Supporting Information for

Ultra-Narrow Bandgap Non-Fullerene Organic Solar Cells with Low Voltage Losses and Large Photocurrent

Jianqiu Wang,^{‡ab} Shenkun Xie,^{‡ab} Dongyang Zhang,^{ab} Rong Wang,^{ab} Zhong Zheng,^b Huiqiong Zhou,^b and Yuan Zhang^{*a}

^aSchool of Chemistry, Beijing Advanced Innovation Center for Biomedical Engineering,

Beihang University, Beijing 100191, P. R. China

^bCAS Key Laboratory of Nanosystem and Hierachical Fabrication, CAS Center for

Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing

100190, P. R. China

[‡] These authors have equally contributed to this work.

*Address correspondence to <u>yuanzhang@buaa.edu.cn</u>

Experimental Section

Materials: All materials for the active layer were purchased from Solarmer, Inc (Beijing) and used as received.

Device fabrication: The patterned indium-tin-oxide (ITO) coated glass substrates (10 Ω per square) were cleaned sequentially in detergent, de-ionized and ethanol by sonication and then blow-dried by high-purity nitrogen. All pre-cleaned ITO substrates treated by UV-ozone for 15 minutes. Subsequently, were poly(3,4ethylenedioxythiophene):poly (styrene sulfonate) solution was spin-coated on ITO substrates at 4000 rpm for 30 s and annealed at 160 °C for 10 min in air. Then the PEDOT:PSS coated ITO substrates were transferred into a nitrogen-purged glove box. The solutions used for solar cell active layers were prepared by dissolving PTB7-Th:IEICO-4F, PBDB-T:ITCC and PTB7-Th:PC₇₁BM (D:A ratio = 1:1.5, 1:1 and 1:1.5w/w, respectively) in chlorobenzene (CB) at a polymer weight concentration of 15 mg/ml, 10 mg/ml, and 12 mg/ml, respectively with using 1,8-iodooctane (DIO) as solvent additives. The active layers were casted from these BHJ solutions atop PEDOT:PSS and thermally annealed at 100 °C for 10 min. After that, 5 nm of PFN-Br was spun-coat atop the BHJ films as the electron transporting layer. Finally, 80 nm of Al cathode was thermally evaporated onto PFN-Br under high vacuum, yielding an effective device area of 4.0 mm².

Characterization: Current-voltage (*J-V*) characteristics of solar cells were measured in a high-purity nitrogen-filled glove box using a Keithley 2400 source meter under AM 1.5G irradiation (100 mW/cm²) provided by an XES-70S1 (SANYOU Electric Co., Ltd.) solar simulator (AAA grade, 70mm×70mm photobeam size) and calibrated by a standard silicon reference cell. The external quantum efficiency (EQE) spectra of solar cells were measured by a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co. Ltd., Taiwan). Ultraviolet-visible (UV-Vis) absorption spectra of neat and blend films were obtained using a Shimadzu UV-3101 PC spectrometer. Irradiation-dependent solar cell testing was performed by applying a filter wheel with customized optical densities between the samples and light source to obtain desired illumination intensities. Single-carrier devices were fabricated based on the same active layers used for solar cells but different electrodes and interlayers. hole-only and electron-only devices were in a configuration of The ITO/PEDOT:PSS/active layer/Au and ITO/ZnO/active layer/PFN-Br/Al, respectively. Double-carrier devices adopted with the same structure as solar cell devices (ITO/PEDOT:PSS/active layer/PFN-Br). Dark J-V curves characteristics of all carrier devices were measured under dark conditions using a Keithley 4200 semiconductor parameter analyzer. The mobility of hole, electron and double carriers were calculated by fittings using Mott-Gurney law. The reduction factor γ was quantified based on the extracted mobilities, according to the relation,

$$\gamma = \frac{16\pi}{9} \frac{\mu_h \mu_e}{\mu_{double}^2 - (\mu_h + \mu_e)^2}$$

where μ_{double} is the effective mobility of double carriers in the solar cell, and μ_h , μ_e are the mobility of holes and electrons carriers, respective. Impedance analysis of solar cells was carried out under different light intensities by using an electrochemical workstation. The impedance data were fitted by using the ZView program. TPC measurements were performed by a customized transient measurement systems (Physike Technology Co., Ltd) with using a pulsed semiconductor laser (Coherent, Inc.) GIWAXS measurements were performed on a Xenocs Xeuss SAXS/WAXS beamline system. Atomic force microscopy (AFM) images were acquired on a Multimode 8 HR (Bruker, Inc.) microscope system in the tapping mode.



Fig. S1 UV-Vis-NIR absorption spectroscopy of neat donor and acceptor films used in this study.



Fig. S2 (a)-(c) *J-V* characteristics of solar cells measurement at different light intensities (P_{light}) based on active layers of PTB7-Th:IEICO-4F, PBDB-T:ITCC, and PTB7-Th:PC₇₁BM. (d-f) PCE, V_{OC} and J_{SC} of various BHJ solar cells as a function of P_{light} .



Fig. S3 a) Device structures of double carriers. b) Dark J–V characteristics of double carrier devices based on PTB7-Th:IEICO-4F, PBDB-T:ITCC, and PTB7-Th:PC₇₁BM BHJ films. Lines are fittings using the Mott–Gurney law in the spacecharge-limited current (SCLC) regime.

Table S1. Mobilities of electrons, holes and double carriers (solar cell) in the comparedall blend films.

BHJ	Electron-only	Hole-only	Solar cell
	(m²/Vs)	(m²/Vs)	(double carriers)
			(m²/Vs)
PTB7-Th:IEICO-4F	7.21E-05	2.11E-04	1.79E-03
PBDB-T:ITCC	2.52E-04	1.15E-04	6.09E-04
PTB7-Th:PC ₇₁ BM	5.70E-04	2.03E-03	4.72E-03



Fig. S4 Normalized photocurrent decay kinetics at various biases of solar cells containing active layers of (a) PTB7-Th:IEICO-4F, (b) PBDB-T:ITCC, and (c) PBDB-T:PC₇₁BM.



Fig. S5 (a)-(c) Nyquist plots of impedance spectroscopy measured on various solar cells containing active layers of PTB7-Th:IEICO-4F, PBDB-T:ITCC, and PTB7-Th:PC₇₁BM. Chemical capacitance of solar cells determined at open-circuit condition as a function of (d) P_{light} and (e) V_{oc} . (f)-(h) Recombination resistance versus P_{light} characteristics of solar cells.



Fig. S6 (a) Topogaraphic (left panels) and phase (right panels) images of various BHJ blend films captured by AFM. (b), (c) 2D GIWAXS patterns measured on various BHJ films. (c) Line-cut profile curves of 2D GIWAXS along out-of-plane (face-on) and in-plane (edge-on) directions.