Supporting Information

Direct Observation of the Charge Transfer States from a Non-Fullerene Organic Solar Cell with a Small Driving Force

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Experimental Section

Materials. The polymer donor PM6 was synthesized according to the previous literature.[1] The acceptor Y6 was purchased and directly used from Solarmer Materials Inc. Other chemicals and solvents were purchased from Damas-beta, Acros Organics and Sigma-Aldrich.

Fabrications of OSC devices with different mixing ratio of PM6:Y6. The OSC devices with the structure of ITO/PEDOT: PSS/active layer/PFN-Br/Ag were fabricated as the following steps: the patterned indium tin oxide (ITO, 8 Ω $\square^{-1}$) substrates were cleaned by detergent, deionized water, acetone and isopropanol in sequence. Then drying the substrates by N_2. After treatment in an ultraviolet ozone cleaner for 20 minutes, PEDOT:PSS was deposited on the clean ITO substrate by spin-coating the PEDOT:PSS solution (Heraeus Clevios PVP Al 4083) under 5000 rpm for 40 s. Then the device was annealed on a hot stage at 150°C for 10 minutes and transferred to a glove box. The active layer blend were dissolved in chloroform (CF) with different mass ratios of donor and acceptor at a total concentration of 18 mg mL^{-1}. Before the spin coating process, 0.5% 1-chloronaphthalene (CN) (v/v, CN/CF) was added as solvent additive. The blend solution was spin-coated on the substrate with 2000-3000 rpm for 40 s and followed by 100°C thermal treatment for 5 minutes. The solution of PFN-Br that is dissolved in methanol with a concentration of 0.5 mg mL^{-1} was spin-coated over the active layers at 3000 rpm for 30 s. Finally, 100 nm Ag (15nm for transmission EA measure) was deposited on the active layer at a rate of 0.8 Ås^{-1} by thermally evaporated under high vacuum (4×10^{-4} Pa).

EQE$_{PV}$-EL. EQE spectra were measured with a system composing a 500 W Xe light source (Zolix X500A), a monochromator (Newport CS260), an optical chopper, calibrated photo-detectors (Thorlabs DET100A2), a low-noise current pre-amplifier (SR570) and a lock-in amplifier (SR830). EL were measured by EN1700 near-infrared fiber spectrometer (Choptics Instruments).

Electro-absorption. We first used a monochromator to convert the light generated by the xenon lamp into monochromatic light. Then made the monochromatic light have a certain frequency by a chopper so that it can be recognized by the lock-in amplifier. The transmission mode is applied for more accurate data fitting, and the reflection mode is used for the study of CTS.A small sinusoidal voltage with a frequency of 1 kHz was superimposed on the reverse DC bias to modulate the internal electric field in the device. The reverse DC bias was used to avoid charge injection. Calibrated silicon and germanium photodetectors are used to detect the reflected or the transmitted signals. The current amplifier and the lock-in amplifier were connected to the detector. The reference for the lock-in amplifier was set to the first harmonic frequency. The final signal is the ratio of signals with and without AC field modulation. In order to reduce noise, each data point was obtained by averaging 16 measurements. All the experiments were all carried out at room temperature.

Ultra-violet photoelectron spectroscopy. UPS were measured with Escalab 250Xi ultra-high vacuum surface analysis system equipped with a He-discharge lamp providing He-I photons of 21.22 eV.

Temperature dependent measurement. Liquid nitrogen was used to lower the

temperature of the sample. A silicon diode was attached to the back of the tested device to accurately monitor the temperature. During the V_{OC} measurement, the sample was only exposed to the AM 1.5G source for less than 1 second to minimize the temperature rise (< 0.5K) due to irradiation.

Transient photovoltage measurement. The solar cell is continuously irradiated using a light source meter (Keithley 2400) and an AAB-grade AM 1.5G simulator (Zolix SS150), that promotes a constant and stable V_{OC}. After reaching a stable photobias ($\sim V_{OC}$), the solar cell is excited with an additional short-lived laser pulse to generate a perturbation of photovoltage ($\Delta V << V_{OC}$). The solar cell is connected to an oscilloscope (Tektronix MDO3024), with an input resistance of 1MΩ, to record the periodic signal over time.
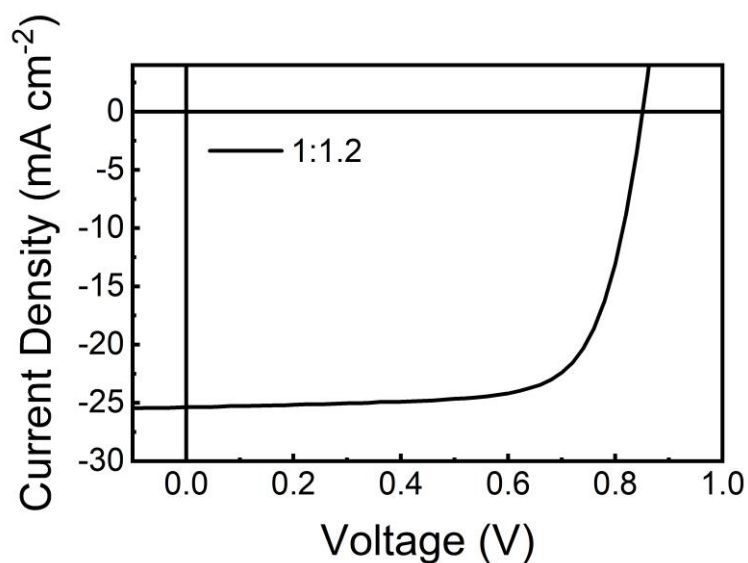
**Figure S1**. J-V characteristics of PM6:Y6 (1:1.2)
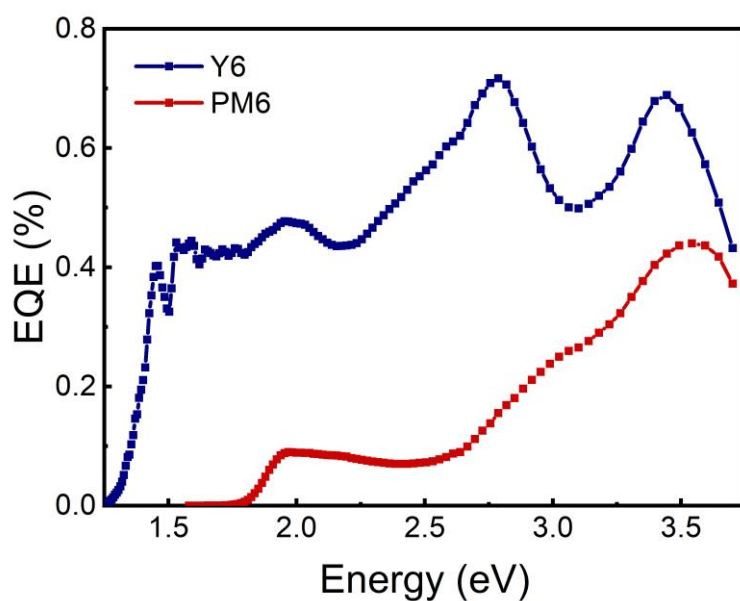
Figure S2. EQE spectrum of pristine Y6-only device and pristine PM6-only device.

First, Y6 does not show a distinctive plateau region which is typical for polymers with a larger E_B. Second, the EQE values around the first excitonic transition is one order of magnitude higher than that in most donor polymers. The results suggest that Y6 has a much smaller exciton binding energy than most donor polymers.[2]
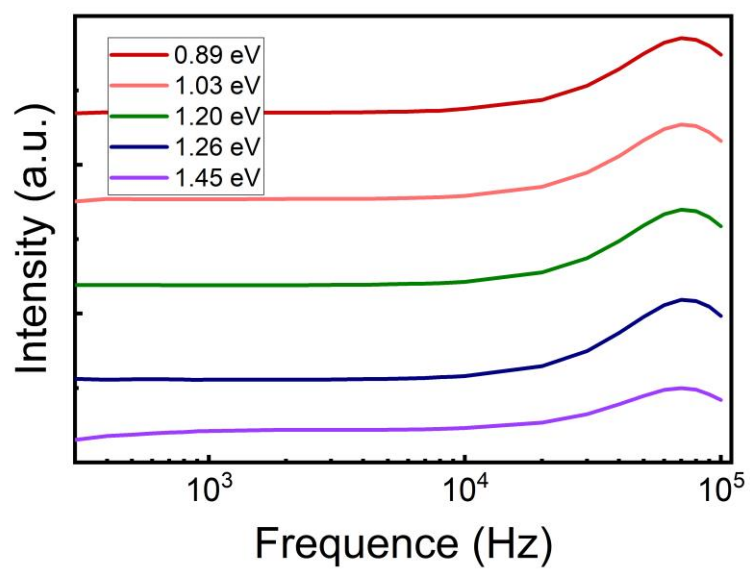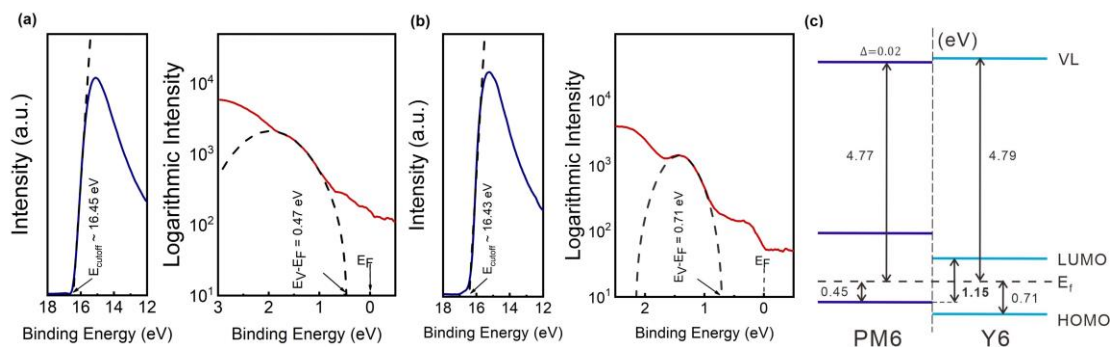
Figure S3. The frequency dependence EA signals of PM6:Y6 (1:1.2) measured at different proving wavelength.
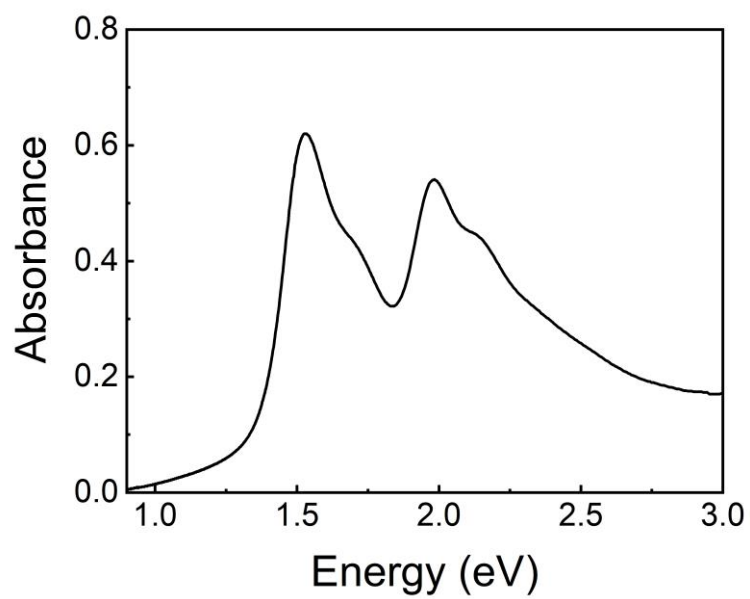
**Figure S4**. The absorbance of a PM6:Y6 (1:1.2) film.
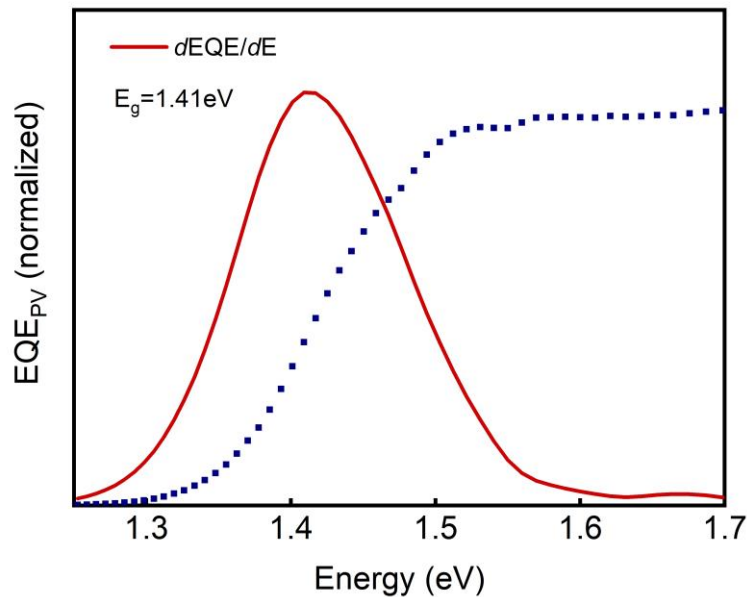
Figure S5. EQE_PV of a PM6:Y6 device and its derivative dEQE/dE. The photovoltaic gap E_g of the blend is determined from the maximum of the derivative.

Figure S6. (a-b) UPS results of PM6, Y6 (logarithmic scale). **c** Energy level alignment of PM6:Y6.

Here, we regarded the intensity of 10 as the baseline when we extracted the difference between the Fermi level and HOMO of both PM6 and Y6.[3] As a result, the E_F and E_{HOMO} of PM6 are determined as -4.77 and -5.22 eV respectively, and those of Y6 are -4.79 and -5.50 eV respectively. In this case, $E_{CT}^{UPS\text{-}Log}$ value is 1.15 eV.
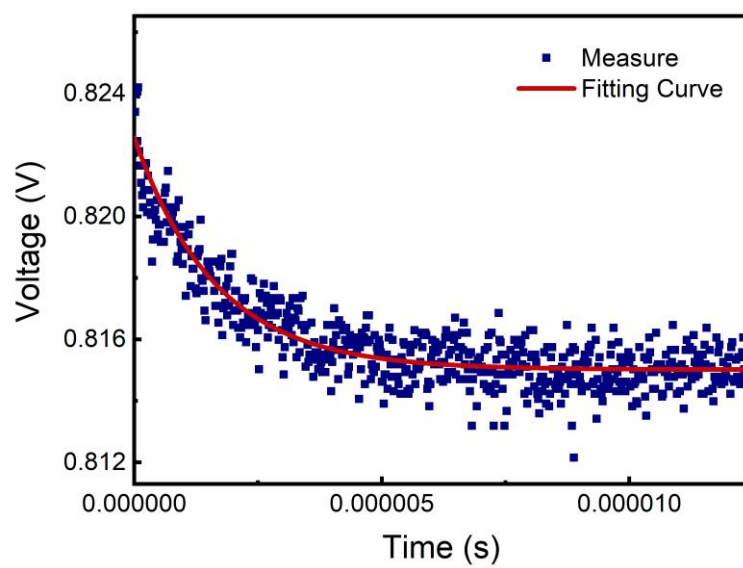
Figure S7. The measured and fitted transient photovoltage decay of PM6:Y6 (1:1.2)

devices.

Note S1. Derivation of fitting equation for isotropic materials.

The fitting equation of electroabsorption can be correlated the Stark effect and measured light intensity.[4] The perturbation level absorption ($\Delta\alpha$) changes can be described in the form of Taylor expansion:

$$\Delta\alpha \approx \Delta E \frac{\partial\alpha}{\partial E} + \frac{1}{2}\Delta E^2 \frac{\partial^2\alpha}{\partial E^2} \tag{S1}$$

Where ΔE is the change of transition energy. L. Sebastain et al.[4] proposed that, with an external electric field, ΔE is defined as the difference between the shift of the excited state energy and the shift of the ground state energy:

$$\Delta E = -\Delta\mu_z \cdot F - \frac{1}{2}\Delta p \cdot F^2 \tag{S2}$$

$\Delta\mu_z$ is the change of the dipole moment, Δp is the change of average polarizability tensor upon excitation. Therefore, the change of absorption coefficient can be expressed by combing Equation S1 and S2:

$$\Delta\alpha \approx \left(-\Delta\mu_z F - \frac{1}{2}\Delta p F^2\right)\frac{\partial\alpha}{\partial E} + \frac{1}{2}\left(-\Delta\mu_z F - \frac{1}{2}\Delta p F^2\right)^2 \frac{\partial^2\alpha}{\partial E^2} \tag{S3}$$

$\Delta\mu_z$ is meaningful to a single molecule. For the bulk film, which is assumed to be isotropic, the change of dipole moment along the electrical field can be positive or negative with equal probability. So in Equation S3, the terms that contain the $\Delta\mu_z$ vanish. And dipole moment in any dimension is the same in magnitude, thus:

$$\Delta\mu_x{}^2 = \Delta\mu_y{}^2 = \Delta\mu_z{}^2 = \frac{1}{3}\Delta\mu^2 \tag{S4}$$

Here, we get the absorption coefficient ($\Delta\alpha$) changes:

$$\Delta\alpha \approx \frac{1}{2}\Delta p F^2 \frac{\partial\alpha}{\partial E} + \frac{1}{6}\Delta\mu^2 F^2 \frac{\partial^2\alpha}{\partial E^2} \tag{S5}$$

Considering the relationship between the absorption coefficient and absorbance A, Equation S5 can be further expressed as:

$$\Delta\alpha \approx \frac{1}{0.86}\Delta p F^2 \frac{\partial A}{D\partial E} + \frac{1}{2.58}\Delta\mu^2 F^2 \frac{\partial^2 A}{D\partial E^2} \qquad (S6)$$

D is the thickness of the active layer. Finally, we can get the fitting equation:

$$-\frac{\Delta T}{T} = \Delta\alpha \cdot d \approx \frac{1}{0.86}\Delta p F^2 \frac{d\partial A}{D\partial E} + \frac{1}{2.58}\Delta\mu^2 F^2 \frac{d\partial^2 A}{D\partial E^2} \qquad (S7)$$

Table S1. Extracted fitting parameters of Δp and $\Delta\mu$ as well as the thickness of the active layer (d) by Equation S7.

Active layer	d (± 5 nm)	$\Delta\mu$ (D)	Δp ($Cm^2\,V^{-1}$)
PM6	90	4.23	12.9×10^{-20}
Y6	70	8.98	7.70×10^{-20}
PM6:Y6 (1:1.2)	100	14.5	21.2×10^{-20}

d is determined by AFM.

Supplementary References:

(1) Zhang, M.; Guo, X.; Ma, W.; Ade, H.; Hou, J. A Large-Bandgap Conjugated Polymer for Versatile Photovoltaic Applications with High Performance. *Adv. Mater.* **2015**, *27*, 4655-4660.

(2) Li, H. W.; Guan, Z.; Cheng, Y.; Lui, T.; Yang, Q.; Lee, C. S.; Chen, S.; Tsang, S. W. On the Study of Exciton Binding Energy with Direct Charge Generation in Photovoltaic Polymers. *Adv. Electron. Mater.* **2016**, *2*, 1600200.

(3) Endres, J.; Kulbak, M.; Zhao, L.; Rand, B. P.; Cahen, D.; Hodes, G.; Kahn, A. Electronic structure of the CsPbBr3/polytriarylamine (PTAA) system. *J. Appl. Phys.*

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(4) Sebastain, L.; Weiser, G.; Bassler, H. Charge transfer transitions in solid tetracene

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