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2D expanded conjugated polymers with non-fullerene acceptor for efficient polymer solar cells

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Materials

All reactions were carried out under Ar. Common solvents were dried and purified by standard procedures. All column chromatography was performed with the use of silica gel 200-300 mesh. Monomer and polymers were synthesized according to reported procedures.[1] Other reagents were purchased from commercial sources and used directly unless otherwise noted.

Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AVANCE-III 600 spectrometer with tetramethylsilane (TMS) as an internal standard. UV-vis absorption spectra were obtained on a Lambda25 spectrophotometer. The molecular weights of the polymers were measured by GPC using 1, 2, 4-trichlorobenzene (TCB) as the solvent and polystyrene as the standard under 150 °C. TGA was performed on a SDT Q600 with a heating rate of 10 °C/min under a nitrogen atmosphere. Cyclic Voltammetry was measured on a CHI660D electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) in acetonitrile at a scan rate of 100 mV/s. The three-electrode system was composed of glass carbon electrode coated with the sample film as the working electrode, Pt wire as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. Potentials were referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple by using ferrocene as a standard. Ultraviolet photoelectron spectroscopy (UPS) was perfromed on the Thermo Scientific ESCALab 250Xi. The gas discharge lamp was used for UPS, with helium gas admitted and the He I (21.22 eV) emission line employed. The helium pressure in the analysis chamber during analysis was about 2×10^{-8} mbar. The data were acquired with -10 V bias. Atomic Force Microscope measurements were performed using an Agilent 5400 in tapping mode under ambient conditions. Grazing incidence wide angle X-ray scattering (GIWAXS) patterns were acquired by beam line BL16B1 (Shanghai Synchrotron Radiation Facility). The ground-state geometries of BDT-DTBT molecules were fully optimized with DFT method under B3LYP/6-31G(d, p) level.[2]

Fabrication of Photovoltaic Devices

Conventional PSC devices were fabricated with the configuration of ITO/PEDOT:PSS/polymer:ITIC/Ca/Al. The ITO-coated glasses with a nominal sheet resistance of 15 Ω/sq were cleaned in an ultrasonic bath with detergent, ultrapure water, acetone, and isopropyl alcohol subsequently. After a 10 min oxygen plasma treatment, a thin layer of PEDOT:PSS (30 nm) was spin-coated onto the ITO anode and then dried at 160 °C for 20 min. The polymer and ITIC were dissolved in chlorobenzene with total concentration of 25 mg/mL. The solution was stirred overnight and spin-coated on the PEDOT:PSS layer. The thickness of the active layer was ~100 nm. Finally, 10 nm Ca and 100 nm Al layers were successively thermal evaporated onto the active layer at a pressure of 4.0×10^{-4} Pa. The active area of the device in this work was 0.1 cm^2. The current density-voltage (*J-V*) characteristics were recorded with a Keithley2420 source measurement under AM 1.5G illumination (100 mW/cm^2) from a Newport solar simulator. A standard silicon solar cell was used to calibrate the light intensity. The external quantum efficiencies (EQE) of the PSCs were measured using a certified Newport incident photon conversion efficiency (IPCE) measurement system.

Charge carrier mobility was measured using the space charge limited current (SCLC) model.[3] Hole - or electron-only diodes were fabricated with a configuration of ITO/PEDOT:PSS/polymer:ITIC/Au for holes and ITO/ZnO/polymer:ITIC/Ca/Al for electrons by taking current-voltage in the range of 0-5 V and fitting the results to a space charge limited current. 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 square law,

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

where ε is the static dielectric constant of the medium and μ is the carrier mobility, *V* is the voltage drop across the device, and *L* is the polymer thickness.

General procedure for the synthesis of polymers

Monomer **1** (0.2 mmol), monomer **2** (0.2 mmol), $Pd_2(dba)_3$ (1.8 mg, 0.002 mmol) and $P(o\text{-tol})_3$ (3.6 mg, 0.012 mmol) were dissolved into 6 mL toluene in a 25 mL round bottom flask protected by argon. The flask was purged three times with successive vacuum and argon filling cycles. The oil bath was heated to 110 °C gradually, and the reaction mixture was stirred for 18 h at 110 °C under argon atmosphere. After cooling, the mixture was cooled to room temperature and precipitated in 200 mL methanol. The precipitate was filtered and washed with methanol and hexane successively in a soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 40 °C overnight.

PBDTTz-BP, GPC: *Mn*= 35 kg mol^{-1}, PDI = 2.31, *Td* = 370 °C. Elem. Anal. calcd (%) for $(C_{92}H_{113}F_2N_3O_2S_4)_n$: C, 75.73; H, 7.81; N, 2.88. Found: C, 75.87; H, 7.92; N, 2.83.

PBDTTz-N, GPC: *Mn*= 27 kg mol^{-1}, PDI = 3.53, *Td* = 389 °C. Elem. Anal. calcd (%) for $(C_{88}H_{109}F_2N_3O_2S_4)_n$: C, 75.12; H, 7.81; N, 2.99. Found: C, 75.31; H, 7.95; N, 3.05.

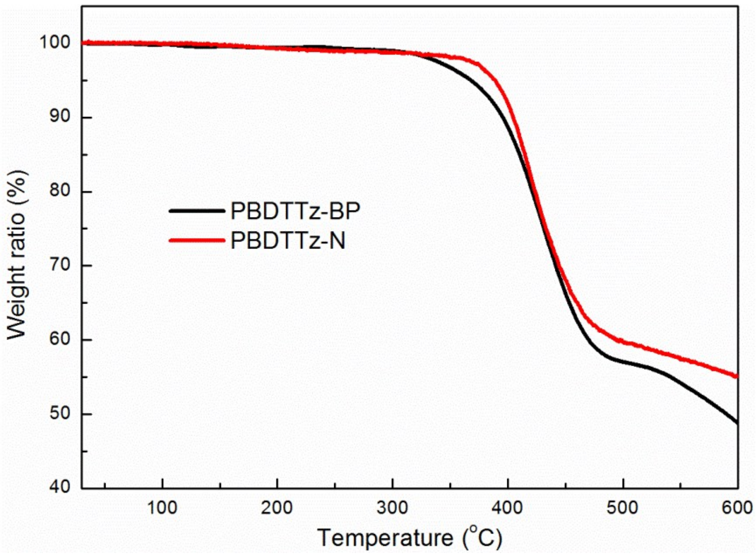

Fig. 1S TGA curve of polymers PBDTTz-BP and PBDTTz-N at a heating rate of 10 ^{o}C min^{-1} under nitrogen.

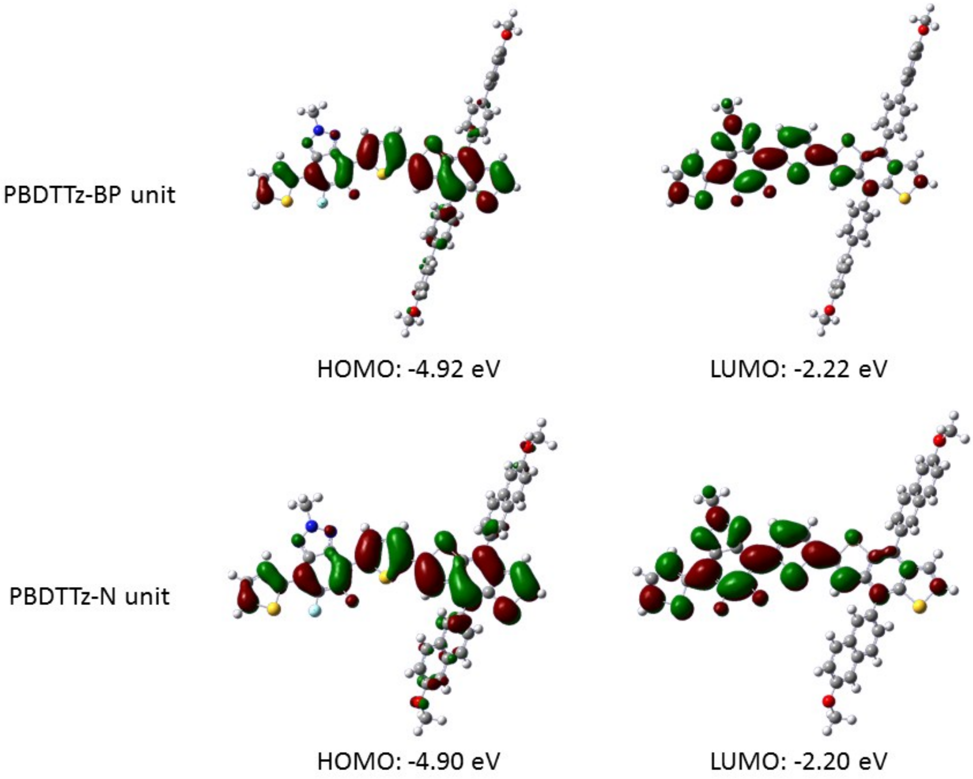

Fig. 2S Optimized molecular geometries and frontier molecular orbitals for PBDTNP-DTBO and PBDTBP-DTBO obtained by DFT calculations.

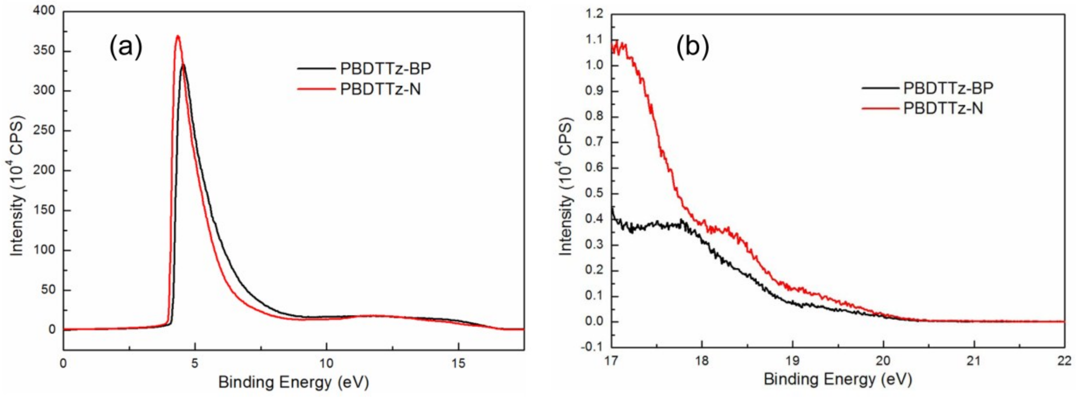

Fig. 3S UPS spectrum of the onset (a) and the secondary edge region (b) of the polymers PBDTTz-BP and PBDTTz-N.

Table 1S Photovoltaic device parameters for conventional configuration solar cells with PBDTTz-BP and PBDTTz-N.

polymer	D:A ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)[b]
PBDTTz-BP	1:1.5	0.82	15.7	0.44	5.69 (5.45)
	1:1	0.81	17.7	0.56	8.03 (7.92)
	1.5:1	0.81	16.5	0.44	5.83 (5.77)
	1:1[a]	0.83	15.0	0.56	6.99 (6.83)
PBDTTz-N	1:1.5	0.73	16.8	0.43	5.27 (5.19)
	1:1	0.75	18.0	0.49	6.61 (6.45)
	1.5:1	0.74	16.2	0.47	5.63 (5.50)
	1:1[a]	0.71	15.8	0.51	5.72 (5.57)

[a] With CN as additive. [b] Average PCEs in brackets for 10 devices.

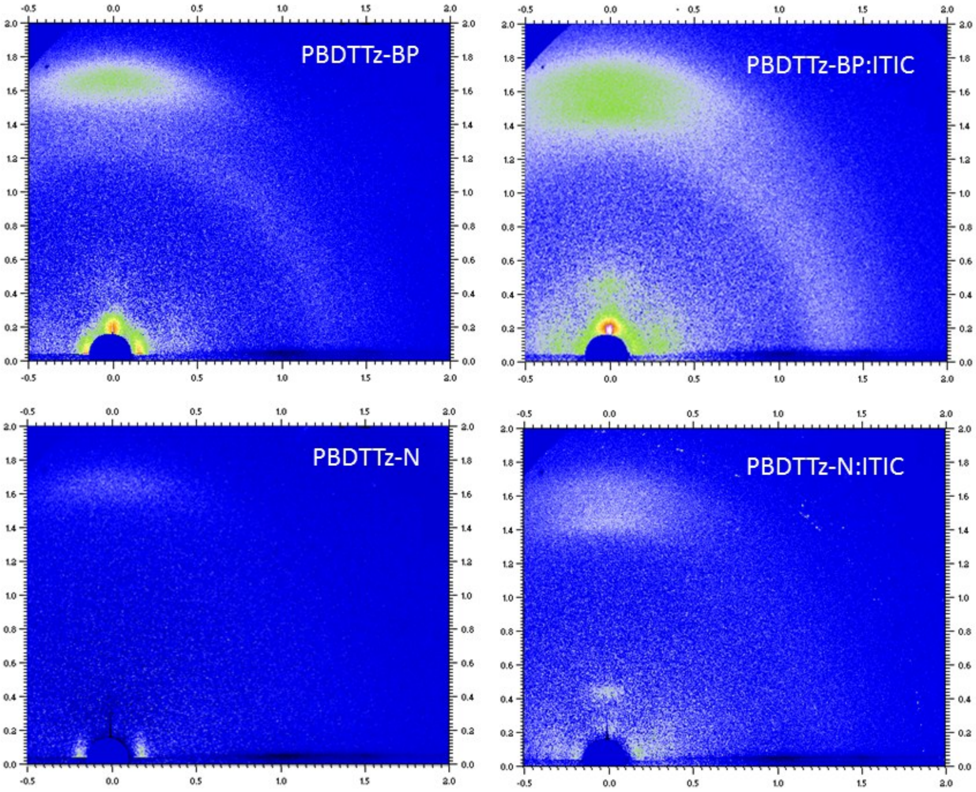

Fig. 4S 2D GIWAXS patterns of neat and blend films for PBDTTz-BP and PBDTTz-N.

Table 2S The hole (μ_h) and electron (μ_e) mobilities of PBDTTz-BP or PBDTTz-N: ITIC blended films.

blend	CN(%)	μ_h(cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_e/μ_h
PBDTTz-BP: ITIC	0	1.32×10^{-4}	0.38×10^{-4}	0.29
PBDTTz-BP: ITIC	1	1.57×10^{-4}	8.13×10^{-4}	5.18
PBDTTz-N: ITIC	0	1.25×10^{-5}	3.41×10^{-4}	27.3
PBDTTz-N: ITIC	1	3.66×10^{-5}	4.09×10^{-4}	11.2

Reference

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