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. PC$_{60}$BM and PC$_{70}$BM were purchased from Nano-C Company. PBDTTT-C and PBDTTDPP were synthesized in our lab. All other starting chemicals and solvents were purchased from Sigma-Aldrich Company.

Measurements and Instruments. All new compounds were characterized by ^{1}H NMR and ^{13}C-NMR spectroscopy performed on a Bruker ARX-400 spectrometer. Chemical shifts were reported in ppm relative to the singlet of CDCl$_3$ at 7.26 ppm and 77 ppm for ^{1}H-NMR and ^{13}C-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 (Bu$_4$NPF$_6$) 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. The polymer materials used were P3HT, PBDTTT-C and PBDTTDTP, with fullerene derivatives $PC_{70}BM$ and H120. The polymer donor was co-dissolved with the fullerene acceptor in o-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-diiodooctance was used as a solvent additive to further improve the final device performances. ITO-coated glass substrates ($15\Omega/cm^2$) 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 the ITO surface which was pretreated by ultraviolet ozone for 15 min. Low-conductivity PEDOT: PSS was chosen to minimize the measurement error from the 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 (<0.1 ppm O_2 and H_2O). A polymer/fullerene composites 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 ^{o}C for 10 mins. A Ca layer (20 nm) and an Al layer (100 nm) were deposited via thermal evaporation in sequence under 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 mW/cm^2 using a

Newport Thermal Oriel 91192 1000W solar simulator (4 in. × 4 in. beam size). The light intensity was determined by a monosilicon detector calibrated by National Renewable Energy Laboratory (NREL) to minimize spectral mismatch.

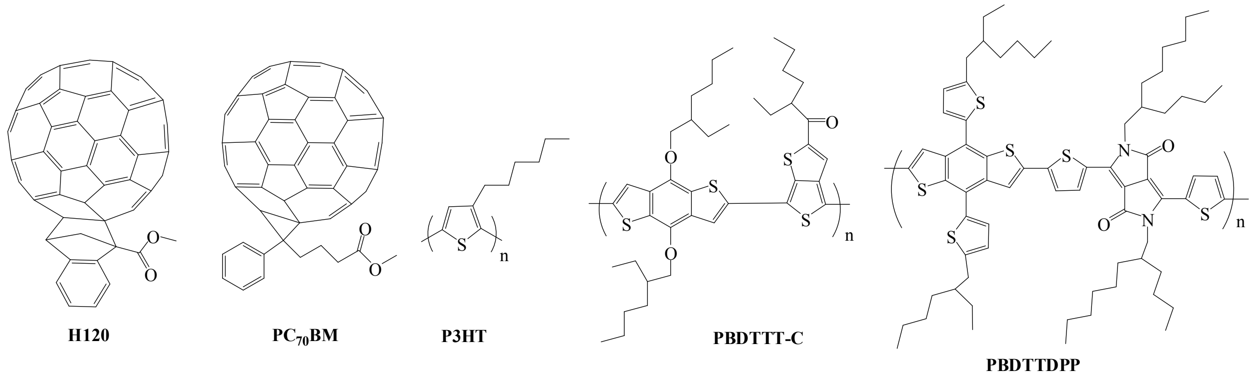
Electron Mobility Testing: Electron mobility is an important parameter of the fullerene acceptor materials for photovoltaic application. Here, we investigated the electron mobility of H120 and $PC_{70}BM$ with the space-charge-limited current (SCLC) model with a device structure of ITO/CsCO3/P3HT:Fullerene derivative (100 nm)/Ca/Al. The electron mobility can be calculated by the following equation:

$$J_{sclc} = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \frac{(V - V_{bi})^2}{L^3}$$

Herein, J_{sclc} stands for current density, L is the thickness of the device, V is the applied potential, V_{bi} is the built-in potential, ε_0 is Vacuum permittivity and its value is 8.85×10^{-12} (F/m), ε_r is the permittivity of the active layer in the device and its value was taken as 3 (F/m), and μ_0 is the electron mobility of the fullerene materials. The results are plotted as log (J_{sclc}) vs. log(V), as shown in **Figure S3**. Electron mobility of H120 and $PC_{70}BM$ are 6.32×10^{-4} $cm^2/V.s$ and 9.55×10^{-4} $cm^2/V.s$ calculated from the intercept of the corresponding lines on the axis of log (J_{sclc}). The results indicate that H120 has slightly lower electron mobility than $PC_{70}BM$.

Synthesis of H120

A solution of methyl 1H-indene-3-carboxylate (1.4 g, 8 mmol) and C70 (0.86 g) in 80 mL dichlorobenzene was heated to reflux for 20 hr, and then cooled to room temperature. The reaction mixture was added drop wise while stirring into 450 mL methanol, the solid was collected and absorbed by silica gel, and purified by a silica gel column using toluene as eluent. The first fraction is the unreacted C_{70} (0.28 g). The second fraction is the compound H120 as a brown solid (0.23 g), yield is 22.6%.). ^{1}H-NMR ($CS_2/CDCl_3$ =3:1, 400MHZ) δ (ppm) 7.87(d, 1H), 7.62(d, 1H), 7.47(m, 2H), 4.83(t, 1H), 4.07(d, 1H), 3.85(s, 3H), 3.12(d, 1H). ^{13}C-NMR ($CS_2/CDCl_3$ =3:1, 400MHZ) δ (ppm):169.79, 155.57, 154.29, 152.85, 147.28, 146.45, 146.33, 146.18, 146.10, 146.00, 145.64, 145.58, 145.47, 145.41, 145.36, 145.28, 145.18, 144.66, 144.58, 144.50, 144.44, 143.22, 143.13, 142.93, 142.80, 142.69, 142.63, 142.31, 142.26, 142.20, 142.11, 142.01, 141.95, 141.73, 140.44, 139.92, 139.81, 139.11, 137.88, 137.62, 137.45, 137.38, 129.06, 128.42, 127.78, 69.32, 56.54, 52.23, 48.72, 47.92. MALDI-TOF for $C_{81}H_{10}O_2$, calculated: 1015.46, analyzed: 1015.23.



Scheme S1. Structures of H120, $PC_{70}BM$, P3HT, PBDTTT-C and PBDTTDPP

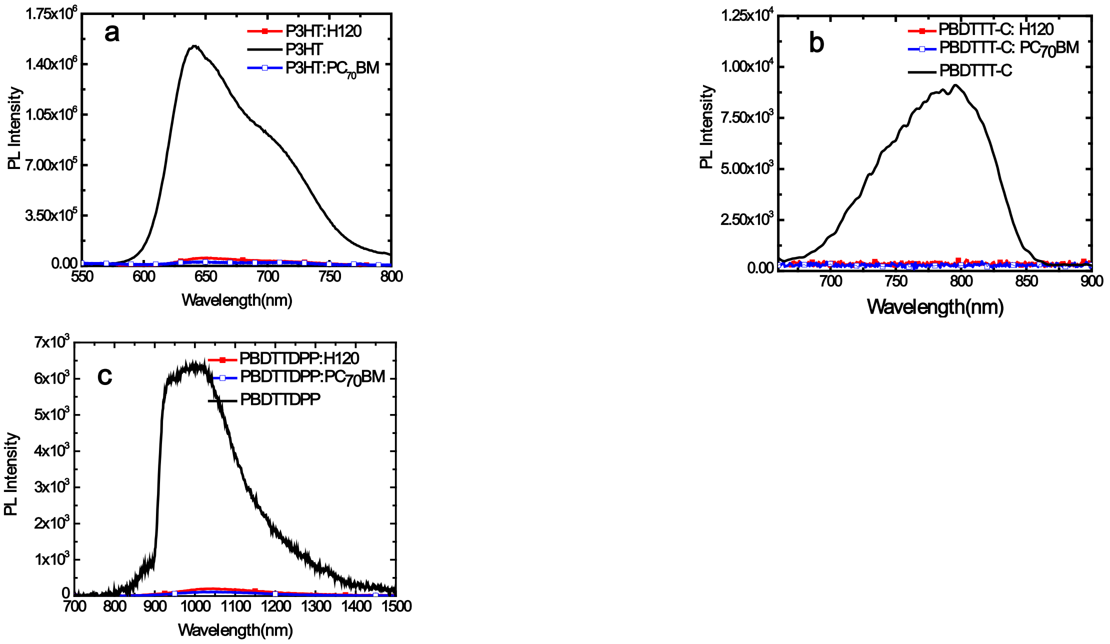


Figure S1. Photoluminescence spectra of the P3HT, PBDTTT-C and PBDTTDPP pure films, and their mixed films with H120 and $PC_{70}BM$.

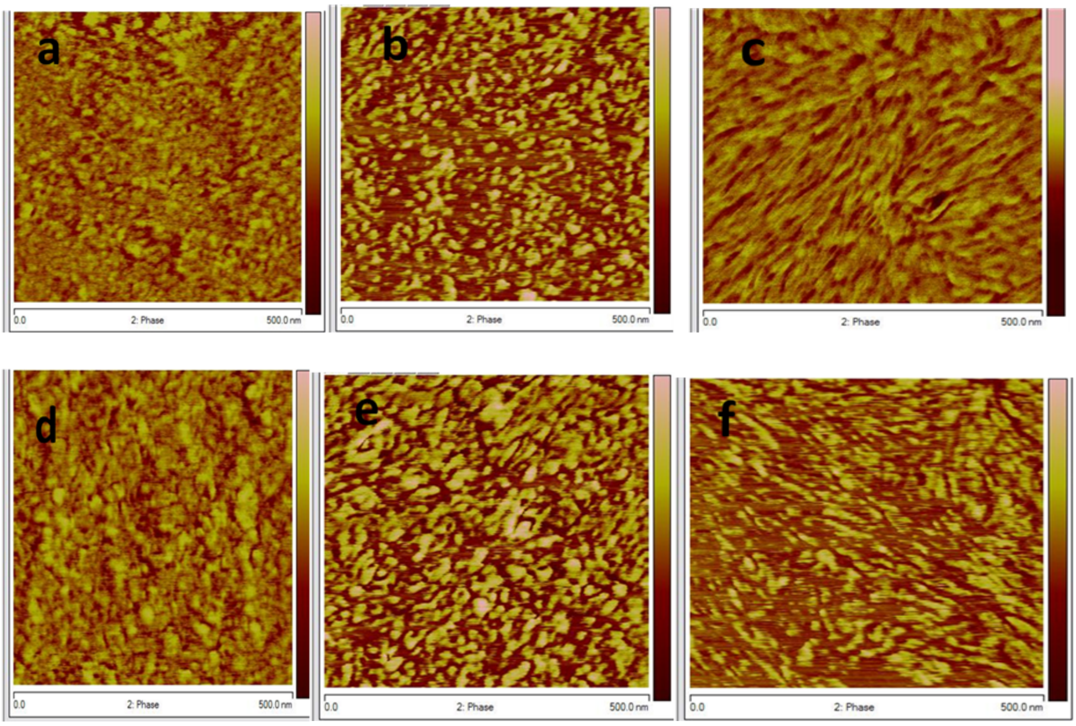


Figure S2. AFM Phase Images of (a)P3HT/ $PC_{70}BM$; (d) P3HT/ H120;(b) PBDTTT-C / $PC_{70}BM$;(e)PBDTTT-C/ H120; (c) PBDTTDPP/ $PC_{70}BM$; (f) PBDTTDPP/H120.

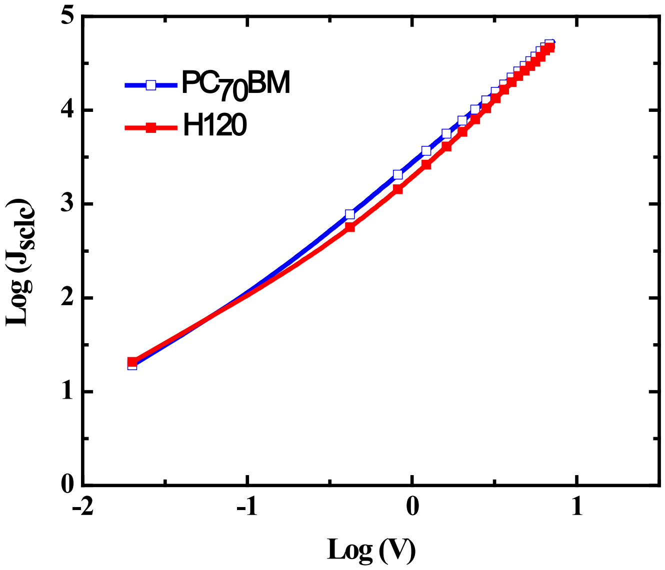


Figure S3. Current-voltage data from the device is ITO/$CsCO_3$/P3HT:Fullerene derivative (100 nm)/Ca/Al, plotted in the format log (J_{sclc}) vs log (V), where J_{sclc} is the current density and V is the applied potential. The line is the fit to the experimental data points.