Supporting Information

Synergistic Effect of Solvent and Polymer Additives on Solar Cell Performance and Stability of Small Molecule Bulk Heterojunction Solar Cells

Hyo-Sang Lee,[a,b] *Hyungju Ahn,*[c] *Jea Woong Jo,*[a] *BongSoo Kim,*[d] *and Hae Jung Son**[,a,b]

[a] Photo-electronic Hybrids Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea.

[b] Green School (School of Energy and Environment), Korea University, Seoul 02841, Republic of Korea

[c] Pohang Accelerator Laboratory, Kyungbuk, Pohang 790-784, Republic of Korea.

[d] Department of Science Education, Ewha Womans University, Seoul 03760, Republic of Korea

*Corresponding Author: Hae Jung Son: E-mail: hjson@kist.re.kr

Materials

The p-DTS(FBTTh$_2$)$_2$ and PCDTBT were purchased from Nano clean tech. PC$_{71}$BM was purchased from EMindex. A chlorobenzene (anhydrous, 99.8%), 1,8-diiodooctane (contains copper as stabilizer, 98%), polyethylenimine (80% ethoxylated), 2-methoxyethanol (anhydrous, 99.8%), and molybdenum(VI) oxide (99.5%) were purchased from Sigma-Aldrich. P1[S1,S2] and P2[S3,S4] were synthesized by following the methods reported in the literatures (P1: M_n = 14,000 Da; P2: M_n = 25,000).

Organic solar cell fabrication

The patterned ITO-coated glass substrates (15 Ω/sq., 2.5 × 2.5 cm^2) were cleaned ultrasonically in isopropyl alcohol, acetone, isopropyl alcohol for each 10 min. The ITO glass substrates were then treated with UV/ozone for 20 min. The clean ITO substrate was then spin-coated with a 30 nm thick layer of polyethylenimine ethoxylated (PEIE) solution (0.2 wt% diluted in 2-methoxyethanol) at 5000 rpm for 60 s, then baked in air at 100 ℃ for 10 min. The photoactive layer was spin-coated on the top of the PEIE layer using a chlorobenzene solution containing p-DTS(FBTTh$_2$)$_2$ and [6,6]-phenyl-C$_{71}$-butyric acid methyl ester (PC$_{71}$BM) (33 mg/mL) at ratio of 3:2 (w/w), with and without additives-either DIO (0.4, 1, and 3 v/v % by total solvent volume), polymer (2, 6, and 20 w% by total solid weight), or both; the thickness of the photoactive layer was 80–110 nm. Finally, a 4 nm thick MoO_3 and a 100 nm thick Al layer were thermally evaporated through a shadow mask at a pressure of less than 3 × 10^{-6} Torr with a deposition rate of ~5 Å/s. The active area of each device was 0.20, 0.12 cm^2.

Characterization

Transmission electron microscope (TEM) samples were prepared by detaching an active layer film from an ITO/PEDOT:PSS substrate at the surface of deionized water and picking it up with a carbon film 200 mesh copper grid. TEM images were measured using a FEI Titan TM 80-300, operating at an accelerating voltages of 80–300 kV. Differential scanning calorimetry (DSC) curves were recorded on a Perkin-Elmer Pyris 1 DSC instrument from 30 to 340 ℃ at a heating rate of 10 ℃/min under nitrogen atmosphere. 2D-GIXD measurement was conducted at PLS-II 9A U-SAXS beamline of Pohang Accelerator Laboratory in Korea. In 2D-GIXD experiment, the wavelength of the incident X-ray was 1.12 Å and the sample to detector distance was 224 mm. Diffraction angles were calibrated by a pre-calibrated sucrose (Monoclinic, P21, a = 10.8631 Å, b = 8.7044 Å, c = 7.7624 Å, , β = 102.938°).

Device measurements

The current density versus voltage (*J-V*) characteristics of organic solar cell devices were recorded on a Keithley model 2400 source measuring unit. A class-A solar simulator with a 1000 W Xenon lamp (Yamashita denso, YSS-50S) equipped with a KG-5 filter served as a light source. Its light intensity was adjusted to AM 1.5 G 1 sun light intensity (100 mW/cm^2) using a National Renewable Energy Laboratory (NREL) calibrated mono Si solar cell. The external quantum efficiency (EQE) was measured as a function of wavelength from 300 to 900 nm on an incident photon-to-current conversion equipment (PV measurement Inc.). Calibration was performed using a silicon photodiode G425, which is National Institute of Standard and Technology (NIST) calibrated as a standard. For hole and electron mobility measurements, hole-only (or electron-only) devices were fabricated with a structure of ITO/PEDOT:PSS/small-molecule:polymer:$PC_{71}BM$/Au (or ITO/Al/small-molecule:polymer:$PC_{71}BM$/Al). Mobilities in the small-molecule:$PC_{71}BM$ blend film were determined from *J–V* curves in dark by space charge limited current (SCLC) method, based on the following equation:

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

where ε_o is the permittivity of free space, ε_r is the dielectric constant of the small-molecule:$PC_{71}BM$ bulk heterojunction film, μ is the mobility, $V=V_{appl}-V_{bi}-V_a$ (where V_{appl} is the applied bias, V_{bi} is the built-in potential due to the difference in electrical contact work function, and V_a is the voltage drop due to contact resistance and series resistance across the electrodes), and L is the thickness of the photo-active layer. The current density versus voltage characteristics were also recorded on a Keithley model 2400 source measuring unit.

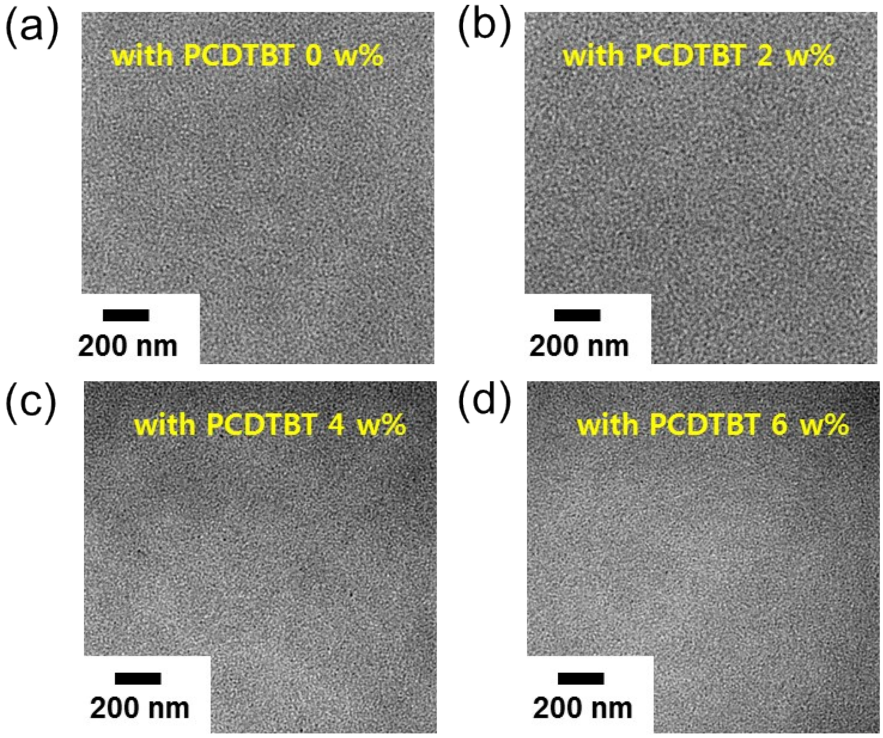

Figure S1. TEM images of p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM films prepared using various contents of PCDTBT without DIO.

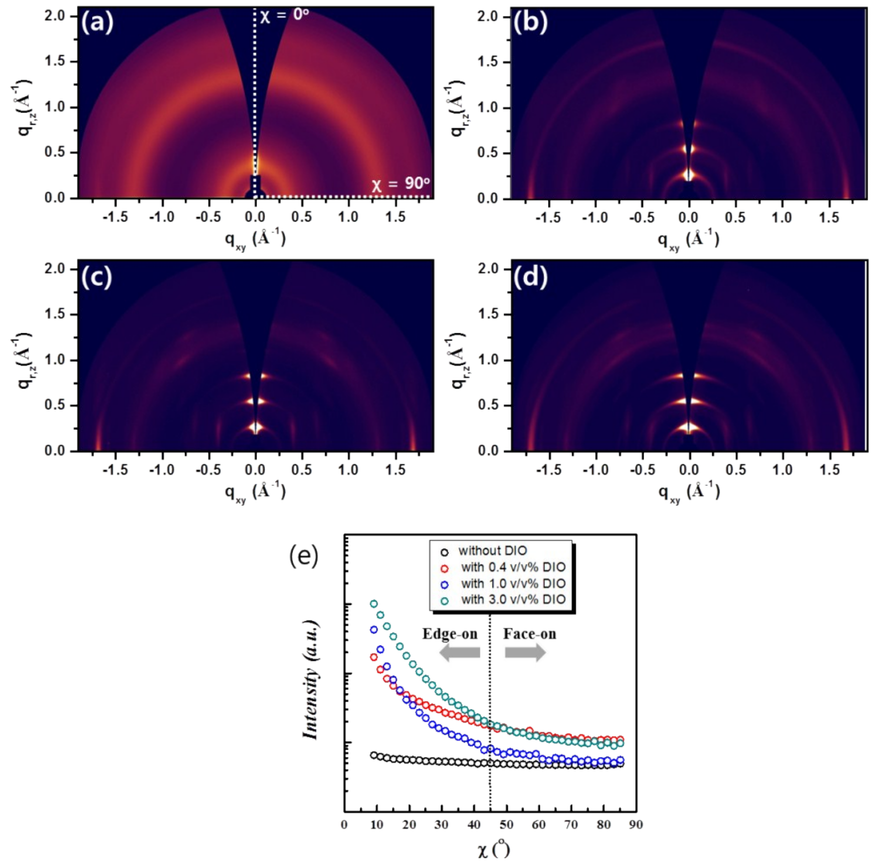

Figure S2. GIXD images of p-DTS($FBTTh_2$)$_2$:$PC_{71}BM$ films prepared using different DIO contents of (a) 0 v/v%, (b) 0.4 v/v%, (c) 1 v/v%, and (d) 3 v/v%. (e) Azimuthal intensity scan of (100) reflection of the blend film.

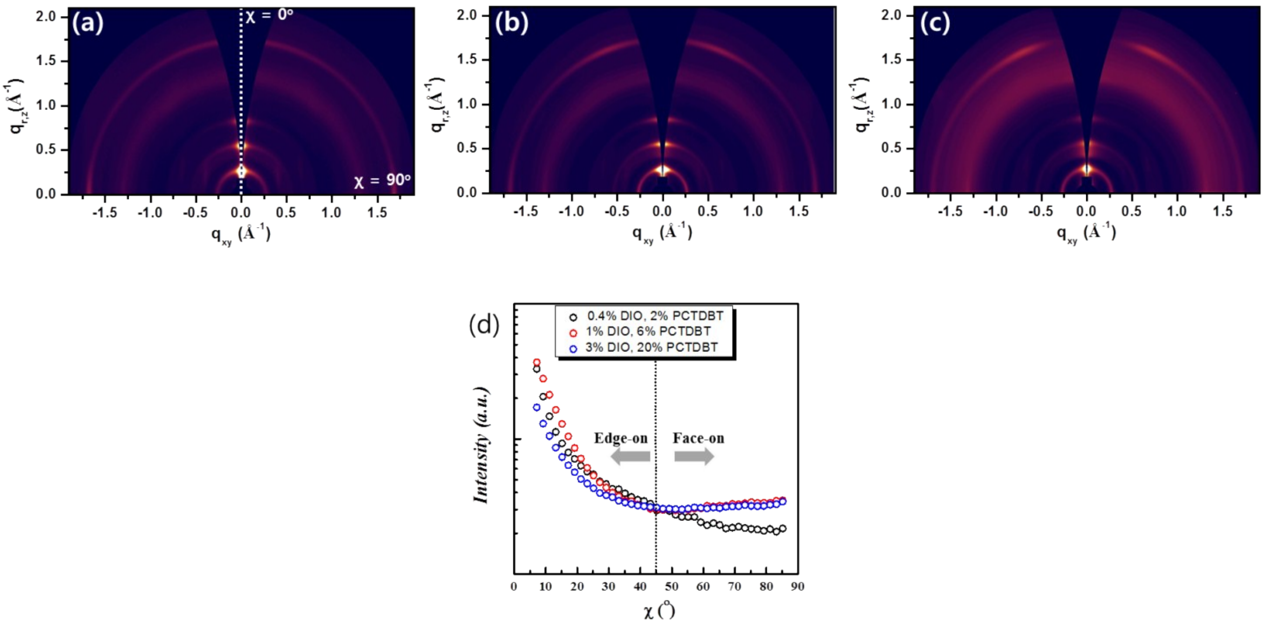

Figure S3. GIXD images of p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM films prepared using different DIO and PCDTBT contents of (a) 0.4 v/v % DIO and 2 w% PCDTBT, (b) 1 v/v % DIO and 6 w% PCDTBT, and (c) 3 v/v % DIO and 20 w% PCDTBT. (e) Azimuthal intensity scan of (100) reflection of the blend film.

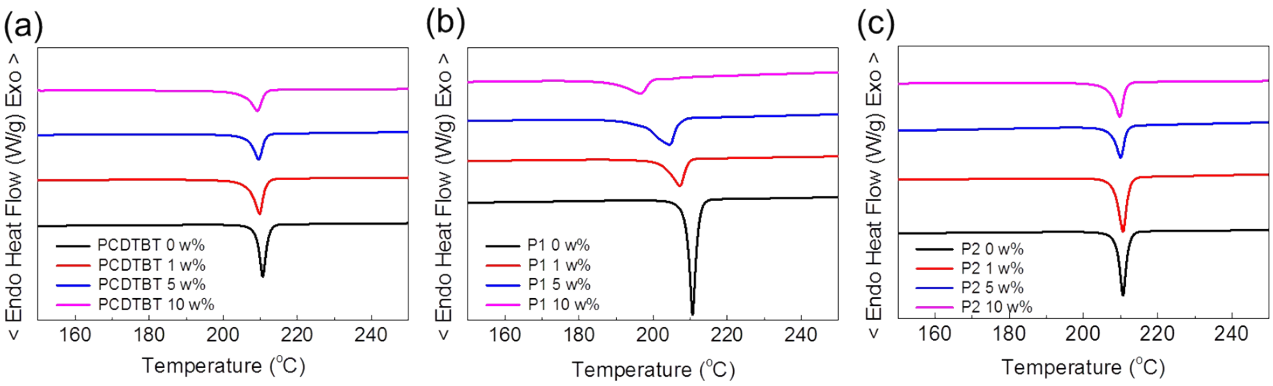

Figure S4. DSC curves of p-DTS(FBTTh$_2$)$_2$ blended with (a) PCDTBT, (b) P1, and (c) P2

Table S1. SCLC mobilities of hole (or electron) only devices fabricated by various DIO and PCDTBT contents and ratios of electron and hole mobilities.

condition	hole mobility ($cm^2V^{-1}s^{-1}$)	electron mobility ($cm^2V^{-1}s^{-1}$)	ratio of mobilities (electron/hole)
0 v/v% DIO	2.59×10^{-4}	5.60×10^{-4}	2.16
0.4 v/v% DIO	5.64×10^{-4}	9.50×10^{-4}	1.68
0.4 v/v% DIO/ 2 w% PCDTBT	7.94×10^{-4}	1.00×10^{-3}	1.25

References

S1 I. Osaka, M. Shimawaki, H. Mori, I. Dori, E. Miyazaki, T. Koganezawa and K.Takimiya, *J. Am. Chem. Soc.* 2012, **134**, 3498-3507.

S2 J. W. Jo, S. Bae, F. Liu, T. P. Russell and W. H. Jo, *Adv. Funct. Mater.* 2014, **25**, 120-125.

S3 R. B. Aich, N. Blouin, A. Bouchard and M. Leclerc, *Chem. Mater.* 2009, **21**, 751-757.

S4 P. O. Morin, T. Bura, B. Sun, S.I. Gorelsky, Y. Li and M. Leclerc, *ACS Macro Lett*. 2015, **4**, 21-24.