

Supporting Information

Ternary Non-fullerene Polymer Solar Cells with a High Crystallinity *n*-Type Organic Semiconductor as the Second Acceptor

Lian Zhong,^{a,b} Haijun Bin,^b Yongxi Li,^c Ming Zhang,^d Jianqiu Xu,^e Xiaojun Li,^{a,b} He Huang,^{a,b} Qin Hu,^g Zuo-Quan Jiang,^c Jing Wang,^d Chunfeng Zhang,^e Feng Liu*,^d Thomas P Russell,^g Zhanjun Zhang*,^a and Yongfang Li*,^{a,b,f}*

^a School of Chemical Science, University of Chinese Academy of Sciences, Beijing 100049, China.

^b Beijing National Laboratory of Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China;

^c Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou 215123, China.

^d Department of Physics and Astronomy and Collaborative Innovation Center of IFSA (CICIFSA), Shanghai Jiao Tong University, Shanghai 200240, China;

^e National Laboratory of Solid State Microstructures, School of Physics and Collaborative Innovation Center of Advanced Microstructures, Nanjing University;

^f Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, China;

^g Polymer Science and Engineering Department, University of Massachusetts Amherst, MA 01003, USA

E-mail: liyf@iccas.ac.cn (Y. F. L), zhangzj@ucas.ac.cn (Z.J. Zhang),

fengliu82@sjtu.edu.cn (F. Liu), cfzhang@nju.edu.cn

Experimental Section

Materials: All chemicals and solvents were purchased from J&K, Alfa Aesar and TCI Chemical Co. IDIC was bought from Solarmer Materials, Inc. J61 and PDINO were

prepared according to our previous publications. The acceptor BT-IC was used as received.

Device fabrication: We fabricated the PSCs with the traditional sandwich device structure of ITO /PEDOT: PSS/Active layer/PDINO/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, and isopropanol for 15 min, dried under a nitrogen stream, and subsequent ultraviolet-ozone treatment for 20 min. A thin layer of PEDOT: PSS (poly-(3,4-ethylenedioxythiophene): poly (styrene sulfonate)) was deposited through spin-coating atop the pre-cleaned ITO-coated glass from a PEDOT: PSS aqueous solution (Baytron P VP AI 4083 from H. C. Starck) at 4200 rpm and dried subsequently at 150 °C for 15 min in air. Then the device was transferred to a nitrogen glove box, where the active blend layer of J61, IDIC and BT-IC was spin-coated atop the PEDOT: PSS layer. The weight ratio of donors and acceptors was kept at 0.9:1 (w/w), and blend solution with a total blend polymer concentration of 9 mg mL⁻¹ in chloroform, without using any additives. To optimize the active layer thickness, the spin-coating rates and the concentrations of the J61: IDIC: BT-IC solutions were varied. The optimized conditions are with a spin-coating rate of 2700 rpm. The active layers were annealed at 140 °C for 2 min. Then spun cast PDINO (1 mg/ml) as electron transport layer at 3000 rpm for 30 s. Finally, the Al cathode (80 nm) was deposited at 5×10⁻⁵ Pa. The active area of the device was 4.6 mm².

Solar Cell characterization: The devices were tested under AM 1.5G solar illumination at 100 mW/cm² using a Newport solar simulator. The current density–voltage (*J–V*) characteristics were measured on a computer-controlled Keithley 2450 Source-Measure Unit. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan).

Measurements: UV–vis absorption spectra of the active layers were measured on a Hitachi U-3010 UV–vis spectrophotometer. The thickness of the thin films was

measured by a profilometry (Ambios Tech.XP-2). PL spectra were measured with an Edinburgh FLS980 fluorescence spectrophotometer. The surface morphology of thin films was measured by atomic force microscope (AFM, Bruker-ICON2-SYS) in the tapping mode. The bulk morphology of thin films was measured by transmission electron microscopy (TEM, JEM-2100F).

SCLC Measurements: Hole and electron mobilities were measured using the SCLC model. ITO/PEDOT: PSS/Active-layer/Au for hole-only devices and ZnO/Active-layer/PDINO/Al for electron-only devices. The SCLC mobilities were calculated by MOTT-Gurney equation:

$$J = \frac{9\varepsilon_r\varepsilon_0\mu V^2}{8L^3} \quad (1)$$

Where J is the current density, ε_r is the relative dielectric constant of active layer material usually 2-4 for organic semiconductor, herein we use a relative dielectric constant of 4), ε_0 is the permittivity of empty space, μ is the mobility of hole or electron and L is the thickness of the active layer.

GIXD Characterization: Grazing incidence x-ray diffraction (GIXD) characterization of active layer was performed at beamline 7.3.3, Advanced Light Source (ALS), Lawrence Berkeley National Lab (LBNL). X-ray energy was 10 keV and operated in top off mode. The scattering intensity was recorded on a 2D detector (Pilatus 2M) with a pixel size of 172 μm (1475 \times 1679 pixels). The samples were \sim 10 mm long in the direction of the beam path, and the detector was located at a distance of 300 mm from the sample center (distance calibrated by AgB reference). The incidence angle was chosen to be 0.16° (above critical angle) for GIXD measurement. OPV samples were prepared on PEDOT: PSS covered Si wafers in a similar manner to the OPV devices. RSoXS was performed at beamline 11.0.1.2 Lawrence Berkeley National Lab. Thin films was flowed and transferred onto Si_3N_4 substrate and experiment was done in transition mode.

Ultrafast transient absorption spectroscopy Characterization: A Ti: sapphire regenerative amplifier (Libra, Coherent Inc.) was employed for TA spectroscopy measurements. For fs-resolved TA experiment, the pump-probe delay was enabled by a translation stage. An optical parametric amplifier (Oper A Solo, Coherent Inc.) pumped by the regenerative amplifier was used to generate the pump beam with tunable wavelengths. The probe beam is a broadband supercontinuum light source. The visible and infrared probe sources are generated by focusing a small portion of the femtosecond laser beam onto a sapphire plate or a YAG plate, respectively. The chirp of the supercontinuum probe was corrected with an error to be less than 100 fs over the whole spectral range. The TA signal was then analyzed by a high speed silicon/InGaAs CCD for visible/infrared detection with a monochromator (Acton 2358, Princeton Instrument) at 1 kHz enabled by a custom-built control board from Entwicklungsbuero Stresing. The angle between the polarized pump and probe beams was set at the magic angle. For ns TA spectroscopy, we used a frequency-doubled sub-nanosecond laser (Picolo AOT MOPA, Inno Las) at 532 nm (pulse duration ~ 0.8 ns) to excite the samples. The laser was synchronized to the probe pulse with a desired delay by an electronic delay generator (SRS DG645, Stanford Research System). The temporal resolutions for fs-TA and ns-TA were better than 0.2 ps and 0.8 ns, respectively.

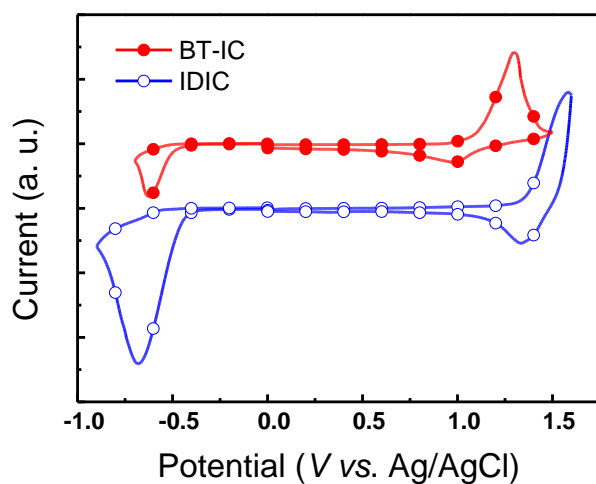


Figure S1. Cyclic voltammograms of the acceptor IDIC and BT-IC thin films

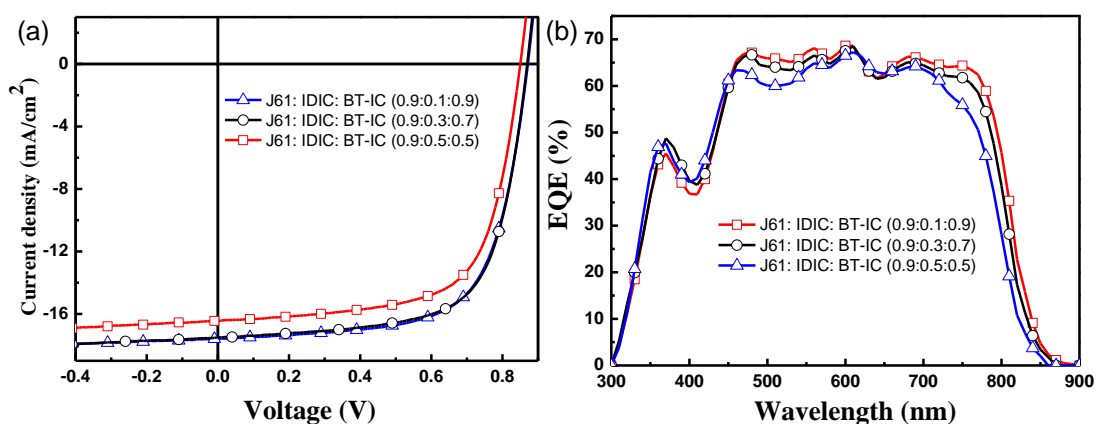


Figure S2. (a) J - V curves of the ternary PSCs under the illumination of AM1.5G, 100 mW/cm², (b) The EQE curves of the corresponding ternary PSCs.

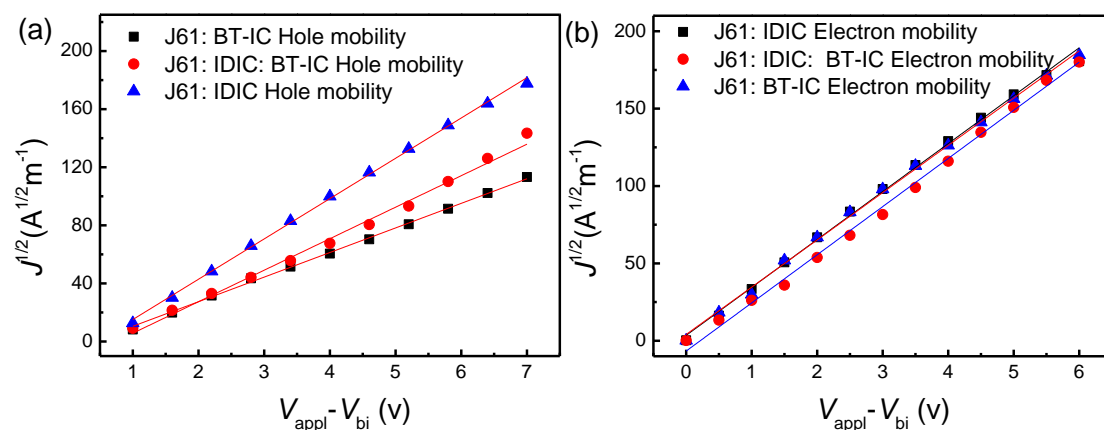


Figure S3. Current density-voltage curves for (a) the hole and (b) electron mobility measurements of the blend films: of J61: BT-IC, J61: IDIC: BT-IC and J61: IDIC. Solid lines are the fitting lines of the data.

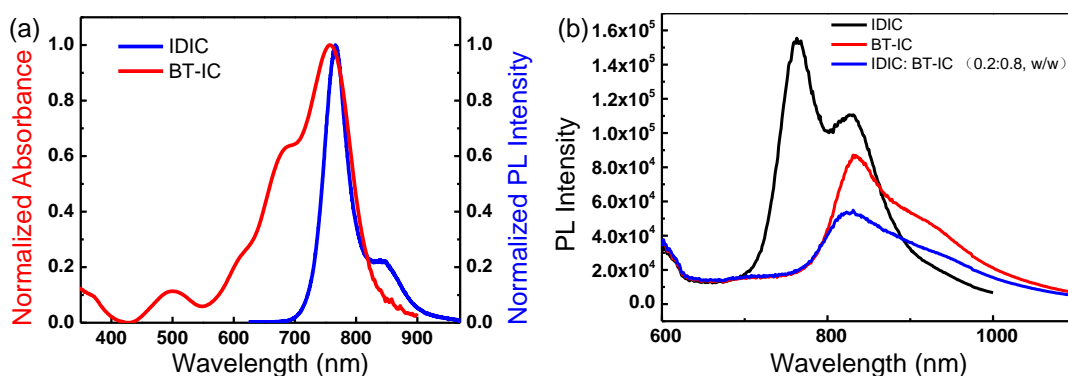


Figure S4. (a) PL spectrum of IDIC and absorption spectrum of BT-IC; (b) PL spectra of IDIC, BT-IC and the blend films of IDIC: BT-IC (0.2:0.8, w/w), excited at 468 nm

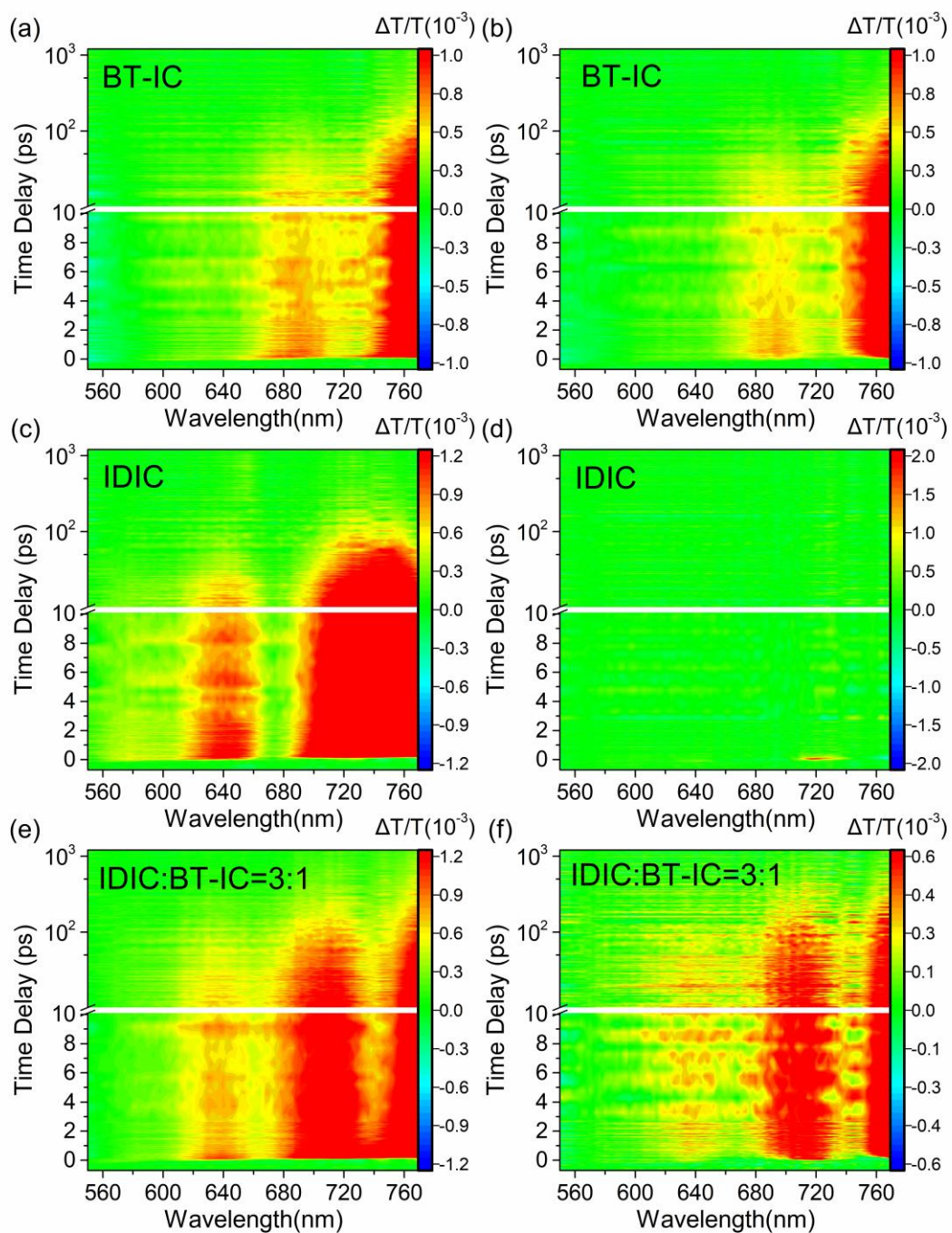


Figure S5. Transient absorption signal recorded from IDIC, BT-IC neat films and their blended film excited by 650 nm (a), (c), (e) and by 800 nm (b), (d), (f).

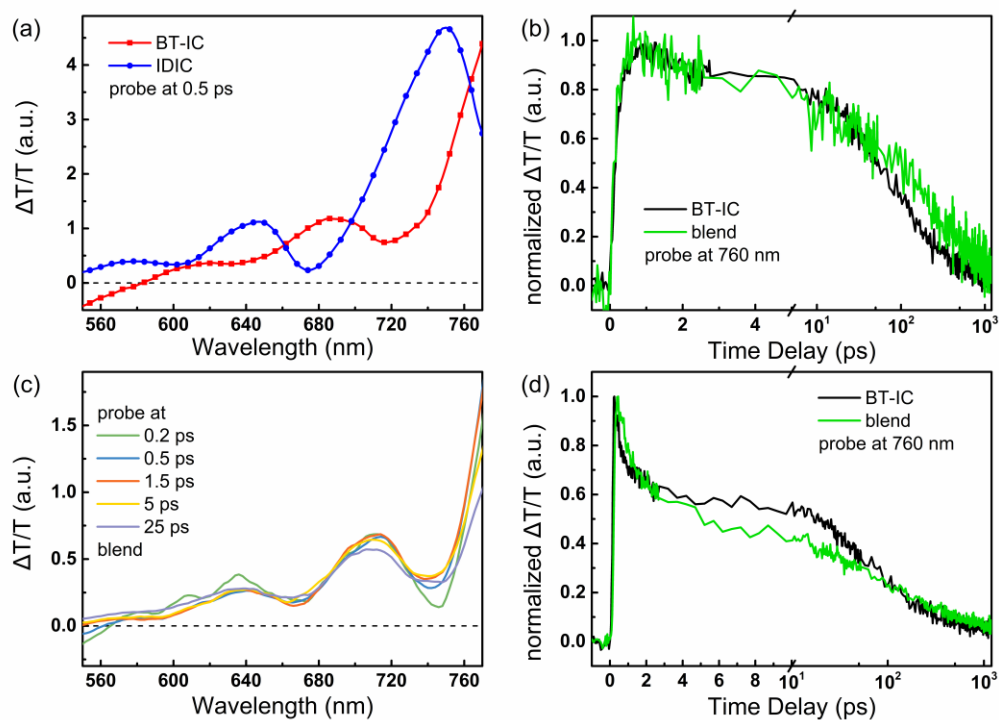


Figure S6. (a) TA spectra of IDIC and BT-IC neat films probed at 0.5 ps excited at 650 nm, 800 nm excited (b) normalized dynamic curve of BT-IC neat film and blended film; (c) TA spectra of blend at different time delays. (d) Normalized dynamic curve of BT-IC and blend probed at 760 nm with pump at 650 nm.

Table S1. The lamellar distances, the π - π -stacking distances and the coherence length of the films

Films	d[100] (\AA)	CCL[100] (\AA) ^a	d[010] (\AA)	CCL[010] (\AA)
J61	25.99	54.39	3.61	21.63
IDIC	16.46	155.55	3.48	29.28
BT-IC	20.50	123.02	3.47	27.33
J61: IDIC: BT-IC	25.99	80.11	3.59	28.54
J61: IDIC	25.54	85.21	3.49	45.49
J61:BT-IC	25.71	63.84	3.58	25.63

^a Calculated from Scherrer equation: $\text{CCL} = 2\pi\kappa/\Delta q$, where Δq is the full-width at half-maximum of the peak and κ is a shape factor (0.9 was used here).

Table S2. The hole (μ_e)/electron mobilities (μ_h) of the blend active layers

Weight ratio of J61: IDIC: BT-IC	Thickness (nm)	$10^{-4}\mu_h$ $\text{cm}^2\text{v}^{-1}\text{s}^{-1}$	$10^{-4}\mu_e$ $\text{cm}^2\text{v}^{-1}\text{s}^{-1}$	μ_e/μ_h
0.9: 0: 1	100	0.98	3.12	3.19
0.9: 0.2: 0.8	100	1.79	3.24	1.81
0.9: 1: 0	100	2.17	3.21	1.48