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聚 3-己基噻吩:非富勒烯太阳能电池中的量子效率损失和电压损失

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Quantum Efficiency and Voltage Losses in P3HT:Non-fullerene Solar Cells

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SI-1 Device characterizations

J–V characterization and light intensity dependent *J–V* measurements

The *J–V* characteristic curves of the OSCs were measured by a standard solar simulator (AM 1.5G) with an intensity of 100 mW·cm^{-2} (Newport, verasol-2). A Keithley 2400 source meter was used to collect the current from the solar cell under different voltages. The light intensity dependent *J–V* measurements were carried out by using a series of neutral density filters.

Highly sensitive EQE (sEQE) measurements

A highly sensitive homo-built setup was used to measure the sEQE/EQE spectra, which includes a halogen lamp (LSH-75, Newport), a monochromator (CS260-RG-3-MC-A, Newport), a chopper, a current amplifier and a phase-locked amplifier (SR830, Newport), and the overtone signals from the monochromator were blocked by a group of long pass filters (600, 900, 1100 nm).

Internal quantum efficiency (IQE)

IQE spectra of the OSCs were determined by dividing the measured EQE spectra by the transfer matrix model simulated EQE spectra. The optical constants of the active layers and the passive layers in the solar cells were determined using variable-angle spectroscopic ellipsometry (VASE, J. A. Woollam M-2000 UI).

Transient photovoltage (TPV) decay measurements

TPV measurement setup consists of two LED lamps. One of the LED was driven by a direct current provided by a Keithley 2400 source meter. This LED was used to provide bias illumination, and the intensity of the bias illumination was controlled by the current injected into the LED. The second LED was driven by an arbitrary function generator (Tektronbix, AFG3022C). This LED provided pulsed illumination to the solar cell. The time interval between the two adjacent pulses was set to be 5 ms. An oscilloscope (Tektronix, MDO4104C) was used to record the transient voltage signal from the solar cell under an open-circuit condition. An exponential attenuation function was used to fit the transient voltage decay signal for the determination of the charge carrier life time. Note, in the life time vs bias photovoltage plots, the bias photovoltage values were corrected by the difference in E_{CT} of the solar cells being compared. The correction of the photovoltage values allows us to compare the life time values of the solar cells with similar free charge carrier concentrations in the devices, thus, to compare the decay rate constant of free charge carriers (K) for the devices.

Photoluminescence (PL) measurements

PL spectra were taken using a fluorescence spectrometer (KYMERA-328I-B2, Andor technology LTD) coupled to an Si EMCCD camera (DU970P-BVF, Andor) for the wavelength range of 400–1000 nm, and an InGaAs camera (DU491A-1.7, Andor) for the wavelength range of 900–1600 nm. A super-continuous white laser (SuperK EXU-6, NKT photonics) and a visible light narrowband filter (SR-VIS-HP8, NKT photonics) was used to provide the monochromatic light with a wavelength of 550 nm to excite the films for the PL measurements.

Atomic force microscopy (AFM)

The thin films for the AFM measurements were prepared using the same processing conditions used for the active layers of the OSCs. The atomic force microscope used in this work was MFP-3D-BIO from Oxford Instruments in a tapping mode.

Molecular dynamics (MD) simulations

MD simulations were carried out by using Material Studio6.0 software package. The active systems based on P3HT:Y6/ZY-4Cl were simulated by using Compass force field. There were 15 polymers and a few acceptor molecules in each cubic cell. Each polymer consists 26 repeating units, and the D : A weight ratios was kept to 1 : 1. The initial simulations were performed at low density (0.1 g·cm^{-3}), and the polymers and acceptors in the cells were randomly distributed. The construction process of the initial cells was done using the Amorphous Cell package in Materials Studio, and the sizes of the initial cells were 11.70 nm × 11.70 nm × 11.70 nm, 12.94 nm × 12.94 nm × 12.94 nm and 12.95 nm × 12.95 nm × 12.95 nm, respectively. The MD simulations were carried out from 650 K (500 ps) to 423 K (500 ps) by using the constant-temperature, constant-pressure ensemble (NPT) ensemble. There are three successive NPT simulations of 600 K for 100 ps, 550 K for 100 ps and 500 K for 100 ps in above process. And then to 423 K (1 ns) at a pressure of 1 atmosphere. After the simulation of the annealing process at the 423 K, the cooling from 423 to 300 K was done in three successive NPT simulations (400 K for 100 ps, 350 K for 100 ps and 300 K for 1 ns). The cutoff for the summation of van der Waals interactions was 1.25 nm.

SI-2 Details regarding the determination of the bandgap of the active layers in OSCs

The tail of EQE spectrum originates from the absorption of the lowest energy state (CT state) of the active layer, which was measured by a sensitive EQE measurement setup. To determine the CT state properties, including E_{CT} and λ, we used the equation derived in the framework of Marcus theory, to fit the lower energy part of the EQE spectrum:

$$\mathrm{EQE}(E) = \frac{fE}{\sqrt{4\pi\lambda kT}} \exp\left(-\frac{(E_{CT} + \lambda + E)^2}{4\lambda kT} \right)$$

where E is photon energy, and f is a pre-factor, proportional to the density of the CT complex formed at the donor-acceptor interfaces (N_{CTC}) and the absorption oscillator strength of CT state (f_{osc}).

In order to improve the accuracy of fitting, we employed two boundary conditions. The first boundary condition put an upper limit for the fit result, which was made based on the assumption that E_{CT} was the effective energy of the band gap for OSCs, therefore, the radiative voltage loss values derived from the EQE fitting must not exceed that derived using the Shockley-Queisser theory. The second boundary put a lower limit for the fit results, and it was made based on the assumption that the absorption strength of CT state was always weaker than that of the singlet states. Thus, the peak value of the fitting curve must be smaller than 10% of the above gap EQE value (the strongest CT state absorption reported for organic donor-acceptor blends was in the bimolecular crystal of PBTTT:PCBM, in which the peak value of CT state EQE is about 5%, compared to that of the singlet EQE value (Adv. Mater. **2017,** *29*, 1702184)).

SI-3 Chemical structures and optical absorption spectra for the active materials

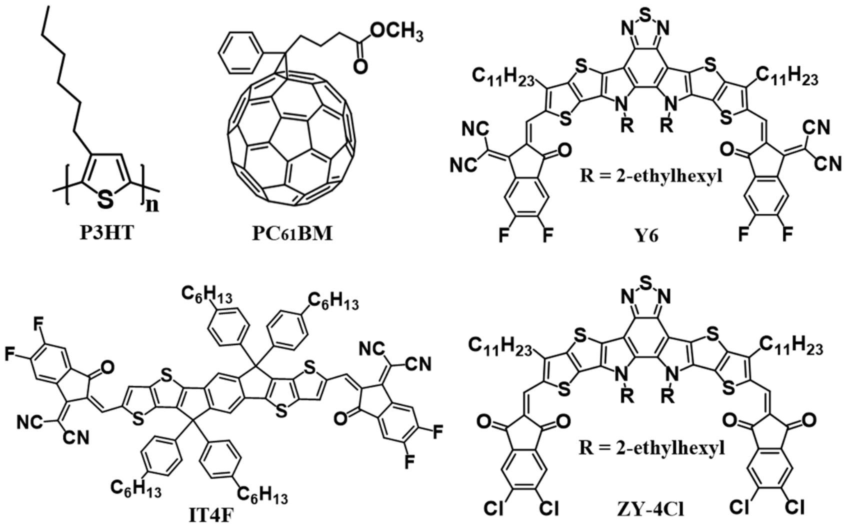

Fig. S1 Chemical structures for P3HT, $PC_{61}BM$, Y6, IT4F and ZY-4Cl.

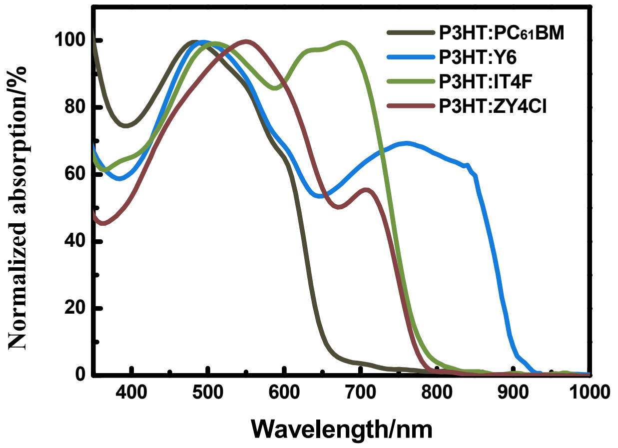

Fig. S2 Optical absorption spectra for the P3HT-based blend films. All the films were annealed at 150 °C for 10 min.

SI-4 Details regarding the optimization of the solar cells

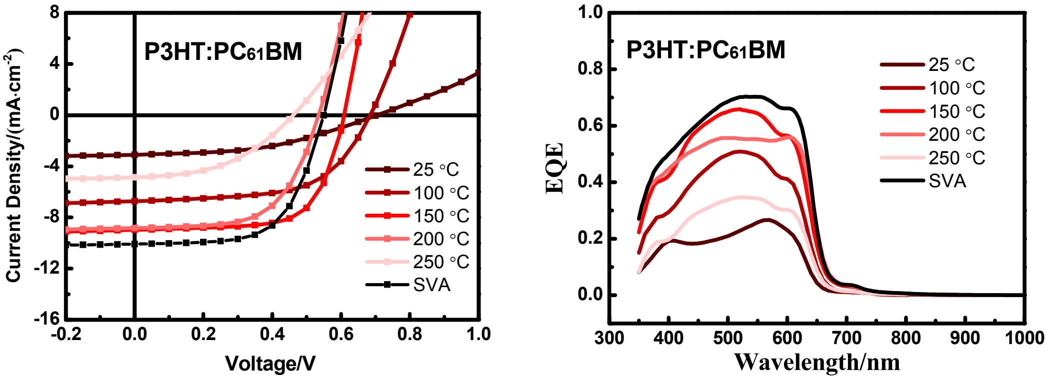

Fig. S3 *J–V* curves and EQE spectra of the solar cells based on $P3HT:PC_{61}BM$, with the active layer cast from the *o*DCB solution (1 : 1 wt ratio, 35 mg·mL^{-1}), and SVA stands for solvent vapor annealing.

Table S1 PV performance for the OSCs based on $P3HT:PC_{61}BM$.

Active layer	Annealing temperature [a]	PCE/(%)	J_{sc}/(mA·cm^{-2})	V_{oc}/V	FF/%
$P3HT:PC_{61}BM$	RT	0.97	3.10	0.705	44.3
$P3HT:PC_{61}BM$	100 °C	2.74	6.73	0.684	59.5
$P3HT:PC_{61}BM$	150 °C	3.66	8.96	0.612	66.9
$P3HT:PC_{61}BM$	200 °C	2.84	8.83	0.535	60.0
$P3HT:PC_{61}BM$	250 °C	1.02	4.87	0.461	45.5
$P3HT:PC_{61}BM$	SVA	3.45	10.08	0.550	62.2

[a] RT stands for room temperature, SVA stands for solvent vapor annealing.

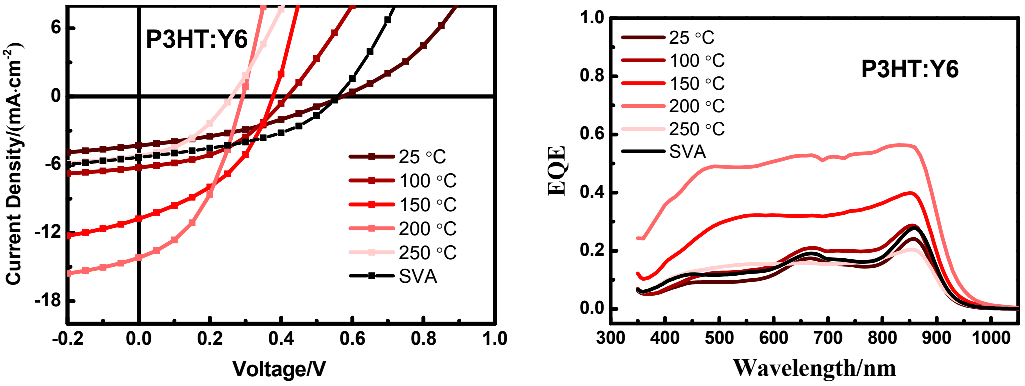

Fig. S4 *J–V* curves and EQE spectra of the solar cells based on P3HT:Y6, with the active layer annealed at different temperatures. Note that the active layers are cast from the oDCB solution (1 : 1 wt ratio, 22 mg·mL^{-1}).

Table S2 PV performance for the OSCs based on P3HT:Y6.

Active layer	Annealing temperature [a]	PCE/%	J_{sc}/(mA·cm^{-2})	V_{oc}/V	FF/%
P3HT:Y6	RT	0.88	4.32	0.572	35.6
P3HT:Y6	100 °C	0.94	5.85	0.417	38.6
P3HT:Y6	150 °C	1.70	10.77	0.377	42.0
P3HT:Y6	200 °C	1.73	14.20	0.292	41.8
P3HT:Y6	250 °C	0.55	5.25	0.261	40.1
P3HT:Y6	SVA	1.29	5.36	0.559	43.0

[a] RT stands for room temperature, SVA stands for solvent vapor annealing.

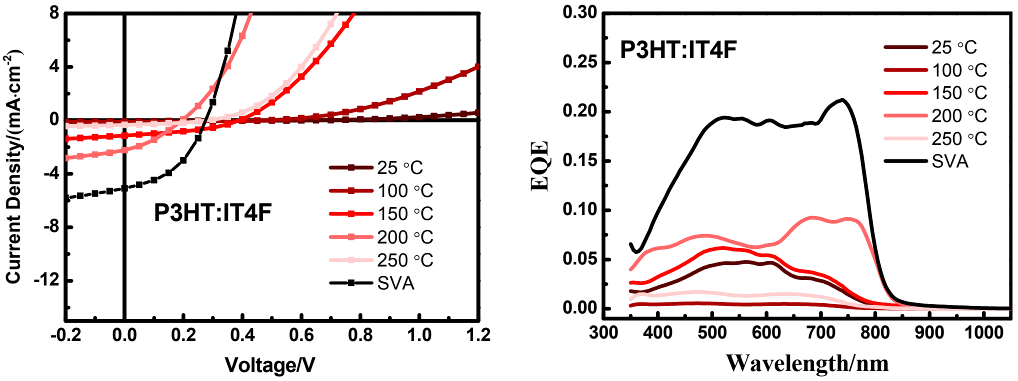

Fig. S5 J–V curves and EQE spectra of the solar cells based on P3HT:IT4F, with the active layer cast from the oDCB solution (1 : 1 wt ratio, 22 mg·mL^{-1}).

Table S3 PV performance for the OSCs based on P3HT:IT4F.

Active layer	Annealing temperature [a]	PCE/%	J_{sc}/(mA·cm^{-2})	V_{oc}/V	FF/%
P3HT:IT4F	RT	0.01	0.07	0.636	31.1
P3HT:IT4F	100 °C	0.02	0.11	0.468	37.4
P3HT:IT4F	150 °C	0.18	1.14	0.389	39.6
P3HT:IT4F	200 °C	0.14	2.23	0.196	33.1
P3HT:IT4F	250 °C	0.03	0.34	0.284	36.2
P3HT:IT4F	SVA	0.61	5.08	0.275	43.5

[a] RT stands for room temperature, SVA stands for solvent vapor annealing.

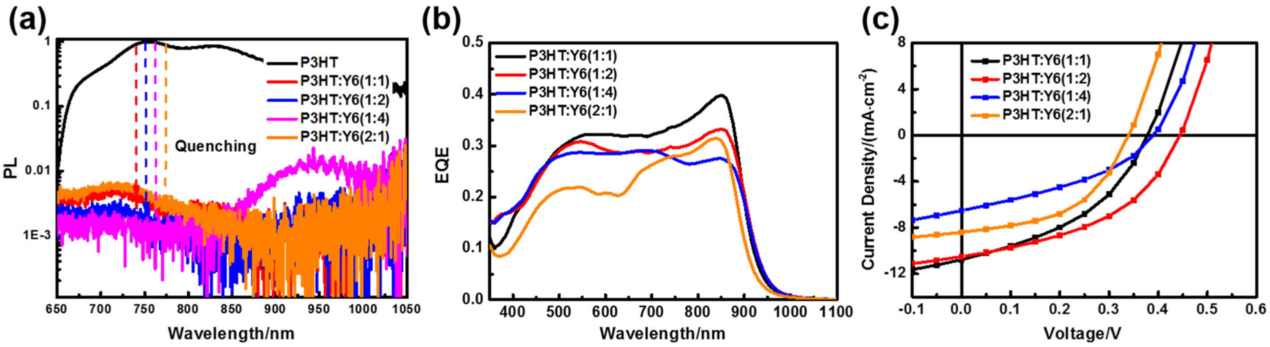

Fig. S6 (a) PL spectra, (b) J–V characteristic curves, and (c) EQE spectra for the OSCs based on P3HT:Y6 with different D : A weight ratios.

Table S4 PV performance and V_{loss} related parameters for the OSCs based on P3HT:Y6 with different D : A weight ratios.

Device	V_{oc}/V)	E_{CT}/eV	$\Delta V_{oc,rad}$/V	ΔV_{nr}/V	ΔV_{r}/V	V_{loss}/V	λ/eV	f/eV^2	J_{sc}/(mA·cm^{-2})	PCE/(%)
P3HT : Y6 (2 : 1)	0.34	1.04	0.91	0.57	0.13	0.70	0.37	7.5E-3	8.39	1.40
P3HT : Y6 (1 : 1)	0.38	1.17	0.94	0.56	0.23	0.79	0.26	1.6E-2	10.77	1.70
P3HT : Y6 (1 : 2)	0.44	1.17	0.95	0.51	0.22	0.73	0.26	1.9E-2	10.51	2.10
P3HT : Y6 (1 : 4)	0.39	1.12	0.92	0.53	0.20	0.73	0.29	1.2E-2	6.52	0.96

Table S5 V_{ph} values of TPV measurements for the solar cells based on P3HT:PC$_{61}$BM, P3HT:Y6, P3HT:IT4F and P3HT:ZY-4Cl.

V_{ph}/V)	1	2	3	4	5	6	7	8
P3HT:PC$_{61}$BM	0.593	0.569	0.550	0.534	0.515	0.499	0.461	0.435
P3HT:Y6	0.315	0.291	0.283	0.261	0.237	0.213	0.201	0.181
P3HT:IT4F	0.358	0.339	0.324	0.296	0.264	0.244	0.212	0.189
P3HT:ZY-4Cl	0.810	0.801	0.791	0.770	0.753	0.732	0.710	0.680

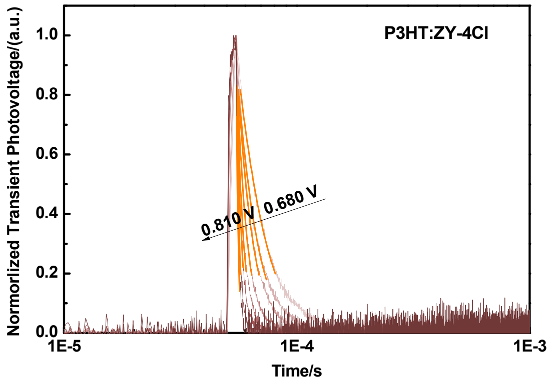

Fig. S7 TPV decay signals from the TPV measurements for the solar cells based on P3HT:ZY-4Cl.

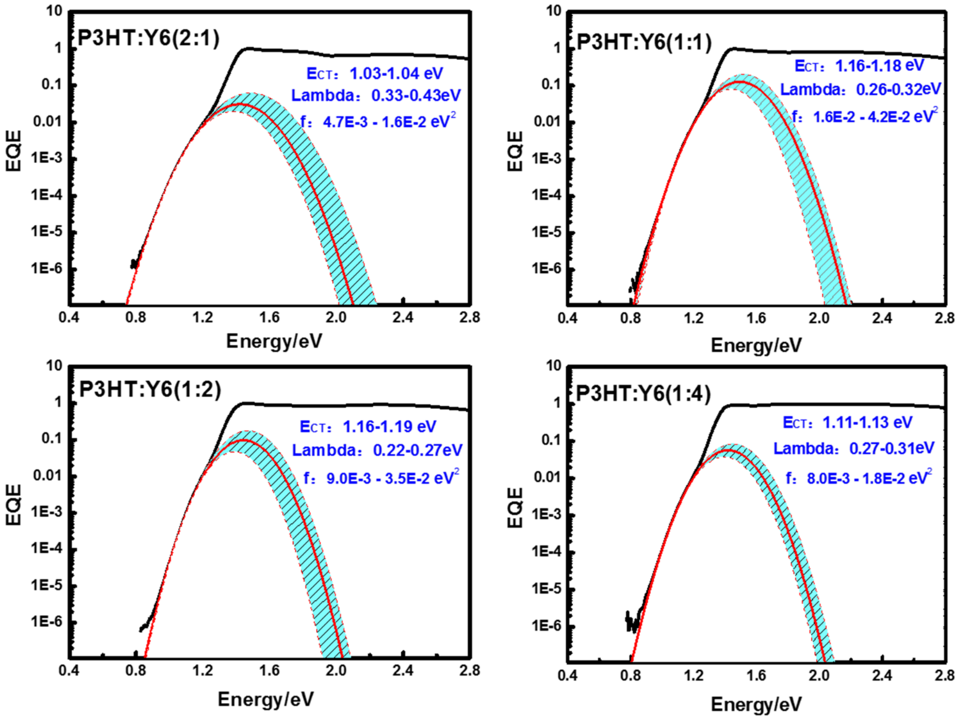

Fig. S8 sEQE spectra of the OSCs based on P3HT:Y6 with different D : A ratios.

The dashed lines represent the upper and the lower limits for the fitting curves.