Supporting Information

J71 based ternary organic photovoltaics exhibiting 13.65% efficiency

Chunyu Xu^a, Jian Wang^b*, Zijin Zhao^a, Jinhua Gao^a, Zhenghao Hu^a, Xiaoling Ma^a, Xiaoli Zhang^c, Fujun Zhang^a*

^a Key Laboratory of Luminescence and Optical Information, Ministry of Education, Beijing Jiaotong University, 100044, Beijing, China.

^b College of Physics and Electronic Engineering, Taishan University, 271021, Taian, Shandong Province, China.

^c State Centre for International Cooperation on Designer Low-Carbon & Environmental Materials, School of Materials Science and Engineering, Zhengzhou University, 450001, Zhengzhou, Henan Province, China.

*E-mail: <u>wangjian@tsu.edu.cn</u> (Jian); <u>fjzhang@bjtu.edu.cn</u> (Fujun)

Experimental details

The patterned indium tin oxide (ITO) coated glass substrates (sheet resistance 15 Ω /square) were consecutively cleaned in ultrasonic baths containing detergent, deionized water and ethanol, respectively. The cleaned ITO substrates were blow-dried by high pure nitrogen gas and then treated by oxygen plasma for 1 min to improve its work function and clearance. Subsequently, poly-(3,4-ethylenedioxythiophene):poly-(styrenesulphonicacid) (PEDOT:PSS) (clevios P VP Al 4083, purchased from H.C. Starck co. Ltd.) solution was spin-coated to fabricated thin films on the cleaned ITO substrates by spin-coating method at 5000 round per minute (RPM) for 40 s, and then annealed at 150 °C for 15 minutes in ambient condition. After annealing treatment, the ITO substrates coated PEDOT:PSS films were transferred to a high-purity nitrogenfilled glove box to fabricate active layers. The used materials J71, BTP-BO-4Cl and ITIC (purchased from Solarmer Materials Inc) were dissolved in chloroform and stirred for 4 h to prepare 16 mg/ml blend solutions. The proportions of BTP-BO-4Cl:ITIC are 1:0, 0.75:0.25, 0.5:0.5, 0.4:0.6, 0.3:0.7, 0.2:0.8, 0:1 and the weight ratio of donors to acceptor is kept constant as 1:1.2. The blend solutions were spin-coated on PEDOT:PSS films at 2000 RMP for 30s in a high purity nitrogen-filled glove box to fabricate the active layers. Then, the active layers were annealed by CS₂ vapor for 60s then annealed at 100 °C for 5 min. Afterwards, a PDIN cathode interlayer was spin-coated onto active layers at 5000 RPM for 30s. Finally, 100 nm Al was deposited by thermal evaporation with a shadow mask. The active area is approximately 3.8 mm², which is defined by the overlapping area of ITO anode and Al cathode.

The current density-voltage (*J-V*) curves of all organic solar cells were measured in a high-purity nitrogen-filled glove box using a Keithley 2400 source meter. AM 1.5G irradiation at 100 mW/cm² was provided by a XES-40S2 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, 70×70 mm² photobeam size), which was calibrated by standard silicon solar cells (purchased from Zolix INSTRUMENTS CO. LTD). The external quantum efficiency (EQE) spectra of organic solar cells were measured in air conditions by a Zolix Solar Cell Scan 100. The ultraviolet-visible (UV-Vis) absorption spectra of neat and blend films were obtained using a Shimadzu UV-3101 PC spectrometer. Transmission electron microscopy (TEM) images of the active layers were obtained by using a JEOL JEM-1400 transmission electron microscope operated at 80 kV.



Fig. S1. EQE spectral difference between ternary OPVs and BTP-BO-4Cl based binary OPVs.



Fig. S2. The *J-V* curves of (a) BTP-BO-4F based binary, (b) the optimized ternary and (c) ITIC based binary OPVs under different light intensity.

Table S1. The μ_h , μ_e and μ_h/μ_e values in the binary and the optimized ternary active layers.

ITIC wt%	$\mu_{h} (cm^{2}V^{-1}s^{-1})$	$\mu_{e} (cm^{2}V^{-1}s^{-1})$	μ_h/μ_e
0	3.26×10 ⁻⁴	1.62×10 ⁻⁴	2.01
60	3.75×10 ⁻⁴	2.22×10-4	1.69
100	4.18×10-4	2.71×10-4	1.54