Supporting Information

Molecular design toward efficient polymer solar cells processed by green solvents

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Materials**:** All chemicals and solvents were reagent grades and purchased from Aldrich, Alfa Aesar and TCI Chemical Co. respectively. (4,8-bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b’] dithiophene-2,6-diyl)bis(trimethylstannane) and 2-triethylene glycol monoether carboxylate -4,6-dibromothieno[3,4-b]thiophene were synthesized by the literature methode [1,2], 4,6-dibromothieno[3,4-b]thiophene-2-carboxylate, $PC_{61}BM$ and $PC_{71}BM$ were purchased from Solarmer Materials Inc.

1-(3-carboxypropyl)-1-phenyl[6,6]C61 acid (*$PC_{61}BA$*): Acetic acid (50mL) and HCl (30 mL) were added to a solution of $PC_{61}BM$ (500 mg, 0.55 mmol) in 100 mL of toluene, and the mixed solution was heated to refluxed for 18 h. After the reaction, the mixture was evaporated, the crude product was treated with methanol, and centrifuged to collect the suspension. This procedure was repeated with diethyl ether, toluene, and twice with diethyl ether, to yield 400 mg (80%) of $PC_{61}BA$.

[6,6]-Phenyl-C61-butyric acid diethylene glycol monoether ($PC_{61}B$-DEG): To a mixture of Dicyclohexylcarbodiimide (DCC, 158 mg, 0.77 mmol), 4-dimethylaminopyridine (DMAP, 39 mg, 0.32 mmol) and $PC_{61}BA$ (570 mg, 0.64 mmol) in dichloromethane (20 ml) and carbon disulfide (20 ml) were added diethylene glycol monoether (84 mg, 0.7 mmol) at room temperature. The reaction mixture was stirred over night and concentrated in vaccum. Deionized Water was added to the residue and extracted with chloroform. The solvent was removed in vacuum and the residue was purified via chromatography with toluene: acetone (10:1, v/v) as eluent to give the expected product (yield: 380 mg, 59%). ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.94 (d, 2H), 7.55 (t, 2H), 7.49 (t, 1H), 4.25 (t, 2H), 3.72 (t, 2H), 3.62 (t, 2H), 3.55 (t, 2H), 3.38 (s, 3H), 2.92 (t, 2H), 2.55 (t, 2H), 2.18 (t, 2H). ^{13}C-NMR (400 MHz, $CDCl_3$), δ (ppm): 173.06, 148.84, 147.83, 145.21, 145.17, 145.10, 145.01, 144.81, 144.69, 144.53, 144.45, 144.03, 143.78, 143.01, 142.95, 142.26, 142.20, 142.15, 140.77, 138.07, 137.59, 132.12, 128.45, 128.26, 79.90, 77.22, 71.91, 70.52, 59.12, 51.90, 34.00, 33.68, 30.93, 22.37. Elemental analysis calcd (%) for $C_{76}H_{23}O_4$: C 91.28, H 2.32; found: C 91.36, H 2.38. m/z = 999.

[6,6]-Phenyl-C61-butyric acid triethylene glycol monoether (PC$_{61}$B-TEG): Compound was prepared via the same method as that for the synthesis of PC$_{61}$B-DEG except the triethylene glycol monoether was used instead of diethylene glycol monoether (yield: 65%). ^{1}H-NMR (400 MHz, CDCl$_3$), δ (ppm): 7.95 (d, 2H), 7.57 (t, 2H), 7.49 (t, 1H), 4.24 (t, 2H), 3.70 (t, 2H), 3.67 (t, 2H), 3.64 (t, 2H), 3.56 (t, 2H), 3.53 (t, 2H), 3.37 (s, 3H), 2.92 (t, 2H), 2.57 (t, 2H), 2.21 (t, 2H). ^{13}C-NMR (400 MHz, CDCl$_3$), δ (ppm): 173.05, 148.84, 147.83, 145.87, 145.21, 145.10, 144.81, 144.69, 144.44, 144.03, 143.78, 143.01, 142.95, 142.26, 142.20, 142.15, 141.01, 138.07, 137.59, 136.75, 132.12, 128.46, 128.26, 79.90, 77.22, 71.95, 70.61, 69.14, 63.68, 59.08, 51.90, 33.98, 33.68, 30.93, 22.36. Elemental analysis calcd (%) for $C_{76}H_{23}O_4$: C 89.73, H 2.61; found: C 89.68, H 2.54. m/z = 1043.

[6,6]-Phenyl-C61-butyric acid dipropylene glycol monomethyl ether (PC$_{61}$B-DPG): Compound was prepared via the same method as that for the synthesis of PC$_{61}$B-DEG except the dipropylene glycol monomethyl ether was used instead of diethylene glycol monoether (yield: 49%). ^{1}H-NMR (400 MHz, CDCl$_3$), δ (ppm): 7.95 (d, 2H), 7.56 (t, 2H), 7.49 (t, 1H), 4.21 (d, 2H), 3.88 (m, 1H), 3.70 (d, 2H), 3.66 (m, 1H), 3.36 (s, 3H), 2.90 (t, 2H), 2.63 (t, 2H), 2.20 (t, 2H), 1.93 (m, 3H), 1.82 (m, 3H). ^{13}C-NMR (400 MHz, CDCl$_3$), δ (ppm): 173.12, 153.93, 148.84, 147.87, 145.88, 145.21, 145.16, 145.09, 144.81, 144.76, 144.67, 144.52, 144.44, 144.02, 143.78, 143.05, 142.95,

142.23, 142.20, 141.00, 138.07, 137.59, 136.79, 128.47, 128.26, 79.94, 77.23, 52.00, 49.76, 35.67, 33.79, 32.80, 30.93, 30.17, 26.39, 25.32, 22.83. Elemental analysis calcd (%) for $C_{78}H_{27}O_4$: C 91.13, H 2.65; found: C 91.10, H 2.62. m/z = 1027.

[6,6]-Phenyl-C61-butyric acid tripropylene glycol monomethyl ether ($PC_{61}B$-TPG): Compound was prepared via the same method as that for the synthesis of $PC_{61}B$-DEG except the tripropylene glycol monomethyl ether was used instead of diethylene glycol monoether (yield: 52%). ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.95 (d, 2H), 7.56 (t, 2H), 7.48 (t, 1H), 4.21 (d, 2H), 3.91 (m, 1H), 3.88 (m, 1H), 3.76 (m, 1H), 3.70 (d, 2H), 3.64 (t, 2H), 3.38 (s, 3H), 2.92 (t, 2H), 2.65 (t, 2H), 2.20 (t, 2H), 1.96 (m, 3H), 1.83 (m, 3H), 1.75 (m, 3H). ^{13}C-NMR (400 MHz, $CDCl_3$), δ (ppm): 173.12, 153.95, 148.83, 147.87, 145.88, 145.21, 145.09, 144.81, 144.76, 144.68, 144.02, 143.78, 143.15, 143.01, 142.95, 142.23, 142.15, 141.01, 140.77, 138.07, 137.59, 136.79, 132.12, 128.48, 128.26, 79.94, 77.24, 56.33, 52.00, 49.75, 35.68, 34.36, 33.80, 32.81, 30.98, 30.94, 26.40, 25.33, 24.74, 22.83. Elemental analysis calcd (%) for $C_{81}H_{33}O_5$: C 89.57, H 3.06; found: C 89.66, H 3.13. m/z = 1085.

[6,6]-Phenyl-C71-butyric acid diethylene glycol monoether ($PC_{71}B$-DEG): Compound was prepared via the same method as that for the synthesis of $PC_{61}B$-DEG except the $PC_{71}BA$ was used instead of $PC_{61}BA$ (yield: 62%). ^{1}H-NMR (400 MHz, $CDCl_3$), δ (ppm): 7.91 (d, 2H), 7.53 (t, 2H), 7.43 (t, 1H), 4.30 (t, 2H), 3.71 (t, 2H),

3.68 (t, 2H), 3.57 (t, 2H), 3.40 (s, 3H), 2.51 (t, 2H), 2.48 (t, 2H), 2.17 (t, 2H). ^{13}C-NMR (400 MHz, CDCl$_3$), δ (ppm): 172.99, 156.00, 155.28, 152.17, 151.94, 151.50, 151.14, 150.90, 150.54, 149.44, 149.15, 148.85, 148.58, 148.43, 147.98, 147.58, 147.38, 146.87, 145.94, 144.90, 144.10, 143.94, 143.76, 143.36, 142.66, 141.75, 140.96, 139.30, 138.92, 137.30, 134.02, 133.85, 132.85, 131.62, 130.78, 128.94, 79.94, 77.24, 71.92, 70.53, 59.14, 35.93, 34.11, 33.92, 30.94, 21.69. Elemental analysis calcd (%) for $C_{86}H_{33}O_5$: C 92.22, H 2.07; found: C 91.98, H 1.98. m/z = 1119.

Polymerization of PBDTTT-S-TEG: 4,8-bis(5-((2-ethylhexyl)thio)thiophen-2-yl)benzo[1,2-b:4,5-b'] dithiophene-2,6-diyl)bis(trimethylstannane) (0.29g, 0.3 mmol), 2-triethylene glycol monoether-4,6- dibromo-3-fluorothieno [3,4-b]thiophene-2-carboxylate (0.146g, 0.3 mmol), dry toluene (8 ml) and dry DMF (1.5 ml) were added to a 50 mL double-neck round-bottom flask. The reaction container was purged with argon for 20 min to remove O_2, and then Pd $(PPh_3)_4$ (20 mg) was added. After another flushing with argon for 20 min, the reactant was heated to reflux for 40 h. The reactant was cooled down to room temperature and poured into n-Hexane (200 mL), then centrifuged to get dark brown solid. The solid was dried under vacuum. Yield: 146 mg (65%). Elemental analysis calcd (%) for $C_{32}H_{24}O_5S_8$: C 51.59, H 3.25. found: C 51.46, H 3.19.

Devices fabrication and characterization: Polymer solar cell devices with the structure of ITO/PEDOT-PSS/PBDTTT-S-TEG:fullerene derivatives/Ca/Al were fabricated under conditions as follows: patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10-15 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After oxygen plasma cleaning for 10 min, a 40 nm thick poly (3, 4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast onto the ITO substrate and then dried by baking in an oven at 150 ^{o}C for 15 min. The active layer, with a thickness in the range of 80-100 nm, was then deposited on top of the PEDOT: PSS layer by spin-coating from a 15 mg ml^{-1} blend solution of PBDTTT-TEG and fullerene derivatives, followed by the common methanol treatment.[3] The thickness of the active layer was controlled by changing the spin speed during the spin-coating process and measured on an BRUKER DEKTAK XT profilometer. Finally, 20 nm Ca and 100 nm Al layer were successively deposited in vacuum onto the active layer at a pressure of ca. 3×10^{-4} Pa. The overlapping area between the cathode and anode defined a pixel size of 4 mm^2. Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of nitrogen drybox containing less than 5 ppm oxygen and moisture. The mobility was measured by the space charge limited current (SCLC) method by a hole-only device with a structure of ITO/PEDOT: PSS/Active layer/Au or an electron-only device with a structure of ITO/TIPD/Active layer/Al and estimated through the Mott-Gurney equation.

Instruments:

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker arx-400 spectrometer. Absorption spectra were taken on a Hitachi U-3010 UV-Vis spectrophotometer. The molecular weight of polymers was measured by GPC method, and polystyrene was used as a standard with THF as eluent. TGA measurement was performed on a Perkin Elmer TGA 4000. DSC measurement was performed on a Mettler Toledo DSC 1. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with glassy carbon disk, Pt wire, and Ag/Ag^{+} electrode as working electrode, counter electrode, and reference electrode respectively in a 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. AFM measurements were performed on Bruker veeco MultiMode 8 Atomic Force Microscope. TEM images were obtained from a JEOL 2200FS instrument at 160 kV accelerating voltage in bright field mode . The power conversion efficiencies of the resulting polymer solar cells were measured under 1 sun, AM 1.5G (air mass 1.5

global) (100 mW cm^{-2}) using a XES-70S1 (SAN-EI ELECTRIC CO., LTD.) solar simulator (AAA grade, 70 mm x 70 mm photo-beam size). 2 x 2 cm^2 Monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology CO., Ltd.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

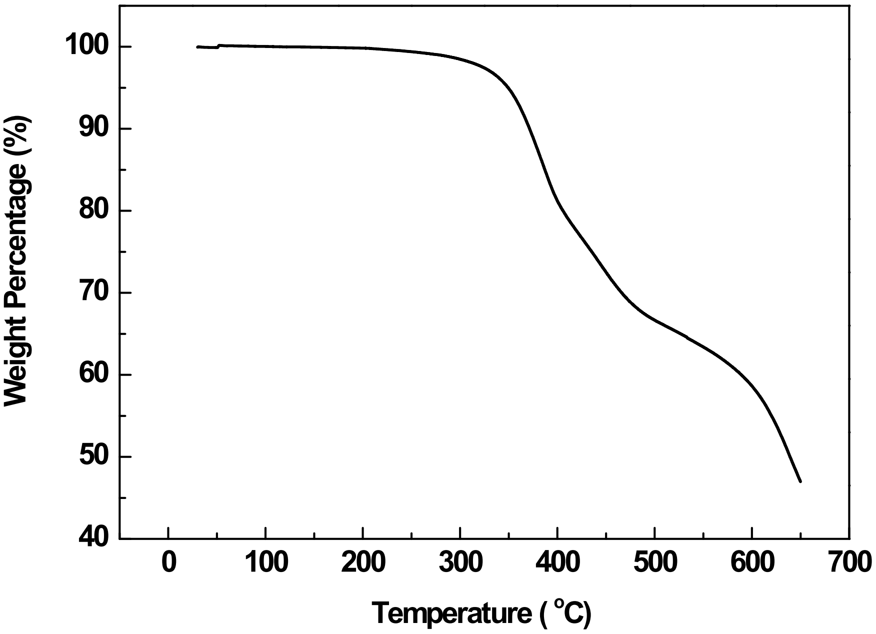

Figure S1. TGA measurements of PBDTTT-S-TEG with 5 ℃ min^{-1} under inert atmosphere.

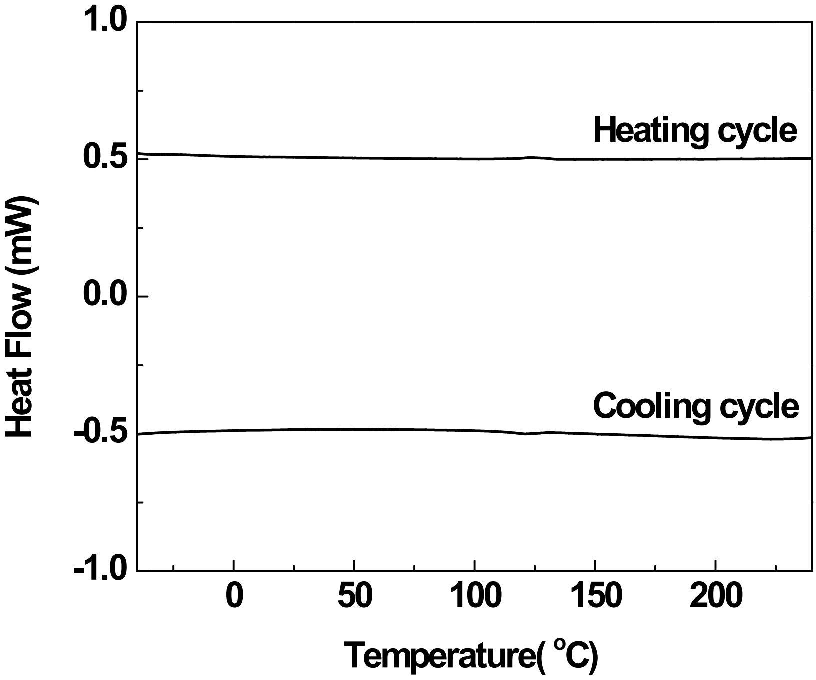

Figure S2. DSC thermogram of the PBDTTT-S-TEG under inert atmosphere at the rate of 10 °C min^{-1}.

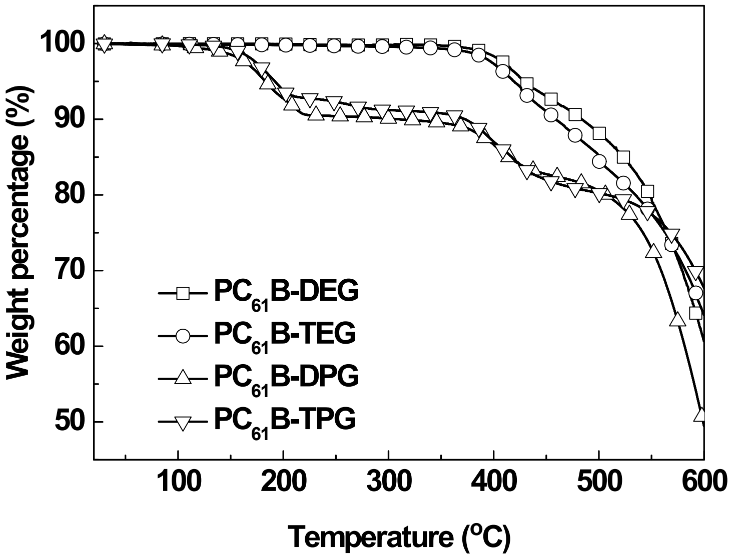

Figure S3. TGA measurements of C[60] derivatives with 5 ℃ min^{-1} under inert atmosphere.

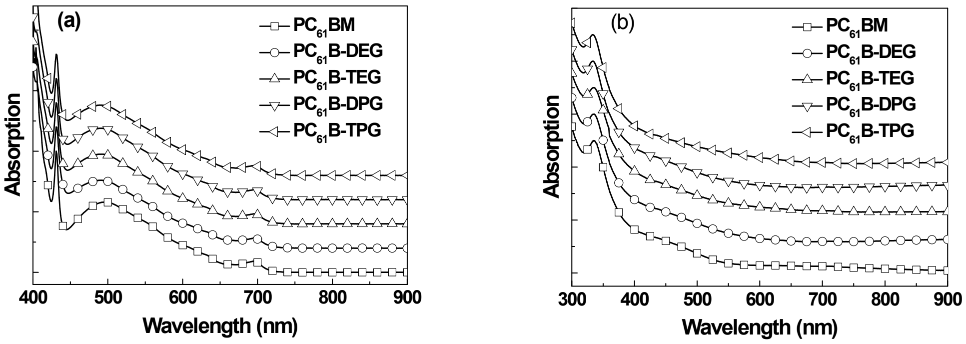

Figure S4. The absorption spectra of the C[60] fullerene derivatives used in this work a) in chloroform and b) in the solid films casted from chloroform solution.

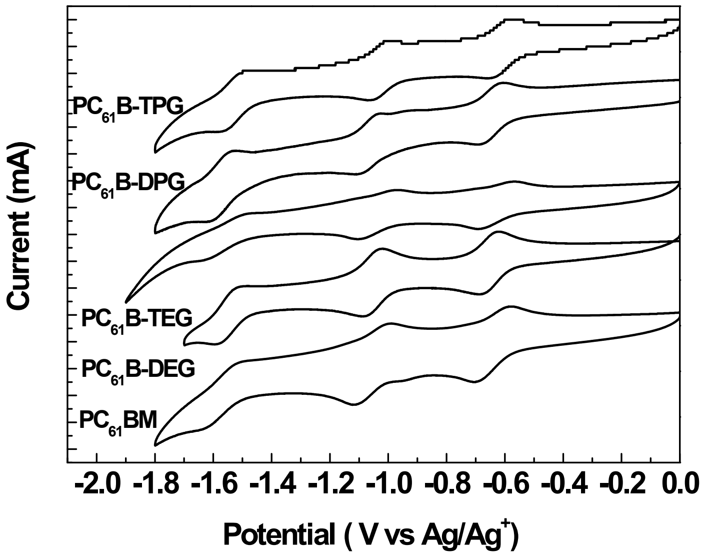

Figure S5. Cyclic voltammograms of C[60] derivatives in a mixed solution of o-DCB/acetonitrile (2:1, *v/v*) with 0.1 M Bu_4NPF_6 at 20 mV s^{-1}.

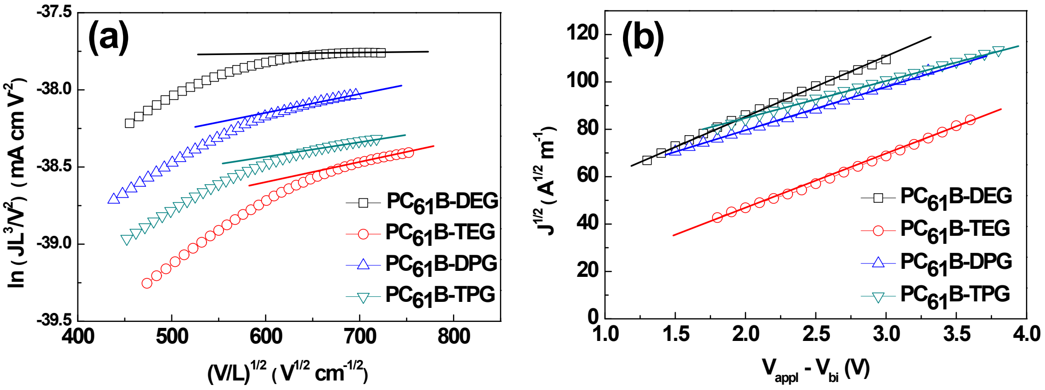

Figure S6. (a) the hole mobility and (b) electron mobility of the blend film based on PBDTT-S-TEG/C[60] derivatives, respectively.

Table S1. Charge carrier mobility of the blend film based on PBDTTT-S-TEG/C[60] derivatives in different solution processing conditions.

Processing solvents	Acceptor	Hole mobility (cm^2 V^{-1} s^{-1})	Electron mobility (cm^2 V^{-1} s^{-1})
o-DCB	$PC_{61}B$-DEG	1.36 x 10^{-4}	1.56 x 10^{-4}
	$PC_{61}B$-TEG	3.12 x 10^{-5}	0.85 x 10^{-4}
	$PC_{61}B$-DPG	4.80 x 10^{-5}	0.72 x 10^{-4}
	$PC_{61}B$-TPG	2.50 x 10^{-5}	4.67 x 10^{-5}
Anisole	$PC_{61}B$-DEG	1.33 x 10^{-4}	2.27 x 10^{-4}

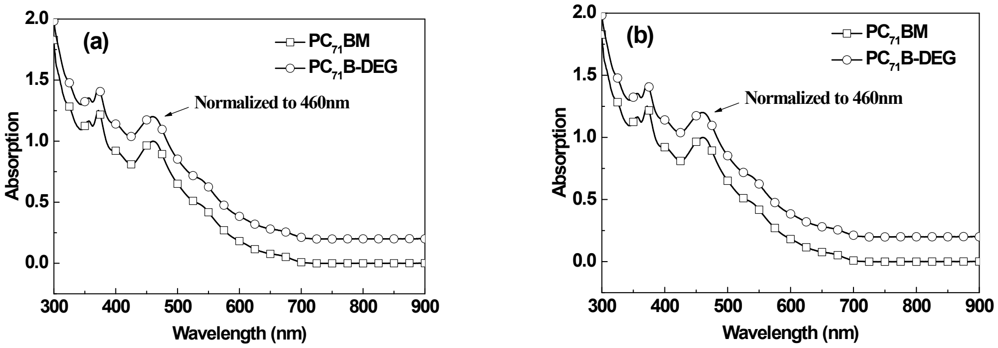

Figure S7. the UV-vis absorption spectra of the C[70] derivatives (a) in chloroform solution and (b) in solid films.

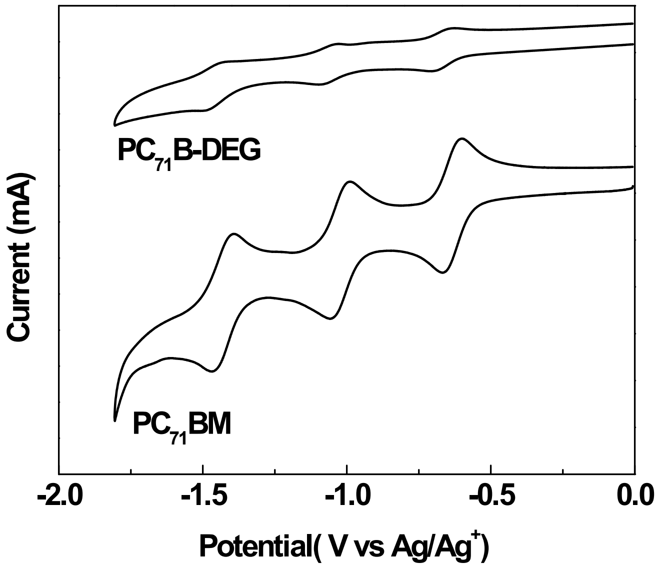

Figure S8. the CV measurement of C[70] derivatives in a mixed solution of o-DCB/acetonitrile (2:1, *v/v*) with 0.1 M Bu_4NPF_6 at 20 mV s^{-1}.

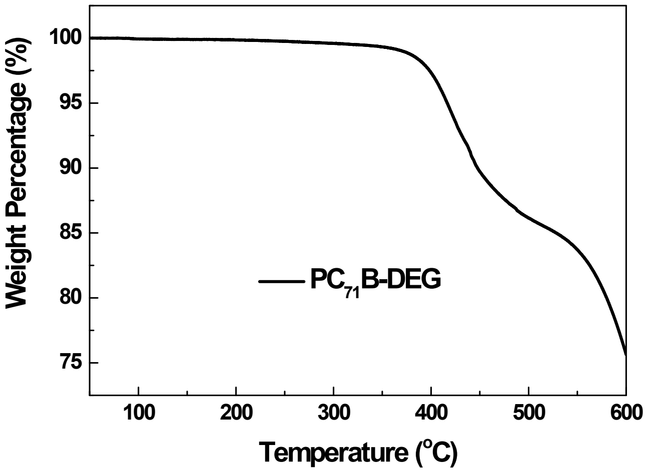

Figure S9. TGA measurements of $PC_{71}B$-DEG with 5 ℃ min^{-1} under inert atmosphere.

Table S2. Device performance in DCB or anisole processing as applying C[70] fullerene derivatives as acceptor.

Acceptor	Processing solvents	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%) best	PCE (%) average
$PC_{71}BM$	DCB	0.748	13.81	46.23	4.77	4.60
$PC_{71}B$-DEG	DCB	0.746	12.91	47.26	4.55	4.50
	Anisole	0.746	12.41	48.57	4.50	4.46

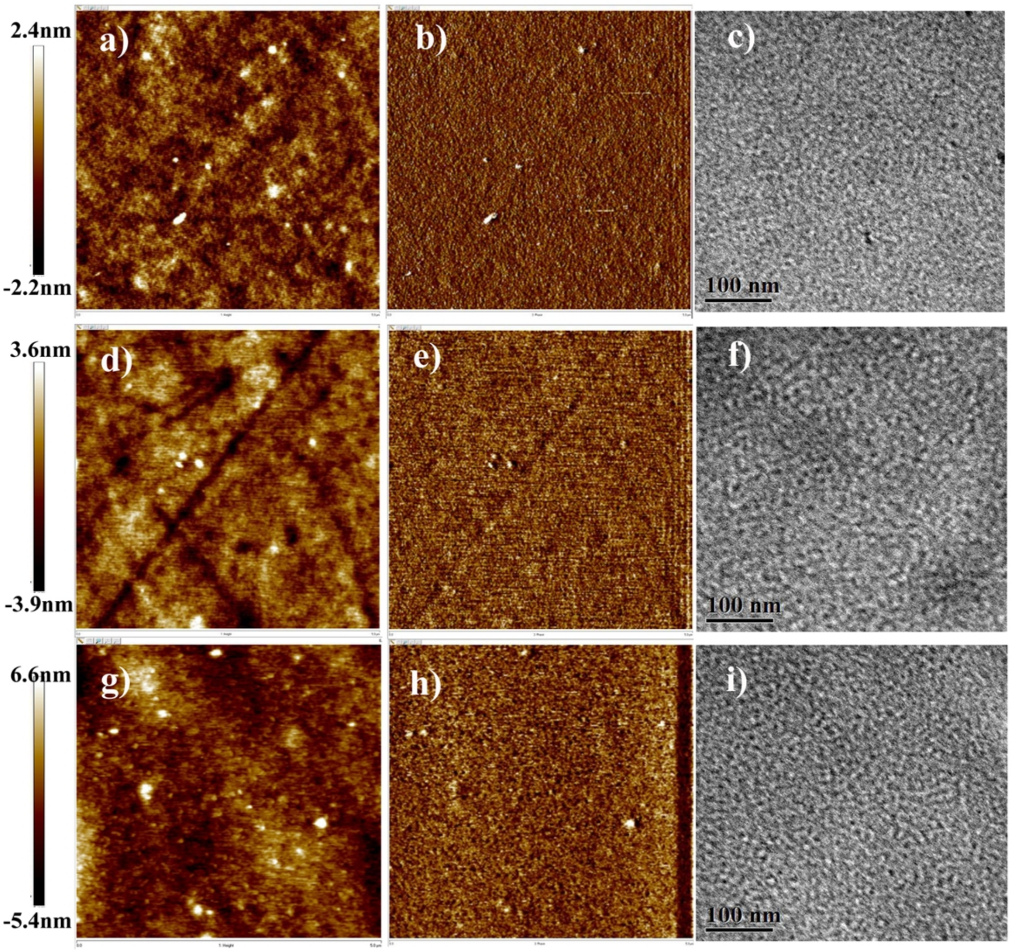

Figure S10. morphology investigation of (a-c) the blend film based on PBDTTT-S-TEG/ $PC_{71}BM$ processed with *o*-DCB and the blend films based on PBDTTT-S-TEG/ $PC_{71}B$-DEG processed with (d-f) *o*-DCB and (g-i) anisole, respectively.

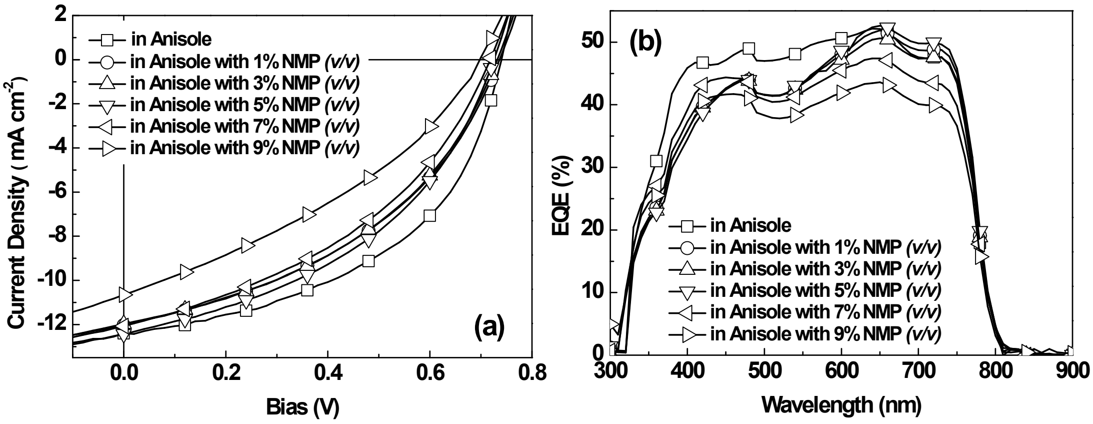

Figure S11. (a) I-V curves of the device based on PBDTTT-S-TEG/ $PC_{71}B$-DEG fabricated from anisole solution with different NMP amounts as additive and (b) the corresponding EQE measurements.

Table S3. the photovoltaic performance of the devices based on PBDTT-S-TEG/ $PC_{71}B$-DEG casted from anisole with different amounts of additives.

additive	amount (*v/v*)	V_{oc} (V)	J_{sc} (mA cm-2)	FF (%)	PCE (%)
NMP	N/A	0.746	12.41	48.57	4.50
NMP	1%	0.737	12.02	41.97	3.71
NMP	3%	0.732	11.99	42.16	3.70
NMP	5%	0.725	12.43	43.23	3.90
NMP	7%	0.718	12.07	40.38	3.50
NMP	9%	0.698	10.64	35.31	2.62
DIO	5%	0.734	12.49	42.02	3.86
DT	5%	0.739	11.52	41.24	3.51

[1] C. H. Cui, W. Y. Wong, Y. F. Li, *Energy Environ. Sci.* **2014**, *7,* 2276.

[2] Y. Chen, S. Q. Zhang, Y. Wu, J. H. Hou, *Adv. Mater.* **2014**, 26, 2744.

[3] H. Zhou, Y. Zhang, J. Seifter, S. D. Collins, C. Luo, G. C. Bazan, T. Nguyen, A. J. Heeger, *Adv. Mater.* **2013**, *25*, 1646.