Electronic Supplementary Information

Enhancing Marangoni Flow by Inner Side Chain Engineering in Nonfullerene Acceptors for Reproducible Blade Coating-Processed Organic Solar Cell Manufacturing

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Experimental Section

Material and characterization

4,7-bis(6-(2-butyloctyl)thieno[3,2-b]thiophen-2-yl)-5,6-dinitrobenzo[c][1,2,5]thiadiazole, 2,2'-((2Z,2'Z)-((3,9-bis(2-butyloctyl)-12,13-bis(2-ethylhexyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (L8-i-EH), 2,2'-((2Z,2'Z)-((3,9,12,13tetrakis(2-butyloctyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4e]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1divlidene))dimalononitrile (L8-i-BO) were synthesized according to previously reported methods.^{1, 2} The other chemicals and reagents were purchased from Sigma-Aldrich, Tokyo Chemical Industry Co., Ltd, and Alfa Aesar Chemical Company and used without any further purification. All solvents are ACS and anhydrous grade by distillation. 1D ¹H NMR and ¹³C NMR spectra of the intermediates and the target product were recorded on a Bruker AVANCE III HD 400 MHz spectrometer using deuterated CDCl₃ as solvent and tetramethylsilane (TMS) as an internal standard. (Figure S8-S11). For measuring UV-vis spectra of synthesized materials, their solutions (4.00 mg mL⁻¹ chloroform) were used, and the films were prepared by deposition from the 4.00 mg mL⁻¹ concentrated chloroform solution via the spin-casting method at 700 rpm. The optical bandgaps were estimated from the absorption onset of the ascast thin films. CV measurements were performed on an Iviumstat.h with a three-electrode cell system in a nitrogen bubbled 0.1 M tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu₄NPF₆) solution in acetonitrile at a scan rate of 100 mV⁻¹ s⁻¹ at room temperature. An Ag/Ag⁺ electrode, platinum wire, and material-coated glassy carbon electrode were used as the reference electrode, counter electrode, and working electrode, respectively. The Ag/Ag⁺ reference electrode was calibrated using a Fc/Fc⁺ redox couple as an internal standard, whose oxidation potential was set at -4.8 eV with respect to the zero-vacuum level. HOMO and LUMO energy levels of NFAs were obtained from the equation HOMO (eV) = $-(E_{ox}^{onset} - E_{ox}^{onset})$ $E_{\rm Fc}^{\rm onset}$ + 4.8) and LUMO (eV) = -($E_{\rm red}^{\rm onset}$ - $E_{\rm Fc}^{\rm onset}$ + 4.8). The TGA curves were evaluated with a Q500 (TA Instruments) with a scan rate of 5 °C min⁻¹.



Scheme S1. Synthetic route of L8-*i*-EB.

Material synthesis

 Synthesis
 of
 3,9-bis(2-butyloctyl)-12,13-bis(2-ethylbutyl)-12,13-dihydro

 [1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2

g]thieno[2',3':4,5]thieno[3,2-b]indole (1). In two-neck round-bottom flask, 4,7-bis(6-(2-butyloctyl)thieno[3,2-b]thiophen-2-yl)-5,6-dinitrobenzo[c][1,2,5]thiadiazole (0.5 g, 0.60 mmol) and triethyl phosphite (6 mL) were dissolved in anhydrous *o*-dichlorobenzene (6 mL) under argon atmosphere. The mixture was stirred and heated at 180 °C overnight. After cooling to room temperature, the reaction mixture was extracted with DI water and dichloromethane and the organic phase dried over magnesium sulfate. After concentrating the organic phase under reduced pressure, the residue was transferred to two-neck round-bottom flask. Then, potassium carbonate (0.41 g, 0.30 mmol), potassium iodide (0.50 g, 0.30 mmol), 2-ethylbutyl bromide (0.39 g, 2.38 mmol), and dimethylformamide (25 mL) were added into the flask and refluxed overnight under argon atmosphere. After cooling to room temperature, the reaction mixture was extracted with DI water and dichloromethane as an eluent to obtain the yellow solid (0.24 g, 42%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 6.99 (s, 2H),

4.62 (d, *J* = 7.8 Hz, 4H), 2.75 (d, *J* = 7.2 Hz, 4H), 2.00 (m, 4H), 1.45 – 1.14 (m, 32H), 1.10 – 0.80 (m, 20H), 0.67 (t, *J* = 7.4 Hz, 12H).

Synthesis of 3,9-bis(2-*butyloctyl*)-*12,13-bis*(2-*ethylbutyl*)-*12,13-dihydro- [1,2,5]thiadiazolo*[*3,4-e*]*thieno*[2'',3'':4',5']*thieno*[2',3':4,5]*pyrrolo*[*3,2-*

g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-dicarbaldehyde (2). To a two-neck round-bottom flask, anhydrous dimethylformamide (1.6 mL), phosphorus oxychloride (1.9 mL), and 1,2-dichloroethane (2 mL) were added and stirred at room temperature for an hour. Then, the mixture was transferred dropwise to the solution of compound 1 (0.23 g, 0.24 mmol) in 1,2-dichloroethane (6 mL) and stirred at 120 °C overnight. The reaction mixture was quenched with concentrated solution of sodium hydrogen carbonate, extracted with dichloromethane, and dried over magnesium sulfate. The residue was purified by column chromatography with hexane and dichloromethane as an eluent to afford the orange solid (0.22 g, 89%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 10.12 (s, 2H), 4.65 (d, *J* = 7.8 Hz, 4H), 3.11 (d, *J* = 7.4 Hz, 4H), 2.14 – 1.90 (m, 4H), 1.48 – 1.20 (m, 32H), 1.04 – 0.85 (m, 20H), 0.69 (t, *J* = 7.4 Hz, 12H)

Synthesis of 2,2'-((2Z,2'Z)-((3,9-bis(2-butyloctyl)-12,13-bis(2-ethylbutyl)-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-

g]thieno[2', 3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methaneylylidene))bis(5,6-difluoro-3oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (L8-i-EB). In two-neck roundbottom flask, compound 2 (0.2 g, 0.20 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.21 g, 0.9 mmol) were dissolved in chloroform (25 mL). Then, pyridine (1 mL) was added to the solution. The mixture was stirred at 75 °C overnight. The reaction mixture was quenched with DI water, extracted with chloroform, and dried over magnesium sulfate. After concentrating the reaction mixture under reduced pressure, the residue was purified by column chromatography with hexane and chloroform, yielding a dark blue solid (0.26 g, 92%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.16 (s, 2H), 8.58 (dd, *J* = 10.0, 6.5 Hz, 2H), 7.72 (t, *J* = 7.5 Hz, 2H), 4.77 (d, *J* = 8.0 Hz, 4H), 3.20 (d, *J* = 7.6 Hz, 4H), 2.09 (m, 4H), 1.51 – 0.80 (m, 52H), 0.75 (t, *J* = 7.4 Hz, 6H), 0.65 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 186.08, 159.67, 153.61, 151.96, 147.61, 145.36, 137.75, 135.75, 135.68, 134.02, 133.64, 130.51, 127.86, 120.11, 115.13, 114.56, 113.68, 113.65, 112.94, 112.65, 112.56, 112.46, 68.80, 55.55, 41.53, 40.10, 33.64, 33.40, 31.84, 29.64, 28.89, 26.61, 23.03, 22.67, 14.11, 14.09, 10.13.

Device fabrication and characterization

The OSC devices fabricated with the conventional configuration were of glass/ITO/PEDOT:PSS/active layer/PNDIT-F3N-Br/Ag. The patterned ITO-coated glass substrate was cleaned using detergent, DI water, acetone, and isopropanol for 15 min for each step, subsequently. After the ITO glass substrates were treated with UV-ozone for 15 min, PEDOT:PSS (Bayer Baytron4083) was spin-coated at 4000 rpm onto the ITO substrate, followed by annealing at 150 °C for 20 min in air. The PM6:NFA (1:1.2 weight ratio) were dissolved in chloroform at a concentration of 16 mg mL⁻¹ with 0.15 vol% of 1,8-diiodooctane as an additive and stirred at room temperature for 1 h. The blend solution was blade-coated onto the PEDOT:PSS. The height of the blade from the substrate was fixed at a distance on 200 µm. The amount of the casted solution was 15 µL and the blade speed was optimized for each system. Notably, the temperature of the substrate was maintained at 45 °C. Then, a methanol solution of PNDIT-F3N-Br (2.0 mg mL⁻¹) was deposited onto the active layer via spin-coating at 3000 rpm for 30 s. Finally, 100 nm Al was thermally evaporated under vacuum ($<3.0 \times 10^{-6}$ Pa). The J-V characteristics were measured on a Keysight B2900 sourcemeter under the illumination of an AM 1.5G solar simulator with an intensity of 100 mW cm⁻². The EQE measurements were conducted using a Model QE-R3011 (Enli Technology) in ambient air. The surface energy and surface tension were measured by contact angles and pendent drop method using SmartDrop (Femtofab Co., Ltd., Korea). The surface energy of the acceptors and PM6 was evaluated by measuring the contact angles using two different solvents: DI water and ethylene glycol (EG) on each neat film and calculated via the Owens-Wendt model. The investigation of thin-film morphology was performed using optical microscope, surface profiler, AFM and GIWAXS measurements. The optical images of film depending on the blade speed were obtained using measurement microscope (Axio Scope A1). The thickness of the active layers was measured using a stylus profilometer (P6, KLA Tencor). The samples were prepared by spin-coating on the glass substrate for AFM and silicon substrate for GIWAXS using the solution of NFAs (2 mg mL⁻¹ in CF) for the neat film and the optimized device fabrication condition for the blend films. AFM was measured via a Hitachi AFM5100N in the tapping mode. GIWAXS analysis was conducted using a PLS-II 6D U-SAXS beamline in Pohang Accelerator Laboratory (South Korea). The X-rays coming from the in-vacuum undulator (IVU) were monochromated at 11.564 keV (wavelength of 1.07216 Å). The X-ray beam was irradiated with an incidence angle of <0.15° within 100 s. GIXD patterns were recorded by a 2D CCD detector with a sample-to-detector distance (SDD) of 237.7 mm. The approximate crystalline coherence length (CCL) was extracted using the Scherrer equation.

$$CCL = \frac{K\lambda}{\beta \cdot \cos \theta} \tag{1}$$

where K is the Scherrer constant, λ is the wavelength (nm) if the X-ray beam used, β is the fill width at half-maximum, and θ is the Bragg angle.



Fig. S1 (a) UV-vis absorption spectra in the CF solution and (b) as film state.

 Table S1 Optical and electrochemical properties from UV-vis absorption spectra and cyclic voltammetry.

| | λ _{sol} ^{max} [nm] | λ _{film} ^{max} [nm] | λ _{onset} [nm]ª | Eg ^{opt} [eV]² | E _{HOMO} CV [eV] ^b | E _{LUMO} CV [eV] ^b |
|------------------|---|--|-----------------------------|----------------------------|---|---|
| L8- <i>i</i> -EB | 731 | 803 | 880 | 1.41 | -5.68 | -3.98 |
| L8- <i>i</i> -EH | 731 | 805 | 883 | 1.40 | -5.72 | -3.99 |
| L8- <i>i</i> -BO | 731 | 813 | 875 | 1.42 | -5.80 | -3.97 |

^{*a*} Optical band gaps were determined from the onset of the UV-vis absorption spectrum of the thin films; ^{*b*} Energy levels were estimated from the onset of the oxidation/reduction potential of CV curves.



Fig. S2 (a) Cyclic voltammetry of L8-*i*-EB, L8-*i*-EH, and L8-*i*-BO. (b) Energetic diagram of PM6, L8-*i*-EB, L8-*i*-EH, and L8-*i*-BO.

| Blade speed [mm s ⁻¹] | V _{oc} [V] | J _{SC} [mA cm ⁻²] | FF [%] | PCE [%] |
|--------------------------------------|---------------------|--|--------|---------|
| 9 | 0.864 | 23.56 | 72.77 | 14.79 |
| 12 | 0.864 | 25.06 | 74.04 | 16.03 |
| 15 | 0.867 | 26.01 | 73.28 | 16.52 |
| 18 | 0.862 | 25.94 | 73.83 | 16.51 |
| 21 | 0.850 | 25.88 | 73.13 | 16.09 |
| 24 | 0.850 | 24.21 | 72.99 | 15.02 |
| 27 | 0.856 | 24.53 | 72.89 | 15.30 |
| 30 | 0.851 | 24.83 | 71.35 | 15.08 |

 Table S2 Photovoltaic parameters depending on blade speed for PM6:L8-*i*-EB based devices.

| Blade speed [mm s ⁻¹] | V _{oc} [V] | J _{SC} [mA cm⁻²] | FF [%] | PCE [%] |
|--------------------------------------|---------------------|---------------------------|--------|---------|
| 9 | 0.888 | 22.72 | 77.59 | 15.66 |
| 12 | 0.889 | 23.10 | 76.92 | 15.79 |
| 15 | 0.892 | 24.50 | 76.42 | 16.70 |
| 18 | 0.890 | 25.14 | 76.24 | 17.06 |
| 21 | 0.886 | 25.81 | 75.24 | 17.20 |
| 24 | 0.883 | 25.13 | 74.62 | 16.56 |
| 27 | 0.885 | 24.40 | 73.98 | 15.98 |
| 30 | 0.884 | 24.26 | 74.13 | 15.91 |

 Table S3 Photovoltaic parameters depending on blade speed for PM6:L8-*i*-EH based devices.

 Table S4 Photovoltaic parameters depending on blade speed for PM6:L8-i-BO based devices.

| Blade speed [mm s ⁻¹] | V _{oc} [V] | J _{SC} [mA cm ⁻²] | FF [%] | PCE [%] |
|--------------------------------------|---------------------|--|--------|---------|
| 9 | 0.859 | 24.82 | 71.66 | 15.28 |
| 12 | 0.856 | 24.45 | 73.75 | 15.42 |
| 15 | 0.867 | 24.11 | 74.84 | 15.65 |
| 18 | 0.875 | 23.55 | 76.56 | 15.77 |
| 21 | 0.876 | 24.24 | 76.21 | 16.18 |
| 24 | 0.870 | 24.28 | 75.33 | 15.91 |
| 27 | 0.861 | 24.38 | 73.29 | 15.38 |
| 30 | 0.852 | 23.80 | 71.00 | 14.40 |



Fig. S3 Light intensity dependence of (a) J_{SC} , and (b) V_{OC} .



Fig. S4 GIWAXS images of neat and blend films for (a, e) PM6:L8-*i*-EB, (b, f) PM6:L8-*i*-EH, and (c, g) PM6:L8-*i*-BO blade-coated films. In-plane scattering line-cut profiles (dotted lines) and out-of-plane scattering line-cut profiles (solid lines) for (d) neat and (h) blend films.

| | Out-of-plane | | | | |
|----------------------|-----------------------------|-----------------------|---------|--|--|
| Neat film | π-π stacking peak | | | | |
| | <i>q</i> [Å ⁻¹] | <i>d</i> -spacing [Å] | CCL [Å] | | |
| L8- <i>i</i> -EB | 1.730 | 3.632 | 51.5 | | |
| L8- <i>i</i> -EH | 1.758 | 3.575 | 54.5 | | |
| L8- <i>i</i> -BO | 1.821 | 3.450 | 94.4 | | |
| Blend film | | π-π stacking peak | | | |
| | q [Å-1] | <i>d</i> -spacing [Å] | CCL [Å] | | |
| PM6:L8- <i>i</i> -EB | 1.717 | 3.659 | 53.4 | | |
| PM6:L8- <i>i</i> -EH | 1.793 | 3.540 | 62.2 | | |
| PM6:L8- <i>i</i> -BO | 1.814 | 3.463 | 98.1 | | |

Table S5 GIWAXS parameters of the neat and blend films.



Fig. S5 Contact angle images of neat films.

| | Contact angle [º] | | Surface energy [mJ m⁻²] |
|------------------|----------------------|-----------------|----------------------------|
| | Water | Ethylene glycol | V ^{total} |
| L8- <i>i</i> -EB | 89.6 | 59.3 | 29.42 |
| L8- <i>i</i> -EH | 92.4 | 59.8 | 30.26 |
| L8- <i>i</i> -BO | 95.6 | 60.1 | 33.06 |

Table S6 Contact angles and calculated surface energies.



Fig. S6 The illustration of expected Marangoni flow for each NFAs dissolved solution.



Fig. S7 2D height images of AFM for a) PM6:L8-*i*-EB, b) PM6:L8-*i*-EH, and c) PM6:L8-*i*-BO spin-coated blend films.

| PM6:L8- <i>i</i> -EB | V _{oc} [V] | J _{sc} [mA cm ⁻²] | FF [%] | PCE [%] |
|----------------------|---------------------|--|--------|---------|
| # 1 | 0.861 | 26.29 | 73.32 | 16.60 |
| # 2 | 0.850 | 25.39 | 74.12 | 16.00 |
| # 3 | 0.845 | 26.74 | 74.65 | 16.86 |
| # 4 | 0.845 | 26.33 | 74.32 | 16.53 |
| # 5 | 0.844 | 26.24 | 74.51 | 16.51 |
| # 6 | 0.855 | 25.86 | 74.13 | 16.39 |
| # 7 | 0.851 | 26.17 | 72.06 | 16.05 |
| # 8 | 0.838 | 26.62 | 73.18 | 16.33 |
| # 9 | 0.854 | 25.16 | 72.69 | 15.61 |

Table S7 Photovoltaic parameters of 9 devices on one substrate for PM6:L8-*i*-EB.

| PM6:L8- <i>i</i> -EB | V _{oc} [V] | J _{SC} [mA cm ⁻²] | FF [%] | PCE [%] |
|----------------------|---------------------|--|--------|---------|
| # 1 | 0.880 | 24.48 | 71.11 | 15.31 |
| # 2 | 0.873 | 26.41 | 73.70 | 17.01 |
| # 3 | 0.874 | 25.80 | 74.90 | 16.90 |
| # 4 | 0.870 | 26.01 | 72.04 | 16.31 |
| # 5 | 0.871 | 26.16 | 72.80 | 16.58 |
| # 6 | 0.867 | 25.86 | 72.36 | 16.22 |
| # 7 | 0.869 | 26.18 | 73.61 | 16.75 |
| # 8 | 0.866 | 26.72 | 70.05 | 16.23 |
| # 9 | 0.882 | 25.89 | 75.32 | 17.20 |

 Table S8 Photovoltaic parameters of 9 devices on one substrate for PM6:L8-i-EH.

Table S9 Photovoltaic parameters of 9 devices on one substrate for PM6:L8-*i*-BO.

| PM6:L8- <i>i</i> -EB | V _{oc} [V] | J _{sc} [mA cm⁻²] | FF [%] | PCE [%] |
|----------------------|---------------------|---------------------------|--------|---------|
| # 1 | 0.860 | 22.68 | 74.22 | 14.47 |
| # 2 | 0.857 | 26.24 | 71.37 | 16.05 |
| # 3 | 0.851 | 24.64 | 70.91 | 14.88 |
| # 4 | 0.861 | 25.10 | 72.31 | 15.63 |
| # 5 | 0.863 | 26.33 | 73.32 | 16.66 |
| # 6 | 0.856 | 25.48 | 73.26 | 15.99 |
| # 7 | 0.862 | 26.03 | 68.63 | 15.41 |
| # 8 | 0.851 | 23.34 | 70.20 | 13.95 |
| # 9 | 0.849 | 23.37 | 70.11 | 13.92 |



Fig. S8 ¹H NMR spectra of compound 1.



Fig. S9 ¹H NMR spectra of compound 2.



Fig. S10 ¹H NMR spectra of L8-*i*-EB.



Fig. S11 ¹³C NMR spectra of L8-*i*-EB.

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