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Supporting information

Achieving 31% Efficiency in Organic Photovoltaic Cells Under Indoor Light Using A Low Energetic Disorder Polymer Donor

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Experimental Procedures

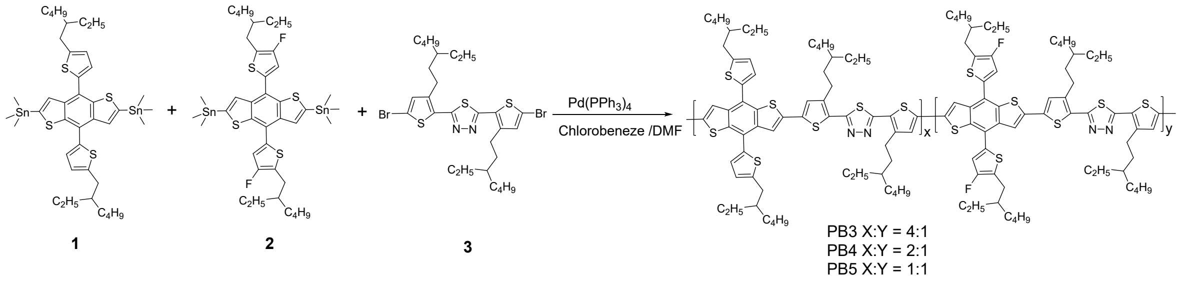

Figure S1. The synthetic route of PB3, PB4 and PB5.

Raw materials

In a 25 ml flask, monomer 1/monomer 2 (0.16 mmol/0.04 mmol; 0.13 mmol/0.07 mmol; 0.1 mmol/0.1 mmol) and **X** (0.20 mmol) monomer 3 (132.1 mg, 0.20 mmol) were dissolved in 7 ml chlorobenzene and 0.7 ml DMF, and the flask was flushed with argon for 10 min. Then 20 mg of $Pd(PPh_3)_4$ was added into the solution, and the mixture was flushed with argon for another 15 min. The solution was heated to 120°C for 8-18 hours. After cooling to ambient temperature, the polymer was precipitated in 200 ml of methanol, filtered through a Soxhlet thimble. The precipitate was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was precipitated from 100 ml of methanol. The precipitates were collected and dried under vacuum overnight to get final polymers as red solid. PB3 (180 mg, 83%), M_n = 71.4 kg mol^{-1}, Đ =2.95; PB4 (182 mg, 83%), M_n = 81.2 kg mol^{-1}, Đ =2.71; PB5 (179 mg, 81%), M_n = 69.8 kg mol^{-1}, Đ =2.48. Besides, the M_n/Đ values of PB2 and PB2F are 80.3 kg mol^{-1}/2.76 and 84.6 kg mol^{-1}/2.49, respectively.

Materials

PEDOT:PSS (clevios P VP Al 4083) is purchased from H.C. Starck co. Ltd. BTP-eC9 is purchased from Solarmer Materials Inc. and used as received. PB2, PB2F and FTCC-Br are synthesized according to our previous reports.[1-3]

Sample characterizations

1H NMR information is obtained by using the Bruker AV-400 and 75 MHz NMR spectrometer. Gel permeation chromatography (GPC) is used to collect the molecular weight and the polydispersity (PDI) by using trichlorobenzene as eluent at 140°C on a PL GPC-220 instrument. The energy levels are measured via CV measurements on a CHI650D electrochemical workstation in a 0.1 mol l^{-1} tetrabutylammonium hexafluorophosphate acetonitrile solution. The absorption in solution and film states are measured by a Hitachi UH5300 spectrophotometer. GIWAXS measurements are conducted on a Xeuss 2.0 SAXS/WAXS system (Xenocs SA, France). Cu Kα X-ray source (GeniX3D Cu ULD), generated at 50 kV and 0.6 mA, is utilized to produce X-ray radiation with a wavelength of 1.5418 Å. A semiconductor detector (Pilatus 300 K, DECTRIS, Swiss) with a resolution of 487×619 pixels (pixel size = 172 × 172 μm^2) is used to collect the scattering signals. The incident angle was 0.3°. AFM height and phased images were collected via a Bruker Nanoscope V AF microscope.

TA measurements were performed on an Ultrafast Helios pump-probe system in collaboration with a regenerative amplified laser system from Coherent. An 800 nm pulse with a repetition rate of 1 kHz, a length of 100 fs, and an energy of 7 mJ pluse^{-1}, was generated by an Ti:sapphire amplifier (Astrella, Coherent). Then the 800 nm pulse was separated into two parts by a beam splitter. One part was coupled into an optical parametric amplifier (TOPAS, Coherent) to generate the pump pulses at various wavelength. The other part was focused onto a sapphire plate and a YAG plate to generate white light supercontinuum as the probe beams with spectra covering 420-800 nm and 750-1600 nm, respectively. The time delay between pump and probe was controlled by a motorized optical delay line with a maximum delay time of 8 ns. The pump pulse is chopped by a mechanical chopper with 500 Hz and then focused on to the mounted sample with probe beams. The probe beam was collimated and focused into a fiber-coupled multichannel spectrometer with CCD sensor. The energy of pump pulse was measured and calibrated by a power meter (PM400, Thorlabs).

OPV cell fabrication procedures

The ITO substrates were consecutively cleaned in detergent, deionized water, acetone, and isopropanol, respectively. The ITO glasses were then treated with ultraviolet-ozone for 30 mins. PEDOT:PSS thin films with about 15 nm were spin-coated on the cleaned ITO-substrates. In order to prevent the high conductivity of PEDOT:PSS interface layer, before spin-coating, the PEDOT:PSS solution was diluted with deionized water (1:1). Then, the

PEDOT:PSS-coated substrates were annealed at 150°C for 15 mins in atmosphere. The active layers were obtained by spin-coating the optimized solutions (polymers:NFAs=1:1 wt% in CB with addition of 0.5% volume ratio of DIO; 10 mg ml^{-1} for polymers) on the PEDOT:PSS layers. The active layers are annealed at 100°C for 10 min and then 5 nm PDINN layers were spin-coated the active layers. Finally, 100-nm-thick Ag layers were deposited onto the active layers. The effective areas of the outdoor and indoor used cells are is 0.06 and 1.0 cm^2, respectively.

The *J-V* curves of the OPV cells were recorded under AM1.5G illumination of 100 mW cm^{-2}. The radiative intensity was calibrated by the standard silicon solar cell. QE-R3011 (Enli Technology Co., Ltd) was used to collect the EQE spectra. A high-precision fiber-optics spectrometer (Maya2000 Pro, Ocean Optics) was used to collect the emission spectra and illumination intensities of the indoor light sources. Highly-sensitive EQE (HEQE) was measured using an integrated system (PECT-600, Enlitech) EQEEL and EL spectra were collected by applying external voltage (0-5 V) through the corresponding OPV cells (ELCT-3010, Enlitech).

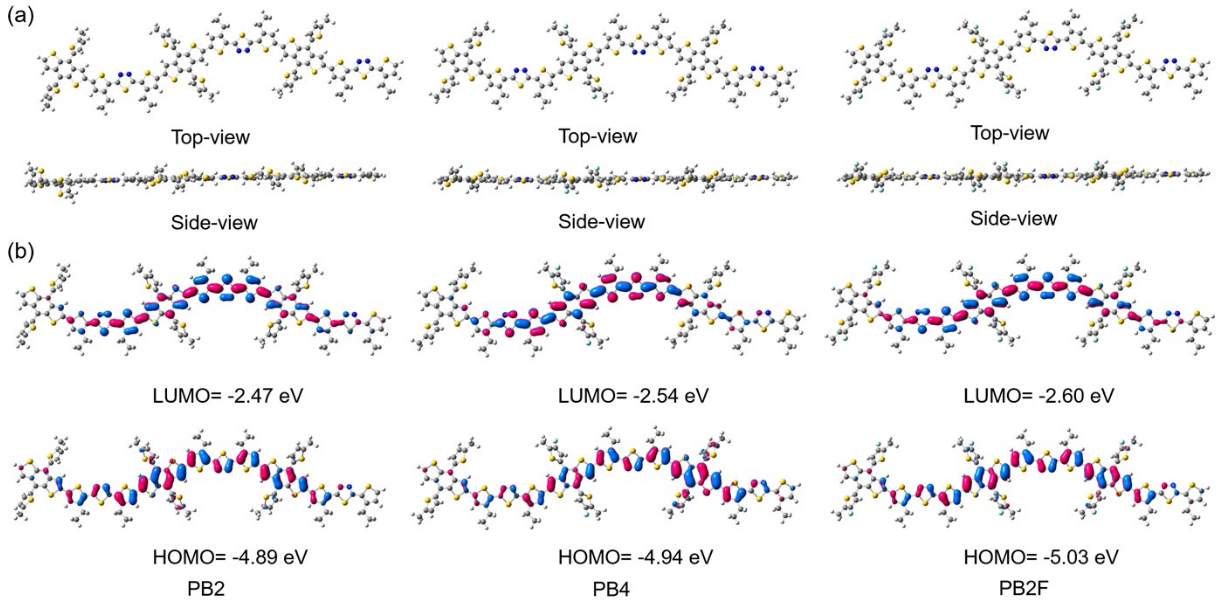

Figure S2. (a) The top-/side-views of optimized stable molecular geometries and (b) the calculated HOMO and LUMO levels of PB2, PB4 and PB2F.

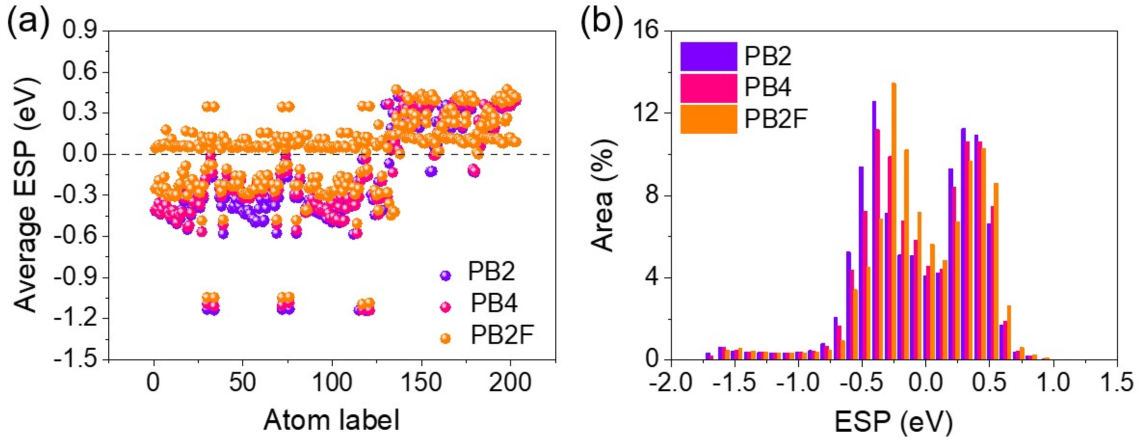

Figure S3. (a) Averaged ESP values of the atoms in the conjugated backbones and (b) the ESP area distributions of PB2, PB4 and PB2F.

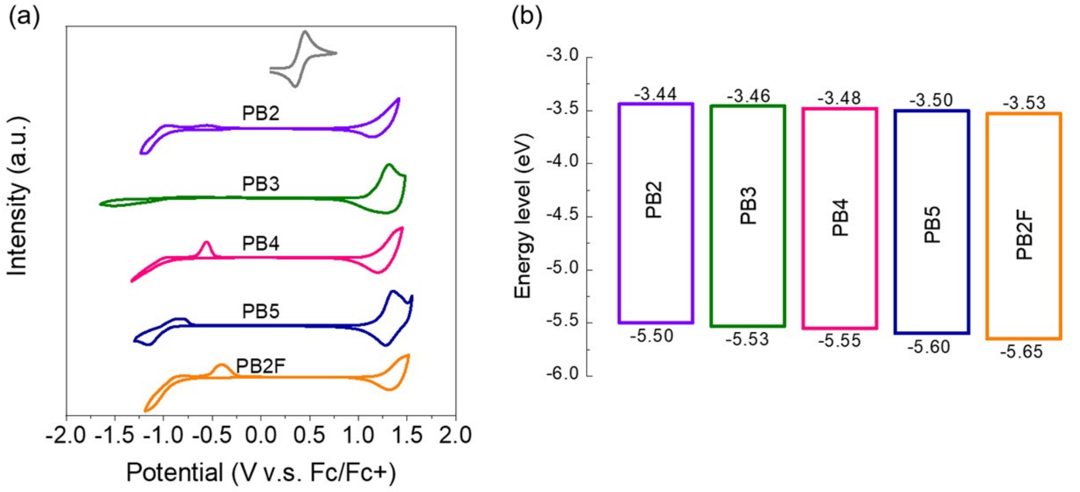

Figure S4. CV curves and energy levels of the polymers.

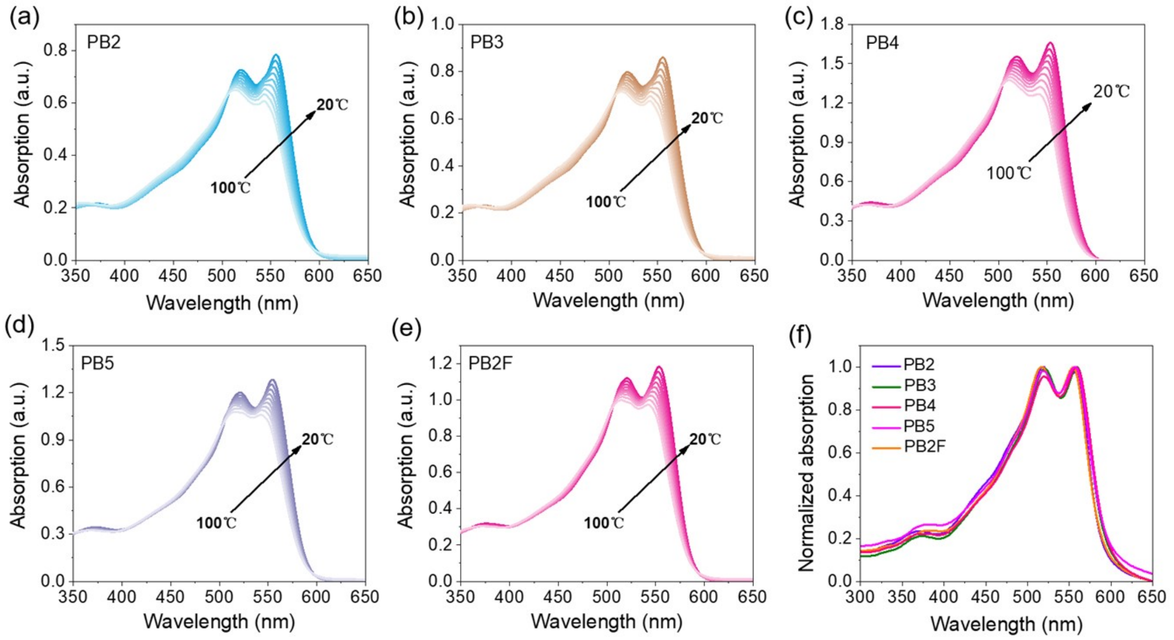

Figure S5. (a-e) The absorption spectra of the polymers (PB2-5 and PB2F) in solution states at various temperatures. (f) The normalized absorption spectra of PB2-5- and PB2F-based neat films.

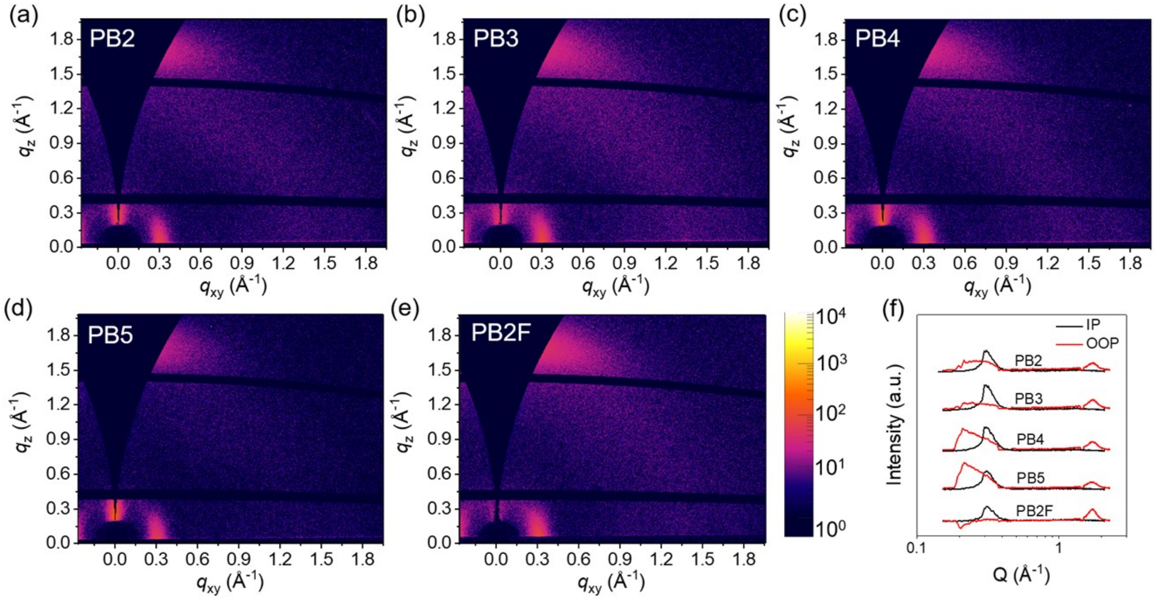

Figure S6. The 2D GIWAXS patterns and line cut profiles of the neat polymers-based films.

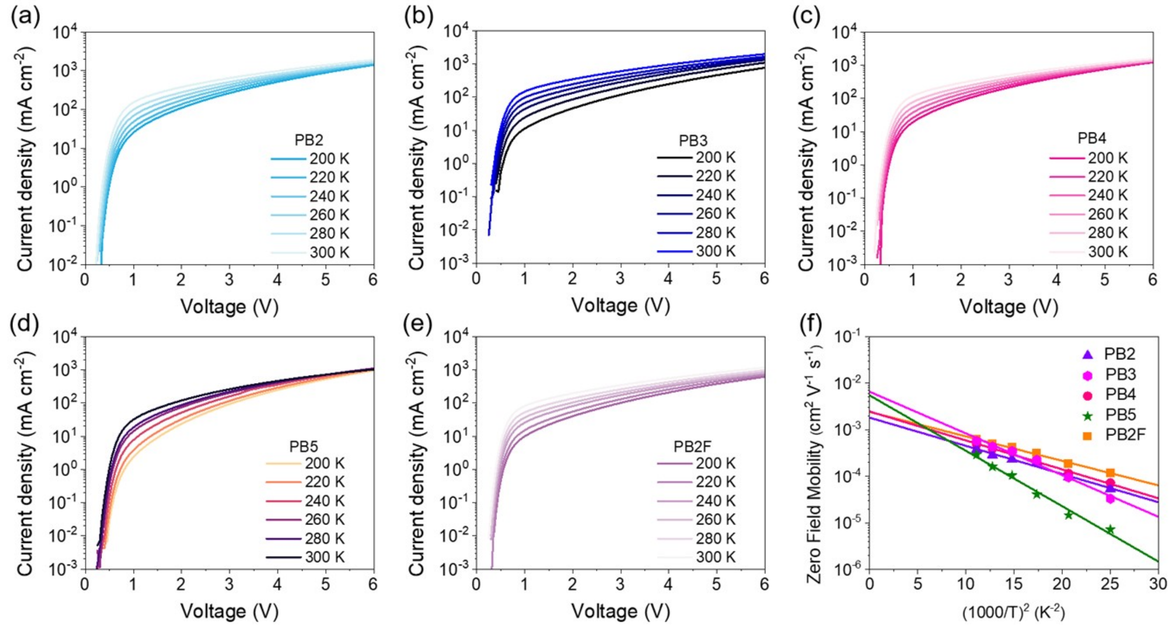

Figure S7. (a-e) The *J-V* curves of the hole-only devices based on PB2-5 and PB2F neat films with various temperatures. (f) Hole mobilities of the PB2-5- and PB2F-based films as a function of $1/T^2$ using SCLC derived data.

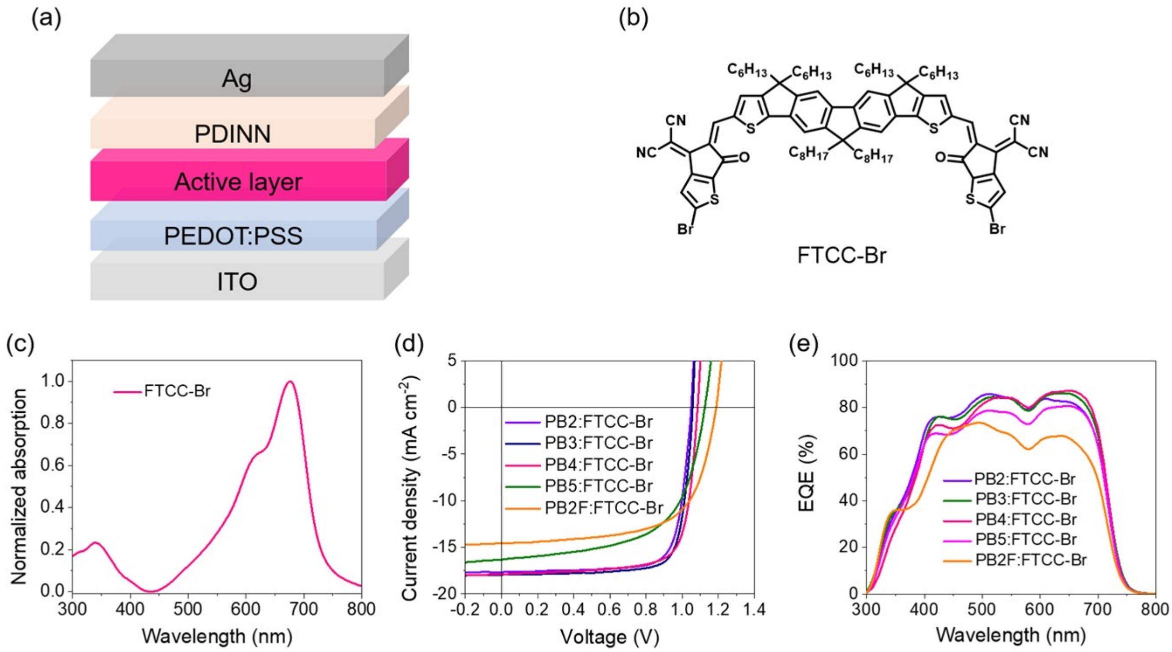

Figure S8. (a) Schematic of the device structure used in this work. (b) The chemical structure of FTCC-Br. (c) The normalized absorption spectrum of the FTCC-Br-based neat film. (d) The *J*-*V* curves of polymers:FTCC-Br-based cells under AM 1.5G, 100 mA cm^{-2}. (e) The EQE spectra of polymers:FTCC-Br-based cells.

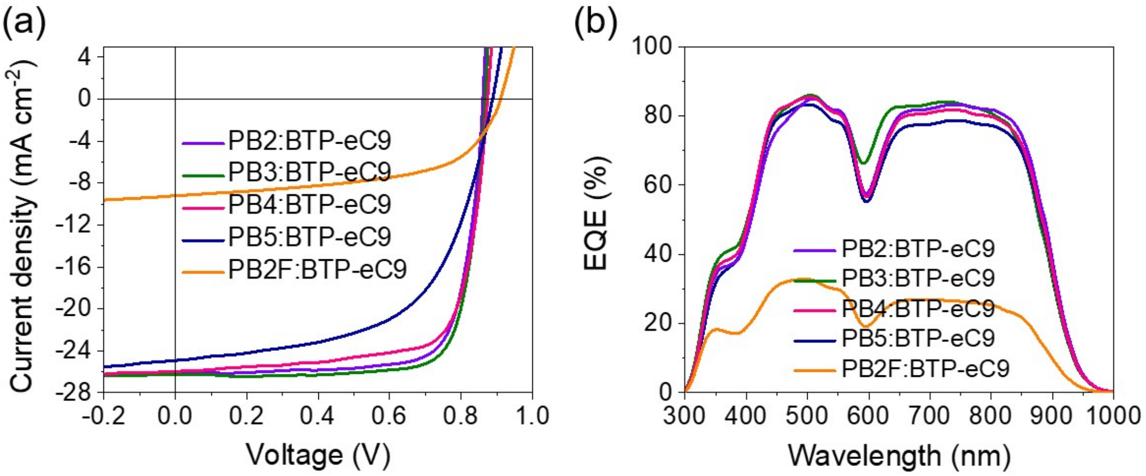

Figure S9. (a) The *J*-*V* curves of polymers:BTP-eC9-based cells under AM 1.5G, 100 mA cm^{-2}. (b) The EQE spectra of polymers:BTP-eC9-based cells.

Table S1. Summary of photovoltaic parameters of polymers:BTP-eC9 based device under AM 1.5G, 100 mW cm^{-2}.

Devices	V_{OC} (V)	J_{SC} (mA cm^{-2})	*Cal.* J_{SC} (mA cm^{-2})	FF (%)	PCE$^{(a)}$ (%)
PB2:BTP-eC9	0.861	26.15	25.44	78.21	17.61 (17.19±0.30)
PB3:BTP-eC9	0.867	26.26	25.81	80.32	18.28 (17.93±0.25)
PB4:BTP-eC9	0.874	25.97	25.23	74.75	16.97 (16.57±0.26)
PB5:BTP-eC9	0.888	24.89	24.43	58.57	12.95 (12.57±0.22)
PB2F:BTP-eC9	0.910	9.20	8.62	57.15	4.79 (4.62±0.13)

$^{(a)}$ Average values with standard deviation are obtained from six devices.

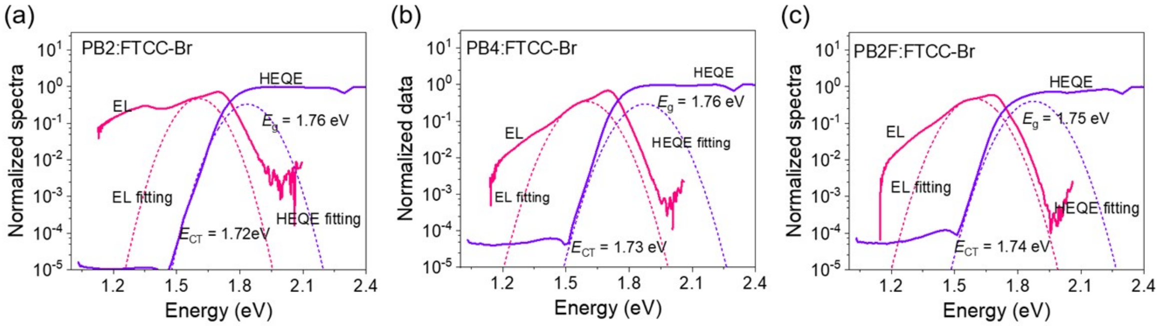

Figure S10. The normalized and fitted HEQE and EL curves of the polymers:FTCC-Br-based cells.

Table S2. Detailed E_{loss} parameters of the polymers:FTCC-Br-based cells.

Devices	E_g (eV)	E_{loss} (eV)	E_{CT} (eV)	ΔE_{CT} (eV)	$\Delta E_{\mathrm{non\text{-}rad}}$ (eV)
PB2:FTCC-Br	1.76	0.71	1.72	0.04	0.30
PB4:FTCC-Br	1.76	0.67	1.73	0.03	0.23
PB2F:FTCC-Br	1.75	0.56	1.74	0.02	0.14

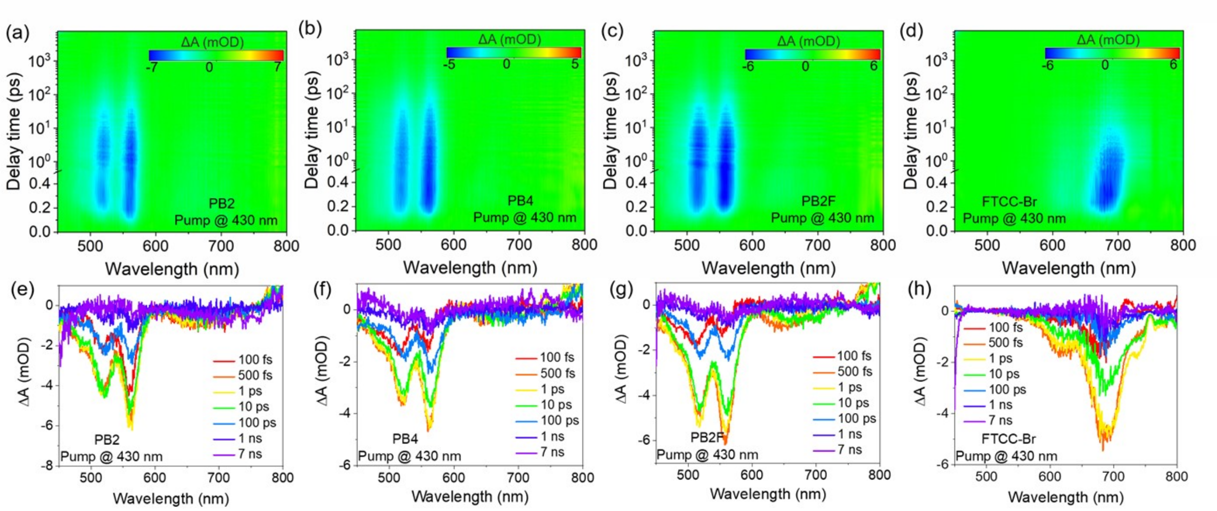

Figure S11. The TA images and the corresponding TA spectra with various decay times with an excitation wavelength of 430 nm.

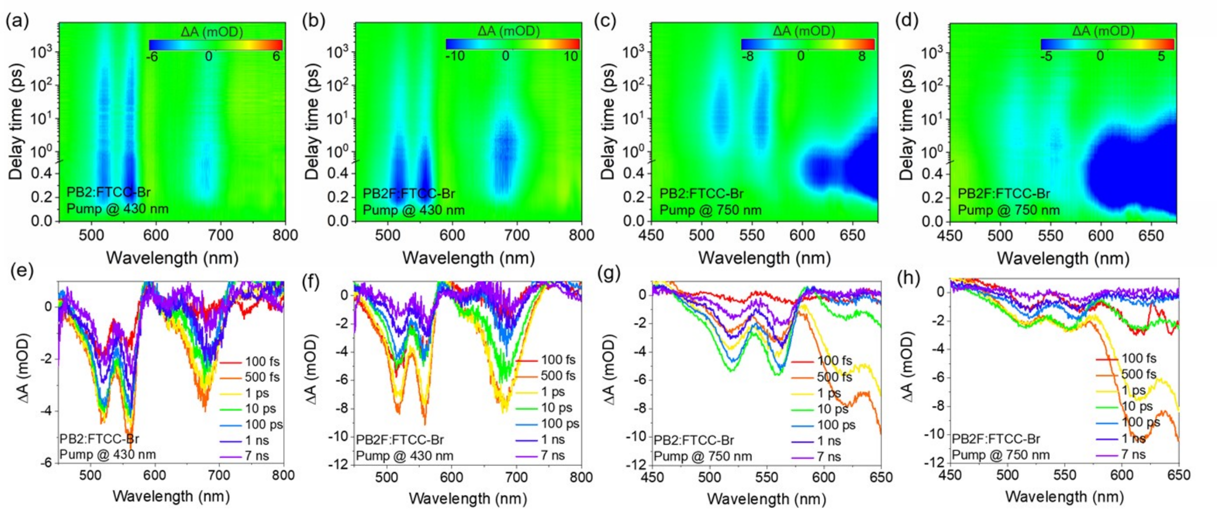

Figure S12. The TA images and the corresponding TA spectra with various decay times with excitation wavelengths at 430 and 750 nm.

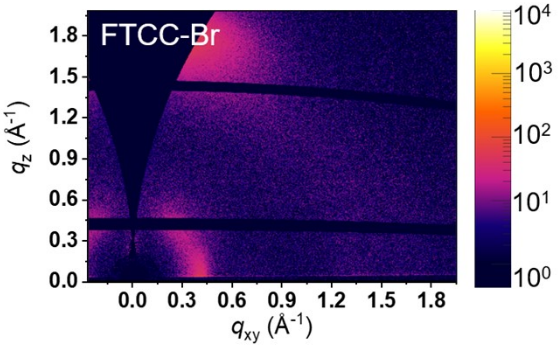

Figure S13. The 2D GIWAXS pattern of FTCC-Br neat film.

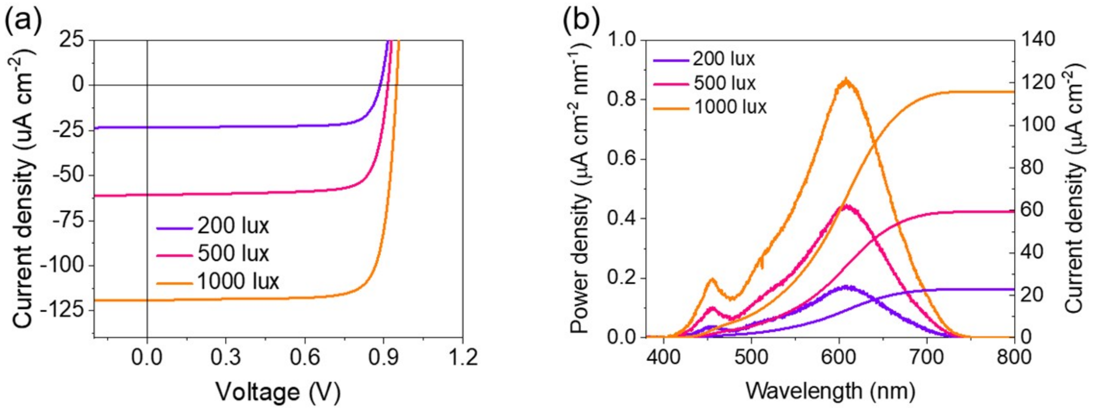

Figure S14. (a) J-V curves of the 1.0 cm^2 PB3:FTCC-Br-based cell under 200, 500 and 1000 lux (2700 K LED). (c) Photon fluxes power densities and the corresponding integral current densities of the PB3:FTCC-Br-based cell under 200, 500 and 1000 lux.

Table S3. The detailed device parameters of PB3:FTCC-Br under the light source of 2700 K LED.

Intensity (lux)	**P_{in} (μW cm^{-2})**	**V_{OC} (V)**	**J_{SC} (μA cm^{-2})**	***Cal.* J_{SC} (μA cm^{-2})**	**FF (%)**	**P_{out} (μW cm^{-2})**	**PCE$^{(a)}$ (%)**
200	60.2	0.895	23.33	22.81	77.26	16.13	26.80 (26.36±0.38)
500	156.1	0.918	60.78	59.22	79.19	44.18	28.31 (27.96±0.31)
1000	305.7	0.954	119.06	115.86	80.72	91.68	30.00 (29.65±0.27)

$^{(a)}$ Average values with standard deviation are obtained from six cells.

Table S4. The detailed device parameters of PB4:FTCC-Br comparisons with the state-of-the-art literature under the low-light intensity.

Device	**Intensity (lux)**	**P_{in} (μW cm^{-2})**	**V_{OC} (V)**	**J_{SC} (μA cm^{-2})**	**FF (%)**	**P_{out} (μW cm^{-2})**	**PCE (%)**	**Device area (cm$^{2)}$**	**Ref.**
PB4:FTCC-Br	1000	305.7	0.967	119.87	82.0	95.05	31.09	1.0	This work
PM6:IT-4F:ITIC-Th	500		0.75	73.18	77.10	42.79	30.11	0.11	4
	1000		0.76	145.42	75.58	83.53	28.14	0.11	4
D18:FCC-Cl	1000	318	0.955	123.0	79.8	93.5	29.4	0.059	5
	1000	318	0.955	120	79.0	90.6	28.5	0.85	5
PB2:FTCC-Br	1000	314	0.943	123.8	81.1	94.7	30.2	1.0	6

Table S5. The detailed device parameters of 10 cm^2 PB4:FTCC-Br under the light source of 2700 K LED.

Intensity (lux)	P_{in} (μW cm^{-2})	V_{OC} (V)	J_{SC} (μA cm^{-2})	FF (%)	P_{out} (μW cm^{-2})	PCE (%)
200	60.2	0.901	21.71	72.97	14.27	23.78
500	156.1	0.926	57.25	77.93	41.31	26.46
1000	305.7	0.953	115.21	79.78	87.59	28.65

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