

From Isoindigo to Dibenzonaphthyridinedione: A Building Block for Wide-bandgap Conjugated Polymers with High Power Conversion Efficiency

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General Procedures and Experimental Details

All glassware was completely dried before use. Reagents and solvents were purchased from commercial suppliers or purified by standard techniques. Reactions were monitored by thin-layer chromatography by exposing to UV-light irradiation at 254 and 365 nm and/or immersion in a phosphomolybdic acid staining solution followed by drying. Column chromatography was carried out by using silica gel 200–300 mesh. ^1H NMR and ^{13}C NMR spectra were attained from a Bruker AVANCE-III 600 MHz with tetramethylsilane (TMS) as an internal standard at 298K and CDCl_3 or $\text{DMSO}-d_6$ was used as the solvent. The coupling constants J are given in Hz. Cyclicvoltammetry (CV) curves were measured by dropping cast of polymer film on the working electrode. The measurement were performed on an electrochemistry workstation (CHI660D, Chenhua Shanghai) in anhydrous argon saturated acetonitrile solution ($10^{-3} \text{ mol L}^{-1}$) of 0.1 M tetrabutylammoniumhexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) at room temperature by three-electrode system, which utilize glassy carbon electrode as the working electrode, Pt as the counter electrode and a Ag/AgCl as the reference electrode at a potential scan rate of 0.1 V s^{-1} . The potential of reference electrode in acetonitrile was identified by using ferrocene as internal standard. The UV-Vis spectra were collected with a Hitachi U-4100 UV-Vis spectrophotometer in an anhydrous *o*-dichlorobenzene solution ($2.5 \times 10^{-5} \text{ mol L}^{-1}$) or on a piezoid dropping casted of polymer solution. HRMS were recorded with a Bruker Apex IV FTMS. Gel permeation chromatography (GPC) was performed on Waters 1151 pump and UV-Vis monitor (700 nm) using 1,2,4-trichlorobenzene (TCB) as eluent (150°C). AFM patterns were collected with Digital Instrument NanoScope IIIa. Bright field transmission electron microscopy (TEM) data were acquired using a HITACHI H-7650 electron microscope. TGA patterns were collected with TGA Q50 V20.13 Build 39. The grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at beamline BL16B1 of the Shanghai Synchrotron Radiation Facility (SSRF). Samples were prepared on Si substrates using the same preparation conditions as for devices. The 10 keV X-ray beam was incident at a grazing angle of 0.2° .

Device Fabrication and Characterization

Two types of conventional OSCs were fabricated, and the device structures are shown as follows: (A) ITO/V₂O₅/Polymer: PC₇₁BM/Ca/Al, (B) ITO/PEDOT: PSS/Polymer: PC₇₁BM/Ca/Al. ITO-coated glass was ultrasonically washed in detergent, deionized water, acetone, and 2-propanol sequentially for 20 min each. Afterward, the cleaned ITO-coated glass was exposed to oxygen plasma to remove organic contaminants and to increase the size of the wetting envelope. The V₂O₅ layer was prepared through spin coating a vanadium (V) triisopropoxide oxide alcohol solution (2.5% (v/v)) at 4000 rpm on ITO substrates and then was treated under O₂ plasma for 10 min without the need for hydrolysis with moisture or annealed. PEDOT: PSS films were prepared by spin coating its aqueous solution on ITO-coated glass at 4000 rpm for 30 s and then thermally annealed at 150 °C for 30 min. Subsequently, the modified ITO-coated glass was moved to the glove box. Polymers and PC₇₁BM were dissolved in *o*-DCB. The solution was stirred overnight at room temperature, and then heated for 1 hour at 100 °C before spin-coated on V₂O₅ or PEDOT: PSS modified ITO-coated glass to form the active layer. The devices were then deposited by Ca (10 nm)/Al (100 nm) as cathode through a shadow mask under high vacuum (~10⁻⁴ Pa). The thickness of the active layer was controlled by changing the spin speed and was estimated using Veeco Dektak 150 surface profiler. The devices area was 0.1 cm² defined by a shadow mask. Current density-voltage (*J-V*) characteristics of the OSCs were recorded using Keithley 2420 source measurement unit under the illumination of AM 1.5G (100 mW cm⁻², Newport solar simulator). Light intensity was calibrated with a standard silicon solar cell. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system. Hole mobility was measured using the space charge limited current (SCLC) model with device configuration of ITO/PEDOT: PSS/polymer: PC₇₁BM/MoO₃/Ag by taking current-voltage in the range of 0-5 V and fitting the results to a space charge limited form for hole-only device. In the presence of carrier traps in the active layer, a trap-filled-limit (TFL) region exists between the ohmic and trap-free SCLC regions. The SCLC behavior in the trap-free region can be characterized by using the Mott-Gurney equation,

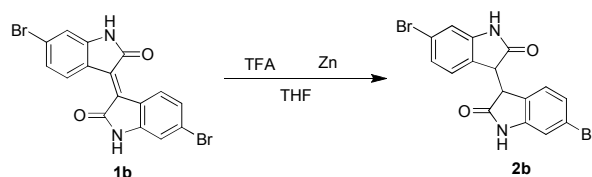
$$J = \frac{9\epsilon\mu V^2}{8L^3}$$

where ϵ is the static dielectric constant of the medium and μ is the carrier mobility, L is the polymer

thickness, and V is the voltage drop across the device. $V = V_{\text{app}} - V_{\text{bi}} - V_{\text{S}}$, where V_{app} is the voltage applied to the device, and V_{bi} is the built-in voltage resulting from the relative workfunction difference between the two electrodes, V_{S} is the voltage drop due to contact resistance and series resistance across the electrodes.

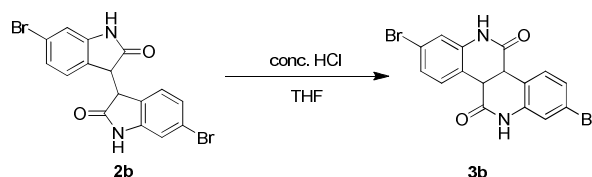
Synthetic procedures

6,6'-dibromo-[3, 3'-biindoline]-2, 2'-dione (**2b**).



TFA (4.7 ml, 60 mmol) was added dropwise to a cooled (0°C) suspension of **1b** (1 g, 2.39 mmol) and activated Zn dust (940 mg, 14.5 mmol) in THF (125 ml) solution. The mixture was stirred at r.t. for 1 hour. Then the mixture was precipitated into a stirring H₂O (500 ml). The white solid **2b** obtained were collected on a filter and washed with H₂O and dried under reduced pressure. Since compound **2b** is unstable in solution state and could be easily oxidized back to **1b**, therefore it was directly used for the next step without further purification (1.03 g, quantitative). ¹H-NMR (DMSO-*d*₆, 600 MHz) δ : 10.51 (s, 2H), 7.09 (d, J = 8.02 Hz, 2H), 6.95 (s, 2H), 6.75 (d, J = 8.02 Hz, 2H), 4.19 (s, 2H). ¹³C-NMR (DMSO-*d*₆, 150 MHz) δ : 176.33, 145.45, 126.83, 125.72, 124.47, 121.46, 112.71, 45.70. ESI-HRMS: Calcd. for [M+H]⁺: 420.9182, found: 420.9185.

2, 8-dibromo-10b, 12-dihydrodibenzo[c, h][2, 6]naphthyridine-5, 11(4bH, 6H)-dione(**3b**).

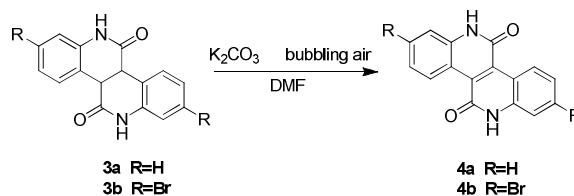


A suspension of **2b** (1 g, 2.38 mmol) in conc. HCl (10 ml) and THF (20 ml) was added to a Schlenk tube. The mixture was stirred for 10 hours at 100 °C. The mixture was then cooled down to r.t. and the precipitate was collected on a filter and washed with water, ethanol and ethyl acetate to give a white solid **3b** which was pure enough to carry out on next step (609 mg, 61%). ¹H-NMR (DMSO-*d*₆, 600

MHz) δ : 10.58 (s, 2H), 7.20-7.16 (m, 4H), 7.06 (s, 2H), 4.23 (s, 2H). ^{13}C -NMR (DMSO- d_6 , 150 MHz) δ : 168.29, 139.53, 132.29, 125.12, 121.28, 120.13, 118.01. ESI-HRMS: Calcd. for $[\text{M}+\text{H}]^+$: 420.9182, found: 420.9183.

dibenzo[c, h][2, 6]naphthyridine-5, 11(6H, 12H)-dione (4a)

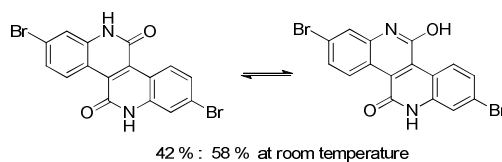
or 2, 8-dibromodibenzo[c, h][2, 6]naphthyridine-5, 11(6H, 12H)-dione (4b).



To a solution of **3a** or **3b** in DMF (0.01 M) was added K_2CO_3 (4 Eq.). The suspension was stirred for 48 hours with air bubbling into the system. The yellow solid **4a** or **4b** (almost quantitative) obtained was filtered and washed with water then THF before drying under reduced pressure, which was to carry out on next step. Because of the low solubility of **4a** or **4b** in the conventional organic solvents, it was difficult to purify the sample and to get the high-quality ^{13}C -NMR spectra. We were also unable to get a HRMS data. However, its structure could be easily identified after alkylation.

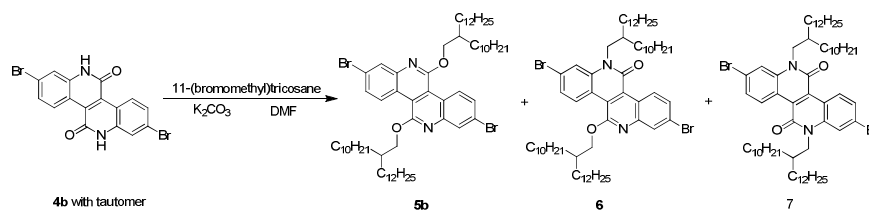
4a: ^1H -NMR (DMSO- d_6 , 600 MHz) δ : 12.43 (s, 2H), 9.79(d, $J=8.43$ Hz, 2H), 7.60 (t, $J=7.67$ Hz, 2H), 7.46 (d, $J=8.32$ Hz, 2H), 7.32 (t, $J=7.77$ Hz, 2H).

Partial tautomerization of **4b** was observed, presumably due to re-aromatization:



4b in *bis*-lactam form: ^1H -NMR (DMSO- d_6 , 600 MHz) δ : 12.54 (s, 2H), 9.68 (d, $J=9.05$ Hz, 2H), 7.62 (s, 2H), 7.48 (d, $J=9.05$ Hz, 2H). **4b** inlactam/quinolinol form: ^1H -NMR (DMSO- d_6 , 600 MHz) δ : 12.00 (s, 1H), 9.14 (s, 1H), 8.23 (d, $J=8.15$ Hz, 1H), 8.18 (s, 1H), 8.08 (d, $J=8.67$ Hz, 1H), 7.65 (s, 1H), 7.63 (d, $J=8.61$ Hz, 1H).

2, 8-dibromo-5, 11-bis((2-decyltetradecyl)oxy)dibenzo[c, h][2, 6]naphthyridine (5b).



To a suspension of K_2CO_3 (995 mg, 7.2 mmol) in DMF (20 ml) was added **4b** (600 mg, 1.44 mmol) and 11-(bromomethyl)tricosane (2.35 g, 5.76 mmol). The mixture was stirred at 100 °C for 48 hours before filtration. The filtrate was concentrated under reduced pressure. The obtained crude product was then purified by column chromatography on silica gel eluted with petroleum ether to give a white solid compound **5b** (1.1 g, 70%), light yellow liquid **6** (154 mg, 10%) and yellow solid **7** (trace). **5b** was then further purified by recrystallization before polymerization.

5b: 1H -NMR ($CDCl_3$, 600 MHz) δ : 9.33 (d, $J=9.25$ Hz, 2H), 8.13 (s, 2H), 7.61 (d, $J=9.25$ Hz, 2H), 4.67 (d, $J=5.54$ Hz, 4H), 2.08 (m, 2H), 1.70-1.20 (m, 80H), 0.90 (m, 12H). ^{13}C -NMR ($CDCl_3$, 150 MHz) δ : 159.59, 145.61, 129.71, 129.28, 128.11, 123.36, 122.72, 119.46, 70.44, 37.59, 31.95, 31.94, 31.93, 30.02, 29.71, 29.69, 29.67, 29.37, 29.37, 26.96, 22.71, 22.70, 14.14. ESI-HRMS: Calcd. for $[M+H]^+$: 1091.6537, found: 1091.6548.

6: 1H -NMR ($CDCl_3$, 600 MHz) δ : 9.79 (d, $J=9.29$ Hz, 1H), 9.27 (d, $J=9.15$ Hz, 1H), 8.07 (s, 1H), 7.63 (s, 1H), 7.62 (d, $J=9.24$ Hz, 1H), 7.43 (d, $J=9.08$ Hz, 1H), 4.62 (s, 2H), 4.43 (s, 2H), 2.02 (m, 2H), 1.60-1.00 (m, 80H), 0.87 (m, 12H). ^{13}C -NMR ($CDCl_3$, 150 MHz) δ : 160.94, 158.73, 145.74, 138.98, 130.66, 129.33, 129.27, 128.95, 128.05, 125.21, 124.33, 124.02, 121.23, 121.17, 117.69, 116.19, 70.60, 46.86, 37.56, 36.18, 31.96, 31.93, 31.92, 31.86, 31.58, 30.03, 29.96, 29.70, 29.67, 29.62, 29.61, 29.57, 29.51, 29.37, 29.36, 29.34, 29.26, 26.96, 26.50, 22.70.

7: 1H -NMR ($CDCl_3$, 600 MHz) δ : 9.72 (d, $J=9.20$ Hz, 2H), 7.59 (s, 2H), 7.44 (d, $J=9.20$ Hz, 2H), 4.40 (s, 4H), 2.03 (m, 2H), 1.50-1.10 (m, 80H), 0.87 (m, 12H). ^{13}C -NMR ($CDCl_3$, 150 MHz) δ : 160.50, 138.93, 130.71, 126.59, 125.91, 124.98, 117.44, 117.31, 47.10, 36.29, 31.95, 31.93, 31.56, 29.99, 29.70, 29.67, 29.63, 29.59, 29.38, 29.35, 26.49, 22.71, 22.70, 14.14.

Procedures for Stille Polymerization and Polymer Purification.

PDBND-2T: **5b** (109.3 mg, 0.1 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (49.2 mg, 0.1 mmol), $Pd_2(dba)_3$ (1.1 mg, 1.2 mmol%), $P(o\text{-tol})_3$ (2.9 mg, 9.6 mmol%) and 2.5 mL of toluene were added to a Schlenk tube. The tube was charge with argon through a freeze-pump-thaw cycle for three times. The

mixture was stirred for 72 hours at 110 °C. And then the mixture was precipitated into methanol (100 mL). The precipitate was filtered and purified via Soxhlet extraction for 8 hours with methanol, 12 hours with hexane, and finally was collected with chloroform. The chloroform solution was then concentrated and precipitated into methanol (100mL) to give a yellow solid (92 mg, 84%).

PDBND-TVT: 5b (109.3 mg, 0.1 mmol), (*E*)-1, 2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (51.8 mg, 0.1 mmol), Pd₂(dba)₃ (1.1 mg, 1.2 mmol%), P(*o*-tol)₃ (2.9 mg, 9.6 mmol%) and 2.5 mL of toluene were added to a Schlenk tube. The tube was charge with argon through a freeze-pump-thaw cycle for three times. The mixture was stirred for 72 hours at 110 °C. And then the mixture was precipitated into methanol (100 mL). The precipitate was filtered and purified via Soxhlet extraction for 8 hours with methanol, 12 hours with hexane, and finally was collected with chloroform. The chloroform solution was then concentrated and precipitated into methanol (100 mL) to give an orange solid (110 mg, 98%).

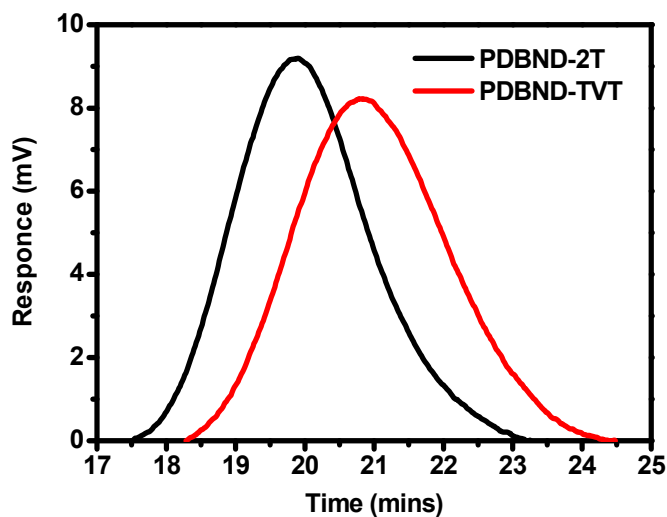


Figure S1. Gel permeation chromatography (GPC) results of PDBND-2T and PDBND-TVT.

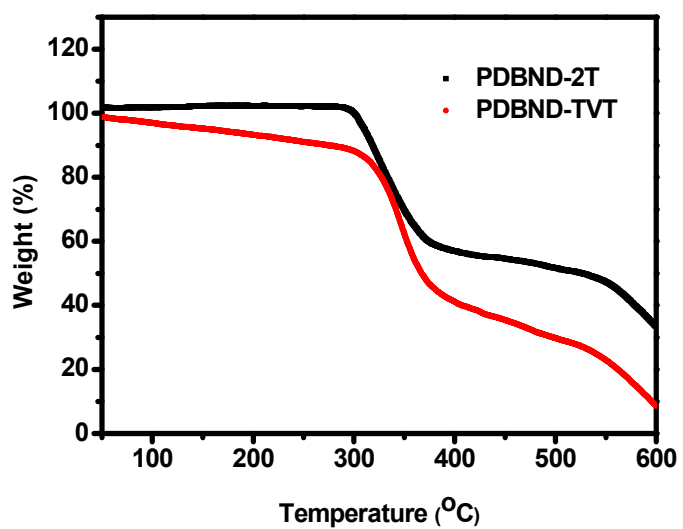


Figure S2. TGA plots of PDBND-2T and PDBND-TVT.

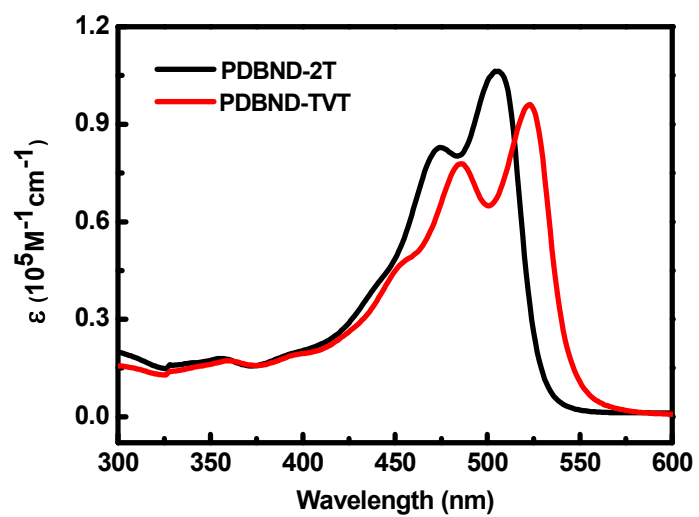


Figure S3. The UV-Vis absorption spectra of PDNBD-2T and PDBND-TVT in *o*-DCB with concentration of 1×10^{-5} M.

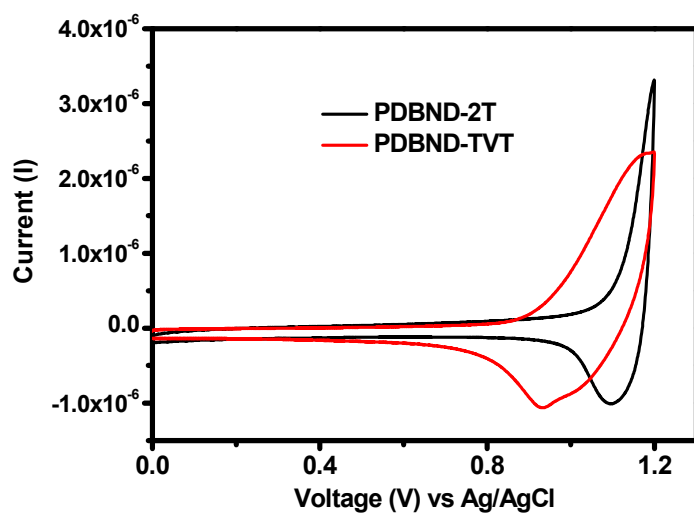


Figure S4. The electrochemical cyclic voltammetry measurement of PDBND-2T and PDBND-TVT film.

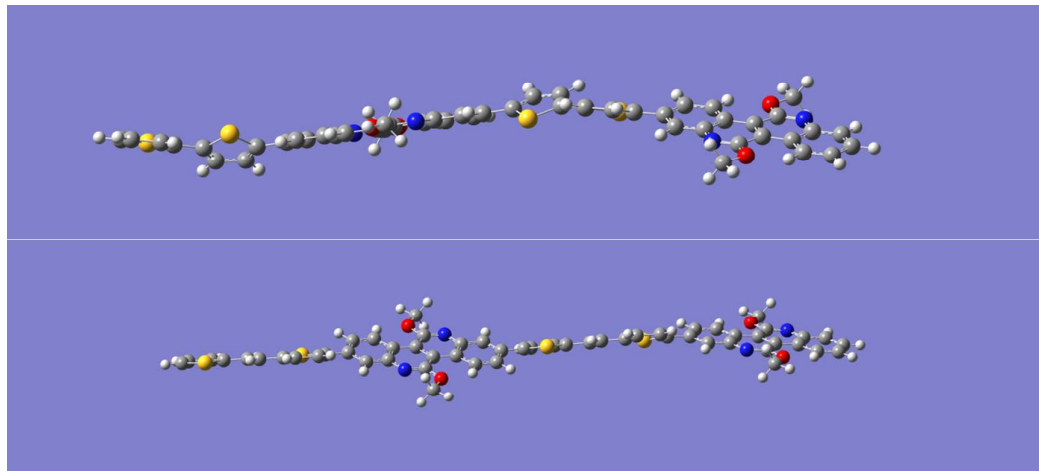


Figure S5. Top sight of energy-minimized structure of PDBND-2T (top) and PDBND-TVT (bottom).

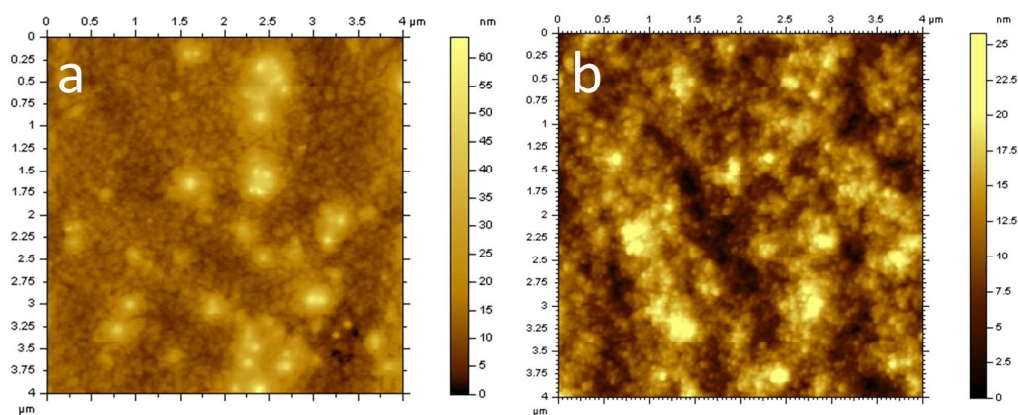


Figure S6. AFM height images the active layers containing PDBND-2T: PC₇₁BM (a) and PDBND-TVT: PC₇₁BM (b) in weight ratio of 1: 2.

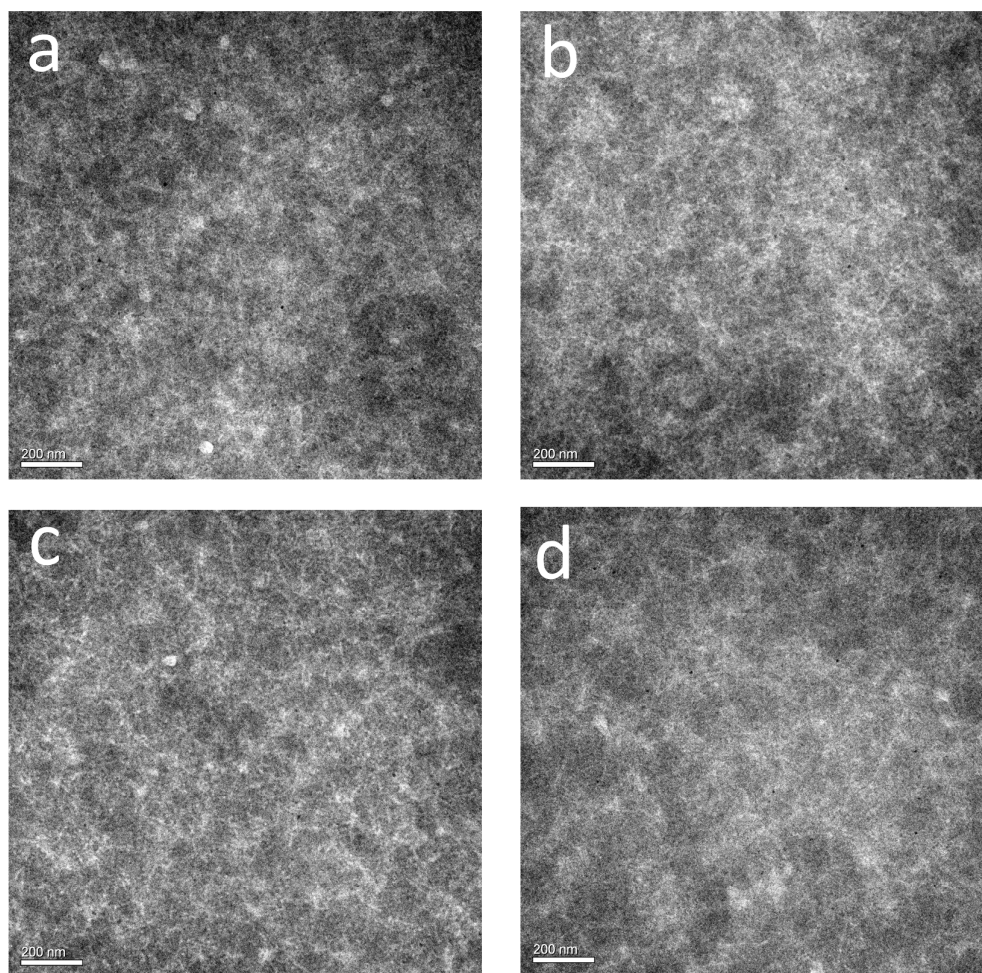


Figure S7. TEM images of the active layers containing PDBND-TVT: PC₇₁BM in weight ratios of a) 1: 1.5, b) 1: 2, c) 1: 2.5, and d) 1: 3.

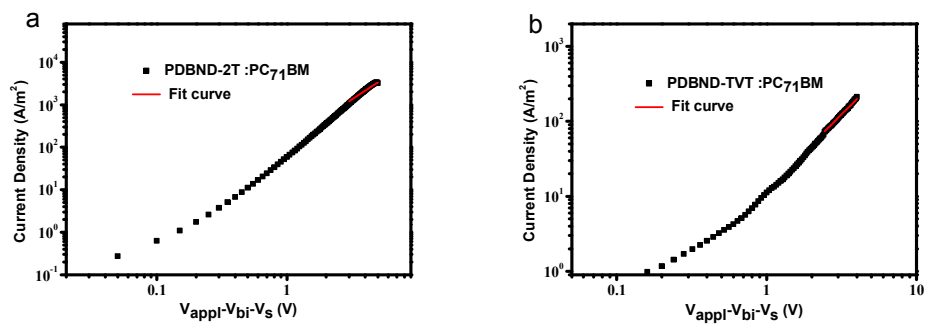


Figure S8. Space-charge-limited current (SCLC) density-voltage curves of hole only devices of PDBND-2T and PDBND-TVT blended film (1: 2, w/w).

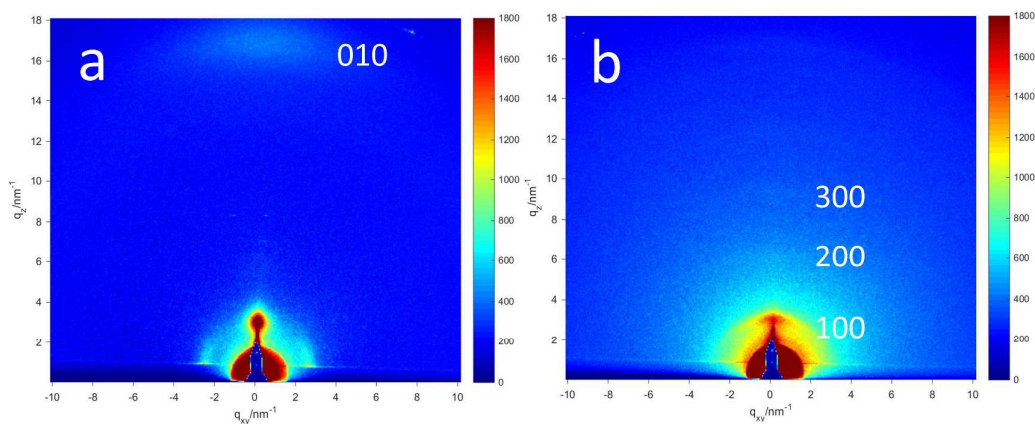
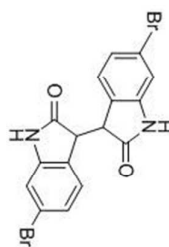
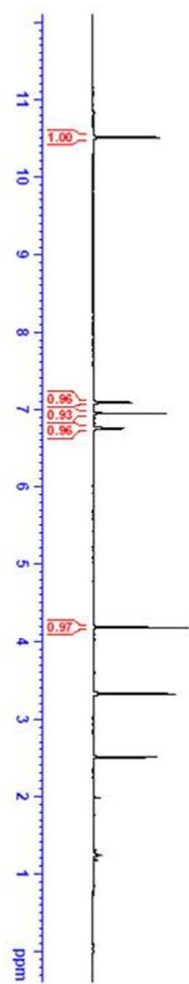


Figure S9. 2D GIWAXS patterns of a) PDBND-2T and b) PDBND-TVT neat film

¹H and ¹³C NMR spectra



—10.512

7.095
7.093
7.082
7.079
6.948
6.945
6.761
6.747

—4.190

