Supplementary Information for

Film-depth-dependent Crystallinity for Light Transmission and Charge Transport in Semitransparent Organic Solar Cells

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Fig. S1 Light absorption spectra (before normalization) of PTB7-Th:acceptor blends showing the tunable crystallinity upon solvent additives.



Fig. S2 Dependence of J_{SC} , FF and V_{OC} on acceptor-related absorption peak of acceptors, as extracted from Fig. 2a and Table 1 in the main text. The less crystalline PTB7-Th:FNIC1 and more crystalline PTB7-Th:FNIC2 are shown in different part of the graph, respectively. The solid lines are guides to eyes.

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Parameter	Symbol	Numerical value
Band gap	$\mathrm{E_{gap}}^{\mathrm{a}}$	1.22 eV
Eff. density of states	N _c , N _v	$10^{26} \mathrm{m}^{-3}$
Initial electron mobility	$\mu_{n0}{}^a$	1.5×10 ⁻⁷ m ⁻³
Initial hole mobility	$\mu_{p0}{}^a$	1.4×10 ⁻⁷ m ⁻³
Relative dielectric constant	3	3.4
Dissociation parameter	β	$5 \times 10^8 \text{ V} \cdot \text{s} \cdot \text{m}^{-2}$
Adjustment factor	w	10

Table S1 | Overview of the parameters in the numerical simulation.

^aThe numerical value is extracted from the experimental result in previous work¹.

Transfer matrix method





As shown in Fig. S3, in-situ oxygen plasma etching can divide active layer into several sublayers, and each sublayer's absorption spectrum can be calculated by difference of adjacent absorption value. Furthermore, each sublayer's extinction coefficient k_i can be calculated from the absorption spectrum (refractive index n_i set is 2, since its value do not differ much from layer to layer).² With each layer's n_i and k_i of the whole device, transfer matrix can be built between adjacent layers, and total electric field at an arbitrary position x can be calculated. The calculation process is as ref. 3. Assuming the device is illuminated under AM 1.5G condition, energy dissipation Q(x)

and exciton generation rate G(x) can be obtained on the basis of electric field distribution:

$$Q(x) = \frac{2\pi\varepsilon_0 ckn \left| E(x) \right|^2}{\lambda} \tag{1}$$

$$G(x) = \int_{\lambda_1}^{\lambda_2} \frac{\lambda}{hc} Q(x,\lambda) d\lambda$$
⁽²⁾

Calculating charge transfer levels from FLAS

As shown in Fig. 1 in the main text, the absorption peaks of neat PTB7-Th and FNIC2 layer are 699.65 nm and 794 nm, relatively, and the HOMO of PTB7-Th is - 5.22 eV while the LUMO of FNIC2 is -4.00 eV as shown in ref. 1. If the aggregate form of organic molecules is J-aggregates, absorption exhibits red-shifted behavior. So we use each sublayer's absorption peak to describe the crystallization fluctuation of the active layer. Red-shift indicates a higher crystallinity while blue-shift indicates a lower crystallinity. Using the neat PTB7-Th and FNIC2 layer as standard, thus a sublayer's donor's HOMO E_{v} and acceptor's LUMO E_{c} are as follows:

$$E_{c} = -4.00 + \left(\frac{1240}{\lambda_{pa}} - \frac{1240}{794}\right)$$
(3)

$$E_{\nu} = -5.22 + \left(\frac{1240}{\lambda_{pd}} - \frac{1240}{699.65}\right)$$
(4)

Here, λ_{pa} is the peak of acceptor's absorption, while λ_{pd} is the peak of donor's absorption. However, in the active layer, the absorbance of a layer can be approximatively regarded as the sum of every component's absorbance, which means that the peak of each component's absorption extracted from FLAS directly is inaccurate because cumulative absorption leads a shift to components' peak position.

So the other's absorption component should be eliminated to ensure the accuracy of peak position. In a sublayer, the total absorption λ_{tot} is

$$\lambda_{tot} = R_d \lambda_d + R_a \lambda_a + \Delta \tag{5}$$

where R_d and R_a are the component ratio of donor and acceptor, λ_d and λ_a are the absorption of donor and acceptor, relatively. Δ is the error component, which indicates the red-shift and blue-shift behavior. So when a component's energy level is calculated, the other's influence to absorption need to be excluded. For instance, if the peak of acceptor is to be calculated, $R_d\lambda_d$ needs to be subtracted.

Numerical simulation

The drift-diffusion model used in this work is from the reference of Blakesley et al⁴. Besides that, to take the change of energy level into consideration, we add the quasielectric field (QEF) to drift-diffusion equations, as introduced by Wang et al⁵. The parameters used in the simulation is provided in Table S1.

Considering the active layer of organic solar cells as a one dimensional model whose length is 100 nm, the Poission's equation that should be solved firstly is as follow

$$\frac{\partial^2}{\partial x^2}\psi(x) = \frac{q}{\varepsilon} \Big[n(x) - p(x) \Big]$$
(6)

where the *q* is the elementary charge, ε is the dielectric constant, and $\psi(x)$ is the electric potential. n(x) and p(x) are the intensity of electron and hole, respectively. The current continuity equations and drift-diffusion equations are

$$\frac{\partial}{\partial x}J_{n(p)}(x) = \pm qU(x) \tag{7}$$

$$J_{n(p)} = -qn(p)\mu_{n(p)}F_{n(p)} \pm \mu_{n(p)}k_bT\frac{\partial}{\partial x}n(p)$$
(8)

$$F_{n(p)} = -\frac{\partial}{\partial x} \left[\psi(x) + w E_{c(v)}(x) \right]$$
(9)

where $J_{n(p)}$ is the current density of electron (hole), U(x) is the neat exciton generation rate, $\mu_{n(p)}$ is the mobility of electron (hole), k_b is Boltzmann's constant, and T is the temperature set as 300 K. As mentioned above, QEF ($F_{n(p)}$) is added into the equation. The gradient of HOMO/LUMO energy level ($E_{c(v)}$) contributes to the build-in electric field in device. Lastly, w is an adjustment factor to increase the effect of energy level to electric field for more accurate simulation, which is arbitrarily added by us, because the energy levels of localized states could leap acutely from one site to neighbor ones in the active layer, not varying continuously along the film-depth direction.

Setting the contact between the boundary of active layer and corresponding electrode is Ohmic Contact. Under steady-state condition, considering the recombination and decay of free carriers, the continuity equation becomes

$$U = PG - (1 - P)R \tag{10}$$

Here *G* is exciton generation rate, and *R* is carriers' recombination rate, which used Langevin recombination model $(R_L=qnp(\mu_h+\mu_e)/\varepsilon\varepsilon_0)$ with a reduced combination coefficient⁴ (R= γR_L , $\gamma=1/\beta(\mu_h+\mu_e)$). *P* is the probability of electron-hole pair dissociation. To simplify the calculation, the model of Braun⁶ is used to calculate *P*

$$P = \frac{\beta(\mu_p + \mu_n)}{\beta(\mu_p + \mu_n) + \sqrt{-2b} / J_1(2\sqrt{-2b})}$$
(11)

$$b = \frac{e^3 E(x)}{8\pi\varepsilon\varepsilon_0 k_b^2 T^2} \tag{12}$$

Here, β is dissociation parameter, J_1 is the first-order Bessel function, E(x) is the electric field, and ε_0 is the permittivity of free space.

Gaussian disorder model is used to calculate mobility⁷:

$$\mu_{n(p)}(x) = \mu_{n(p)0} \exp\left\{-0.42\hat{\sigma}^2 + 0.5(\hat{\sigma}^2 - \hat{\sigma}) \left[2n(p)(x)/N_{c(v)}\right]^{\delta}\right\}$$
(13)

$$\delta = 2 \frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - 0.3266}{\hat{\sigma}^2} \tag{14}$$

Here, $\hat{\sigma} = \sigma / k_b T$ is the amount of disorder relative to thermal energy, the value

of standard deviation is extracted by fitting the absorption of active layer to a Gaussian

distribution, because absorption intensity at a range of wavelength reveals the charge's

hopping among energy levels.

Supplementary References

- J. Wang, J. Zhang, Y. Xiao, T. Xiao, R. Zhu, C. Yan, Y. Fu, G. Lu, X. Lu, S. R. Marder and X. Zhan, J. Am. Chem. Soc., 2018, 140, 9140-9147.
- 2. S. Gao, L. Bu, Z. Zheng, X. Wang, W. Wang, L. Zhou, J. Hou and G. Lu, *AIP Advances*, 2017, **7**, 045312.
- 3. X. Zhao, B. Mi, Z. Gao and W. Huang, *Sci. China Phys. Mech. Astron.*, 2011, **54**, 375-387.
- 4. J. C. Blakesley and D. Neher, *Phys. Rev. B*, 2011, 84, 075210.
- 5. Z. Wang, Y. Hu, T. Xiao, Y. Zhu, X. Chen, L. Bu, Y. Zhang, Z. Wei, B. B. Xu and G. Lu, *Adv. Opt. Mater.*, 2019, **7**, 1900152.
- 6. C. L. Braun, J. Chem. Phys., 1984, 80, 4157-4161..
- W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. Blom, D. M. de Leeuw and M. A. Michels, *Phys. Rev. Lett.*, 2005, **94**, 206601.