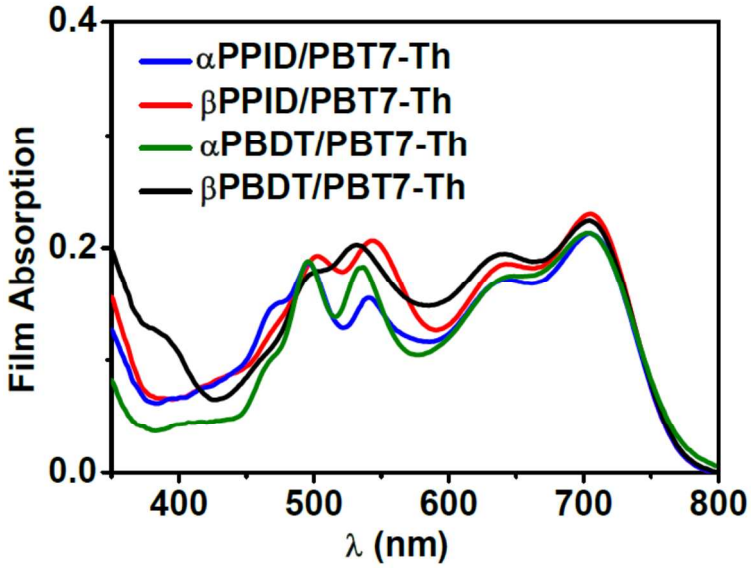

Figure S7. The film absorption spectrum of αPPID/PBT7-Th; βPPID/ PBT7-Th; αPBDT/PBT7-Th; βPBDT/PBT7-Th.

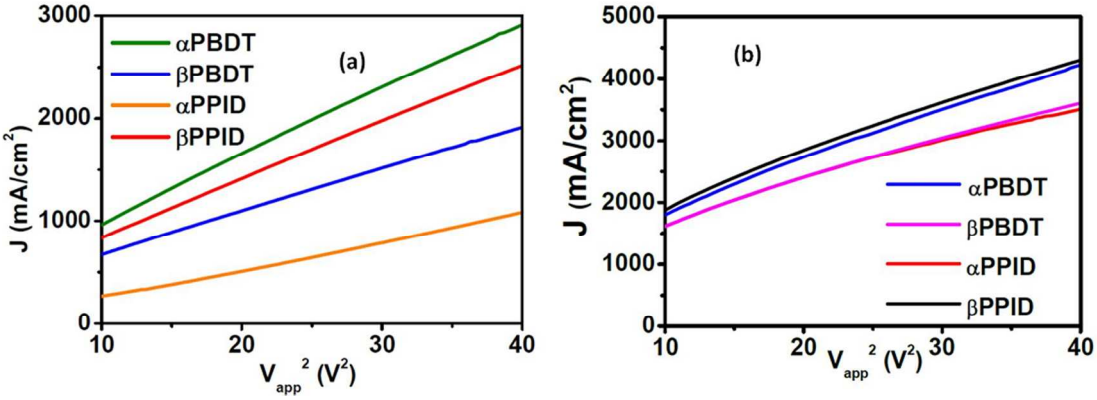

Figure S8. a) Electron mobility for the blend films of αPPPID, βPPID, αPBDT, βPBDT /PTB7-TH; b) Hole mobility for the blend films of αPPPID, βPPID, αPBDT, βPBDT /PTB7-TH.

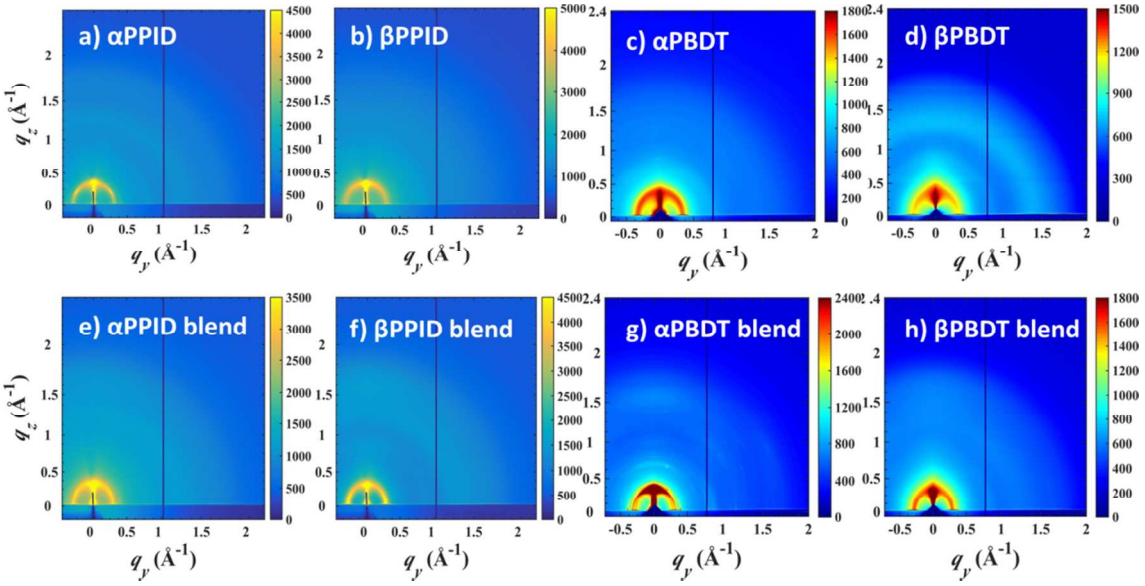

Figure S9. 2D GIWAXS patterns of films on PEDOT:PSS-modified Si substrates. a–h, 2D GIWAXS patterns of pristine αPPID (a), pristine βPPID (b), pristine αPBDT (c), pristine βPBDT (d), PTB7-TH: αPPID (1:1.5) (e), PTB7-TH: βPPID (1:1.5) (f), PTB7-TH: αPBDT (1:1.5) (g) and PTB7_TH: βPBDT (1:1.5) (h).

4. References

(1) Zhang, J.; Singh, S.; Hwang, D. K.; Barlow, S.; Kippelen, B.; Marder, S. R. 2-Bromo perylene diimide: synthesis using C–H activation and use in the synthesis of bis(perylene diimide)–donor electron-transport materials *J. Mater. Chem. C.* **2013**, *33*, 5093-5100.
(2) Jiang, W.; Ye, L.; Li, X.; Xiao, C.; Tan, F.; Zhao, W.; Hou, J.; Wang, Z. Bay-linked perylene bisimides as promising non-fullerene acceptors for organic solar cells. *Chem. Commun.* **2014**, *50*, 1024-1026.
(3) Minabe, M.; Nakada, K. Hydrogenation of pyrene and catalytic inter conversion of hydropyrenes. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1962-1966.