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Supporting Information

Optimized Active Layer Morphology via Side-Chain Atomic Substituents to Achieve Efficient and Stable All-Polymer Solar Cells

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1. Measurements and characterization

UV-visible spectra: UV-visible spectra were recorded on a Shimadzu UV-3600 spectrophotometer at room temperature. All UV-vis experiments for solutions were performed in *o*-DCB with sample concentration of 0.05 mg mL^{-1}. Films were prepared by spin coating *o*-DCB solutions on glass substrates.

Thermogravimetric analyses (TGA): TGA measurements were performed on a Netzsch TG 209 F3 under the protection of nitrogen gas at a heating rate of 10 °C min^{-1} with a nitrogen flow rate of 20 mL min^{-1}.

Differential scanning calorimetry (DSC): DSC measurements were determined using a NETZSCH DSC 200 F3 Maia with about 5 mg samples. DSC measurements were carried out at a heating/cooling rate of 10 °C/min in the temperature range of 30 to 350 °C. DSC samples were prepared from solution. The materials were dissolved in chloroform at a total concentration of 10 mg/mL and stirred overnight at 50 °C. The solution was then drop cast on a glass substrate and kept under a nitrogen atmosphere for 48 h to remove the residual solvents.

Fabrication of solar cells: Patterned indium tin oxide (ITO) glass substrates were pre-cleaned sequentially by sonicating in a detergent bath, then with deionized water, acetone, and isopropanol at room temperature and in a boiled isopropanol bath, each for 10 minutes. The substrates were subjected to ultraviolet/ozone treatment at room temperature for 5 minutes. Then PEDOT:PSS (CLEVIOS^{TM} P VP AI 4083 from Heraeus) was spin-coated on the ITO glass substrates at 3000 rpm for 40 seconds to give a thickness of 40 nm, followed by baking at 140 °C for 15 minutes. The substrates were transferred to a nitrogen-filled glove box. The active layer consisting of a blend of the corresponding donor and NOE10 (1.5:1/2:1 by weight) was spin-coated from a chloroform solution, giving a thickness of 100 nm. After that, a layer of PFN-Br (5 nm) was spin-coated from a methanol solution (0.5 mg mL^{-1}) at a spin speed of 2000 rpm for 20 seconds. Finally, a layer of Ag (90 nm) was thermally evaporated at a pressure of 4×10^{-7} Torr.

Current density–voltage (*J–V*) characteristics: The $J-V$ characteristics were recorded on a computer-controlled Keithley 2400 source meter under 1 sun, the AM1.5 G spectra came from a class solar simulator (Enlitech, Taiwan), and the light intensity was 100 mW cm^{-2} as calibrated by a China General Certification Center-certified reference monocrystal silicon cell (Enlitech).

External quantum efficiencies (EQEs): The EQE spectra measurements were performed on a commercial QE measurement system (QE-R3011, Enlitech). The light intensity at each wavelength was calibrated by a standard single-crystal Si photovoltaic cell.

PL quenching experiments. The PL quenching experiments were recorded on a Shimadzu RF-6000 spectrometer at different excitation wavelengths for the corresponding films.

Fabrication and characterization of single-carrier devices. Single-carrier devices were fabricated to measure hole and electron mobility by using the space-charge-limited current (SCLC) method. The device structures of the hole-only devices and electron-only are ITO/PEDOT:PSS (40 nm)/active layer (100 nm)/MoO_x (12 nm)/Ag (90 nm) and ITO/ZnO (40 nm)/active layer (100 nm)/Ca (10 nm)/Al (100 nm), respectively. The mobility was determined by fitting the dark current to the model of a single-carrier SCLC model, which is described by the equation $J = (9/8)\varepsilon_0\varepsilon_r\mu((V^2)/(d^3))$, where J is the current, μ is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layers, and V is the effective voltage. The effective voltage was obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_{s}) from the series resistance of the whole device except for the active layers from the applied voltage (V_{appl}), $V = V_{\mathrm{appl}} - V_{\mathrm{bi}} - V_{\mathrm{s}}$. The charge carrier mobility can be calculated from the slope of the $J^{1/2}{\sim}V$ curves.

Grazing incidence wide-angle X-ray scattering (GIWAXS): The X-ray diffraction measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11–3 with an area detector (Rayonix mar CCD225). The X-ray beam with an energy of 12.735 keV and an incidence angle of 0.12° was used. The sample was kept in a helium chamber to avoid air scattering. Data reduction was performed using Igor software with Nika package.

Atom force microscopy (AFM): AFM images were obtained by using a Bruker Multimode 8 Microscope AFM in tapping-mode.

Transmission electron microscopy (TEM): Transmission electron microscopy images were collected from a JEM-2100F transmission electron microscope operated at 200 kV.

Tapping AFM-IR+: A neaSNOM from neaspec/attocube was used to perform tapping AFM-IR measurements. IR absorption is mapped by detecting the mechanical response of an AFM cantilever upon sample stimulation by pulsed IR light. Within the microscope, a parabolic mirror focuses a pulsed, tunable QCL laser onto a PtIr coated AFM probe operating in intermittent contact mode.

Contact angle measurements: The contact angle tests were performed on a Dataphysics OCA40 Micro surface contact angle analyzer. The surface energy of the polymers was characterized and calculated by the contact angles of the two probe liquids with the Owens and Wendt equation: $(1 + \cos\theta)\gamma_{\mathrm{pl}} = 2(\gamma_{\mathrm{s}}^{\mathrm{d}}\gamma_{\mathrm{pl}}^{\mathrm{d}})^{1/2} + 2(\gamma_{\mathrm{s}}^{\mathrm{p}}\gamma_{\mathrm{pl}}^{\mathrm{p}})^{1/2}$, where$\gamma_{\mathrm{s}}$ and γ_{pl} are the surface energy of the sample and the probe liquid, respectively. The superscripts *d* and *p* refer to the dispersion and polar components of the surface energy, respectively.[1]

2. Additional Figures and Tables

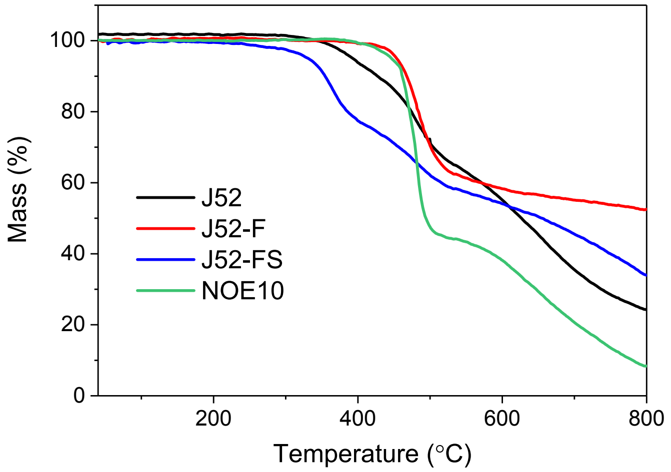

Figure S1. TGA thermograms of the polymers.

Table S1. Photovoltaic parameters of the J52/-F/-FS:NOE10 solar cells with various fabricating conditions under AM1.5G illumination (100 mW cm^{-2}).

Donor	D:A	Solvent	Annealing (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
J52	1:1	CF+2%DIO	150	0.69	5.8	0.39	1.55
	1.5:1	CF+2%DIO	150	0.69	6.3	0.40	1.71
	2:1	CF+2%DIO	150	0.71	3.8	0.47	1.25
		CF+0.7%DIO	150	0.74	13.9	0.65	6.73
		CF+2%DPE	150	0.79	15.1	0.73	8.73
J52-F	1:1	CB+2%DIO	150	0.90	8.1	0.65	4.70
	1.5:1	CB+2%DIO	150	0.89	10.3	0.66	6.00
		CB+2%DPE	110	0.91	11.4	0.71	7.29
			150	0.91	11.2	0.75	7.65
			170	0.90	11.2	0.67	6.83
		CF+2%DIO	150	0.89	10.0	0.68	6.01
		CF+2%DPE	150	0.90	12.9	0.71	8.30
		CF+2%CN	150	0.89	6.1	0.55	2.98
	2:1	CB+2%DIO	150	0.88	8.6	0.42	3.20
J52-FS	1:1	CB+2%DIO	150	0.89	5.3	0.40	1.84
	1.5:1	CB+2%DIO	150	0.90	4.4	0.40	1.56
	2:1	CB+2%DIO	150	0.91	2.8	0.41	1.05
		CB+2%DPE	130	0.93	7.3	0.50	3.41
			150	0.95	7.1	0.58	3.85
			170	0.93	7.4	0.49	3.36
		CF+2%DPE	150	0.91	5.9	0.48	2.57

[a] Determined by integrating the EQE with the AM1.5G solar spectrum.

[b] Calculated using J_{sc} (EQE).

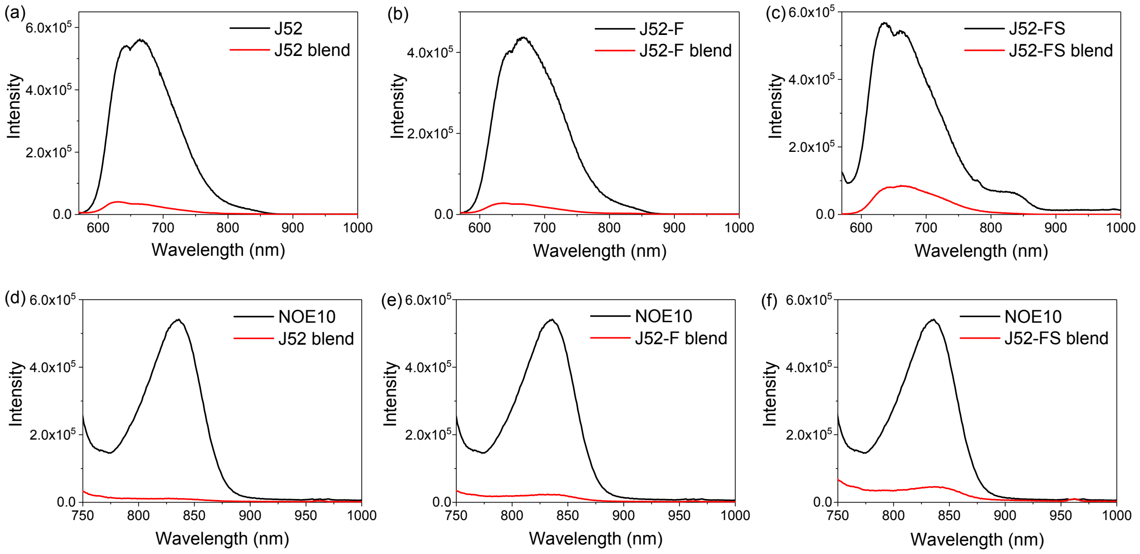

Figure S2. (a-c) PL spectra of the J52, J52-F, J52-FS neat films and blend films with photoexcitation at 580 nm; (d-e) PL spectra of the NOE10, and the blend films excited at 720 nm.

Table S2. The photoluminescence quenching efficiency of the J52, J52-F, J52-FS blend films.

Blend film	ΔPL_D	ΔPL_A
J52:NOE10	96%	98%
J52-F:NOE10	94%	96%
J52-FS:NOE10	92%	85%

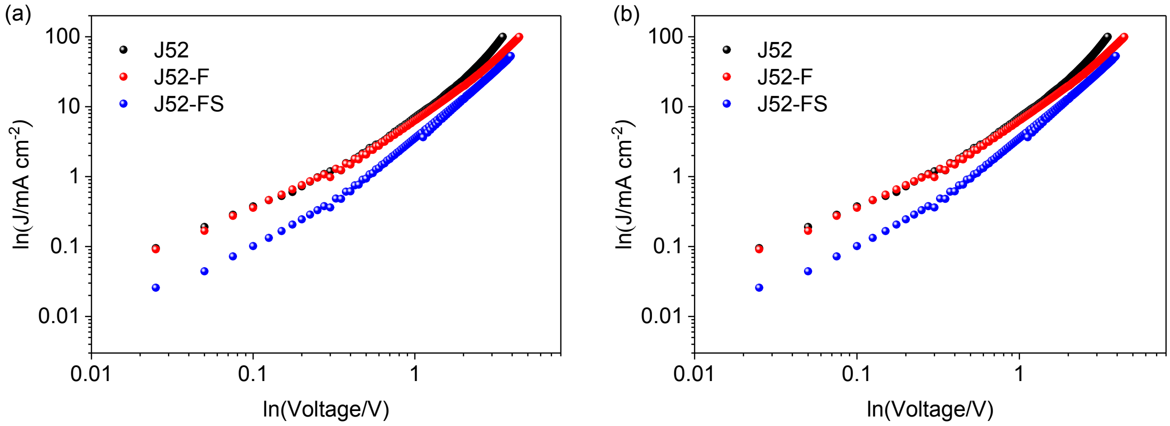

Figure S3. (a) Current density versus voltage characteristics of hole-only devices with a structure of ITO/PEDOT:PSS/J52/-F/-FS:NOE10/MoO$_x$/Ag. (b) Current density versus voltage characteristics of electron-only devices with a structure of ITO/ZnO/J52/-F/-FS:NOE10 /Ca/Al.

Table S3. Lattice parameters of the neat films and blend films.

Sample	Lamellar				π-Stacking			
	q (Å^{-1})	(100) distance (Å)	FWHM$^{a)}$ (Å^{-1})	CCL$^{b)}$ (Å)	q (Å^{-1})	π–π distance (Å)	FWHM$^{a)}$ (Å^{-1})	CCL$^{b)}$ (Å)
J52	0.29	21.66	0.107	58.69	1.77	3.55	0.41	15.32
J52-F	0.26	24.15	0.154	40.78	1.76	3.57	0.31	20.26
J52-FS	0.28	22.43	0.175	35.89	1.76	3.57	0.40	15.70
J52:NOE10	0.28	22.43	0.089	70.56	1.73	3.63	0.43	14.60
J52-F:NOE10	0.27	23.26	0.089	70.56	1.76	3.57	0.35	17.94
J52-FS:NOE10	0.26	24.15	0.083	75.66	1.75	3.59	0.39	16.10

a) FWHM represents full-width at half maximum;

b) CCL represents crystal coherence length.

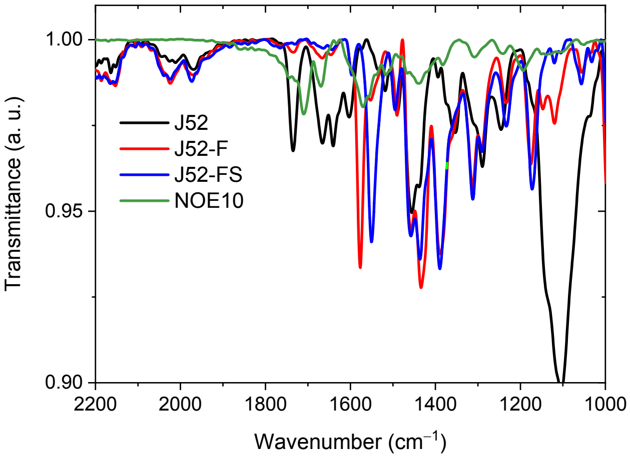

Figure S4. FT-IR spectra of J52 (black line), J52-F (red line), J52-FS (blue line) and NOE10 (green line).

Table S4. The characteristic peak of pure donor and acceptor in blend films.

Blend film (D:A)	Donor	Acceptor
J52:NOE10	J52@1310 cm^{-1}	NOE10@1710 cm^{-1}
J52-F:NOE10	J52-F@1385 cm^{-1}	NOE10@1710 cm^{-1}
J52-FS:NOE10	J52-FS@1385 cm^{-1}	NOE10@1710 cm^{-1}

Table S5. The relevant parameters for calculating the Flory-Huggins interaction parameters of the various blends.

Blend film (D:A)	T_m^0 (ºC)	T_m (ºC)	Φ_2	ΔH_f (J g^{-1})
J52:NOE10	338.75	303.52	0.609	7.25
J52-F:NOE10	338.75	309.81	0.501	7.25
J52-FS:NOE10	338.75	336.71	0.039	7.25

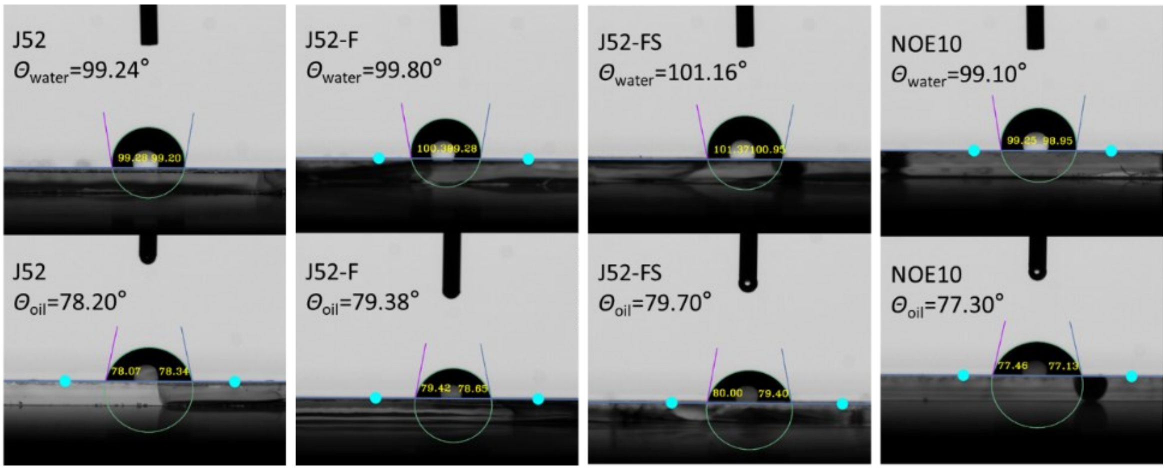

Figure S5. Views of surface contact angle measurements with the pure polymer films. The measurements are carried out by using deionized water and ethylene glycol as the wetting liquid.

Table S6. The surface energy (γ) and solubility parameter (δ) of the neat polymers, and the Flory–Huggins interaction parameters ($\chi_{\mathrm{Donor,Acceptor}}$) between the various donors and NOE10.

Sample	Surface energy γ (mN m^{-1})	Solubility parameter δ (MPa$^{1/2}$)^{a}	$\chi_{\mathrm{Donor,Acceptor}}{}^{b}$
J52	16.11	14.72	0.026κ
J52-F	15.76	14.56	0.102κ
J52FS	15.31	14.35	0.281κ
NOE10	16.45	14.88	-

[a] $\delta = K\sqrt{\gamma}$, K=116×10^{3} m$^{-1/2}$

[b] $\chi_{Donor,Acceptor} = \frac{V_0}{RT}(\delta_{Donor} - \delta_{Acceptor})^2, \kappa = \frac{V_0}{RT}$

3. References

[1] D. K. Owens, R. C. Wendt, *J. Appl. Polym. Sci.* 1969, **13**, 1741.