Supporting Information

Origin of Efficient Inverted Nonfullerene Organic Solar Cells: Enhancement of Charge Extraction and Suppression of Bimolecular Recombination Enabled by Augmented Internal Electric Field

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V_{OC} in OSCs is closely associated with the difference in the energy levels between the HOMO of donor and the LUMO of acceptor in the blend layer, and also is related to the difference in the work function of the electrodes.[1,2] The HOMO and LUMO levels in organic semiconducting materials are analogous to the conduction band minimum and valence band maximum in inorganic semiconductors. Generally, the solution-processes organic semiconductor layers used in the OSCs are amorphous. The structural disorders in the organic semiconductors have a significant impact on the performance of OSCs.[3,4] The edges of conduction band minimum and valence band maximum in the amorphous semiconductor materials are not clearly defined, with the band tail states extended into the bandgap.[5,6] Gaussian distribution is often used to approximate the density of the band tail states. The disorder-induced loss in V_{OC} of OSCs is associated with the term $-\sigma^2/kT$, where σ is related to the width of Gaussian distribution, k is the Boltzmann constant and T is the temperature.[7,8] It is important to understand the origin of V_{OC} in OSCs, including the effect of monomolecular and bimolecular recombination processes on V_{OC}.[9,10] Shockley equation is derived based on the classical p-n junction theory and describes the current-voltage behavior of a p-n junction diode. The Shockley equation for a p-n junction diode can be expressed by:[11]

$$J(V_a) = J_0[\exp(\frac{qV_a}{kT}) - 1], \qquad (1)$$

where V_a is the external bias, J_0 is the saturation current under a small reverse bias ($V_a < 0$), q is the elementary charge. In a p-n junction type solar cell, the direction of the photocurrent J_{ph} is opposite to the current caused by a forward bias. Therefore, the Shockley equation for p-n junction type solar cells under illumination becomes:

$$J(V_a) = J_0[\exp(\frac{qV_a}{kT}) - 1] - J_{ph}. \tag{2}$$

At the open circuit condition, the current in the external circuit is 0, i.e. J ($V_a=V_{OC}$) =0，therefore, V_{OC} can be expressed by:

$$V_{oc} = \frac{mkT}{q} \ln(\frac{J_{ph}}{J_0} + 1), \tag{3}$$

where m is dependent on the ideality of the p-n junction diode.

It is easy to see that V_{OC} is a function of light intensity as J_{ph} is directly related to light intensity. J_0 is the dark reverse saturation current and is the fundamental character of a p-n junction diode. Under reverse bias, the dynamic equilibrium of minority carriers results in the saturation dark current density J_0. The dynamic equilibrium of the minority carriers is obtained via the balance between the charge injection and recombination. Therefore, the charge recombination in a p-n junction type solar cell has a great impact on its J–V characteristics.

Following the metal-insulator-metal model, as an approximation, considering the energy level of the HOMO in the organic donor can be analogous to the valence band minimum in the inorganic semiconductor, and that of the LUMO level in the organic acceptor is analogous to the valence band maximum, the charge carrier dynamics inside an OSC can be described [9, 12,13] using the following expressions:[14]

$$np = n_i^2 \exp(\frac{qV_{oc}}{kT}), \tag{4}$$

$$n_i = N_c \exp(-\frac{\Delta E}{2kT}), \tag{5}$$

where n and p are the concentrations of the electrons and holes inside the device, n_i is the intrinsic carrier concentration (electrons and holes) in the organic active layer, N_c is the effective density of states (for both conduction band and valence band), and ΔE is the difference in the energy levels between the LUMO of acceptor and the HOMO of donor. From **Equations S4** and **Equation S5**, V_{OC} can be expressed by:

$$V_{oc} = \frac{\Delta E}{q} + \frac{kT}{q} \ln(\frac{np}{N_c^2}) \ . \tag{6}$$

ΔE may be modified if the Gaussian disorder in the organic semiconductor materials is taken into consideration, V_{OC} can be expressed by:

$$V_{oc} = \frac{\Delta E}{q} - \frac{\sigma^2}{kT} + \frac{kT}{q} \ln(\frac{np}{N_c^2}) \ . \tag{7}$$

The carrier concentration in the device is determined by the dynamics of mobile charge carrier generation and recombination, or mathematically it can be expressed by the following equation:

$$\frac{\partial(n \cdot Vol)}{\partial t} = g_e - r_e , \tag{8}$$

where Vol is the volume of the active region, g_e is the number of photo-generated free electrons per unit time, r_e is the number of free electrons lost to the recombination. Based on the metal-insulator-metal model and the concept expressed by **Equation S8**, taking into consideration of space charge effects, the continuity equation becomes:[15]

$$\frac{1}{q} \frac{\partial}{\partial x} J_n(x) = PG - (1-P)R , \tag{9}$$

where G is the exciton generation rate, P is the exciton dissociation probability and R is the recombination rate. At an open circuit condition, there is no current in the device, and thereby the correlation between I and the charge recombination (R) becomes:

$$R = \frac{PA}{1-P} \cdot I,\qquad(10)$$

where A is the linear coefficient linking the exciton generation rate (averaged photon absorption ratio) and the intensity of the incident light (I). To express V_{OC} as a function of I, a relationship between the recombination R and the density of the free carriers (n/p) is essential. The bimolecular recombination and monomolecular recombination are examined separately. If the bimolecular recombination is the dominant recombination process in the system, the limiting factor on the rate of bimolecular recombination is the possibility to find the recombination partners. Therefore, the bimolecular recombination rate can be expressed as:[16]

$$R = \gamma(np - n_i^2).\qquad(11)$$

Under illumination, the intrinsic carrier concentration n_i, excited by thermal energy and external bias, is much lower than the photo-excited charge carriers. By neglecting the term n_i^2, using **Equation S9**, **Equation S10** and **Equation S11**, the V_{OC} of OSCs and the intensity of light can be related through the following equation:

$$V_{oc} = \frac{\Delta E}{q} - \frac{\sigma^2}{kT} + \frac{kT}{q}\ln[\frac{PA}{\gamma(1-P)N_c^2} \cdot I].\qquad(12)$$

Equation S12 shows a linear relationship between V_{OC} and $\ln I$ with the bimolecular recombination dominant in OSCs. The slope of the V_{OC}–$\ln I$ plot is $\dfrac{kT}{q}$.

If the monomolecular recombination becomes the dominant recombination process in the cell, then the limiting factor of the monomolecular recombination is the possibility finding an effective trap site, the monomolecular recombination rate can be described by Schockley-Read Hall equation:[17,18]

$$R = \frac{C_n C_p \delta(pn - n_i^2)}{C_n(n + n_i) + C_p(p + n_i)}, \qquad (13)$$

where C_n and C_p are the capture coefficients of electrons and holes respectively, δ is the density of the trap sites, p/n is the hole/electron density generated by photoexcitation, n_i is the intrinsic carrier concentration. Under illumination, the concentrations of photo-generated electrons and holes are about the same, i.e., $p \approx n$, since the electrons and holes are generated in pair. The number of photo-generated charge carriers is greater than that of the intrinsic ones, i.e., $p \approx n >> n_i$, **Equation S13** can be simplified as:

$$R = \frac{C_n C_p \delta}{C_n + C_p} \cdot n = \gamma_m \delta \cdot n, \qquad (14)$$

where $\gamma_m = \frac{C_n C_p}{C_n + C_p}$, is a constant. Combing **Equation S7**, **Equation S9** and **Equation S14**, V_{OC} as a function of I having monomolecular recombination process dominated in the cells can be related by:

$$V_{oc} = \frac{\Delta E}{q} - \frac{\sigma^2}{kT} + \frac{kT}{q} \ln[\frac{P^2 A^2}{\gamma_m^2 \delta^2 (1-P)^2 N_c^2} \cdot I^2]. \qquad (15)$$

Equation S15 shows that the V_{OC}−ln$I$ plot has a slope of $2 \cdot \frac{kT}{q}$. For a high performance OSC, the densities of defects and impurities in the active layer are relatively low. The charge

loss via bimolecular recombination is the dominant at open circuit condition.[19] Therefore, the slope of V_{OC}–ln$I$ plot for OSCs is about $\frac{kT}{q}$. However, in some OSCs with a high trap density and a deep average trap depth, the slope of the V_{OC}–ln$I$ plot can be well exceed $\frac{kT}{q}$ or even larger than $2 \cdot \frac{kT}{q}$.[20] It needs further study to explain that the slope is sometimes larger than $2 \cdot \frac{kT}{q}$. In summary, a combination of the V_{OC}–ln$I$ characteristic measurements and transient photo physics studies is a useful approach for analyzing the recombination losses in OSCs.
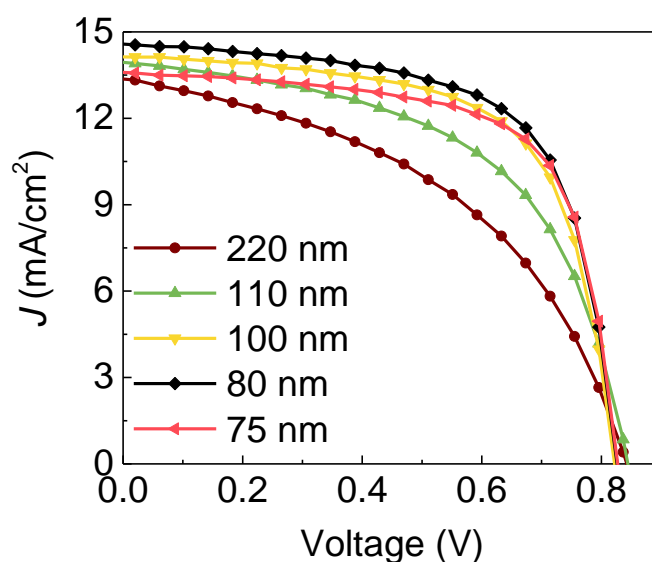

Figure S1. *J*–*V* characteristics measured for a set of PTB7-Th:ITIC-based reverse configuration OSCs with different active layer thicknesses.
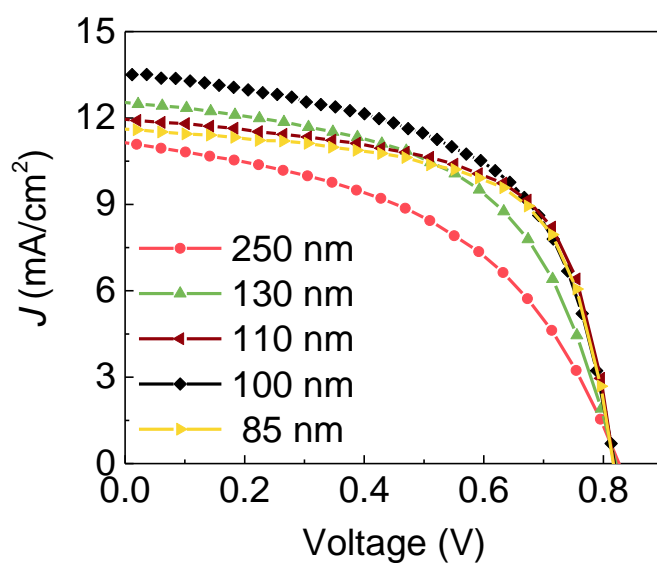
Figure S2. *J–V* characteristics measured for a set of PTB7-Th:ITIC-based regular configuration OSCs with different active layer thicknesses.
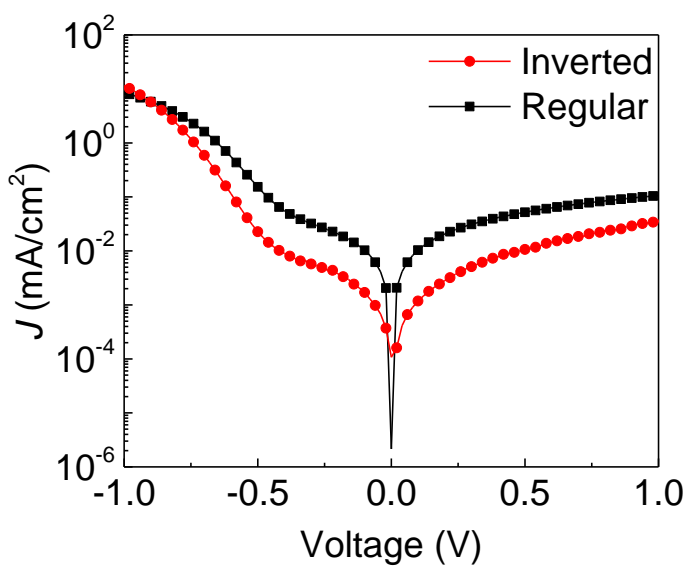

Figure S3. Dark *J–V* characteristics measured for the optimized inverted and regular configuration PTB7-Th:ITIC OSCs.
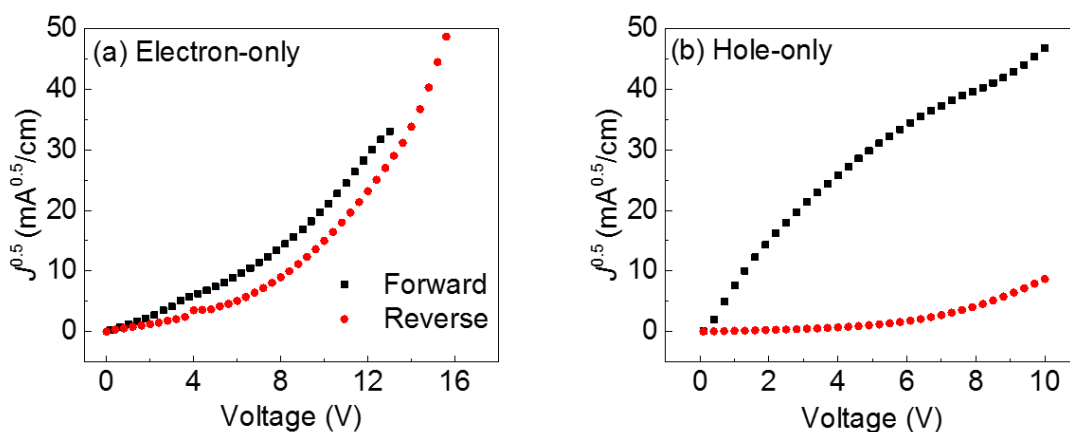
Figure S4. $J^{0.5}-V$ characteristics measured for (a) electron-only and (b) hole-only devices under the forward and reverse biases.
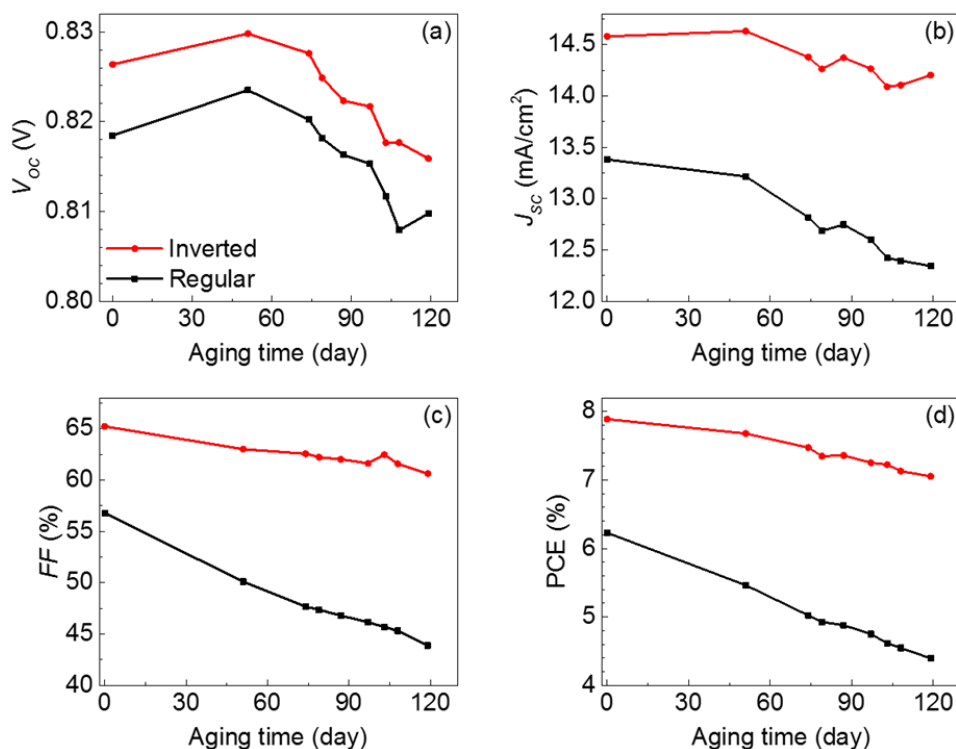

Figure S5. (a) V_{OC} (b) J_{SC} (c) FF (d) PCE as a function of the aging time measured for the encapsulated inverted and regular configuration PTB7-Th:ITIC OSCs.

Table S1. A summary of cell parameters measured for a set of inverted PTB7-Th:ITIC OSCs with different active layer thickness at AM1.5G of 100 mW/cm^2, the values of J_{SC} and PCE are calibrated using $IPCE$ measurements.

Thickness (nm)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
220	0.85	13.36	45.78	5.16
110	0.84	13.94	54.62	6.32
100	0.82	14.13	64.82	7.42
80	0.83	14.58	65.23	7.89
75	0.83	13.59	67.52	6.58

Table S2. A summary of cell parameters measured for a set of regular PTB7-Th:ITIC OSCs with different active layer thicknesses at AM1.5G of 100 mW/cm^2, the values of J_{SC} and PCE are calibrated using $IPCE$ measurements.

Thickness (nm)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
250	0.83	11.14	47.31	4.36
130	0.82	12.54	54.75	5.63
110	0.82	11.95	63.00	6.16
100	0.82	13.38	56.78	6.23
85	0.82	11.61	63.90	6.06

Table S3. The area ratios of XPS spectra N_{1S}/C_{1S}, N_{1S}/S_{2P}, F_{1S}/C_{1S}, F_{1S}/S_{2P} and the relative compositional ratio of ITIC to PTB7-Th obtained from the top surfaces of the PTB7-Th:ITIC blend films deposited on glass, ZnO and PEDOT:PSS.

Substrate	N_{1S}/C_{1S}	N_{1S}/S_{2P}	F_{1S}/C_{1S}	F_{1S}/S_{2P}	ITIC/PTB7-Th ratio
Glass	0.009	0.081	0.019	0.180	0.46
ZnO	0.009	0.075	0.018	0.153	0.50
PEDOT:PSS	0.009	0.082	0.018	0.155	0.51

REFERENCES

(1) Brabec, C. J.; Cravino, A.; Meissner, D.; Sariciftci, N. S.; Fromherz, T.; Rispens, M. T.; Sanchez, L.; Hummelen, J. C. Origin of the Open Circuit Voltage of Plastic Solar Cells. *Adv. Funct. Mater.* **2001**, *11*, 374.

(2) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J.; Design Rules for Donors in Bulk-Heterojunction Solar Cells—Towards 10% Energy-Conversion Efficiency. *Adv. Mater.* **2006**, *18*, 789-794.

(3) Murata, H.; Malliaras, G. G.; Uchida, M.; Shen, Y.; Kafafi, Z. H. Non-Dispersive and Air-Stable Electron Transport in an Amorphous Organic Semiconductor. *Chem. Phys. Lett.* **2001**, *339*, 161-166.

(4) Podzorov, V.; Menard, E.; Borissov, A.; Kiryukhin, V.; Rogers, J. A.; Gershenson, M. E. Intrinsic Charge Transport on the Surface of Organic Semiconductors. *Phys. Rev. Lett.* **2004**, *93*, 086602.

(5) Hulea, I. N.; Brom, H. B.; Houtepen, A. J.; Vanmaekelbergh, D.; Kelly, J. J.; Meulenkamp,

E. A. Wide Energy-Window View on the Density of States and Hole Mobility in Poly(p-Phenylene Vinylene). *Phys. Rev. Lett.* **2004,** *93*, 166601.

(6) Tal, O.; Rosenwaks, Y.; Preezant, Y.; Tessler, N.; Chan, C. K.; Kahn, A. Direct Determination of the Hole Density of States in Undoped and Doped Amorphous Organic Films with High Lateral Resolution. *Phys. Rev. Lett.* **2005**, *95*, 256405.

(7) Celebi, K.; Jadhav, P. J.; Milaninia, K. M.; Bora, M.; Baldo, M. A. The Density of States in Thin Film Copper Phthalocyanine Measured by Kelvin Probe Force Microscopy. *Appl. Phys. Lett.* **2008**, *93*, 083308.

(8) Blakesley, J. C.; Neher, D. Relationship between Energetic Disorder and Open-Circuit Voltage in Bulk Heterojunction Organic Solar Cells. *Phys. Rev. B* **2011**, *84*, 075210.

(9) Shuttle, C. G.; O'Regan, B.; Ballantyne, A. M.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. Bimolecular Recombination Losses in Polythiophene: Fullerene Solar Cells. *Phys. Rev. B* **2008**, *78*, 113201.

(10) Maurano, A.; Hamilton, R.; Shuttle, C. G.; Ballantyne, A. M.; Nelson, J.; O'Regon, B.; Zhang, W. M.; McCulloch, I.; Azimi, H.; Morana, M.; Brabec, C. J.; Durrant, J. R.; Recombination Dynamics as a Key Determinant of Open Circuit Voltage in Organic Bulk Heterojunction Solar Cells: A Comparison of Four Different Donor Polymers. *Adv. Mater.* **2010**, *22*, 4987.

(11) Selberherr, S. Analysis and Simulation of Semiconductor Devices, Springer, Wien, Germany, **1984**.

(12) Chirvase, D.; Chiguvare, Z.; Knipper, M.; Parisi, J.; Dyakonov, V.; Hummelen, J. C. Temperature Dependent Characteristics of Poly(3 hexylthiophene)-Fullerene based

Heterojunction Organic Solar Cells. *J. Appl. Phys.* **2003**, *93*, 3376.

(13) Pivrikas, A.; Juska, G.; Mozer, A. J.; Scharber, M.; Arlauskas, K.; Sariciftci, N. S.; Stubb, H.; Osterbacka, R. Bimolecular Recombination Coefficient as a Sensitive Testing Parameter for Low-Mobility Solar-Cell Materials. *Phys. Rev. Lett.* **2005**, *94*, 176806.

(14) Riedel, I.; Parisi, J.; Daykonov, V.; Lutsen, L.; Vanderande, D.; Hummelen, J. C. Effect of Temperature and Illumination on the Electrical Characteristics of Polymer‐Fullerene Bulk‐Heterojunction Solar Cells. *Adv. Funct. Mater.* **2004**, *14*, 38.

(15) Koster, L. J. A.; Smits, E. C. P.; Mihailetchi, V. D.; Blom, P. W. M. Device Model for the Operation of Polymer/Fullerene Bulk Heterojunction Solar Cells. *Phys. Rev. B.* **2005**, *72*, 085205.

(16) Pope, M.; Swenberg, C. E. Electronic Process in Organic Crystals and Polymers. 2nd edition Oxford University Press, Oxford, USA, **1999**.

(17) Shockley, W.; Read, W. T. Statistics of the Recombinations of Holes and Electrons. *Phys. Rev.* **1952**, *87*, 835.

(18) Hall, R. N. Electron-Hole Recombination in Germanium. *Phys. Rev.* **1952**, *87*, 387.

(19) Koster, L. J. A.; Mihailetch, V. D.; Ramaker, R.; Blom, P. W. M. Light Intensity Dependence of Open-Circuit Voltage of Polymer:Fullerene Solar Cells. *App. Phys. Lett.* **2005**, *86*, 123509.

(20) Mandoc, M. M.; Kooistra, F. B.; Hummelen, J. C.; Boer, B. D.; Blom, P. W. M. Effect of Traps on the Performance of Bulk Heterojunction Organic Solar Cells. *Appl. Phys. Lett.* **2007**, *91*, 263505.