

Electronic Supplementary Information

Experimental Section

Materials

All starting materials and reagents were purchased from commercial sources and used without further purification, unless otherwise mentioned. Toluene (PhMe) and tetrahydrofuran (THF) were distilled over sodium in the presence of benzophenone as indicator. CHCl_3 and CH_2Cl_2 were distilled over calcium hydride.

Instrumentation

^1H and ^{13}C NMR spectra were measured on a Bruker Advance III 600 spectrometer with tetramethylsilane (TMS, $\delta = 0$ ppm) as an internal standard. All GPC analyses were made using 1,2,4-trichlorobenzene (TCB) as eluent at 150 °C and polystyrene standard as reference. UV-vis absorption spectra were performed on Lambda25 spectrophotometer. The density functional theory (DFT) method under B3LYP/6-31G(d,p) level was employed. To simplify the calculations, only two repeating units of each polymer were subjected to the calculations, with alkyl chains replaced by CH_3 groups. Cyclic voltammetry (CV) measurements were taken on a CHI660D electrochemical workstation. The CV experiments were carried out at room temperature with a conventional three-electrode system using a glassy carbon electrode as working electrode, Pt wire as the counter electrode, and saturated calomel electrode as the reference electrode. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6 , 0.1 M) in acetonitrile solution was used as the supporting electrolyte, and the scan rate was 100 mV s^{-1} . Ferrocene/ferrocenium (Fc/Fc^+) was used as the internal standard. Thermal gravimetric analysis (TGA) measurements were performed on STA-409 at a heating rate of 10 °C min^{-1} . Topographic images of the active layers were obtained through atomic force microscopy (AFM) in tapping mode under ambient conditions using an Agilent 5400 instrument. Transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV. Grazing incidence wide-angle X-ray scattering (GIWAXS) patterns were acquired by beamline BL16B1 (Shanghai Synchrotron Radiation Facility).

Photovoltaic device fabrication

The PSCs devices were fabricated with a configuration of ITO/PEDOT:PSS/polymers:PC₇₁BM/Ca/Al. A thin layer of PEDOT:PSS (30 nm, Baytron PH1000) was spin-cast on pre-cleaned ITO-coated glass at 4000 rpm. After baking at 150 °C for 20 min, the substrates were transferred into glovebox. Optimized devices were prepared under the following conditions. The polymer:PC₇₁BM ratio of 1:1.5 (w/w) was dissolved in

chlorobenzene (CB) with a total concentration of 25 mg/mL, followed by 3% 1,8-diiodooctane (DIO) additive (v/v), and then the active layers was spin-coated from the above solution at 100 °C with a speed of 1600 rpm. The effects of solvents, additive concentrations, and blend ratios on device performance were also examined. Finally, a Ca (10 nm)/Al (100 nm) metal top electrode was thermal evaporated onto the active layer under about 2×10^{-4} Pa. The active area of the device was 0.1 cm² defined by shadow mask. The current density–voltage (J – V) characteristics were measured with a Keithley 2420 source measurement unit under simulated 100 mW/cm² (AM 1.5G) irradiation from a 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 measurement system.

Monomer Synthesis

2-octyldodecyl-4,6-dibromothieno[3,4-*b*]thiophene-2-carboxylate (2)

4,6-Dibromothieno[3,4-*b*]thiophene-2-carboxylic acid (3.16 g, 9.24 mmol), 4-dimethylaminopyridine (DMAP) (56 mg, 0.462 mmol) were dissolved in dry CH₂Cl₂ (100 mL) with a round-bottom flask. Then dicyclohexylcarbodiimide (DCC) (2.10 g, 10.17 mmol) was added in several portions. 2-Octyl-1-dodecanol (3.03 g, 10.17 mmol) was added to the reaction mixture at room temperature after 20 minutes and stirred for 24 h under inert atmosphere. The resulting mixture was poured into water and filtrated to remove DCC, then extracted with dichloromethane. The organic layer was concentrated and purified on a silica gel column chromatography to give compound **2** as yellow oil in 76% yield. ¹H NMR (600 MHz, CDCl₃), δ (ppm): 7.53 (s, 1H), 4.22 (d, $J = 5.4$ Hz, 2H), 1.77-1.40 (m, 1H), 1.36-1.25 (m, 32H), 0.89-0.86 (m, 6H). ¹³C NMR (150 MHz, CDCl₃), δ (ppm): 162.54, 145.61, 141.12, 140.49, 123.14, 102.23, 97.04, 68.77, 37.34, 31.94, 31.93, 31.32, 29.92, 29.66, 29.60, 29.56, 29.37, 29.32, 26.73, 22.71, 14.14.

2-octyldodecyl-4,6-di(thiazol-2-yl)thieno[3,4-*b*]thiophene-2-carboxylate (3)

To a solution of compound **2** (1.86 g, 3.00 mmol) and 2-tributylstannyl thiazole (3.38 g, 9.00 mmol) in anhydrous toluene (40 mL), Pd(PPh₃)₄ (170 mg) was added. The mixture was heated at 100 °C for 12 h, and then the mixture was cooled to room temperature. After the solvent removed, the residue was purified by column chromatography (eluent dichloromethane) to give the product as yellow solid in 64% yield. ¹H NMR (600 MHz, CDCl₃), δ (ppm): 8.17 (s, 1H), 7.92 (d, $J = 3.6$ Hz, 1H), 7.90 (d, $J = 3.6$ Hz, 1H), 7.42 (d, $J = 3.6$ Hz, 1H), 7.41 (d, $J = 3.6$ Hz, 1H), 4.29 (d, $J = 6.0$ Hz, 2H), 1.83-1.80 (m, 1H), 1.45-1.25 (m, 32H), 0.89-0.83 (m, 6H). ¹³C NMR (150 MHz, CDCl₃), δ (ppm): 162.28, 160.15, 160.12,

145.12, 143.12, 142.92, 139.46, 128.22, 123.64, 123.20, 109.50, 109.19, 69.10, 37.33, 31.90, 31.89, 29.93, 29.92, 29.66, 29.64, 29.59, 29.55, 29.34, 29.32, 26.74, 22.67, 14.10.

2-octyldodecyl-4,6-bis(5-bromothiazol-2-yl)thieno[3,4-*b*]thiophene-2-carboxylate (4)

To a solution of **3** (1.26 g, 2 mmol) in anhydrous CHCl₃ (40 mL), NBS (4.5 mmol) was added in portions, and then the mixture was refluxed for 4 h. TLC showed the starting material disappeared completely. After the solvent removed, the residue was purified by column chromatography (eluent dichloromethane) to give the product as yellow solid in 74% yield. ¹H NMR (600 MHz, CDCl₃), δ (ppm): 8.07 (s, 1H), 7.70 (s, 1H), 7.60 (s, 1H), 4.28 (d, *J* = 6.0 Hz, 2H), 1.83-1.80 (m, 1H), 1.43-1.25 (m, 32H), 0.88-0.83 (m, 6H). ¹³C NMR (150 MHz, CDCl₃), δ (ppm): 162.31, 160.18, 160.15, 145.17, 145.15, 143.15, 142.94, 139.49, 128.24, 123.66, 123.23, 109.53, 109.22, 69.13, 37.37, 31.93, 31.92, 31.39, 29.96, 29.95, 29.69, 29.66, 29.62, 29.58, 29.37, 29.35, 26.77, 22.69, 14.12.

2,2'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)dithiazole (6)

To a solution of **5** (1.81 g, 2.00 mmol) and 2-bromothiazole (0.98 g, 6.00 mmol) in anhydrous toluene (30 mL), Pd(PPh₃)₄ (115 mg) was added. The mixture was heated at 100 °C for 12 h, and then the mixture was cooled to room temperature. After the solvent removed, the residue was purified by column chromatography (eluent dichloromethane) to give the product as yellow solid in 72% yield. ¹H NMR (600 MHz, CDCl₃), δ (ppm): 8.07 (s, 2H), 7.83 (d, *J* = 3.6 Hz, 2H), 7.36 (d, *J* = 3.6 Hz, 2H), 7.34 (d, *J* = 3.6 Hz, 2H), 6.92 (d, *J* = 3.6 Hz, 2H), 2.89 (d, *J* = 6.6 Hz, 4H), 1.72-1.68 (m, 2H), 1.48-1.35 (m, 16H), 0.98-0.96 (m, 12H). ¹³C NMR (150 MHz, CDCl₃), δ (ppm): 161.84, 146.48, 143.76, 139.58, 138.29, 137.45, 136.09, 128.22, 125.67, 124.76, 122.42, 119.49, 41.46, 34.29, 32.51, 28.94, 25.71, 23.05, 14.20, 10.92.

2,2'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(5-(trimethylstannyl)thiazole) (7)

To a solution of **6** (1.12 g, 1.5 mmol) in anhydrous THF (40 mL), *n*-BuLi (2.3 ml, 1.6 M in hexane) was added dropwise at -78 °C. After 2 h, chlorotrimethylstannane (1.0 M in hexane, 4 mL) was added and the mixture was stirred at room temperature overnight. Then the mixture was extracted by diethyl ether and the combined organic phase was concentrated to give yellow solid. Further purification was carried out by recrystallization using CHCl₃/isopropanol to obtain the pure compound **7** as a yellow solid in 58% yield. ¹H NMR (600 MHz, CDCl₃), δ (ppm): 8.05 (s, 2H), 7.75 (t, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 3.6 Hz, 2H), 6.91 (d, *J* = 3.6 Hz, 2H), 2.87 (d, *J* = 6.6 Hz, 4H), 1.73-1.68 (m, 2H), 1.49-1.33 (m, 16H), 0.98-0.92 (m, 12H), 0.44 (t, 18H). ¹³C NMR (150 MHz, CDCl₃), δ (ppm): 166.53, 149.97, 146.28,

139.51, 138.32, 137.53, 136.27, 131.02, 128.15, 125.60, 124.58, 122.30, 41.45, 34.29, 32.51, 28.96, 25.72, 23.07, 14.23, 10.92, -8.01.

General procedure of polymerization: bis(trimethyltin) monomer **5** or **7** (0.20 mmol), dibromo monomer **4** or **2** (0.20 mmol) were mixed in 4 mL toluene and 1 mL DMF. After being purged with argon for 15 min, Pd (PPh₃)₄ (11.5 mg) was added as the catalyst, and the mixture was then purged with argon for another 25 min. The reaction mixture was refluxed for 24 h. Then the mixture was cooled to room temperature, and the polymer was precipitated by addition of 50 mL methanol and filtered. The precipitate was then subjected to Soxhlet extraction with methanol, dichloromethane, and chlorobenzene. The polymer was recovered as solid from the chlorobenzene fraction by precipitation with methanol. The black solid was dried under vacuum to afford the target polymers.

PTBTz-2, black solid, yield: 53%, M_n : 18.6 kDa, PDI: 2.72.

PTBTz-5, black solid, yield: 64%, M_n : 27.1 kDa, PDI: 3.10.

Thermal properties

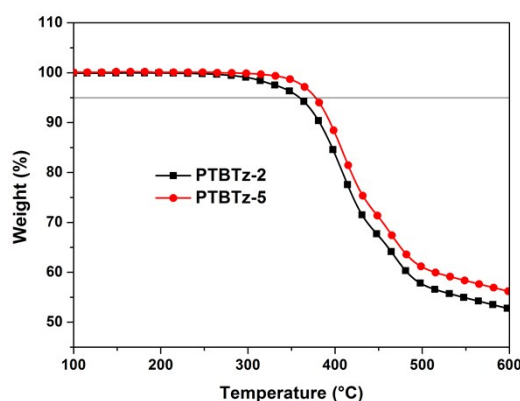


Figure S1. TGA plots of PTBTz-2 and PTBTz-5 with a heating rate of 10 °C/min under the protection of nitrogen.

Optical properties

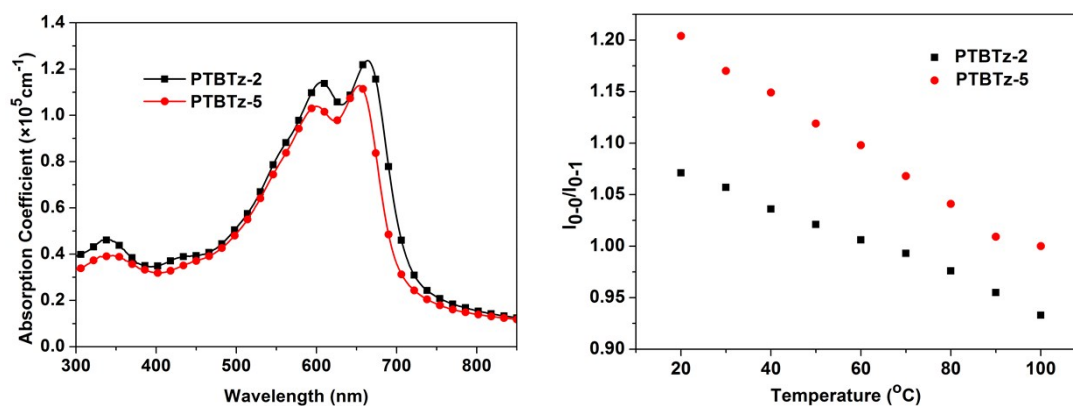


Figure S2. UV-vis absorption spectra of pure polymer films (left) and intensity ratio value of λ_{0-0} and λ_{0-1} of both polymers in solution (right).

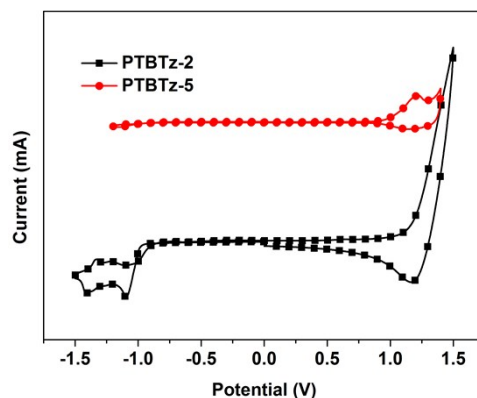


Figure S3. Cyclic voltammograms of the two polymer films.

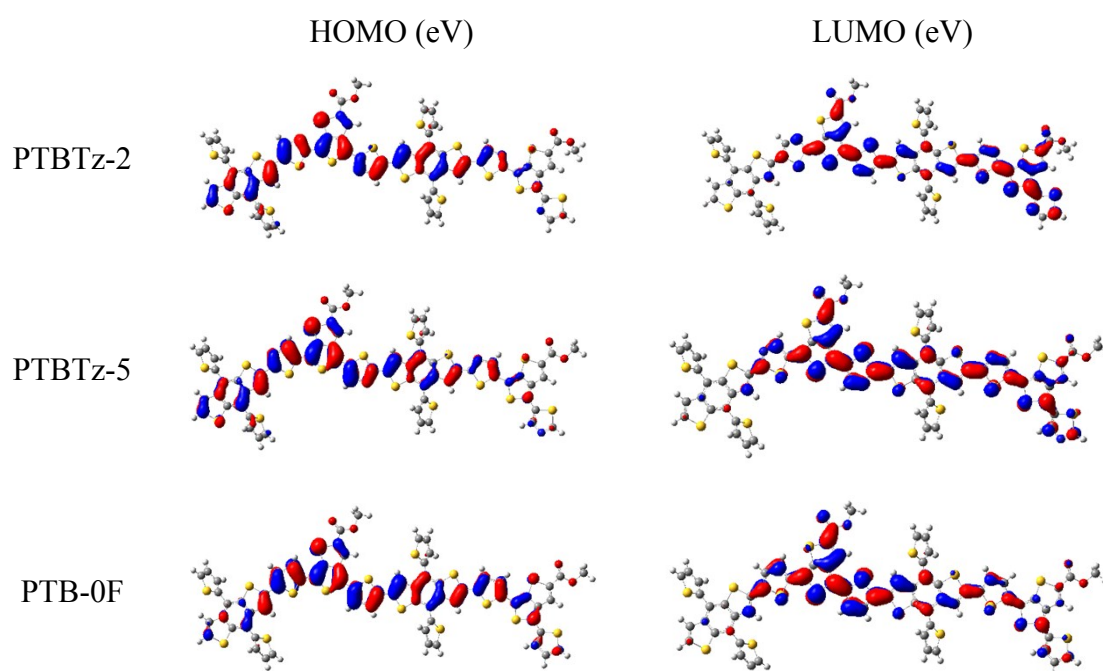


Figure S4. HOMO and LUMO orbital geometries of PTBTz-2, PTBTz-5 and PTB-0F dimer calculated by DFT.

Table S1. Calculated dipole moments with two repeating units for PTBTz-2 and PTBTz-5

| | μ_g (D) | μ_e (D) | $\Delta\mu_{ge}$ (D) |
|---------|-------------|-------------|----------------------|
| PTBTz-2 | 6.44 | 11.27 | 12.13 |
| PTBTz-5 | 5.22 | 5.86 | 9.58 |
| PTB-0F | 5.67 | 6.53 | 1.88 |

μ_g and μ_e represent the dipole moment at ground state and excited state, respectively. $\Delta\mu_{ge}$ indicates the difference between the ground and excited state dipole moments, calculated by $\Delta\mu_{ge} = [(\mu_{gx} - \mu_{ex})^2 + (\mu_{gy} - \mu_{ey})^2 + (\mu_{gz} - \mu_{ez})^2]^{1/2}$, calculated with DFT method at B3LYP/6-31G(d,p) level using Gaussian 09.

Photovoltaic performance

Table S2. The photovoltaic performance of both polymers under different conditions

| Polymers | D/A Ratios | Additive | Solvent | V_{oc} (V) | J_{sc} (mA/cm ²) | FF (%) | PCE (%) |
|----------|------------|----------|---------|--------------|--------------------------------|--------|---------|
| PTBTz-2 | 1:1 | 3% DIO | CB | 0.81 | 16.24 | 65.8 | 8.67 |
| | 0.8:1 | 3% DIO | CB | 0.82 | 16.37 | 68.6 | 9.27 |
| | 1:1.5 | 3% DIO | CB | 0.83 | 16.84 | 69.5 | 9.72 |
| | 1:2 | 3% DIO | CB | 0.84 | 16.08 | 65.9 | 8.95 |
| | 1:1.5 | 0% | CB | 0.87 | 13.43 | 59.3 | 6.93 |
| | 1:1.5 | 2% DIO | CB | 0.84 | 16.72 | 62.5 | 8.75 |
| | 1:1.5 | 2.5% DIO | CB | 0.83 | 16.57 | 67.2 | 9.18 |
| | 1:1.5 | 3% DIO | CB | 0.83 | 16.84 | 69.5 | 9.72 |
| | 1:1.5 | 3.5% DIO | CB | 0.82 | 16.62 | 66.4 | 9.05 |
| | 1:1.5 | 4% DIO | CB | 0.80 | 16.73 | 65.6 | 8.76 |
| | 1:1.5 | 1%CN | CB | 0.86 | 13.53 | 62.8 | 7.31 |
| | 1:1.5 | 3%CN | CB | 0.85 | 14.05 | 64.1 | 7.67 |
| | 1:1.5 | 5%CN | CB | 0.84 | 13.37 | 67.8 | 7.62 |
| | 1:1.5 | 2% DIO | DCB | 0.84 | 16.72 | 62.5 | 8.77 |
| | 1:1.5 | 3% DIO | DCB | 0.84 | 16.50 | 64.9 | 8.99 |
| | 1:1.5 | 4% DIO | DCB | 0.86 | 15.38 | 63.3 | 8.38 |
| PTBTz-5 | 1:1 | 0% | CB | 0.85 | 11.73 | 55.4 | 5.50 |
| | 1:1.5 | 0% | CB | 0.84 | 11.61 | 59.9 | 5.82 |
| | 1:2 | 0% | CB | 0.85 | 10.06 | 54.9 | 4.73 |
| | 1:3 | 0% | CB | 0.84 | 9.25 | 59.3 | 4.59 |
| | 1:1 | 0% | DCB | 0.82 | 11.33 | 54.7 | 5.08 |
| | 1:1.5 | 0% | DCB | 0.84 | 11.85 | 56.0 | 5.57 |
| | 1:2 | 0% | DCB | 0.83 | 10.09 | 56.1 | 4.70 |
| | 1:1.5 | 2% DIO | CB | 0.82 | 12.35 | 62.6 | 6.31 |
| | 1:1.5 | 3% DIO | CB | 0.82 | 13.11 | 64.3 | 6.91 |
| | 1:1.5 | 4% DIO | CB | 0.80 | 12.78 | 63.9 | 6.55 |

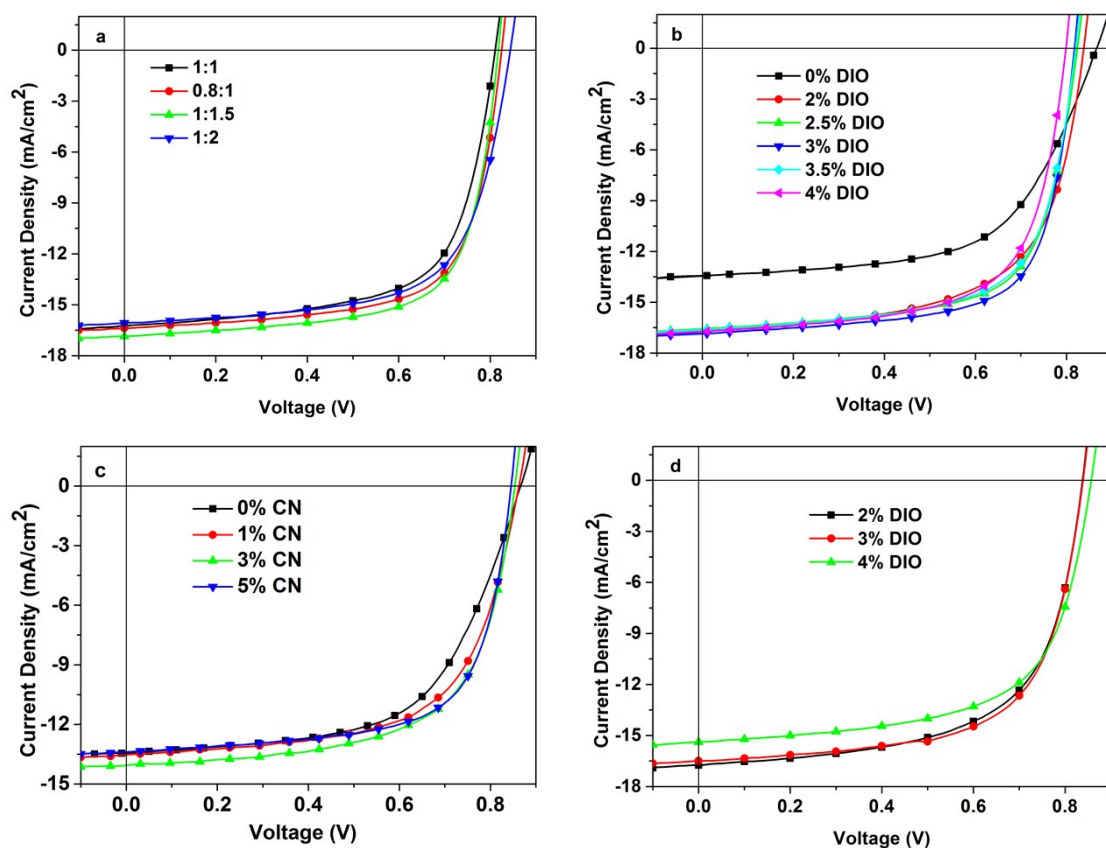


Figure S5. The J - V curves of PTBTz-2 under different conditions. (a) different D/A ratios (CB, 3% DIO), (b) different DIO ratios (CB, 1:1.5 D/A), (c) different CN ratios (CB, 1:1.5 D/A), (d) different DIO ratios (DCB, 1:1.5 D/A).

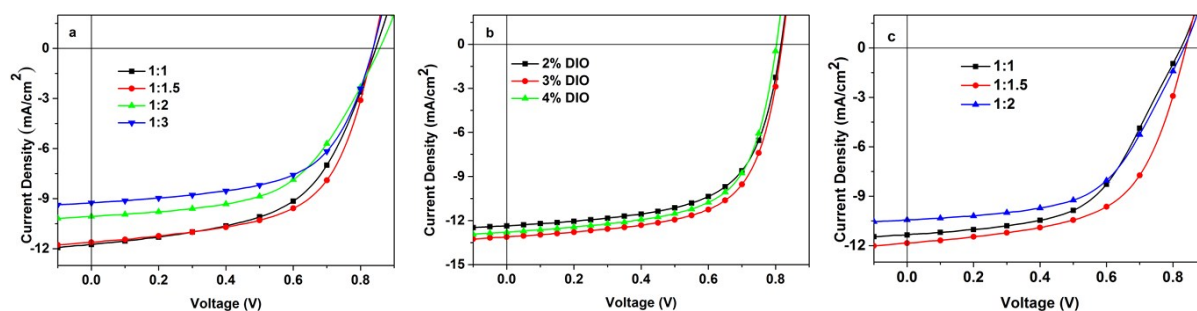


Figure S6. The J - V curves of PTBTz-5 under different conditions. (a) different D/A ratios (CB, without DIO), (b) different DIO ratios (CB, 1:1.5 D/A), (c) different D/A ratios (DCB, without DIO).

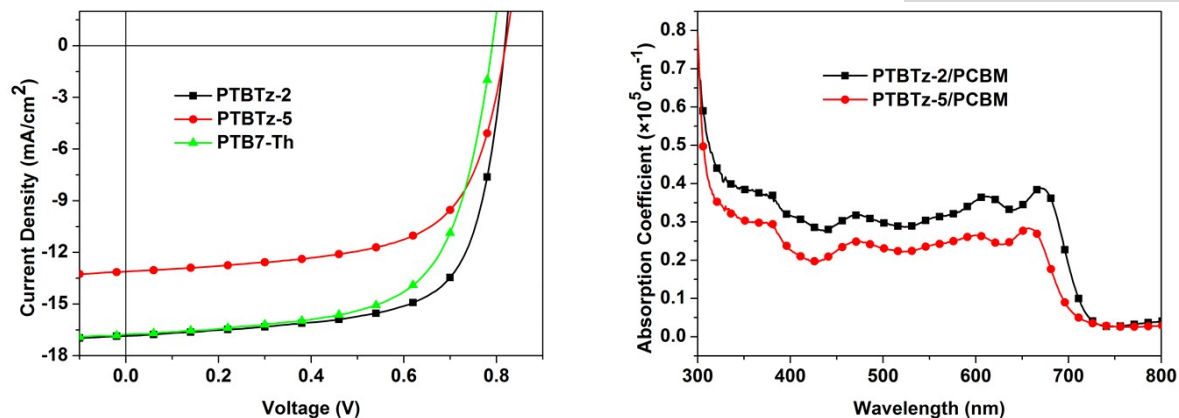


Figure S7. The J - V curves of PTBTz-2, PTBTz-5 and PTB7-Th at optimal condition (left), and the UV-vis absorption spectra of the active layers at optimal condition (right).

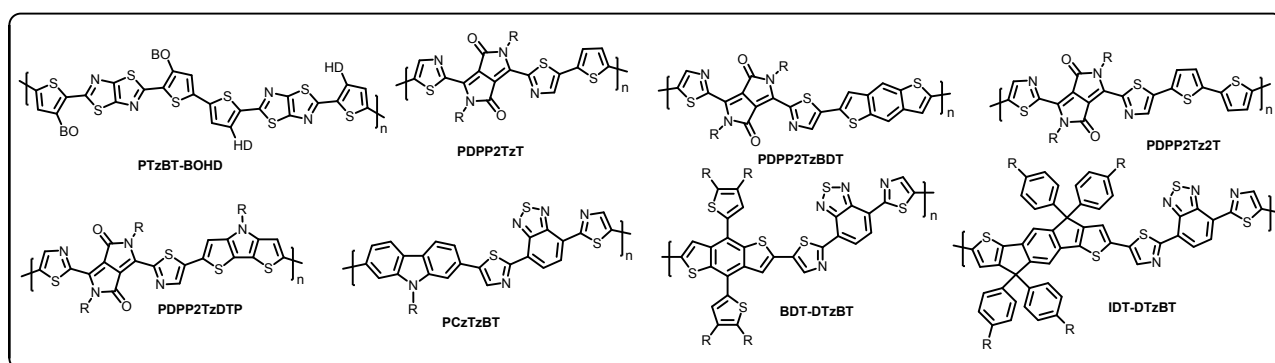


Figure S8. The chemical structures of the reported representative thiazole-containing polymers.

Hole mobility: The hole mobility of the polymer was investigated by the space charge limited current (SCLC) method. The hole only mobility of the blend films was measured with the device structure of ITO/PEDOT:PSS/polymer:PC₇₁BM (100 nm)/Au. The SCLC model is described by

$$J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3} \quad (1)$$

Here, J stands for current density, ε_0 is the permittivity of free space, ε_r is the relative dielectric constant of the transport medium, μ is the hole mobility, V is the internal potential in the device and L is the thickness of the active layer.

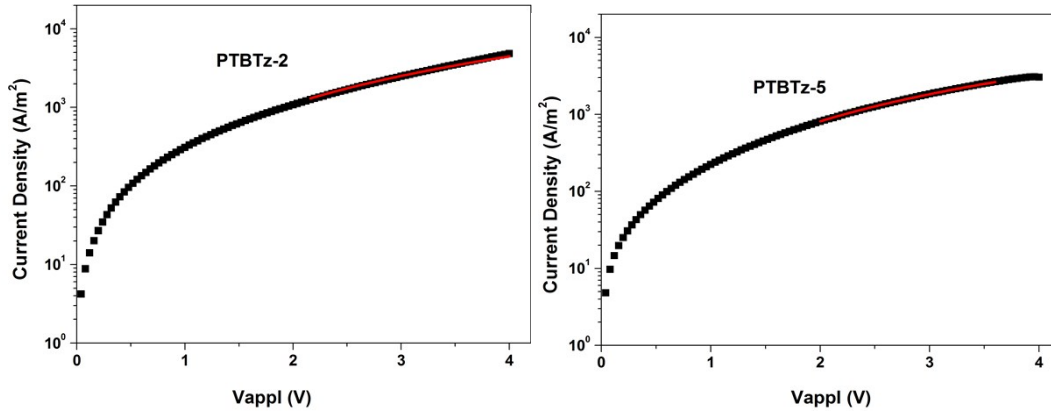


Figure S9. J - V characteristics of the device ITO/PEDOT:PSS/polymer:PC₇₁BM/Au. The symbols are experimental data for the transport of holes, and the solid lines are fitted according to SCLC model.

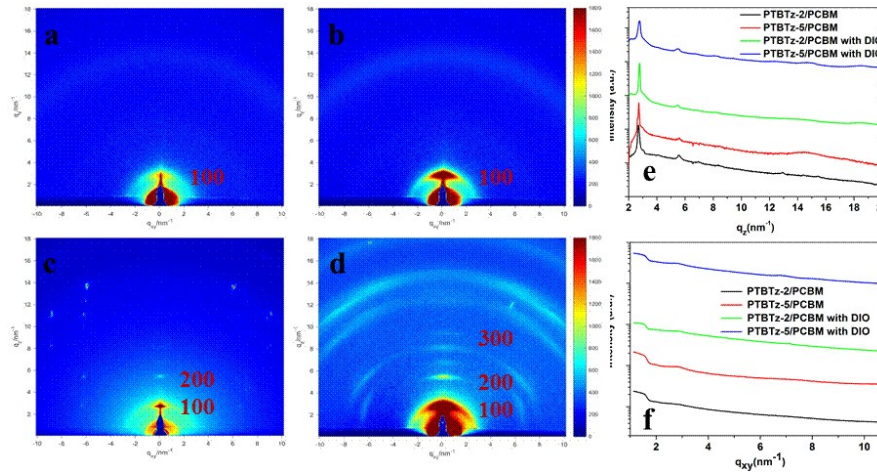


Figure S10. GIWAXS images of PTBTz-2(5)/PC₇₁BM blend films, (a), (c) for PTBTz-2 without or with DIO, respectively. (b), (d) for PTBTz-5 without or with DIO, respectively. The out-of-plane (e) and in-plane (f) GIWAXS 2D patterns of blend films with and without 3% DIO.

Table S3 GIWAXS data of PTBTz-2(5)/PC₇₁BM blend films

| | $h00$ peak (nm ⁻¹)/lamella (Å) | | |
|------------------------------------|--|------------|------------|
| | 100 | 200 | 300 |
| PTBTz-2/PC ₇₁ BM | 2.701/23.2 | 5.565/22.5 | |
| PTBTz-2/PC ₇₁ BM+3% DIO | 2.768/22.7 | 5.485/22.9 | |
| PTBTz-5/PC ₇₁ BM | 2.716/23.1 | 5.58/22.5 | --- |
| PTBTz-5/PC ₇₁ BM+3% DIO | 2.767/22.7 | 5.496/22.8 | 8.105/23.2 |