Supporting information

The Synergistic Effect of Fluorine Atom and Alkyl Chain Positions in Enhancing Organic Photovoltaic Open-circuit Voltage and Morphology Miscibility

Jianling Ni, Hui Kang, Xiaonan Xue, Bing Zheng, Yuan Zhang*and Lijun Huo*

J. Ni, H. Kang, X. Xue, B. Zheng, Prof. Y. Zhang, Prof. L. Huo School of Chemistry Beihang University Beijing 100191, China. E-mail: <u>yuanzhang@buaa.edu.cn</u>; <u>huolijun@buaa.edu.cn</u>

Materials: Unless otherwise stated, all the solvents and reagents were obtained from commercial sources and were utilized without further purification. Compounds 1 were commercially available from Solarmer Materials Inc. All the reactions were conducted under the protection of a nitrogen atmosphere unless otherwise noted. Anhydrous THF was obtained through distillation from sodium benzophenone under nitrogen.

Synthesis of compound 4:

1,3-dibromo-5-fluorobenzene (compound 2) (2.82 g, 11.12 mmol) was dissolved in anhydrous ether (100 mL) at -50° C, and n-butyllithium (2.4 M solution in hexane, 5.10 mL, 12.23 mmol) was added to the sample dropwise under nitrogen atmosphere. After the mixture was stirred under this temperature for 2 h, the compound 3 (0.7 g, 3.18 mmol) was added in one portion into the reaction mixture. Subsequently, the mixture was stirred at room temperature for 2 h, a solution of SnCl₂.2H₂O (4.90 g, 21.7 mmol) in 10% HCl was added to one portion under an ice bath condition. Then, the mixture

was restored up to 50°C and stirred for 2 h. Finally, the mixture was poured into water and extracted with dichloromethane (DCM). The combined organic phases were dried with anhydrous MgSO₄ and further concentrated under a reduced pressure. The crude product was purified by recrystallization with petroleum ether to afford compound 4 as pale yellow powder (1.28 g, 75.0%). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (s, 2H), 7.52-7.50 (d, J = 7.0 Hz, 2H), 7.44-7.38 (t, J =8.1 Hz, 4H), 7.33-7.21 (d, J = 8.0 Hz, 2H). ¹³C NMR (CDCl₃, 25 °C): δ 161.2, 138.0, 135.9, 128.3, 123.1, 122.3, 119.3, 118.95, 115.7, 115.4.

Synthesis of compound 5:

The Grignard reagent (2- ethylhexyl)magnesium bromide (1.0 M solution in hexane, 5.59 mL, 5.59 mmol) was added dropwise to the mixture of compound 4 (1.00 g, 1.86 mmol) and catalyst [PdCl₂(dppf)]CH₂Cl₂ (40 mg) in 50 mL of anhydrous THF at 0°C. Then the mixture was heated to reflux and stirred under argon at this temperature, overnight. After completion of the reaction, 500 mL of water was added to the reaction mixture followed by the addition 1M HCl (until acidic media). The organic phase was separated, washed with water and anhydrous MgSO₄. The solvent was removed under reduced pressure. Excess of initial reagents was distilled off in a vacuum and cube containing the product was passed over a short column of silica gel in petroleum ether to give the compound **5** (0.90 g, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7. 43-7.42 (d, J = 7.2 Hz, 2H), 7.33-7.29 (t, J = 9.2 Hz 4H), 7.23-7.20 (d, J = 9.0 Hz 2H), 7.01-6.98 (d, J = 9.0 Hz 2H), 2.64-2.62 (d, 4H), 1.65 (s, 2H), 1.43-1.25 (m, 16H), 0.94-0.87 (m, 12H). ¹³C NMR (CDCl₃, 25 °C): δ 164.6 161.3, 145.2, 140.6, 138.0, 135.9, 129.7, 127.6, 126.0, 122.6, 115.9, 113.7, 41.1, 32.4, 28.9, 25.5, 23.0, 14.1, 10.8.

Synthesis of compound 6:

compound **6** (0.8 g, 1.32 mmol) was dissolved in dry THF (100 mL)at -78° C, and nbutyllithium (2.4 M solution in hexane, 1.66 mL, 3.98 mmol) was added to the sample dropwise. The mixture was stirred under this temperature for 30 min, then restored up to room temperature for 1 h. Me₃SnCl (1 M solution in hexane, 4.62 mL, 4.62 mmol) was added dropwise after cooling down to -78° C and continued to stir for a 30 min. Subsequently, the mixture was stirred overnight by warm up to room temperature. Water (100 mL) was added into the mixture to quench reaction, and extracted twice with dichloromethane. The crude product was purified by recrystallization with ethanol to give the compound **6** (0.86 g, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.09 (s, 2H), 7.05-7.03 (d, J = 8.0 Hz 4H), 6.80-6.77 (d, J = 8.0 Hz 2H), 2.45-2.42 (m, 4H), 1.47 (s, 2H), 1.27-1.06 (m, 16H), 0.74-0.69 (m, 12H), 0.23-0.09 (t, 18H). ¹³C NMR (CDCl₃, 25 °C): δ 145.1 142.6, 141.3, 136.8, 130.3, 128.1, 126.2, 115.7, 113.7, 41.2, 32.5, 28.9, 25.5, 23.1, 14.2, 10.9.

Synthesis of compound L18:

Compound 1 (0.1 mmol) and DTBTT-BO-Br (0.1 mmol) were dissolved into 8 mL of toluene in a flask under nitrogen, respectively. The mixture was flushed with nitrogen for 10 min, and 2.86 mg of Pd₂dba₃ as well as 9.28 mg of P(o-toly)₃ as ligand were added into the flask. The solution was flushed with nitrogen for an additional 25 min. Then, the reaction mixture was stirred for 24 h at 110°C. The polymer was obtained when the cooled solution was precipitated in 100 mL of methanol. Subsequently the polymer was collected by filtration and purified by washing, extracted on a Soxhlet extractor with methanol and hexane in succession. The final product was obtained by precipitating the chloroform solution in methanol. Molecular weight L18: M_n : 12.8 kDa, PDI:2.0.

Synthesis of compound L19:

Compound **6** (0.1 mmol) and DTBTT-BO-Br (0.1 mmol) were dissolved into 8 mL of toluene in a flask under nitrogen, respectively. The mixture was flushed with nitrogen for 10 min, and 2.86 mg of Pd_2dba_3 as well as 9.28 mg of $P(o-toly)_3$ as ligand were added into the flask. The solution was flushed with nitrogen for an additional 25 min. Then, the reaction mixture was stirred for 24 h at 110°C. The polymer was obtained when the cooled solution was precipitated in 100 mL of methanol. Subsequently the polymer was collected by filtration and purified by washing, extracted on a Soxhlet

extractor with methanol and hexane in succession. The final product was obtained by precipitating the chloroform solution in methanol. Molecular weight L19: M_n : 13.5 kDa, PDI:1.8.

Instrumentation: ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer using CDCl₃ as the solvent. The Sn and Br content of polymers was determined by inductively coupled plasma-mass spectrometry (model U Agilent 7800 ICP-MS). The molecular weight of polymers was determined by gel permeation chromatography (GPC) relative to polystyrene standards with chloroform as the eluent. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 1 thermogravimetric analyzer. UV–vis absorption measurements were carried out on a Hitachi (model U-3010) UV–vis spectrophotometer. Cyclic voltammetric (CV) measurements were carried out in a conventional three-electrode cell using a platinum plate as the working electrode, a platinum wire as the counter electrode, and an Ag/Ag⁺ electrode as the reference electrode on a Zahner IM6e Electrochemical workstation in a tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M) acetonitrile solution at a scan rate of 20 mV·s⁻¹.

Device Fabrication and Characterization: An inverted architecture was fabricated with ITO/PEDOT:PSS/active layer/ PNDIT-F3N/Ag. The ITO-coated glass substrates were sequentially ultrasonicated in soap water, deionized water, acetone, and isopropyl alcohol for at least 15 min, and ultimately dried in an oven overnight. The ITO-coated glass substrates were treated by uv-ozone for 10 min. Filter the PEDOT:PSS aqueous solution (Baytron P 4083, from HCStarck) through a 0.45 mm filter, and pre-coat it on the pre-cleaned ITO glass at 5000 rpm for 30 seconds, and then heat the ITO substrate in the air at 150°C annealing for 0.5 h. The polymer donor: Y6 (D:A=1:1.2, 16 mg·mL⁻¹ in total) was dissolved in chloroform (CF) with 1-chloronaphthalene (CN) (0.5%, v/v) additive. The blended solution was spin-coated on the PEDOT:PSS layer at 3000 rpm for 30 s. It is then annealed at 110°C for 10 minutes. Then PNDIT-F3N methanol solution with a concentration of 0.3 mg·mL⁻¹ was deposited on the active layer at a speed of 3000 rpm for 30 seconds to provide a PNDIT-F3N cathode modification layer.

After cooling to room temperature, the sample was transferred to the evaporation chamber. Under the pressure of 1×10^{-5} Pa, about 100 nm of Ag electrode was evaporated and deposited. The device area is 4.0 mm². The active area of the devices is 4.0 mm². Current density-voltage (*J-V*) characteristics were measured by a Keithley 2400 Source Measure Unit, in N₂ atmosphere under an AM 1.5G solar simulator with an irradiation light intensity of 100 mW·cm⁻². The external quantum efficiency (EQE) of the devices was measured by using a QEX10 solar cell EQE measurement system (PV measurements.Inc.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Space-Charge-Limited Current (SCLC): The current density–voltage (J–V) characteristics of the hole or electron only devices are fitted by the Mott–Gurney law: $J = (9/8)\varepsilon_{r}\varepsilon_{0}\mu(V^{2}/L^{3})$

Where J is the current density, ε_r is the dielectric permittivity of the active layer, ε_0 is the vacuum permittivity, L is the thickness of the active layer, μ is the mobility. $V=V_{app}$ - V_{bi} , where V_{app} is the applied voltage, V_{bi} is the offset voltage (V_{bi} is 0 V here). The mobility can be calculated from the slope of the $J^{0.5} \sim V$ curves.

Atomic force microscopy (AFM) Characterization: AFM images were investigated on a Dimension Icon AFM (Bruker) in a tapping mode.

Transmission Electron Microscopy (TEM) Characterization: TEM images were performed on a JEOL JEM-1400 transmission electron microscope. TEM samples were prepared as follows: First, the active layer was spin cast on the top of ITO/PEDOT:PSS substrates; Then, the active layer film was peeled off and floated onto the surface of deionized water; Finally, the floated films were picked up on a carbon film 200 mesh copper grid for TEM measurements.

Contact angle measurements: All the photos were taken by digital camera with macro lens.

Surface Tension Calculation:The contact angles of two different solvent (Water and Glycerol) on neat films of copolymer donors L18, L19, and Y6 were used to calculate the surface tension by equation (1)-(3).

$$\gamma_{Water}(\cos\theta + 1) = \frac{4\gamma_{Water}^{d}\gamma^{d}}{\gamma_{Water}^{d} + \gamma^{d}} + \frac{4\gamma_{Water}^{p}\gamma^{p}}{\gamma_{Water}^{p} + \gamma^{p}}$$
(1)

$$\gamma_{Glycerol}(\cos\theta + 1) = \frac{4\gamma_{Glycerol}^{d}\gamma^{d}}{\gamma_{Glycerol}^{d} + \gamma^{d}} + \frac{4\gamma_{Glycerol}^{p}\gamma^{p}}{\gamma_{Glycerol}^{p} + \gamma^{p}}$$
(2)

$$\gamma = \gamma^{d} + \gamma^{p}$$
(3)

Where θ is the contact angle of neat polymer film, and γ is the surface tension of the film, which is the sum of dispersion (γ^d) and polarity (γ^p) components. γ_{Water} and $\gamma_{Glycerol}$ are the surface tensions of water and glycerol, respectively.

The relationship between surface tension (γ_D, γ_A) and interfacial tension (γ_{D-A}) is as follows:

$$\gamma_{D-A} = \gamma_D + \gamma_A - \frac{4\gamma_D^d \gamma_A^d}{\gamma_D^d + \gamma_A^d} - \frac{4\gamma_D^P \gamma_A^P}{\gamma_D^P + \gamma_A^P}$$
(4)

Where γ_{D-A} is the interfacial tension between donor and acceptor, $\gamma_D^d, \gamma_D^p, \gamma_A^d, \gamma_A^p$ are the dispersion component and the polarity component of the donors and the acceptor respectively, which could be obtained by the contact angle, and the surface tension is equal to the sum of the dispersion component and the polarity component.

The interaction parameter χ :

$$\chi_{D-A} \propto \left(\sqrt{\gamma_D} - \sqrt{\gamma_A}\right)^2 \tag{5}$$

GIWAXS Characterization: The samples for the GIWAXS measurements were prepared on Si substrates using chloroform solutions of the samples.



Figure S1. ¹H NMR spectrum of monomer 3 in CDCl₃.



Figure S2. ¹³C NMR spectrum of monomer 3 in CDCl₃.



Figure S3. ¹H NMR spectrum of monomer 4 in CDCl₃.



Figure S4. ¹³C NMR spectrum of monomer 4 in CDCl₃.



Figure S5. ¹H NMR spectrum of monomer 5 in CDCl₃.



Figure S6. ¹³C NMR spectrum of monomer 5 in CDCl₃.



Figure S7. TGA plots of **L18** and **L19** with a heating rate of 20°C/min under the inert atmosphere.



Figure S8. Cyclic voltammetry (CV) curves of the polymer donor L18 and L19.



Figure S9. *J-V* characteristics of (a) hole-only devices based on **L18** and **L19** neat films; (b) hole-only devices based on the **L18:Y6** and **L19:Y6** blend films; (c) electron-only devices based on the **L18:Y6** and **L19:Y6** blend films.



Figure S10. $J_{\rm ph}$ versus $V_{\rm eff}$ of the devices.



Figure S11. Device storage stability under dark conditions.



Figure S12. Phase images of (a) L18:Y6 and (b) L19:Y6 as cast; (c) L18:Y6 and (d) L19:Y6 under optimized condition; TEM images of (g) L18:Y6 and (h) L19:Y6 as cast.

Table S1. The device parameters of PSCs based on polymer:Y6 with various D:A ratios, concentrations, additive volume content, and annealing temperatures under illumination of AM $1.5G,100 \text{ mW} \cdot \text{cm}^{-2}$.

Active	Ratio	Additive	Concentration	Thermal	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
player	of	(w%)	(mg/ml)	annealing	(V)	(mA·cm ⁻²)	(%)	(%)
	D:A			temperature				
				(°C)				
L19:Y6	1:1.2	0	16	110	0.89	16.8	43.7	6.5
L19:Y6	1:1.2	0.3	16	110	0.9	19.6	43.02	7.6
L19:Y6	1:1.2	0.5	16	110	0.91	22.3	49.8	10.1
L19:Y6	1:1.5	0.5	16	110	0.87	18.4	55.8	8.9
L19:Y6	1:1.2	0.5	14	110	0.9	20.3	61.1	11.1
L19:Y6	1:1	0.5	14	110	0.93	22.9	54.6	11.7
L19:Y6	1:1	0.5	14	90	0.91	22.3	55	11.1
L19:Y6	1:1	0.5	14	150	0.89	23.9	46.1	9.8
L18:Y6	1:1.2	0	16	110	0.87	12.6	42.9	4.7
L18:Y6	1:1.2	0.3	16	110	0.93	13.5	43.4	5.4
L18:Y6	1:1.2	0.5	16	110	0.89	17.3	41.8	6.4
L18:Y6	1:1.5	0.5	16	110	0.91	9.42	38	3.3
L18:Y6	1:1	0.5	16	110	0.93	10.5	36.2	3.5

L18:Y6	1:1.2	0.5	14	110	0.93	13.5	43.5	5.5
L18:Y6	1:1.2	0.5	16	90	0.94	10.7	36.7	3.7
L18:Y6	1:1.2	0.5	16	150	0.9	15.9	42.5	6.1

Table S2. Photovoltaic data of the PSCs under AM 1.5G 100 mW·cm⁻² illumination.

Active layer	$V_{\rm oc}({ m V})$	$J_{ m sc}$	FF (%)	PCE _{max}	References
		$(mA \cdot cm^{-2})$		(%)	
PBDTT:Y6	0.78	19.94	64.4	10.02	Ref.1
PBDTS:Y6	0.81	21.17	65.6	11.25	Ref.1
PBDTF:Y6	0.82	22.73	67.9	12.66	Ref.1
PBDTC1:Y6	0.84	23.16	69.2	13.46	Ref.1
PBDTTO:Y6	0.83	27.03	59	13.29	Ref.2
PBF1-C:Y6	0.74	25.21	66	12.31	Ref.3
PBF1-C-2Cl:Y6	0.83	23.88	66	13.1	Ref.3
PM6-D1:Y6	0.85	26.47	78.7	17.71	Ref.4
PM6-D2:Y6	0.85	26.18	75.6	16.82	Ref.4
PM6-D3:Y6	0.86	26.01	76.1	17.02	Ref.4
PM7:Y6	0.88	25.61	73.3	17.04	Ref.5
PM6:Y6	0.84	25.38	15.55	15.9	Ref.5
PBB:Y6	0.84	4.25	42.36	1.51	Ref.6
PBBSe-H:Y6	0.65	22.23	56.4	8.17	Ref.6
PBBSe-Cl:Y6	0.82	24.07	73.16	14.44	Ref.6
TP-H:Y6	0.85	26.78	73.53	16.76	Ref.7
TP-EH:Y6	0.87	26.09	69.09	15.65	Ref.7
PBDB-TF:Y6	0.82	26.5	69	15	Ref.8
PBDB-TF-TT10:Y6	0.8	25.1	66	13.3	Ref.8
PBDB-TF-TT20:Y6	0.82	25.8	61	12.9	Ref.8
PBDB-TF-TT50:Y6	0.82	24.4	62	12.4	Ref.8
PBDB-TF-T10:Y6	0.84	27.9	70	16.4	Ref.8
PBDB-TF-T20:Y6	0.85	26.5	58	13.1	Ref.8
PBDB-TF-T50:Y6	0.85	23.5	43	8.6	Ref.8
PBNT-S:Y6	0.798	23	60.5	11.1	Ref.9
PBNP-S:Y6	0.81	25.5	69.4	14.3	Ref.9
P-17k:Y6	0.88	22.4	57	11.2	Ref.10
P-30k:Y6	0.86	23.8	75	15.3	Ref.10
P-53k:Y6	0.84	25.6	76	16.3	Ref.10
P-98k:Y6	0.82	25.9	76	16.2	Ref.10

Table S3. The mobilities data of PSCs based neat copolymers and polymer:Y6 blend films.

Active layer	Hole mobility/electron mobility (μ_h)/(μ_e) (cm ² ·V ⁻¹ ·s ⁻¹)	μ_h/μ_e
L19	1.6×10 ⁻³ / -	-
L18	7.13×10 ⁻⁴ / -	-
L19:Y6	3.34×10 ⁻³ /3.32×10 ⁻³	1.006
L18:Y6	5.93×10 ⁻⁴ / 7.57×10 ⁻⁴	0.78

Table S4. Summarized parameters for the surface tension of the films.

	L18	L19	Y6
$\gamma (\mathrm{mN}\cdot\mathrm{m}^{-1})$	31.58	28	21.57

 Table S5. Summarized interaction parameter for the different materials.

	L18:Y6	L19:Y6
$\gamma_{D-A}(\mathrm{mN}\cdot\mathrm{m}^{-1})$	11.69	9.55
$\chi_{D-A} \propto (\sqrt{\gamma_D} - \sqrt{\gamma_A})^2$	0.95	0.42

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