Supporting Information

Ultrafast spectroscopic investigation of the effect of solvent additives on charge photogeneration and recombination dynamics in nonfullerene organic photovoltaic blends

Qingqing Yang,*^a Xitong Li,^b Hao Tang,^{ac}Youzhan Li,^{ac} Yingying Fu,^a Zhanguo Li^b and Zhiyuan Xie*^{ac}

^aState Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P R China

^bCollege of Optoelectronic Engineering, Changchun University of Science and

Technology, Changchun 130022, P R China

°School of Applied Chemistry and Engineering, University of Science and

Technology of China, Hefei 230026, P R China

Corresponding Author

*E-mail: xiezy_n@ciac.ac.cn

*E-mail: qqyang@ciac.ac.cn



Fig.S1 PL spectra of the neat PBDB-TF and IT-4F films and the PBDB-TF:IT-4F(1:1) blend films. These films are pristine or processed with DIO (or CN) additive. All of these samples are excited at 500 nm.



Fig.S2 Integrated scattering profiles of the corresponding 2D GIWAXS patterns of PBDB-TF films prepared with different conditions.



Fig.S3 TA spectra of the IT-4F films prepared with different conditions under excitation at 500nm.



Fig.S4 TA kinetics at 1250 nm for the pristine blend film with the pump fluences ranging from $1.0-3.8 \mu$ J/cm² under excitation at 500 nm.



Fig.S5 TA spectra of the PBDB-TF:IT-4F blend films processed with different conditions under excitation at 750 nm.



Fig.S6 The GSB kinetics at 580nm for the PBDB-TF:IT-4F films prepared with different conditions under excitation at 750nm.

The volume amounts of 1,8-diiodooctane (DIO) additive for PBDB-TF:IT-4F blend organic solar cells were selected to be 0.5% in this work according to the reference¹, at which an optimized photovoltaic performance were obtained. The volume amounts of 1-chloronaphthalene (CN) additive for PBDB-TF:IT-4F blend were optimized based on their photovoltaic performance and the corresponding J-V curves are plotted in Fig.S7. The optimal volume amount of CN is determined to be 1.0%.



Fig.S7 The illuminated J-V curves of PBDB-TF:IT-4F blend solar cells processed

with different volume amounts of CN additive.



Fig.S8 Dark J-V characteristics of PSCs with the PBDB-TF:IT-4F active layerdepositedindifferentconditions.



Fig.S9 *J*^{0.5}-*V* characteristics of (a) electron-only and (b) hole-only devices. The device architectures are ITO/ZnO/active layer/PFN-Br/Al for electron-only devices and ITO/PEDOT:PSS/ active layer/MoO₃/Al for hole-only devices.

Processing condition	A ₁ (%)	$\tau_1^{}(\mathrm{ps})$	A ₂ (%)	$\tau_2^{}(\mathrm{ps})$	A ₃ (%)	$\tau_3^{}$ (ps)	γ ₀ (%)
pristine	38.9	0.46	36.4	5.03	24.1	42.5	0.6
DIO	21.6	3.29	49.8	65.4	23.4	515	6.2
CN	21.7	2.89	47.7	50.8	24.3	434	6.2

Table S1 Exciton kinetic fits in the neat PBDB-TF films prepared with different conditions.

 $\mu_{\rm e}/\mu_{\rm h} \, (10^{-4} {\rm cm}^2 {
m V}^{-1} {
m s}^{-1}$ Processing $V_{\rm OC}(\mathbf{V})$ $J_{\rm SC}$ (mA/cm²) PCE_{max} (%) FF (%) ¹) condition 10.93 (10.67) 0.87 (0.87)^a 17.60 (17.66) 71.4 (69.4) pristine 0.47/2.00 0.5% DIO 0.81 (0.82) 76.2 (75.9) 12.29 (11.89) 19.91 (19.21) 1.42/3.30 1% CN 0.88 (0.88) 20.07 (19.90) 72.0 (70.1) 12.72 (12.22) 1.01/3.06

Table S2 Photovoltaic parameters for the PSCs with the PBDB-TF:IT-4F active layer deposited in different conditions.

^{a)} Average photovoltaic parameter values are obtained from more than 10 devices.

Reference:

¹ W. Li, L. Ye, S. Li, H. Yao, H. Ade and J. Hou, Adv. Mater. 2018, 30, 1707170.