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基于侧链不对称喹喔啉聚合物的高效非富勒烯太阳电池

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Asymmetric Quinoxaline-based Polymer for High Efficiency Non-fullerene Solar Cells

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1. Characterization

^{1}HNMR spectra were recorded using a Bruker AV-500 spectrometer in deuterated chloroform solution at 298 K, unless specified otherwise. Chemical shifts were reported as δ values (ppm) with tetramethylsilane (TMS) as the internal reference. Molecular weight and polydispersity index of the polymer was determined by high temperature gel permeation chromatography (GPC) analysis with polystyrene as standard (Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3 and HT4) using 1,2,4-trichlorobenzene as eluent at a flow rate of 1.0 mL·min^{-1} at 150 °C. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 with a heating rate of 20 K·min^{-1} under nitrogen. UV-Vis absorption spectra were recorded on SHIMADZU UV-2600 spectrophotometer. For the solid state measurements, polymer solution in chloroform was spin-coated on quartz plates. The cyclic voltammetry was recorded with a computer controlled CHI660E electrochemical workstation using polymer films on platinum electrode (1.0 cm^2) as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (0.1 mol·L^{-1}) as the reference electrode in an anhydrous and argon-saturated solution of 0.1 mol·L^{-1} of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile at a scanning rate of 50 mV·s^{-1}. Electrochemical onsets were determined at the position where the current starts to differ from the baseline. The morphologies of the polymer/$PC_{71}BM$ blend films were investigated by atomic force microscopy (AFM, Agilent Technologies, 5500 AFM/SPM System, USA) in contacting mode with a 5 μm scanner. Transmission electron microscope (TEM) measurements were performed in a JEM-2100F.

2. Fabrication and characterization of polymer solar cells.

The PSCs were fabricated with an indium tin oxide (ITO) glass as positive electrode and a ETLs/Al as negative electrode. Patterned ITO glass with a sheet resistance of 10 Ω·□$^{-1}$ was purchased from CSG HOLDING Co. LTD. (China). The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone and isopropanol, and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. Then PEDOT:PSS (poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate)) (Baytron PVP Al 4083, Germany) was filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) filter and spin coated at 3000 r·min^{-1} for 40 s on the ITO substrate. Subsequently, PEDOT: PSS film was baked at 150 °C for 15 min in the air, and the thickness of the PEDOT:PSS layer is about 40 nm. The polymer and o-IDTBR (10 mg·mL^{-1} for polymer) were dissolved inCHCl3overnight and spin-cast at 2500 r·min^{-1} for 90 s onto the PEDOT:PSS layer. Thermal annealing treatment was performed at different temperatures for 10 min. The thickness of the photoactive layer is about 110 nm measured by Ambios Technology XP-2 profilometer. A bilayer cathode consisting of ETLs (~15 nm) capping with Al (~40 nm) was thermal evaporated under a shadow mask with a base pressure of ca. 10^{-5} Pa. The active area of the PSCs is 5 mm^2. The ETLs were simply prepared by spin-coating its water/ethanol solution (1 mg·mL^{-1}) on photoactive layer at 3000 r·min^{-1} for 30 s at room temperature, no thermal annealing or any other post-treatment was performed. Finally, top electrodes were deposited in a vacuum onto the active layer.

Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW·cm^{-2} (Oriel 67005, 500 W), calibrating by a standard silicon cell. *J–V* curves were recorded with a Keithley 236 digital source meter. A xenon lamp with AM 1.5 filter was used as the white light source and the optical power was 100 mW·cm^{-2}. The EQE measurements of PSCs were performed by Stanford Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500 W xenon lamp. A calibrated silicon detector was used to determine the absolute photosensitivity at different wavelengths. All of these fabrications and characterizations were conducted in a glove box.

3. ^{1}H NMR

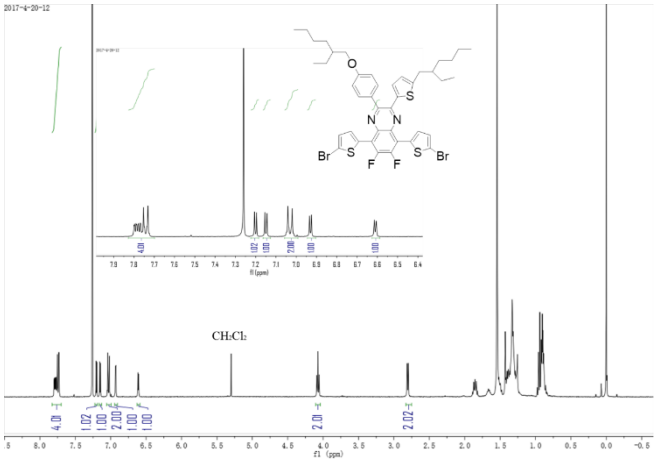

Fig. S1 ^{1}H NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2-(4-((2-ethylhexyl)oxy)-phenyl)-3-(5-(2-ethylhexyl)thiophen-2-yl)-6,7-difluoroquinoxaline.

4. Absorption spectra

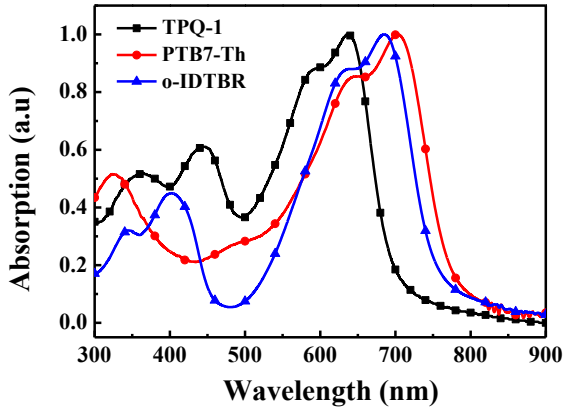

Fig. S2 Absorption spectra of TPQx-1, PTB7-Th and o-IDTBR in thin film.

5. Solar cell performance

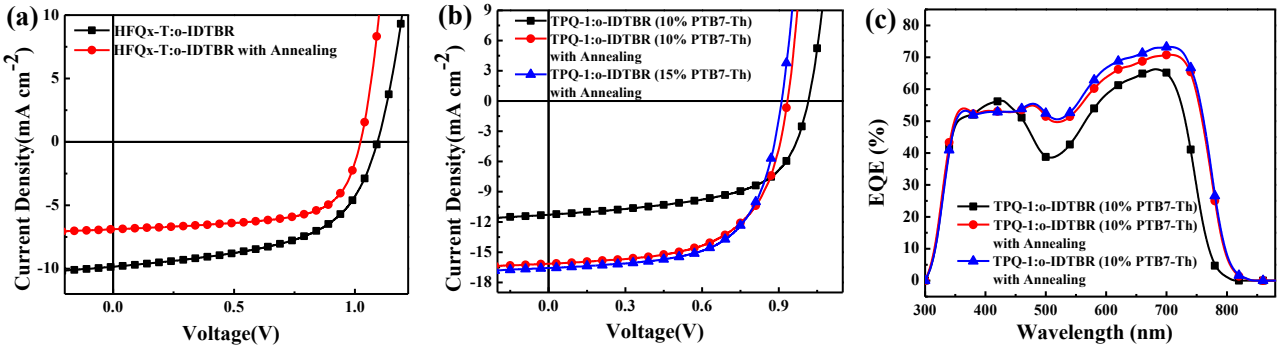

Fig. S3 *J–V* characteristics of the devices based on donor polymers (a) HFQx-T with o-IDTBR, (b) TPQ-1, PTB7-Th with o-IDTBR under illumination of AM 1.5, 100 mW cm^{-2}; (c) EQE spectra of the devices based on donor polymers TPQ-1, PTB7-Th with o-IDTBR.

6. SCLC, J_{ph} versus V_{eff}, and light-intensity dependence of J_{sc}

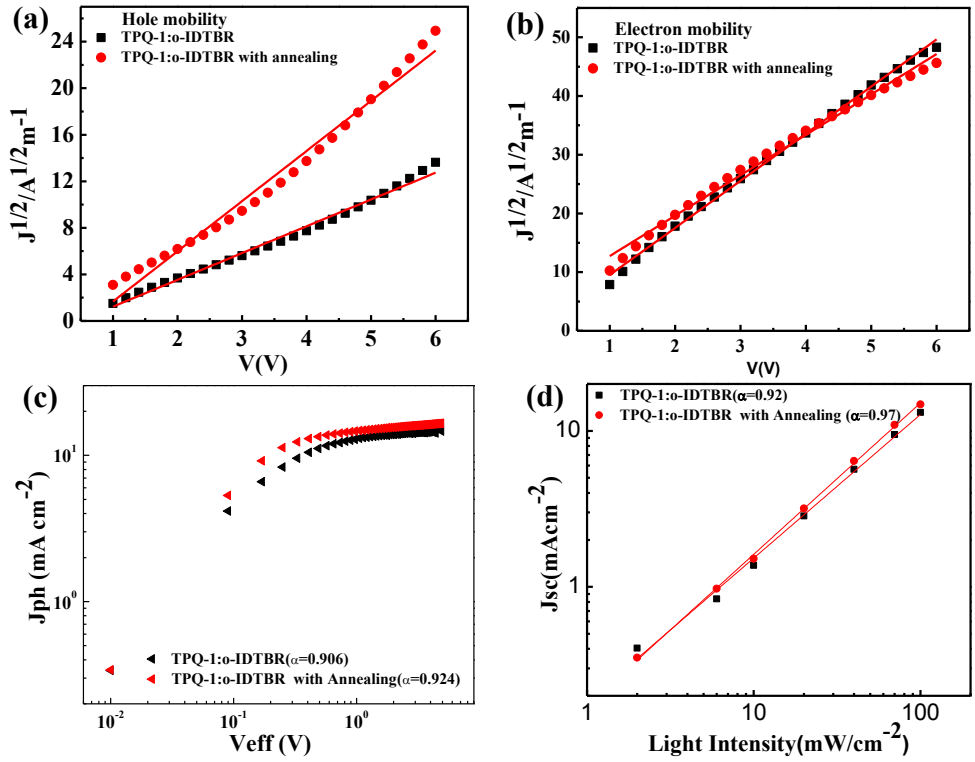

Fig. S4 $J^{1/2}/A^{1/2}$ m^{-1} plots of the blends of TPQ-1/o-IDTBR (a) hole mobilities; (b) electron mobilities measurement by SCLC method. (c) J_{ph} versus V_{eff} and (d) light-intensity dependence of J_{sc} of the corresponding device.

Table S1 The device parameters of PSCs based on TPQ-1:o-IDTBR under illumination of AM 1.5G,100 mW cm^{-2}.

Active layer	V_{oc}/(V)	J_{sc}/(mA cm^{-2})	FF (%)	PCE (%)
TPQ-1 : o-IDTBR = 1 : 1 [a]	0.95	12.57	47.2	5.7
TPQ-1 : o-IDTBR = 1 : 1 [b]	0.90	13.98	59.2	7.5
TPQ-1 : o-IDTBR = 1 : 1 [c]	0.88	13.89	65.2	8.0
TPQ-1 : o-IDTBR = 1 : 1.5 [a]	0.91	13.94	53.5	6.8
TPQ-1 : o-IDTBR = 1 : 1.5 [d]	0.91	13.81	58.4	7.3
TPQ-1 : o-IDTBR = 1 : 1.5 [e]	0.91	14.19	62.4	8.1
TPQ-1 : o-IDTBR = 1 : 1.5 [b]	0.90	14.95	64.3	8.6
TPQ-1 : o-IDTBR = 1 : 1.5 [c]	0.89	12.92	66.5	7.7
TPQ-1 : o-IDTBR = 1 : 1.5 [f]	0.88	13.07	68.0	7.8

[a] As-cast film. [b] With thermal annealing at 110 °C for 10 min. [c] With thermal annealing at 120 °C for 10 min. [d] With thermal annealing at 90 °C for 10 min. [e] With thermal annealing at 100 °C for 10 min. [f] With thermal annealing at 130 °C for 10 min.

Table S3 The device parameters of PSCs based on HFQx-T:o-IDTBR under illumination of AM 1.5G,100 mW cm^{-2}.

Active layer	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
HFQx-T:o-IDTBR =1:1[a]	1.09	9.85	55.0	5.9
HFQx-T:o-IDTBR =1:1[b]	1.02	6.91	64.7	4.6
HFQx-T:o-IDTBR =1:1[c]	1.01	5.08	63.4	3.3
HFQx-T:o-IDTBR =1:1.5[a]	1.02	6.06	63.7	4.0
HFQx-T:o-IDTBR =1:1[a]	1.09	9.85	55.0	5.9

[a] As-cast film. [b] With thermal annealing at 110 °C for 10 min. [c] With thermal annealing at 120 °C for 10 min.

Table S4 Summary of TPQ-1:o-IDTBR device performance of ternary organic solar cells with different PTB7-Th contents.

PTB7-Th content (%)	V_{oc} (V)	J_{sc}/(mA cm^{-2})	FF (%)	PCE (%)
10 [a]	0.95	13.57	53.6	6.9
10 [b]	0.95	14.03	62.4	8.3
10 [c]	0.90	13.74	66.1	8.2
15 [d]	0.92	16.57	63.0	9.6
20[d]	0.94	12.85	61.1	7.4

[a] As-cast film. [b]With thermal annealing at 100 °C for 10 min. [c] With thermal annealing at 120 °C for 10 min. [d]With thermal annealing at 110 °C for 10 min.

7. AFM and TEM

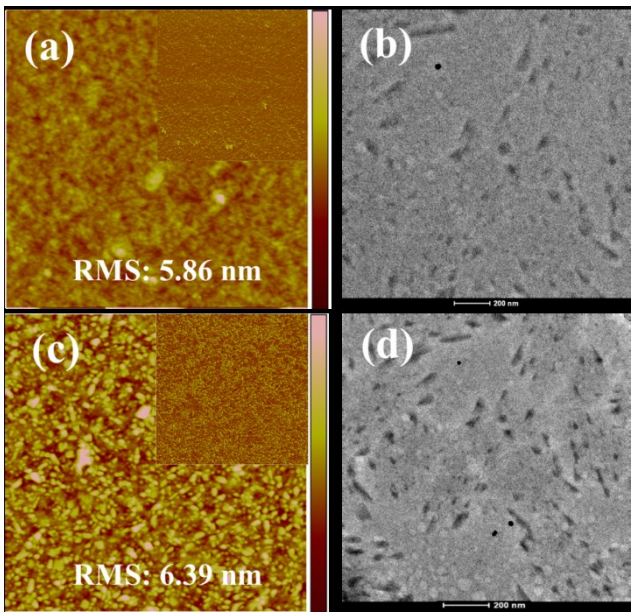

Fig. S5 AFM images of blend films: (a) HFQx-T:o-IDTBR; AFM images of blend films with thermal annealing: (c) HFQx-T:o-IDTBR; TEM images of blend films: (b) HFQx-T:o-IDTBR; TEM images of blend films with thermal annealing: (d) HFQx-T:o-IDTBR.