Supporting Information

Realizing High Efficiency Multiple Blend Polymer Solar Cells Enabled by a Unique Parallel-Series Working Mechanism

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1. Materials and synthetic details

Materials: F8IC was purchased from Derthon Optoelectronic Materials Science Technology Co., LTD with purity of 99%, PC₇₁BM was purchased from Solenne BV (Netherlands) with purity of 99%. Polymer PBDTSF-TZNT,¹ 5-bromo-2-(2'ethylhexyloxy)-1,3-difluoro benzene (1),² diethyl 2,5-di(thieno[3,2-b]thiophen-2yl)terephthalate (2)³ and 3-(dicyano methylidene)indan-1-one (IC)⁴ were synthesized according to previously reported procedures. All the other chemicals were purchased from Aladdin, Adamas, and Innochem and used without further purification. All solvents were freshly distilled immediately prior to use.



Scheme S1. Synthetic route of f8OIC.

Synthesis of compound 3

n-BuLi (1.6 mL, 4.06 mmol, 2.50 M in hexane) was added to a solution of 5-bromo-2-(2'-ethylhexyloxy)-1,3-difluorobenzene (1) (1.30 g, 4.06 mmol) in THF (20 mL) at -78 °C, the mixture was kept at -78 °C for 1 h, then a solution of diethyl 2,5di(thieno[3,2-b]thiophen-2-yl)terephthalate (2) (0.41 g, 0.81 mmol) in THF (30 mL) was added slowly. After that, the mixture was stirred at room temperature overnight and then poured into water and extracted twice with ethyl acetate. The combined organic phase was dried over Na₂SO₄. After removing the solvent, the crude product was charged into a three-neck flask. Acetic acid (40 mL) and concentrated H₂SO₄ (0.4 mL) were added and the mixture was refluxed for 4 h. The mixture was extracted twice with dichloromethane (DCM), the combined organic layer was dried over MgSO₄. The crude product was purified by column chromatography with petroleum ether and dichloromethane (v:v = 5:1) as eluent to obtain compound 3 appeared as a yellow solid (0.43 g, 39.09%). ¹H NMR (400 MHz, CDCl₃, δ/ppm) 7.41 (s, 2H), 7.33-7.35 (m, 4H), 6.77-6.79 (d, J = 8.0 Hz, 8H), 4.00-4.01 (d, J = 4 Hz, 8H), 1.63-1.68 (m, 4H), 1.28-1.45 (m, 32H), 0.87-0.90 (m, 24H). ¹³C NMR (100 MHz, CDCl₃, δ/ppm) 157.15, 157.09, 154.68, 154.61, 151.92, 144.03, 143.39, 142.55, 136.52, 136.44, 136.37, 136.24, 135.62 132.93, 127.39, 120.69, 116.86, 112.11, 111.87, 61.82, 40.19, 30.04, 28.93, 23.46, 23.02, 14.07, 11.01. Anal. Calc'd for (C₇₆H₈₂F₈O₄S₄) (%): C 68.14, H 6.17; found (%): C 69.25, H 6.24.

Synthesis of compound 4

Compound **3** (0.54 g, 0.41 mmol) was dissolved in the mixture of DMF (10 mL) and 1,2-dichloroethane (10 mL). An excess amount of phosphorus oxychloride (1 mL) was added and the mixture was stirred at 80 °C overnight. The reaction was then quenched with saturated sodium acetate solution (10 mL) and stirred for 30 min at room temperature. The mixture was extracted twice with DCM, and the combined organic layer was dried over MgSO₄. The crude product was purified by column

chromatography with petroleum ether and dichloromethane (v:v = 1:1) as eluent to obtain compound **4** as a light yellow solid (0.26 g, 47.02%). ¹H NMR (400 MHz, CDCl₃, δ /ppm) 9.93 (s, 2H), 8.01 (s, 2H), 7.52 (s, 2H), 6.74-6.76 (d, *J* = 8 Hz, 8H), 4.01-4.02 (d, *J* = 4 Hz, 8H), 1.65-1.68 (m, 4H), 1.29-1.47 (m, 32H), 0.87-0.91(m, 24H). ¹³C NMR (100 MHz, CDCl₃, δ /ppm) 157.15, 157.09, 154.68, 154.61, 151.92, 144.03, 143.39, 142.55, 136.52, 136.44, 136.37, 136.24, 135.62, 132.93, 127.39, 120.69, 116.86, 112.11, 111.87, 61.82, 40.19, 30.04, 28.93, 23.46, 23.02, 14.07, 11.01. Anal. Calc'd for (C₇₈H₈₂F₈O₆S₄) (%): C 67.12, H 5.92; found (%): C 67.41, H 6.03.

Synthesis of compound **f80IC**

Compound **4** (0.17 g, 0.12 mmol) and 3-(dicyanomethylidene)indan-1-one (**IC**) (0.24 g, 1.24 mmol) were dissolved in chloroform (30 mL). After that, pyridine (1.0 mL) was added. The mixture was stirred at 80 °C overnight. After cooling down, the reaction mixture was concentrated under vacuum. The crude product was purified by column chromatography with petroleum ether and chloroform (v:v = 1:3) as eluent to obtain compound **f8OIC** as an ink blue solid (0.11 g, 49.68%). ¹H NMR (400 MHz, CDCl₃, δ /ppm) 8.89 (s, 2H), 8.68-8.70 (d, *J* = 8 Hz, 2H), 8.23 (s, 2H), 7.93 (s, 2H), 7.77 (s, 4H), 7.55 (s, 2H), 6.83-6.85 (d, *J* = 8 Hz, 8H), 4.04-4.05 (d, J = 4 Hz, 8H), 1.66-1.67 (m, 4H), 1.25-1.43 (m, 32 H), 0.86-0.90 (m, 24H). ¹³C NMR (100 MHz, CDCl₃, δ /ppm) 188.09, 160.05, 157.24, 154.77, 154.03, 151.92, 145.40, 145.28, 143.73, 140.05, 139.96, 137.89, 136.85, 136.58, 136.17, 135.43, 135.01, 134.73, 125.41, 124.02, 123.79, 118.30, 114.35, 112.08, 111.84, 70.32, 40.21, 30.04, 29.71, 28.93, 23.46, 23.00, 14.05, 11.01. Anal. Calc'd for (C₁₀₂H₉₀F₈N₄O₆S₄) (%): C 70.08,

H 5.19, N 3.21; found (%): C 70.13, H 5.26, N 3.29.

2. Methods, device fabrication and measurements

Methods: ¹H and ¹³C NMR spectra were recorded on a Bruker Avance-400 spectrometer with d-chloroform (CDCl₃) as the solvent and tetramethylsilane (TMS) as internal standard. The elemental analysis was performed on a Thermo Electron SPA Flash EA 1112 series analyzer. Thermogravimetric analysis (TGA) was conducted on a TA Instrument Model SDTQ500 at a heating rate of 10 °C min⁻¹ and under a N_2 flow rate of 90 mL min⁻¹. UV-vis spectra were obtained on a Hitachi U2910 spectrophotometer. Atomic Force Microscopy (AFM) images were obtained by using a Bruker Innova atomic microscope in tapping mode. Cyclic voltammetry measurements were carried out on a CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s⁻¹, with the platinum wire as the counter electrode and the Ag/AgCl as the reference electrode, which was calibrated by the ferrocene/ferrocenium (Fc/Fc⁺) redox couple to be -4.34 eV. Grazing-incidence wideangle X-ray scattering (GIWAXS) measurements were conducted at the PLS-II 9A U-SAXS beamline of Pohang Accelerator Laboratory, Pohang, Korea. Samples for GIWAXS measurements were prepared by spin-coating active blend solutions on top silicon Poly(3,4-ethylenedioxythiophene):polystyrene of а wafer. sulfonate (PEDOT:PSS) (Bay P VP. Al 4083, Bayer AG) was first filtrated through a 0.45 µm nylon filter and then spin-coated on the Si substrates prior to the deposition of the thin film. Photoluminescence (PL) spectroscopy was performed on a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon) excited with a 680 nm light source.

Device Fabrication: The device was fabricated with a conventional structure of ITO/PEDOT:PSS/active layer/OTF/Al. The patterned indium tin oxide (ITO, sheet resistance = 15 Ω square⁻¹) glass substrates were sequentially ultrasonicated with detergent, deionized water, acetone and isopropanol. Then, the ITO glasses were UV treated with for 30 min UV-ozone chamber. Poly(3,4in а ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) (Bay P VP. Al 4083, Bayer AG) was first filtrated through a 0.45 µm nylon filter and then spin-coated on the cleaned ITO substrates at 5000 rpm for 60 s to form a thin layer (35 nm). The substrates were baked on a hot plate at 150 °C for 10 min and transferred into the argon-filled glove box. The polymer:acceptor solution (16 mg mL⁻¹ in chloroform) was prepared and stirred overnight at 60 °C. The active blend solution was spin-coated on the top of PEDOT:PSS layer at a speed of 2500 rpm for 30 s to fabricate the active layer of thickness about 100 nm. OTF solution (0.5 mg mL⁻¹ in ethanol) was spincoated on the top of the active layer to form a thin cathode interlayer (5 nm). Then the aluminum electrode (Al, 100 nm) was finally deposited onto the top of the active layer in an evaporation chamber under high vacuum ($\leq 10^{-6}$ mbar). The device area was exactly fixed at 4.00 mm².

Device measurements: The *I-V* characterization was performed on a computercontrolled Keithley 2400 Source under AM 1.5G (100 mW cm⁻²) using a solar simulator (XES-70S1, SAN-EI), which was calibrated by a standard Si solar cell (AK-200, Konica Minolta, INC.). The EQE values were measured with a Newport QE test Model 77890 (Newport Co. Ltd.) during illumination with monochromatic light from a xenon lamp. The transient photocurrent (TPC) and photovoltage (TPV) decay measurements were conducted using a pulsed double frequency Nd:YAG laser (Brio, 1000 Hz) at a wavelength of 550 nm and an ultra-low light intensity. The dynamics curves were recorded on a sub-nanosecond resolution digital oscilloscope (Tektronix DPO 7104) at a 50- Ω (short-circuit condition for TPC) resistor and a mega Ω (opencircuit condition for TPV).

Charge carrier mobilities: Charge carrier mobilities were measured using the SCLC method, which 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 is the hole or electron mobility, $\varepsilon_{\rm r}$ 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 device and $V = V_{appl} - V_{bi} - V_{a}$, where V_{appl} is the applied voltage to the device, V_{bi} is the built-in voltage and V_a is the drop. Hole-only devices were fabricated with a voltage structure of ITO/PEDOT:PSS/polymer:acceptor/MoO₃/Au. PEDOT:PSS first filtrated was through a 0.45 µm nylon filter and then spin-coated on the cleaned ITO substrates at 5000 rpm for 60 s to form a thin layer (35 nm). The substrates were baked on a hot plate at 150 °C for 10 min and transferred into the argon-filled glove box. A 10 nm of molybdenum oxide (MoO_3) layer was evaporated onto the surface of the active blend film before the evaporation of Au (100 nm) electrode. Electron-only devices were fabricated with a structure of glass/Al/polymer:acceptor/Al. 100 nm of Al electrode was evaporated before and after the active layer spin-coating.

3. Supplementary Figures



Fig. S1 TGA curve of f8OIC.



Fig. S2 CV curves of f8OIC (a) and F8IC (b).



Fig. S3 Plot illustrating the stability of encapsulated devices kept in dark (a) and under continuous illumination (b) under ISOS D1 and L1 conditions.



Fig. S4 J-V^{0.5} curves of the hole-only devices (a) and electron-only devices (b).



Fig. S5 AFM height (a-c) and tapping phase (d-f) images of neat acceptor materials.



Fig. S6 GIWAXS images of F8IC (a), f8OIC (b) and single-acceptor blends containing PC₇₁BM (c) and f8OIC (d).



Fig. S7 *J-V* curves of the electron acceptor-only devices. Device structure: ITO/PEDOT:PSS/acceptor/OTF/A1.

Acceptor	$\mu_{\rm h} (10^{-4}{\rm cm}^2{ m V}^{-1}{ m s}^{-1})$	$\mu_{\rm e} (10^{-4}{\rm cm}^2{ m V}^{-1}{ m s}^{-1})$	$\mu_{ m h}/\mu_{ m e}$
f8OIC	3.4	2.3	1.47
F8IC	2.1	6.6	0.38
f8OIC:F8IC	4.5	5.1	0.88
f8OIC:F8IC:PC71BM	6.4	6.0	1.07

Table S1 Charge carrier mobilities of the single, double and triple-acceptor devices.

Active layer	$V_{\rm oc}$	$J_{ m sc}$	FF	PCE
	[V]	[mA cm ⁻²]	[%]	[%]
f8OIC	0.66	0.252	32.5	0.054
PC ₇₁ BM	0.84	0.091	33.2	0.025
F8IC	0.59	0.166	36.8	0.036
f8OIC:PC71BM	0.88	0.614	59.2	0.320
F8IC:PC71BM	0.72	0.121	32.1	0.028
F8IC:f8OIC	0.60	0.200	35.8	0.043
F8IC:f8OIC:PC71BM	0.80	0.425	42.4	0.144

 Table S2 Device parameters of the electron acceptor-only devices.

4. References

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