Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Enhanced Efficiency of Polymer Solar Cells through Synergetic Optimizing Mobility and Tuning Donor Alloy by adding a High-mobility Conjugated Polymer

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The UV-Vis of P3

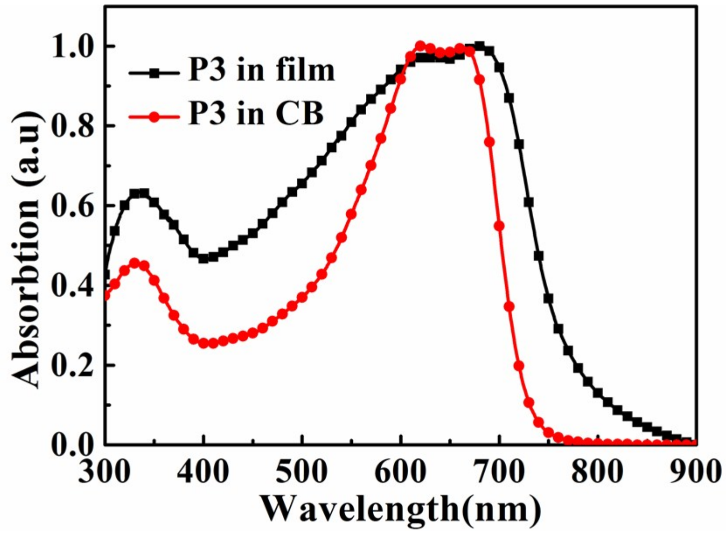

Fig. S1 UV-vis absorption spectra of P3.

Table S1. The fitted lifetime of 750 nm of donor blend films with different DPPT-TT content.

DPPT-TT (wt %)	A_1	$\tau_1(ns)$	A_2	$\tau_2(ns)$
0	1.76	0.56	0.033	3.595
0.5	1.80	0.55	0.037	3.364
1	1.91	0.53	0.045	3.012
2.5	1.98	0.52	0.050	2.866
5	2.13	0.32	0.026	3.256
10	3.04	0.26	0.032	2.727

The lifetimes were fitted using a Gaussian response function (1) convoluted with a bipartite exponential decay function:

$$\Delta y(t) = y_0 + A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) \qquad (1)$$

Photocurrent behavior

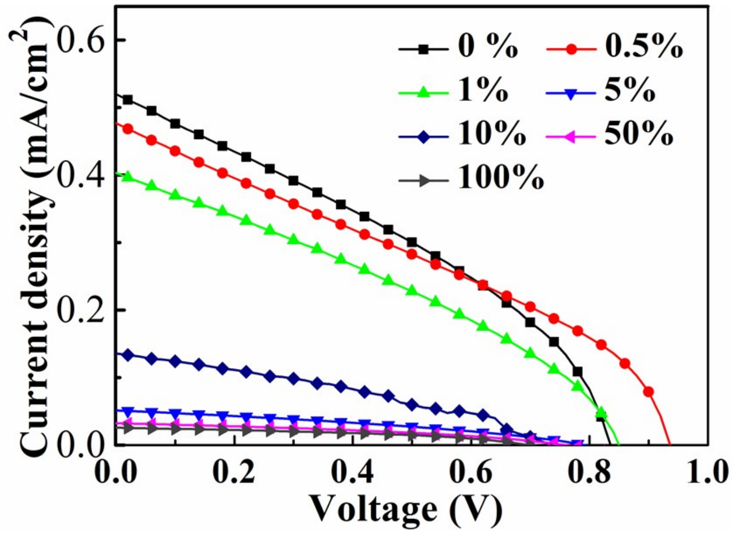

Fig. S2 *J-V* curves of devices with P3, P3:DPPT-TT (DPPT-TT ratio with 0.5% ,1%, 5%, 10%, 50%, respectively) or DPPT-TT as active layers under AM 1.5G illumination with light intensity of 100 mW cm^{-2}.

Calculation of DOS of alloy

In our study, we assume that the donor 1 (D_1) and the donor 2 (D_2) form the donor alloy. Base on Huang's method,[1,2] the following calculation is explicitly for this case. Here, n_1/n_2 is the molecular number of D_1/D_2 of unit mass, l_1/l_2 is the number of quasi-degenerate HOMO of per molecule of D_1/D_2, m_1/m_2 is the weight of D_1/D_2, E_{H1}/E_{H2} is the HOMO of D_1/D_2, E_{He} is the effective HOMO of donor alloy, E_{LUMO} is the LUMO of acceptor. According to the density of state (DOS) model, g_{D1}/g_{D2} is the density of state of D_1/D_2, G_{D1}/G_{D2} is the density of state of per unit weight of D_1/D_2, g_{eff} is the density of state of effective *HOMO* of alloy, G_{eff} is the total state of per unit mass of alloy. We use $V_{OCTernary}$ to represent the V_{oc} of the ternary solar cell. And $V_{OCBinary1}$ and $V_{OCBinary2}$ are the Voc of binary solar cells, donor1: acceptor and donor2: acceptor, respectively.

Then, we can get the equations as blow:

$$g_{D1} = \frac{l_1}{\sigma_1\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H1})^2}{2\sigma_1^2}\right)$$

$$g_{D2} = \frac{l_2}{\sigma_2\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H2})^2}{2\sigma_2^2}\right)$$

$$G_{D1} = \frac{n_1 l_1}{\sigma_1\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H1})^2}{2\sigma_1^2}\right)$$

$$G_{D2} = \frac{n_2 l_2}{\sigma_2\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H2})^2}{2\sigma_{21}^2}\right)$$

Since the donors are simply blended without any chemical reaction, the E_{H1} and E_{H2} do not affect each other. So, the effective density of state can be given

$$G_{eff} = \frac{\frac{m_1 n_1 l_1}{\sigma_1\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H1})^2}{2\sigma_1^2}\right) + \frac{m_2 n_2 l_2}{\sigma_2\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H2})^2}{2\sigma_2^2}\right)}{m_1 + m_2}$$

Introducing ratios $f_1 = m_1/(m_1+m_2)$ and $f_2 = m_2/(m_1+m_2)$, the G_{eff} can be re-expressed as

$$G_{eff} = \frac{f_1 n_1 l_1}{\sigma_1\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H1})^2}{2\sigma_1^2}\right) + \frac{f_2 n_2 l_2}{\sigma_2\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H2})^2}{2\sigma_2^2}\right)$$

We set $N_{e1} = n_1 l_1$ and $N_{e2} = n_2 l_2$. Thus we get

$$G_{eff} = f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H1})^2}{2\sigma_1^2}\right) + f_2 \cdot N_{e2} \cdot \frac{1}{\sigma_2\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H2})^2}{2\sigma_2^2}\right)$$

$$g_{eff} = \frac{f_1 \cdot N_{e1} \cdot \frac{1}{\sigma_1\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H1})^2}{2\sigma_1^2}\right) + f_2 \cdot N_{e2} \cdot \frac{1}{\sigma_2\sqrt{2\pi}}\exp(-\frac{(E-E_{H2})^2}{2\sigma_2^2})}{f_1 \cdot N_{e1} + f_2 \cdot N_{e2}}$$

As g_{D1} and g_{D2} are the Gaussian distributions, the averaged energy level and disorder of g_{eff} can be derived in terms of the standard formulas

$$E_{He} = \int_{-\infty}^{+\infty} E g_{eff}\, dE$$

$$E_{He} = \frac{f_1 \cdot N_{e1} \cdot \int_{-\infty}^{+\infty} \frac{1}{\sigma_1\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H1})^2}{2\sigma_1^2}\right) dE + f_2 \cdot N_{e2} \cdot \int_{-\infty}^{+\infty} \frac{1}{\sigma_2\sqrt{2\pi}}\exp\left(-\frac{(E-E_{H2})^2}{2\sigma_2^2}\right) dE}{f_1 \cdot N_{e1} + f_2 \cdot N_{e2}}$$

$$E_{He} = \frac{f_1 N_{e1} E_{H1} + f_2 N_{e2} E_{H2}}{f_1 N_{e1} + f_2 N_{e2}} \qquad (2)$$

Due to $f_1+f_2=1$, when $N_{e1}=N_{e2}$, the equation (2) can be transfer as

$$E_{He} = f_1 E_{H1} + f_2 E_{H2}$$

In the same time, V_{OC} is calculated by empirical equation[3]

$$V_{OC} = -(E_{HOMO} - E_{LUMO})/e + 0.3V \tag{3}$$

$$V_{OCBinary1} = -(E_{H1} - E_{LUMO})/e + 0.3V \tag{4}$$

$$V_{OCBinary2} = -(E_{H2} - E_{LUMO})/e + 0.3V \tag{5}$$

$$V_{OCTernary} = -(E_{He} - E_{LUMO})/e + 0.3V \tag{6}$$

Combined the equation (2) to (6), the equation (7) can be obtained,

$$V_{OCTernary} = \frac{f_1 \cdot N_{e1} \cdot V_{OCBinary1} + f_2 \cdot N_{e2} \cdot V_{OCBinary2}}{f_1 \cdot N_{e1} + f_2 \cdot N_{e2}} \tag{7}$$

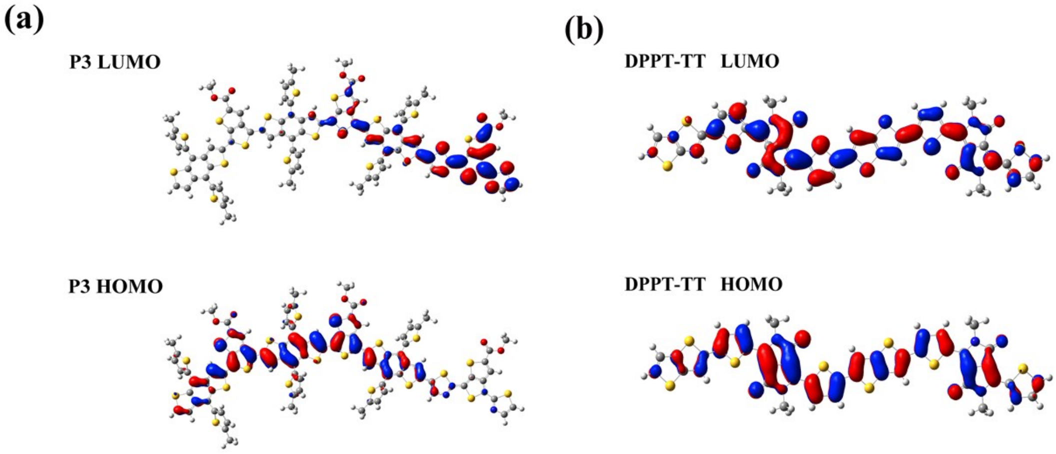

Fig. S3 Pictorial representations of the frontier molecular orbitals of P3 and DPPT-TT from the DFT calculations.

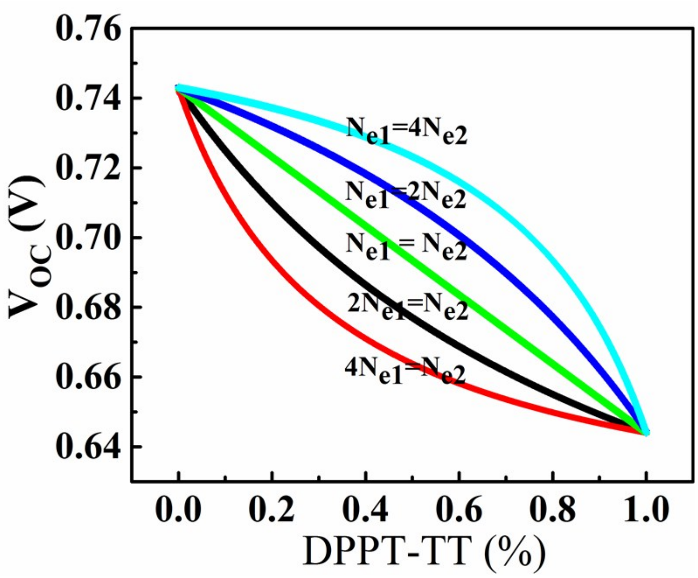

Fig. S4 V_{oc} of PSCs based on different weight ratio of DPPT-TT and simulation curves with different $N_{\mathrm{e1}}/N_{\mathrm{e2}}$, respectively.

Characterization

The cyclic voltammetry (CV) was measured on CHI 600D electrochemical workstations (Shanghai Chenhua) at a scan rate of 50 mV/s with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN) with glass carbon and $Ag/AgNO_3$ electrode as the working and reference electrode, respectively. A ferrocene/ferrocenium redox couple was used as an external standard. The HOMO energy levels were calculated according to the following equations (8), [4]

$$E_{HOMO} = -e\left((\varphi_{ox}^{onset} - \varphi_{ox}^{FC/FC^{+}}) + 4.8\right)(eV) \qquad (8)$$

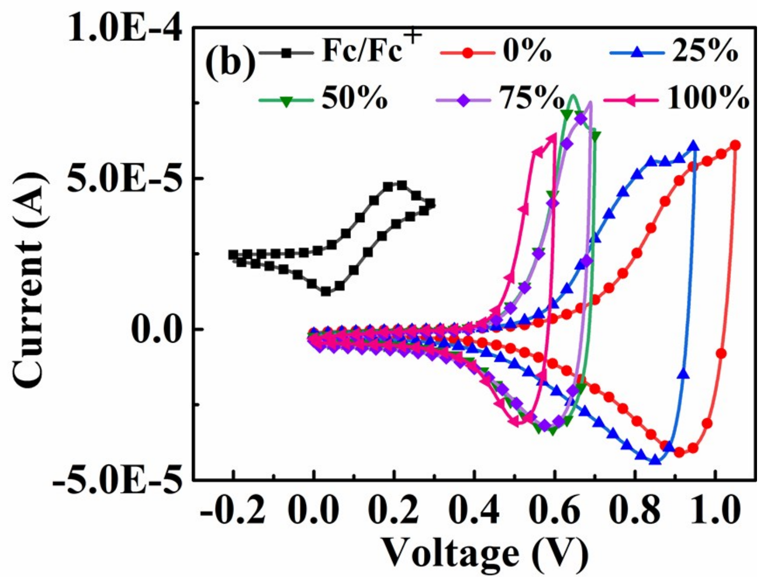

Fig. S5 Cyclic voltammetry (CV) plots of P3:DPPT-TT blend films with different DPPT-TT content.

Surface energy analysis

The interfacial surface energy (γ_{X-Y}) between X and Y in the blend films can be calculated using the equation for interfacial tensions (9),[5]

$$\gamma_{X-Y} = \gamma_X + \gamma_Y - 2\sqrt{\gamma_X \cdot \gamma_Y} \cdot e^{[-\beta(\gamma_X - \gamma_Y)^2]} \qquad (9)$$

where γ_{X-Y} represents the interfacial surface energy between X and Y, β=0.000115 m^4/mJ^2.

The wetting coefficient (ω_c) of a guest material C (DPPT-TT) in blends of host materials A (P3) and B (PC$_{71}$BM), which can predict the location of C in ternary blends, can be calculated using Young's equation (10) ,[6]

$$\omega_c = \frac{\gamma_{C-B} - \gamma_{C-A}}{\gamma_{A-B}} \qquad (10)$$

If the wetting coefficient is larger than unity ($\omega_c > 1$), C will be located in domains of A. If $\omega_c < -1$, C will be located in domains of B. If $-1 < \omega_c < 1$, C will be located at the interface between domains of A and B. The $\omega_{DPPT-TT}$ in P3:PC$_{71}$BM blend films was calculated to be 2.11, which indicate that DPPT-TT molecules may have a tendency to locate at the P3 domain

Table S2. Calculated values of $G_{\max}$ for different incorporating devices.

DPPT-TT (wt %)	P(E.T)	J_{sat} (mA cm^{-2})	G_{max}(m^{-3} s^{-1})
0	0.893	12.47	7.793×10^{27}
0.5	0.920	18.13	1.133×10^{28}
1	0.896	15.18	9.487×10^{27}
2.5	0.895	13.14	8.209×10^{27}
5	0.856	11.62	7.264×10^{27}
10	0.858	12.20	7.628×10^{27}

Hole and electron mobility measurement

The hole-only mobility (μ_h) was characterized from the device with the configuration of ITO/PEDOT:PSS/active layer (110 nm)/MoO_3/Ag, while electron-only mobility (μ_e) was measured from the device with the configuration of ITO/ZnO/active layer (110 nm)/PFN/Al. All the blend films were prepared in accordance with the optimal solar cells conditions. The obtained current-voltage curves were consistent with the Mott-Gurney square law, given by Equation (11),

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{(V_{appl}-V_{bi})^2}{L^3} \qquad (11)$$

Where J is the current density, ε_0 is the permittivity of free space ($\approx 8.85\times10^{-14}$ Fcm^{-1}), ε_r is the relative dielectric constant of the organic active layer ($\approx$3.00), L is the thickness of the active layer, V_{appl} is the applied voltage on the device, V_{bi} is built-in voltage, μ is the mobility. V_{bi} of electron-only device and hole-only device are 0.7 and 0 V, respectively.

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