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Electronic Supplementary Information (ESI)

High Open Circuit Voltage Organic Photovoltaic Cells Fabricated Using 9,9'-Bifluorenylidene as Non-Fullerene Type Electron Acceptor

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25 Experimental

♦ Materials

9H-fluorene, chromium(IV) oxide, activated MnO₂, Lawsson's reagent, titanium(IV) tetrachloride and triethyl amine were purchased from Aldrich and Alfa Aesar. All chemicals were used without further purification.

30 Measurements

¹H and ¹³C NMR spectra were recorded using a Varian 300 spectrometer. The fast atom bombardment mass spectra were measured by using ZMS-DX303 Mass spectrometer (FAB-Mass; JEOL LTD.) and the absorption spectra were measured by using scinco UV-vis Spectrophotometer model s-300. Photoluminescence (PL) spectra were recorded using a Shimadzu RF 5301 PC fluorometer. Fourier-transform infrared (FT-IR) spectra, by using NicoLET 380 spectrometer. Electronic structure

35 calculations were carried out at density functional theory (DFT) level using B3LYP hybrid exchange-correlation functional and 6-31G(d) basis sets. Optimized geometries were confirmed to be local minima with subsequent frequency calculations.

These calculations were conducted using Gaussian 09 package.¹ Atomic force microscopy (AFM) were taken with a Digital Instruments Nanoscope IV. The space-charge limited current (SCLC) hole and electron-only devices were recorded using a MINOLTA CS-2000.

5 • Fabrication of photovoltaic devices

- Composite solutions of P3HT and 9,9'BF or 4,4'BP were prepared using 1,2-dichlorobenzene as the solvent. The concentration was controlled adequately in the range 1.0~2.0 wt%. Polymer photovoltaic devices with a typical sandwich structure of ITO/PEDOT:PSS/P3HT:acceptor/LiF/Al were fabricated. The ITO-coated glass substrates were cleaned by a routine cleaning procedure that involved sonication in a detergent followed by sonication in distilled water, acetone and 10 then 2-propanol. A 40 nm thick layer of PEDOT: PSS (Clevious P VP AI4083) was spin coated on a cleaned ITO substrate after exposing the ITO surface to ozone for 10 min. The PEDOT:PSS layer was baked on hot plate at 150 °C for 15 min. The pre-dissolved composite solution was filtered by using 0.45 µm syringe filters, and the active layer was spin coated on the PEDOT:PSS layer for 800 rpm to a thickness of 100 nm. Finally, a top electrode consisting of a 0.5 nm thick layer of LiF and a 120 nm thick layer of Al was deposited on the polymer active layer under a vacuum of 3 x 10⁻⁶ Torr in a
- 15 thermal evaporator. The current–voltage (*J-V*) characteristics of all the polymer photovoltaic cells were analyzed under simulated solar light (intensity: 100 mW/cm²; AM 1.5 G) provided by an Oriel 300 W solar simulator. Electric data were recorded using a Keithley 2400 source-measure unit, and all characterizations were carried out in an ambient environment. The intensity of the simulated sunlight used was calibrated using a standard Si photodiode detector (BS520, Bunkoh-keiki) which was calibrated at NREL. The thickness of the thin film was measured using a KLA Tencor Alpha-step IQ surface
- 20 profilometer with an accuracy of ±1 nm. The external quantum efficiency (EQE) was measured as a function of the wavelength in the wavelength range 360 to 800 nm using a halogen lamp as the light source, and the calibration was performed by using a silicon reference photodiode. Measurement was carried out after masking all but the active cell area of the fabricated device. The active area of the fabricated devices was 9 mm². All the characterization steps were carried out in an ambient laboratory atmosphere.

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♦ Fabrication of hole- and electron-only devices

To measure the hole and electron mobilities of P3HT:9,9'BF and P3HT:4,4'BP blend, the ITO/MoO₃/blend/ MoO₃/Al and ITO/ZnO/blend/ LiF/Al devices were fabricated for hole-only and electron-only devices, respectively. The SCLC mobilities were estimated using the Mott-Gurney law;

$$J = \frac{8}{9}\varepsilon_r\varepsilon_o\mu\frac{V^2}{L^3}$$

30 Where *J* is the current density, ε_r is the dielectric constant of the 9,9'BF or 4,4'BP, ε_o is the permittivity of the vacuum, μ is the hole or electron mobility, *L* is the film thickness of the blend films, $V = V_{appl} - V_{bi}$, V_{appl} is the applied potential, and V_{bi} is the built-in voltage which results from the difference in the work function of the anode and the cathode.

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Scheme S1. Synthetic routes and chemical structure of 9,9'BF and 4,4'BP.

Synthesis of 9,9'BF and 4,4'BP

5 Synthesis of 9,9-bifluorenylidene (9,9'BF)

To a solution of compound **1** (0.5 g, 2.77 mmol) in toluene (100 ml) was added, Lawesson's reagent (0.56 g, 1.38 mmol). The mixture was refluxed overnight. The solution was concentrated under reduced pressure. The resulting mixture was extracted with ethyl acetate/brine, and then dried with anhydrous MgSO₄. The residue product was purified by column chromatography using hexane/ethyl acetate as the eluents. The resulting solid was recrystallized in dichloromethane and 10 methanol, and then the orange needles were dried in vacuo. A orange needles **9,9'BF** was obtained (0.42 g, 46.1%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.41 (d, 4H), 7.87 (d, 4H), 7.40 (t, 4H), 7.31 (t, 4H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 142.0, 141.2, 138.9, 129.4, 127.5, 127.1, 120.8. FAB-MS (M⁺¹, C₂₆H₁₆): calcd; 328.41, found; 328. FT-IR (KBr,

cm⁻¹): 3050 (aromatic C-H stretch), 1610, 1480 (aromatic C=C stretch), 764 (aromatic C-H out-of-plane bend).

- 15 Synthesis of 4,4'-bicyclopenta[*def*]phenanthrenylidene (4,4'BP)
- Triethylamine (0.74g, 7.31 mmol) and anhydrous chloroform are mixed under N₂ atmosphere at 0 °C. The 1M solution of titanium(IV) tetrachloride (0.54 ml, 4.91 mmol) in dichloromethane are added under nitrogen at 0 °C. The reaction is stirred for 1h at 0 °C and to this reaction mixture of compound **2** (0.5 g, 2.45 mmol) are added and the stirring is continued for further 5h at room temperature. The reaction mixture is then quenched with a saturated solution of NH₄Cl. The organic
- 20 layer is separated and the aqueous layer is extracted with dichloromethane/brine and then dried with anhydrous MgSO₄. The residue product was purified by column chromatography using hexane/ethyl acetate as the eluents. The resulting solid was recrystallized in dichloromethane and methanol, and then the orange needles were dried in vacuo. A orange needles **4,4'BP** was obtained (0.32g, 34.7%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.74 (d, 4H), 7.85 (m, 8H), 7.66 (t, 4H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 143.0, 137.3, 137.1, 128.3, 127.6, 126.1, 125.2, 124.0. FAB-MS (M⁺¹, C₂₆H₁₆): calcd;

25 376.45, found; 376. FT-IR (KBr, cm⁻¹): 3040 (aromatic C-H stretch), 1640, 1440 (aromatic C=C stretch), 731 (aromatic C-H out-of-plane bend).

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Figure S1. (a) TGA and (b) DSC curves of 9,9'BF and 4,4'BP.



Figure S2. UV-vis absorption spectra of 9,9'BF and 4,4'BP. (a) CHCl₃ solution, (b) solid film, (c) with P3HT blend films.



Figure S3. PL quenching spectra of (a) P3HT:9,9'BF and (b) P3HT:4,4'BP in CHCl₃ with increasing concentration of acceptors. (c) PL spectra of pure P3HT, P3HT:9,9'BF (1:0.7), and P3HT:4,4'BP (1:0.7) films.



Figure S4. (a) Cyclic voltammograms of 9,9'BF and 4,4'BP and (b) energy diagrams of the HOMO and LUMO energy levels for the P3HT, 9,9'BF, and 4,4'BP.



Optical						Electrochemical	
Acceptor _	$\lambda_{\max, abs}$ (nm)		λ_{onset} (nm)	$E_{\sigma}^{\text{opt}} (\text{eV})^{\text{a}}$	K _{sv}	НОМО	LUMO
	Solution	Film	-onset ()	5 ()	(M^{-1})	(eV)	(eV)
9,9'BF	246, 273, 460	246, 275, 462	579	2.14	3.21 x 10 ⁵	-5.62	-3.48
4,4'BP	231, 244, 340, 475, 510	224, 344, 479	623	1.99	$3.17 \ge 10^4$	-5.33	-3.34

Table S1. Optical and Electrochemical properties of 9,9'BF and 4,4'BP.

^a Calculated from λ_{onset} of the absorption spectrum of the solid film.

Figure S5. Geometries and frontier molecular orbitals of 9,9'BF and 4,4'BP derived at B3LYP/6-31G(d) level.



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Figure S6. *J-V* curves of the PSCs based on P3HT:9,9'BF (a) pristine, (b) annealing at 90 °C, and (c) annealing at 150 °C under the 1.5 G illumination of 100 mW/cm².



5 Table S2. Photovoltaic performances of the PSCs based on P3HT:9,9'BF with different annealing temperature conditions.

P3HT:9,9'BF	Annealing temp. (°C)	$V_{oc}\left(\mathrm{V} ight)$	J_{sc} (mA/cm ²)	FF	PCE (%)
1 : 0.5		0.84	2.44	0.33	0.68
1 : 0.7	misting	1.05	3.28	0.31	1.07
1 : 1	pristine	0.92	3.33	0.31	0.95
1 : 1.2		0.84	2.30	0.34	0.66
1 : 0.5		0.92	4.36	0.36	1.44
1 : 0.7	00	0.93	4.52	0.41	1.73
1 : 1	90	0.95	4.27	0.42	1.69
1 : 1.2		0.93	4.04	0.38	1.43
1 : 0.5		0.85	1.78	0.31	0.47
1 : 0.7	150	0.85	2.25	0.32	0.61
1 : 1	150	0.80	2.17	0.32	0.56
1 : 1.2		0.85	2.00	0.33	0.56

P3HT:4,4'BP	Annealing temp. (°C)	$V_{oc}\left(\mathrm{V} ight)$	J_{sc} (mA/cm ²)	FF	PCE (%)
1 : 0.5		0.17	0.04	0.25	0.001
1 : 0.7	nuistina	0.18	0.04	0.25	0.002
1 : 1	prisuite	0.22	0.04	0.25	0.002
1 : 1.2		0.24	0.04	0.25	0.002
1 : 0.5		0.26	0.04	0.25	0.002
1 : 0.7	70	0.27	0.03	0.25	0.002
1 : 1	70	0.30	0.05	0.25	0.003
1 : 1.2		0.34	0.04	0.25	0.003
1 : 0.5	00	0.24	0.05	0.25	0.003
1 : 0.7	20	0.24	0.04	0.24	0.003

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1:1		0.34	0.04	0.24	0.004
1 : 1.2		0.35	0.05	0.24	0.005
1 : 0.5		0.24	0.04	0.25	0.003
1 : 0.7	150	0.27	0.04	0.25	0.003
1 : 1	150	0.32	0.05	0.25	0.004
1 : 1.2		0.38	0.06	0.24	0.005

Figure S7. Field-dependent hole mobilities of (a) P3HT:9,9'BF (1:0.7, w/w) and (b) P3HT:4,4'BP (1:0.7, w/w) blend films pristine and after annealing calculated from the hole-only devices by fitting J-V curves in the SCLC regime.



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Table S3. Hole and electron mobilities of P3HT:9,9'BF and P3HT:4,4'BP blend films under the different annealing temperature conditions, calculated using the Mott-Gurney law.

Condition	$\mu_{\rm h} ({\rm cm}^2/{\rm Vs})^{\rm a}$		$\mu_{\rm e} ({\rm cm}^2/{\rm Vs})^{\rm a}$		$\mu_{ m h}$ / $\mu_{ m e}$	
Condition	P3HT:9,9'BF	P3HT:4,4'BP	P3HT:9,9'BF	P3HT:4,4'BP	P3HT:9,9'BF	P3HT:4,4'BP
Pristine	9.06 x 10 ⁻⁵	9.04 x 10 ⁻⁵	1.62 x 10 ⁻⁶	1.74 x 10 ⁻⁸	56	5,195
Annealed at 70 $^{\rm o}{\rm C}$	2.75 x 10 ⁻⁴	1.68×10^{-4}	4.73 x 10 ⁻⁶	2.21 x 10 ⁻⁸	58	7,602
Annealed at 90 °C	3.61 x 10 ⁻⁴	1.92 x 10 ⁻⁴	1.09 x 10 ⁻⁶	3.16 x 10 ⁻⁸	331	6,076
Annealed at 150 ° C	4.98 x 10 ⁻⁴	3.68 x 10 ⁻⁴	6.26 x 10 ⁻⁸	3.47 x 10 ⁻⁸	7,955	10,605

^aHole and electron mobility (cm²/Vs) at the electric field of 500 (V/cm)^{1/2}.

Figure S8. AFM images of (a) ~ (d) P3HT:9,9'BF (1:0.7, w/w) and (e) ~ (h) P3HT:4,4'BP (1:0.7, w/w) blend films.



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