Supporting Information

Octafluoronaphthalene as a thermal-annealing-free volatile solid

additive enables high-performance organic solar cells

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Materials

Chloroform (CF) and methanol solvents were procured from Sigma-Aldrich co. D18-Cl and N3 were bought from Derthon Materials, Inc. Solid additive octafluoronaphthalene (OFNA) was bought from Sigma-Aldrich Co. PEDOT: PSS ((poly-(3,4-ethylenedioxythiophene): poly (styrene sulfonate)) aqueous solution (Baytron P VP AI 4083) was purchased from H. C. Starck co. The patterned Indium tin oxide (ITO) coated glass substrates were purchased from AMG Technology Co. Electron transport layer H75 was synthesized according to the previous publication.

Device fabrication

The organic solar cells (OSCs) were fabricated with the conventional device structure of ITO/PEDOT:PSS/Active layer/H75/Ag. The ITO-coated glass substrates were cleaned using ultrasonic baths by sequential and continuous treatment in detergent,

deionized water, acetone, and isopropanol for 15 mins, then dried at oven under 80 °C overnight. The cleaned ITO-coated glass substrates were subjected to ultraviolet-ozone treatment for 20 minutes (min). A thin layer of PEDOT:PSS was deposited through spin-coating atop the precleaned ITO from a PEDOT: PSS aqueous solution at 4000 rpm and dried subsequently at 150°C for 20 mins in ambient air. Then they were transferred into a nitrogen glove box. The blend solution of D18-Cl:N3 were spincoated atop the PEDOT: PSS layer in nitrogen glove box. The weight ratio of donor and acceptor was kept at 1.0:1.4 (w/w), and the blend solution had a total concentration of 10 mg mL⁻¹ in chloroform. The blend solution was hot stirred at 100 °C for 30 mins, after the materials dissolved well in CF, then the blend solution was cooling down at room temperature. After that, 40 wt% OFNA additives (related to donor and acceptor weight) were added to the blend solution, then the blend solution was stirred for 10 mins under room temperature. The blend solution spun cast on PEDOT: PSS layer with a spin-coating rate of around 2200 rpm and the thickness of the active layer is ≈ 110 nm. The electron transport layer H75 with a concentration of 2 mg mL⁻¹ in methanol was spun cast at 3000 rpm for 30 seconds. Finally, the Ag cathode (100 nm) was deposited by thermal evaporation at a pressure of 3×10^{-5} Pa. The active area of the device was 3.95 mm².

Solar cell measurements

The solar cells were tested under AM 1.5 G solar illumination at 100 mW/cm² by using an SS-X100R simulator (EnliTech. Taiwan). The current density–voltage (J–V) characteristics of solar cells stored in nitrogen glove box, where were measured on a computer-controlled KEISIGHT B2901A Precision Source-Measure Unit (EnliTech. Taiwan). The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 (EnliTech. Taiwan) in ambient air.

SCLC Measurements

Hole and electron mobility were measured using the SCLC model. ITO/PEDOT: PSS (30 nm)/active layer (110 nm)/MoO₃ (8 nm)/Ag (100 nm) for hole-only devices and ITO/ZnO (30 nm)/active layer (110 nm)/H75/Ag (100 nm) for electron-only devices. The SCLC mobilities were calculated by MOTT-Gurney equation:

$$J = \frac{9\varepsilon_{\rm r}\varepsilon_0\mu V^2}{8L^3} \tag{1}$$

Where J is the current density, ε_r is the relative dielectric constant of active layer material usually 2–4 for organic semiconductors, herein we use a relative dielectric constant of 4), ε_0 is the permittivity of empty space, μ is the mobility of hole or electron and L is the thickness of the active layer.

Characterization

TGA was carried out using Q200 (TA Instrument, USA) with heating from 25 to 200 °C at a heating rate of 10 °C/mins in nitrogen flow. The thickness of the active layer was measured by a profilometry (P6, KLA Tencor). The FT-IR absorption spectra were measured on a Varian 670 infrared spectrometer (Varian USA) with wavenumbers ranging from 650 to 4000 cm⁻¹. UV-vis spectra were obtained by a Shimadzu UV-2550 spectrometer. ¹⁹F NMR spectra of the D18-Cl, N3, OFNA additive and their blend were recorded on a Bruker AVANCE III HD 400 MHz spectrometer using deuterated CDCl₃ as solvent and trifluorotoluene in C6D6 as external standard.

Morphology Characterization

The GIWAXS measurement was carried out at the PLS-II 6D U-SAXS and 9A beamline of the Pohang Accelerator Laboratory in Korea. The scattering signal was recorded using a 2-D CCD detector (Rayonix SX165). The X-ray light had an energy of 11.24 KeV. The incidence angle of X-rays was adjusted to 0.09–0.12° to maximize the signal-to-background ratio. AFM images of thin films were obtained using multimode V microscope (Veeco, USA) with a nano scope controller using Si tips (Bruker). Time-of-flight secondary ion mass spectrometry (TOF-SIMS) experiments were conducted using TOF-SIMS M5 (IONTOF GmbH) instrument.



Fig. S1 (a) The chemical structures of materials used in this work. (b) TGA plot of OFNA. (c) FTIR spectrum of the thin films without TA treatment and OFNA powder.



Fig. S2 (a) Absorption spectra of (a) D18-Cl, (b) N3, and (c) their blend films without and with 40 wt% OFNA solid additive.



Fig. S3 (a) Absorption spectra of (a) D18-Cl:OFNA, (b) N3:OFNA, and (c) their blend films: OFNA under TA at 80 °C/ 5 min.



Fig. S4 (a) AFM height and (b) AFM phase images (2 µm scale) of neat films processed without and with 40 wt% OFNA solid additive without TA treatment.



Fig. S5 (a) AFM height and (b) AFM phase images (2 μ m scale) of neat films processed without and with 40 wt% OFNA solid additive under TA at 80 °C/ 5 min.



Fig. S6 ¹⁹F NMR spectra of (a) and (b) D18-Cl, N3, OFNA, and their mixture solution processed by CDCl3 solvent.



Fig. S7 (a) J-V and (b) EQE curves of D18-Cl:N3-based devices processed with different amount of OFNA solid additive.

Table S1 The photovoltaic parameters of the optimized devices based on D18-Cl:N3(1.0:1.4, w/w) with different amount of OFNA solid additive.

D18-Cl: N3	$V_{\rm OC}$ [V]	$J_{ m SC}$ [mA/cm ²]	$J_{ m SC}{}^{ m a}$ [mA/cm ²]	FF [%]	PCE [%]
20 wt% OFNA	0.855	26.94	26.16	77.83	17.92
30 wt% OFNA	0.853	27.35	26.42	78.24	18.26
40 wt% OFNA	0.857	27.53	26.55	78.85	18.59
50 wt% OFNA	0.852	26.79	26.05	79.05	18.05

^{*a*} Integrated J_{SC} from EQE.



Fig. S8 Statistical distribution of PCE (a), V_{OC} (b), J_{SC} (c), and FF (d).



Fig. S9 (a) *J-V*, and (b) EQE, and curves of D18-Cl:N3-based OSCs processed without and with 40 wt% OFNA solid additive under TA at 80 °C/ 5 min.

Table S2 The photovoltaic parameters of the optimized devices based on D18-Cl:N3(1.0:1.4, w/w) with 40 wt% OFNA solid additive under TA at 80 °C/ 5 min.

Blend film	V _{OC} [V]	J _{SC} [mA/cm ²]	$J_{\rm SC}{}^{ m a}$ [mA/cm ²]	FF [%]	PCE [%] (ave.) ^b	
/	0.860 (0.853±0.006)	27.05 (26.92±0.32)	25.88	74.70 (74.63±0.36)	17.39 (17.13±0.22)	
40 wt% OFNA	0.850 (0.846±0.006)	27.98 (27.56±0.44)	26.16	77.05 (77.79±0.42)	18.32 (18.13±0.17)	

^{*a*} Integrated J_{SC} from EQE.

^b The statistical values in brackets were calculated from for 10 devices.

Supplementary discussion 1:

To understand the enhanced J_{SC} and FF values for the target devices with the help of 40 wt% OFNA solid additive compared with the control device counterparts, we subsequently evaluated these devices' charge transport properties and recombination characteristics. We initially used the space-charge-limited current (SCLC) method to study the hole mobility (μ_h) and electron mobility (μ_e) of control and target devices based on D18-Cl:N3 (Fig. S10 and Table S3, ESI⁺).¹ The SCLC measurements show a disparity in hole and electron transport abilities. The target devices have higher μ_h and μ_e values of 1.05 and 1.42×10^{-4} cm² V⁻¹ s⁻¹, while the control device has lower μ_h and μ_e values of 0.71 and $1.11\times 10^{-4}~cm^2~V^{-1}~s^{-1}$ with the larger unbalance between μh and µe than the target devices. More efficient and balanced charge transport in OFNAprocessed devices might account for the higher FF parameters. Also, the dependence of photocurrent (J_{Ph}) on effective voltage (V_{eff}) was then used to investigate the characteristics of charge generation and collection, as shown in Fig. S11a, ESI⁺.² The saturation current (J_{sat}) values were 27.45 and 28.83 mA cm⁻², with exciton dissociation efficiency (Pdiss) values of 97.28% and 98.52% and charge collection efficiency (Pcoll) values of 85.36% and 90.17% for the control and target devices, respectively. Higher saturation current, Pdiss, and Pcoll values in OFNA-processed devices can account for the higher J_{SC} parameters than control devices. The fitted V_{OC} and J_{SC} on light intensity (P) characteristics reveal the charge recombination mechanism.³ The fitted V_{OC}, –P characteristics displayed a larger slope of 1.12 kT/q in the control device; in contrast, that in target device counterparts is very close to kT/q (Fig. S11b, ESI⁺.), indicating that trap-assisted recombination is significantly suppressed in the device based on D18-Cl:N3 with the aid of OFNA solid additive. The fitted $J_{\rm SC}$ –P characteristics displayed similar values and were very close to the unit, implying the bimolecular recombination was suppressed effectively in control and target devices (Fig. S11c, ESI[†]). These results suggest adequately that OFNA-processed devices are helpful in achieving higher J_{SC} and FF values than without additive processed devices.



Fig. S10 Current density-voltage curves for the hole and electron mobility of the devices based on D18-Cl:N3 without and with the 40 wt% OFNA solid additive.

Table S3 The hole (μh) /electron mobilities (μe) values of the devices based on D18-Cl:N3 without and with the 40 wt% OFNA solid additive.



Fig. S11 (a) J_{ph} as a function of effective bias V_{eff} , and (b) V_{oc} and (c) J_{SC} versus light intensity curves of D18-Cl:N3-based OSCs processed without and with 40 wt% OFNA solid additive.



Fig. S12 (a) 2D GIWAXS diffraction patterns, (b) line-cut profiles of D18-Cl and N3based neat films treatment without and with with the 40 wt% OFNA solid additive.



Fig. S13 (a) 2D GIWAXS diffraction patterns, (b) line-cut profiles of D18-Cl and N3based neat films treatment without and with with the 40 wt% OFNA solid additive under thermal annealing at 80 °C for 5 min.



Fig. S14 (a) and (b) 2D GIWAXS diffraction patterns, (c) and (d) line-cut profiles of D18-Cl:N3-based blend films treatment under different conditions.

Table S4 The lamellar distances, the π - π stacking distances, and the crystalline coherence length for the D18-Cl and N3-based neat and blend films treatment under different condition.

	Out-of-Plane π - π stacking				In-plane lamellar stacking			
Films	q (Å ⁻¹)	d-spacing (Å)	Full width at half maxima (FWHM)	Coherence length (Å)	q (Å ⁻¹)	d-spacing (Å)	Full width at half maxima (FWHM)	Coherence length (Å)
D18-C1	1.624	3.871	0.301	19.006	0.299	21.001	0.096	58.876
D18-Cl (TA)	1.627	3.861	0.296	19.281	0.299	21.022	0.094	60.455
D18-Cl: OFNA	1.618	3.882	0.292	19.585	0.303	20.760	0.085	66.905
D18-Cl: OFNA (TA)	1.637	3.838	0.294	19.447	0.304	20.670	0.087	65.194
N3	1.724	3.644	0.216	26.516	0.276	22.758	0.084	67.076
N3 (TA)	1,749	3.593	0.202	28.308	0.283	22.166	0.080	70.822
N3: OFNA	1.736	3.620	0.210	27.188	0.279	22.543	0.084	67.164
N3: OFNA (TA)	1.733	3.363	0.196	29.129	0.279	22.513	0.077	73.167
D18-Cl: N3	1.713	3.669	0.256	22.387	0.296	21.255	0.098	57.863
D18-Cl: N3 (TA)	1.692	3.714	0.242	23.677	0.291	21.595	0.087	64.907
D18-Cl: N3:OFNA	1.704	3.688	0.251	22.759	0.292	21.553	0.092	61.673
D18-Cl: N3:OFNA (TA)	1.705	3.685	0.236	24.263	0.292	21.499	0.087	65.222

Reference

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