

Electronic Supplementary Information

Experimental details

Materials. C60 and C70 were purchased from American Dye Source Inc. P3HT was purchased from Rieke Metals and used as received. PC₆₀BM and PC₇₀BM were purchased from Nano-C Company. All other starting chemicals and solvents were purchased from Sigma-Aldrich Company. PBDTTT-C was synthesized in our lab.

Measurements and Instruments. All new compounds were characterized by ¹H NMR and ¹³C-NMR spectroscopy performed on a Bruker ARX-400 spectrometer. Chemical shifts were reported in ppm relative to the singlet of CDCl₃ at 7.26 ppm and 77 ppm for ¹H-NMR and ¹³C-NMR respectively. Absorption spectra were taken on a Varian Cary 50 ultraviolet-visible spectrometer. The photoluminescence spectra were taken on a Fluorolog-3 Spectrofluorometer. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt disk, Pt wire, and Silver wire as working electrode, counter electrode, and reference electrode respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) o-dichlorobenzene/acetonitrile (5:1) solution. The half potential of Ferrocene in this condition is 0.40 V.

Device Fabrication and Characterization of PSCs. PSCs were fabricated with ITO glass as a positive electrode, Ca/Al as a negative electrode and the blend film of the polymer/fullerene derivatives between them as a photosensitive layer. Here, polymer materials are P3HT and PBDTTT-C, fullerene derivatives are PC₆₀BM, PC₇₀BM, F1 and F2. Polymer donor (or other polymers reported here) was

co-dissolved with fullerene acceptor in 1, 2-dichlorobenzene (DCB) in the weight ratio of 1:1 for P3HT system and 1:2 for PBDTTT-C system with a concentration of 10 mg/mL. For PBDTTT-C systems, 3% (volume) 1,8-diiodooctane were used to further improve the final device performances. ITO-coated glass substrates ($15\Omega/\text{cm}^2$) were cleaned stepwise in detergent, water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried in an oven for 5 h. A thin layer (~ 30 nm) of PEDOT: PSS (Baytron P VP A1 4083) was spin-coated onto ITO surface which was pretreated by ultraviolet ozone for 15 min. Low-conductivity PEDOT: PSS was chosen to minimize measurement error from device area due to lateral conductivity of PEDOT: PSS. After being baked at 120°C for ~ 20 min, the substrates were transferred into a nitrogen-filled glove box. A polymer/fullerene composite. Layer (ca. 100 nm thick) was then spin-cast from the blend solutions at 2500 rpm on the ITO/PEDOT: PSS substrate. For P3HT systems, the films were solvent annealed and then thermally annealed at 150°C for 10 mins. Then the film was transferred into a thermal evaporator which is located in the same glovebox. A Ca layer (20 nm) and an Al layer (100 nm) were deposited in sequence under the vacuum of 2×10^{-6} torr. The effective area of film was measured to be 0.10 cm^2 .

Current-voltage measurement. The fabricated device was encapsulated in a nitrogen-filled glovebox by UV epoxy and cover glass. The current density-voltage (J-V) curves were measured using a Keithley 2400 source-measure unit. The photocurrent was measured under AM 1.5 G illumination at $100\text{ mW}/\text{cm}^2$ using a Newport Thermal Oriel 91192 1000W solar simulator (4 in. \times 4 in. beam size). The

light intensity was determined by a monosilicon detector calibrated by National Renewable Energy Laboratory (NREL) to minimize spectral mismatch.

Synthesis of F1 and F2.

Compound 1. A solution of 4-methyl-1-nitrosopentane (11.4 mL) and vinyl acetate (240 mL) was heated to reflux. A solution of 2-amino-4, 5-dimethoxybenzoic acid (8.4 g) in 120 mL THF was added dropwise into above solution over 30 mins, and then the reaction mixture was heated to reflux for another 15 hs. After removing the solvent, the residue was distilled to obtain the compound 1 as yellow oil. ¹H-NMR (CDCl₃, 400MHZ) δ (ppm) 6.83(s, 1H), 6.70(s, 1H), 5.79(d, 1H), 3.86(s, 3H), 3.85(s, 3H), 3.52(d, 1H), 3.15(d, 1H), 2.10(s, 3H).

F1. A solution of C60 (0.72 g, 1 mmol) and compound 1(0.33 g, 1.5 mmol) in 60 ml 1, 2, 4-trichlorobenzene was heated to reflux for 3 hs. After being cooled to room temperature, the reaction mixture was dropwise added into 500 mL stirred methanol. The solution was centrifuged to remove the solvent, the solid was washed several times using methanol. And then was dissolved in 100 ml dichlorobenzene, adsorbed on silica gel and purified by silica gel column using toluene as eluent to remove the unreacted C60 and then using chloroform/ethyl acetate (9:1) as eluent to obtain F1 (0.49 g). ¹H-NMR (CDCl₃/CS₂ 1:3, 400MHZ) δ (ppm) 7.33(s, 1H), 7.12(s, 1H), 5.27(d, 1H), 4.40(d, 1H), 4.01(s, 6H), 3.45(s, 1H), 2.32(s, 3H). ¹³C-NMR (CDCl₃/CS₂ 1:3, 400MHZ) 169.39, 157.23, 153.96, 150.69, 149.24, 148.51, 147.76, 146.70, 145.79, 144.70, 143.07, 142.16, 140.16, 136.71, 135.08, 130.00, 129.27, 127.09, 113.11, 111.66, 69.35, 63.73, 55.92, 44.30, 21.06. MALDI-TOF for C₇₂H₁₄O₄,

calculated: 942.90, analyzed: 942.65.

F2 A solution of C70 (0.84 g, 1 mmol) and compound 1(0.33 g, 1.5 mmol) in 60 ml 1, 2, 4-trichlorobenzene was heated to reflux for 3 hs. After being cooled to room temperature, the reaction mixture was added dropwise into 500 mL of stirred methanol. The solution was centrifuged to remove the solvent, the solid was washed several times using methanol, and then was dissolved in 100 ml dichlorobenzene, adsorbed on silica gel and purified by silica gel column using toluene as eluent to remove the unreacted C60 and then using chloroform/toluene (3:1) as eluent to obtain F2(0.19 g). ¹H-NMR (CDCl₃/CS₂ 1:3, 400MHZ) δ (ppm) 7.18(s, 1H), 7.05(s, 1H), 4.59(d, 1H), 4.10(d, 1H), 3.90(s, 6H), 3.77(s, 1H), 2.32(s, 3H). ¹³C-NMR (CDCl₃/CS₂ 1:3, 400MHZ) 169.26, 166.06, 164.24, 163.39, 159.67, 155.36, 151.77, 151.38, 150.86, 150.34, 149.88, 149.56, 148.90, 149.24, 148.45, 147.60, 147.01, 145.90, 143.42, 142.97, 140.22, 138.07, 134.16, 133.76, 132.53, 132.13, 131.29, 130.18, 130.00, 129.92, 129.33, 129.00, 128.22, 127.95, 126.91, 125.48, 119.87, 117.32, 113.54, 111.98, 63.19, 56.07, 43.78, 35.72, 34.95, 30.15, 21.32. MALDI-TOF for C₈₂H₁₄O₄, calculated: 1063.02, analyzed: 1063.452.