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Supplementary Information

Effects of morphology evolution on solution-processed small molecule photovoltaics via solvent additive

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Experimental Section

Instruments

The synthesized compounds were characterized with 1H NMR spectra obtained using a Bruker DPX-300 NMR Spectrometer. UV-visible absorption was performed with a Lambda 20 (Perkin Elmer) diode array spectrophotometer. Thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere at a heating rate of 10 °C/min with a Dupont 9900 analyzer. Cyclic voltammetry (CV) was performed using a Power Lab/AD instrument model system in 0.1M solution of tetrabutylammonium hexafluorophospate (Bu4NPF6) in anhydrous acetonitrile as supporting electrolyte at a scan rate of 50 mV/s. A glassy carbon disk (~0.05 cm^2) coated with a thin polymer film, an Ag/AgNO$_3$ electrode, and a platinum wire were used as working electrode, reference electrode, and counter electrode, respectively. Density functional theory (DTF) calculation was carried out for the model compound using the DMol 3 software. In the DMol 3 electronic structure calculations, the all-electron treatment and double numerical polarized (DNP) basis sets were chosen. The density function was treated with the B3LYP hybrid functional. The alpha step surface profilometer (KLA-Tencor USA) was employed for thicknesses measurement. Bright field TEM images of optimized devices were acquired by using a JEOL JEM-2200FS. X-Ray photoelectron spectroscopy (XPS) data was obtanined on a Kratos Axis Nova instrument using 150W Al-K$_\alpha$ radiation at a base pressure of 5 x 10^{-9} torr.

Fabrication and measurment of the organic photovoltaics

In this study, devices were fabricated with the conventional architecture Glass/ITO/PEDOT:PSS/Photoactive Layer/Ca/Al. First of all, ITO patterned glass substrates were cleaned three times using micro-90 cleaning detergent in deionized water, followed by acetone and IPA. These ultrasonically cleaned glass substrates were placed overnight in an oven at 140 °C. Solutions of photoactive materials were prepared with the BDTT-2DPPBFu small molecule to PC$_{71}$BM acceptor in chloroform as processing solvent. The photoactive solution was stirred over 3 h at 50 ^oC for thorough intermixing of donor and acceptor. Glass/ITO substrates were treated in UV-ozone for 15min followed by the spin coating of PEDOT:PSS (AI4083, HERAEUS) at 3000rpm for 60 seconds to get a uniform thickness of 30nm. Substrates were annealed at 150 ^oC for 20minutes before transfer to the nitrogen gas filled glove box, where the photoactive solution was spin coated to get an average thickness of 100nm. Finally, after drying of the photo-active film, these substrates were transferred to the metal deposition chamber to deposit top electrodes. 2nm of calcium (Ca) and 100nm of aluminium (Al) were thermally evaporated under ~ 10^{-6} torr vacuum to get the final/top electrode. The 9mm^2 area of the device was defined by using the aperture.

Photovoltaic properties were characterized under simulated 100 mW/cm^2 AM 1.5G irradiation from a xenon arc lamp with an AM 1.5 global filter. The Simulator (Newport) intensity was set using an NREL-certified silicon diode with an integrated KG5 optical filter. The current density-voltage characteristics of devices are measured using a computer-controlled Keithley 236 source measure unit (Keithley Instruments). The EQE was measured by K3100 spectral IPCE measurement system (McScience, South Korea). All device measurements were carried out in air at room temperature.

SCLC devices fabrication and testing

Mobility measurements of small molecule/$PC_{71}BM$ (w/w, 1.0:1.0) blends were done by a charge-only space-charge limited current (SCLC) method with the following diode structures: ITO/PEDOT:PSS/active layer/Au for hole-only devices and Al/active layer/Al for electron-only devices by taking current-voltage measurements and fitting the results to a space-charge limited form. The charge carrier mobilities were calculated using the SCLC model, where the SCLC is described by: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where J is the current density, L is the film thickness of the active layer, μ_0 is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), V is the internal voltage in the device, and $V = V_{appl} - V_r - V_{bi}$, where

V_{appl} is the applied voltage to the device, V_{r} is the voltage drop due to contact resistance and series resistance between the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

Impedance spectroscopy analysis

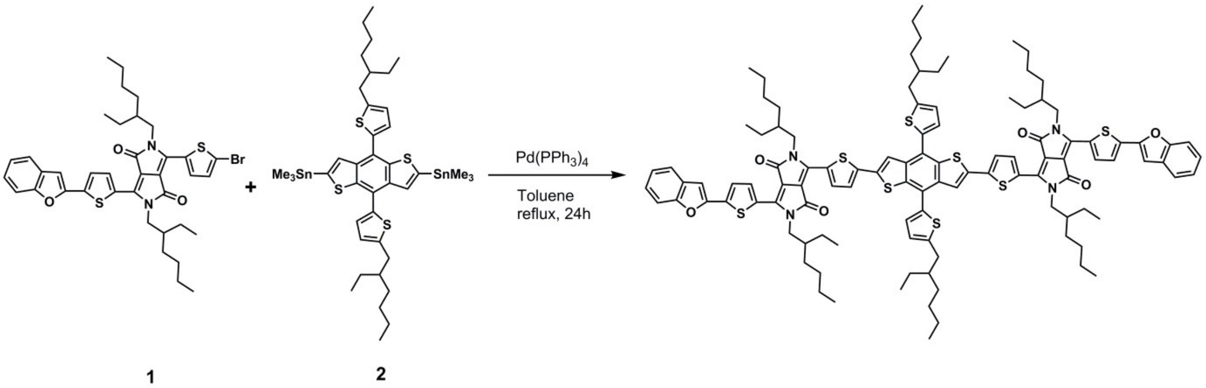
Impedance measurements were conducted with an IviumStat instrument (Ivium Technologies) equipped with a four-wire impedance test interface (in a tow-prove configuration). The impedance response was measured over the range of 1Hz to 30MHz with an oscillation amplitude of 10mV. The impedance was recorded under illumination with a xenon lamp (1 Sun) under open-circuit conditions.

Synchrotron X-ray diffraction analysis

Grazing-incidence wide angle X-ray Scattering (GIWAXS) measurements were conducted at PLS-II 3C beamline of Pohang Acceleartor Laboratory (PAL) in Korea. The X-rays coming from the in-vacuum undulator (IVU) are monochromated using Si(111) double crystals and focused at the detector position using K-B type mirrors. GIWAXS patterns were recorded with a 2D CCD detector (Rayonix SX165) and X-ray irradiation time was 2 ~ 120 seconds dependent on the saturation level of detector. The incidence angle (0.1 ~ 0.14$^{\mathrm{o}}$) was carefully selected to allow for complete penetration of the X-rays into the film.

Materials

All chemicals and solvents were purchased from Aldrich and were used without further purification. The materials 3-(5-(benzofuran-2-yl)thiophen-2-yl)-6-(5-bromothiophen-2-yl)-2-(2-ethylheptyl)-5-(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (1)[1] and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (2)[2] were prepared with previously described methods.



Scheme S1. Synthesis details of small molecule electron donor, BDTT-2DPPBFu.

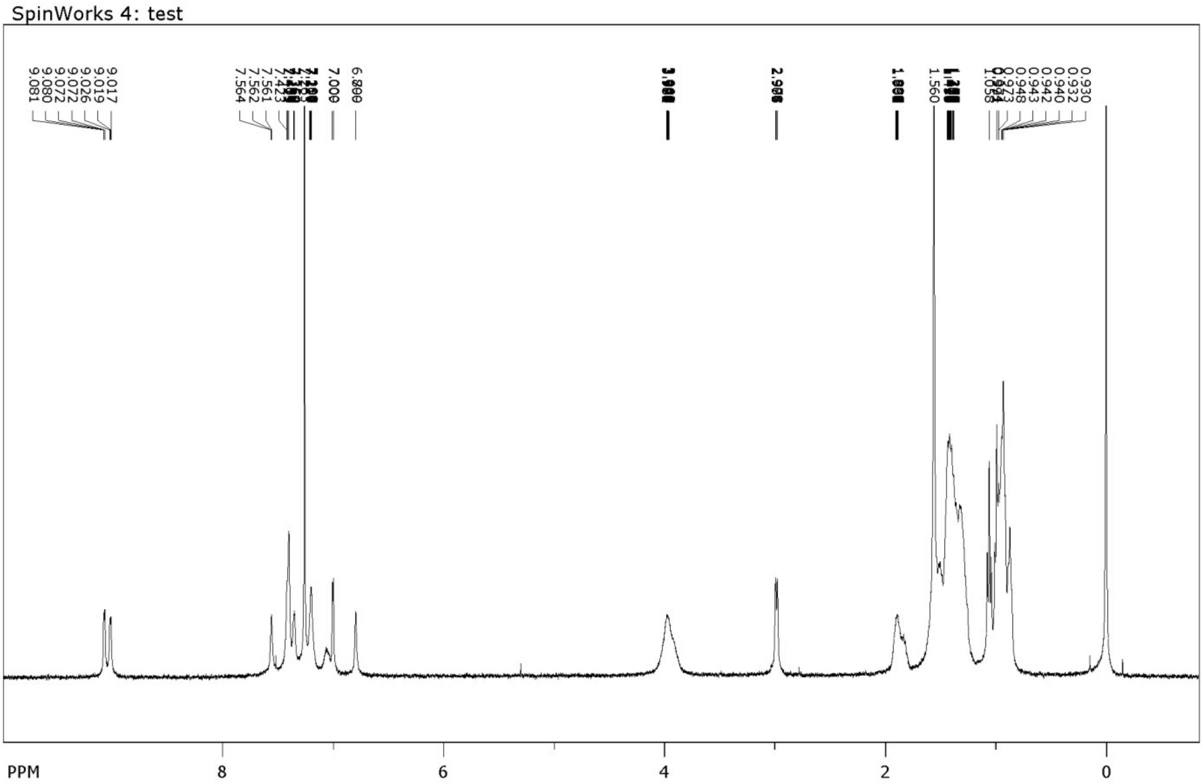
BDTT-2DPPBFu

Compound 1 (191 mg, 0.26 mmol) and compound 2 (114 mg, 0.13 mmol) in toluene (8 mL) were purged by argon for 20 min, and then $Pd(PPh_3)_4$ (10 mg) was added. After being purged for another 20 min, the mixture was stirred and heated to reflux for 8 h. After cooled to room temperature, the solution was poured into water (20 mL) with vigorous stirring and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$ and then rotary evaporated to remove the solvent. The crude product was purified by column chromatography on silica gel affording blue solid as pure product (155 mg, 66 %).

^1H NMR (400 MHz, $CDCl_3$): δ 9.08 (dd, *J* = 21.79Hz, 3.32Hz, 4H), 7.56 (s, 2H), 7.40 (s, 8H), 7.35 (s, 2H), 7.20 (s, 2H), 7.06 (s, 2H), 7.01 (d, *J* = 2.94Hz, 2H), 6.90 (s, 2H), 3.96 (s, 8H), 2.99 (d, *J* = 6.66Hz, 4H), 1.89 (m, 4H), 1.50 (m, 2H), 1.08-0.87 (m, 84H)

^{13}C NMR (400 MHz, $CDCl_3$): δ 165.11, 156.08, 155.57, 143.44, 142.93, 142.67, 138.40, 138.15, 136.32, 135.47, 133.69, 132.52, 132.03, 131.28, 129.35, 128.73, 127.97, 126.80, 125.94, 124.71, 123.36, 120.96, 119.44, 113.66, 111.50, 102.74, 49.53, 41.89, 37.93, 35.24, 32.28, 32.15, 29.60, 29.38, 26.10, 25.37, 23.04, 14.16, 11.94, 11.63 90.79

m/z (MALDI-TOF) 1856.72 ca lcd. for $C_{110}H_{126}N_4O_6S_8$ 1855.75



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(2) J. Zhou, Y. Zuo, X. Wan, G. Long, Q. Zhang, W. Ni, Y. Liu, Z. Li, G. He, C. Li, B. Kan, M. Li, and Y. Chen, *J. Am. Chem. Soc*., 2013, **135**, 8484-8487.

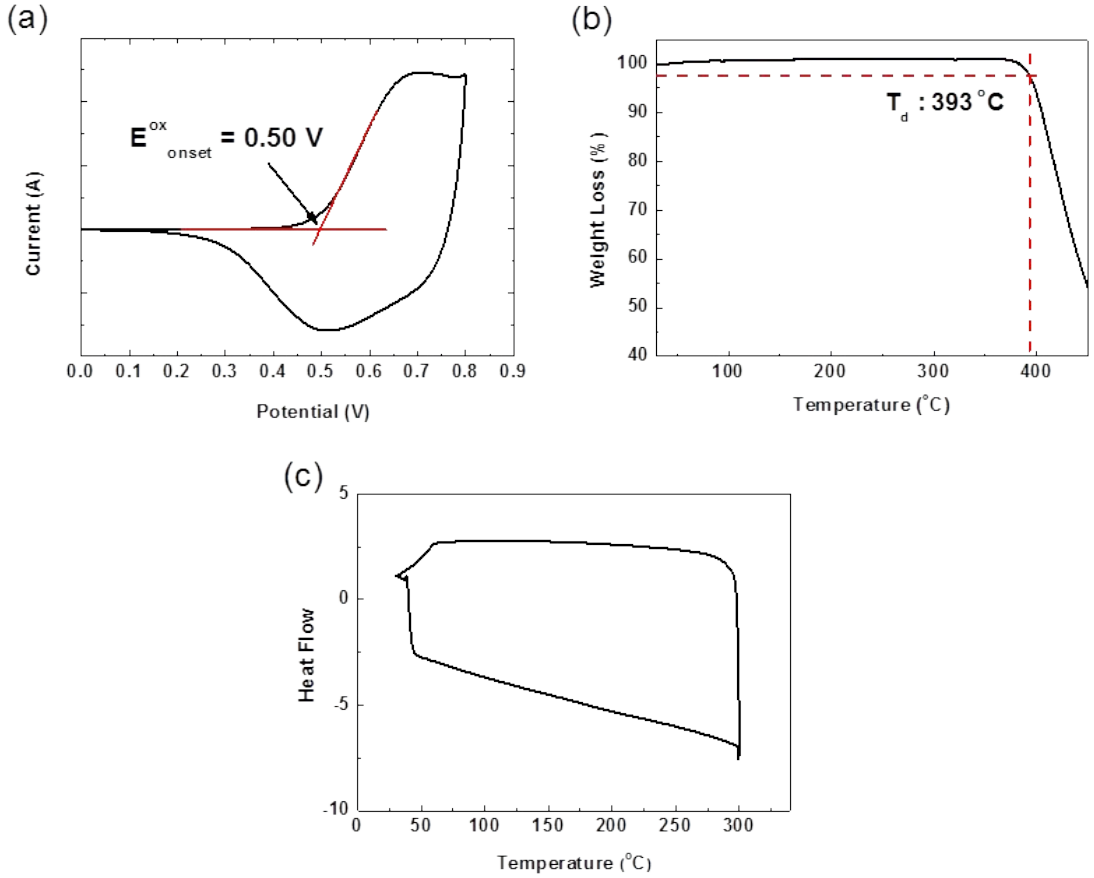

Fig. S1. The BDTT-2DPPBFu small molecule for (a) CV (b) TGA, (c) DSC.

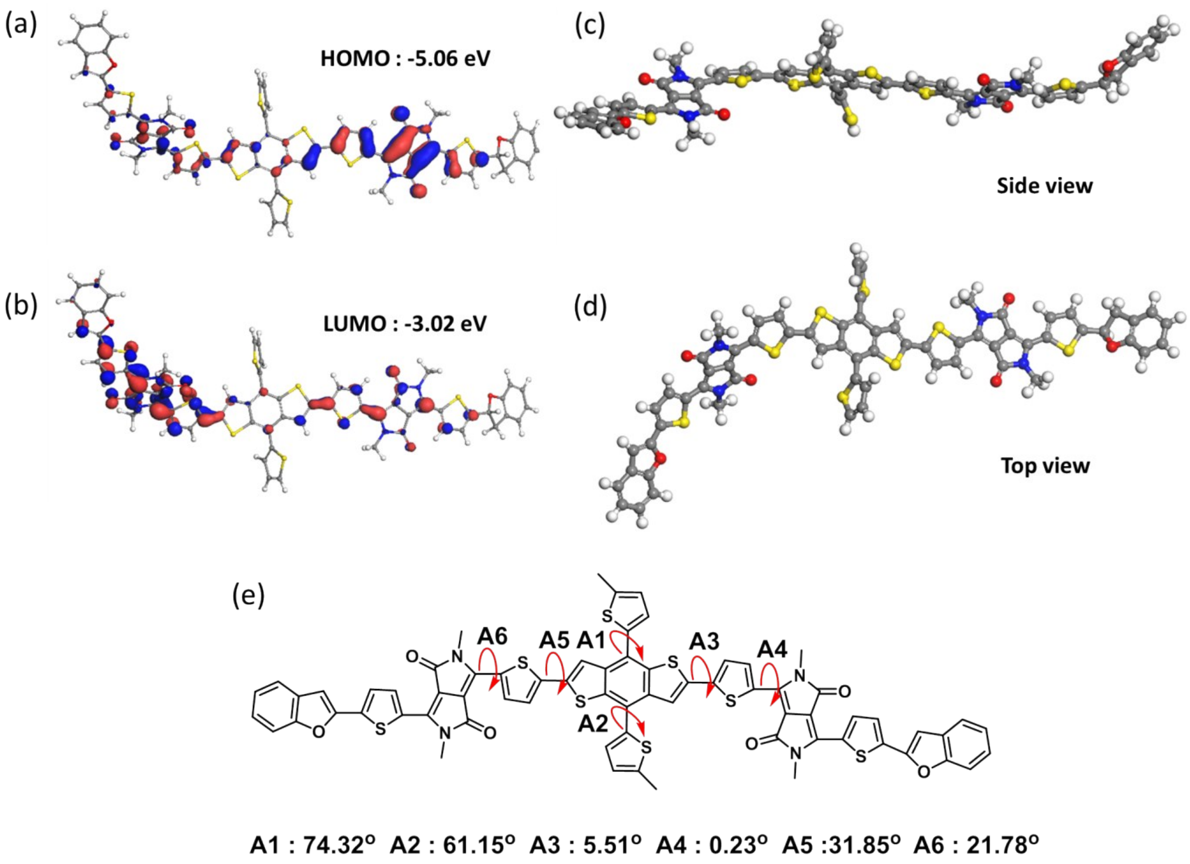

Fig. S2 Electron density of (a) HOMO and (b) LUMO optimized molecular geometries. (c) Side, (d) top view and (e) dihedral angle for the BDTT-2DPPBFu small molecule by DFT calculation.

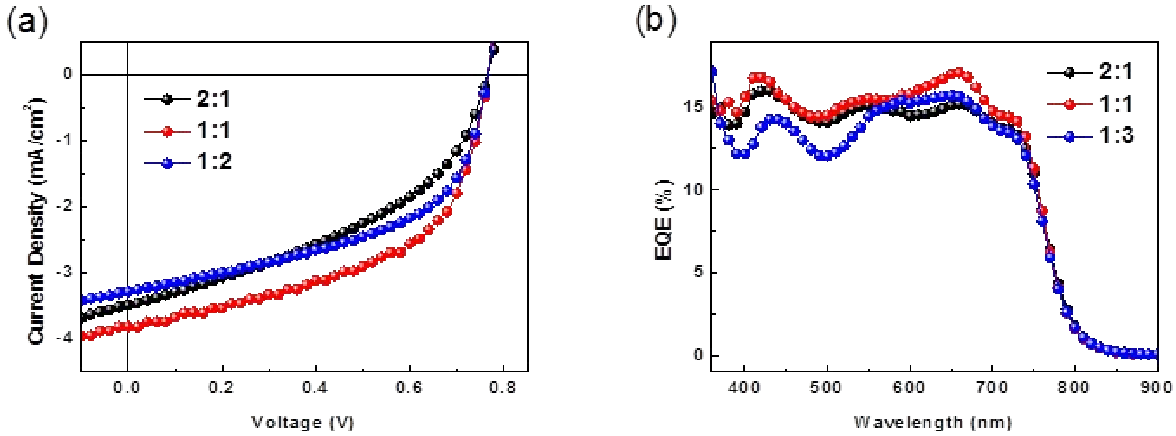

Fig. S3 Results of solar cells with different weight ratios (a) *J-V* characteristics and EQE curves.

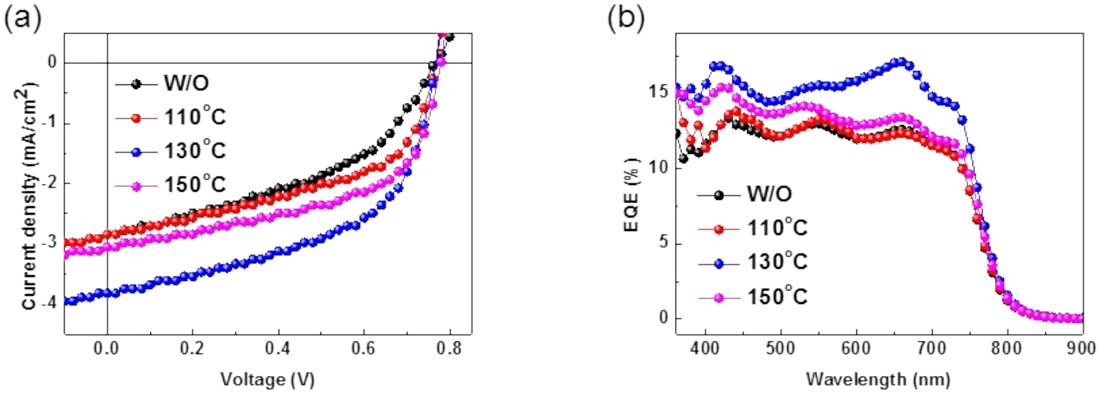

Fig. S4 (a) *J-V* and (b) EQE curves with various thermal annealing temperature on the devices.

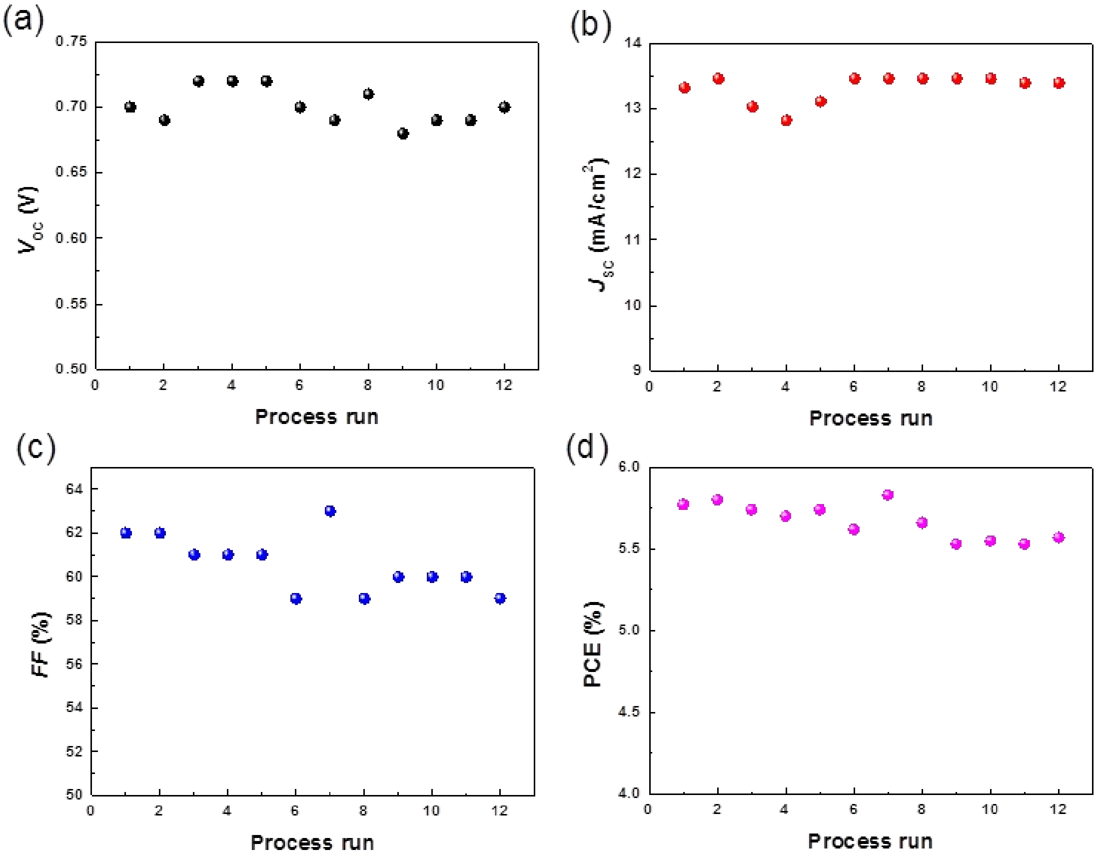

Fig. S5 Photovoltaic parameters for (a) V_{OC}, (b) J_{SC}, (c) *FF*, (d) PCE versus process run of SM-OPVs devices.

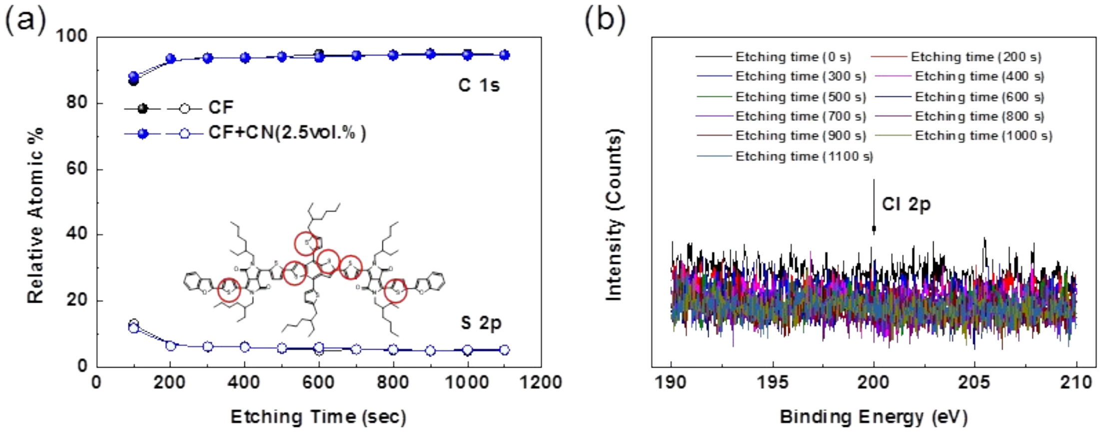

Fig. S6 XPS depth profiles of SM-OPVs (a) XPS peak of C_{1s}, and S_{2p} and (b) Cl_{2p}.

Table S1 Photovoltaic results of BDTT-2DPPBFu:$PC_{71}BM$ dissolved in CF with different weight ratios.

Weight Ratio	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	**PCE** [%]
1.0:0.5	0.77	3.49 (3.62)[a]	42	1.14
1.0:1.0	0.77	3.82 (3.82)[a]	53	1.57
1.0:2.0	0.77	3.29 (3.49)[a]	52	1.31

[a] The value is calculated from EQE data.

Table S2 Thermal annealing effect on photovoltaic results of BDTT-2DPPBFu:$PC_{71}BM$ = 1.0:1.0 dissolved in CF.

Annealing	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	**PCE** [%]
As-cast	0.76	2.84 (3.00)[a]	43	0.94
110°C, 10min	0.77	2.84 (3.03)[a]	51	1.10
130°C, 10min	0.77	3.82 (3.82)[a]	53	1.57
150°C, 10min	0.78	3.06 (3.29)[a]	54	1.29

[a] The value is calculated from EQE data.

Table S3 Summary of the *d*-spacing parameters of edge-on and face-on orientation.

Film	Solvent	(100)[a] [Å]	(010)[a] [Å]	(100)[b] [Å]	(010)[b] [Å]
SM	CF	15.00	-	17.18	3.76
SM:PC$_{71}$BM	CF	15.98	-	17.95	-
	CF+1.0CN	15.89	-	18.16	-
	CF+2.5 CN	17.66	-	19.61	3.66
	CF+4.5 CN	16.39	-	-	-

[a] Calculation from *z*-axis.

[b] Calculation from *xy*-axis.