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Supplementary Information

Fluorination on both D and A Unit in D–A Type conjugated copolymer based on difluorobithiophene and benzothiadiazole for high efficient polymer solar cells

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Experimental Section

Materials

[6,6]-Phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) was obtained from Nano-C. All reagents were purchased from Sigma-Aldrich unless specified and used as received.

Synthesis of polymers

3,3'-Difluoro-2,2'-bithiophene (**1**)¹ and thiophene-flanked 2,1,3-benzothiadiazole derivatives (**2**, **3** and **4**)² were synthesized by following the methods reported in the literatures. For synthesis of 2F polymer, the compounds **1** (70 mg, 0.13 mmol) and **2** (150 mg, 0.13 mmol) were dissolved in a mixture of toluene (10 mL) and DMF (1 mL). After the solution was flushed with N₂ for 20 min, 10 mg of Pd(PPh₃)₄ was added. The

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reaction mixture was stirred for 5 h at 150°C in a microwave reactor. After being cooled to room temperature, the mixture was poured into methanol. The crude product was filtered through a Soxhlet thimble and then subjected to Soxhlet extraction successively with methanol, ethyl acetate, hexane and chloroform. The chloroform fraction was precipitated into methanol to afford the product as a dark green solid (82 mg, 54%). ¹H NMR (500 MHz, CDCl₃): δ (ppm), 8.32-7.50 (m, 4H), 7.05-5.26 (m, 2H), 3.15-0.85 (br, 98H). The 3F and 4F polymers were synthesized by following the same procedure as used in the synthesis of 2F. The compound **2** (69 mg, 0.13 mmol) and **3** (150 mg, 0.13 mmol) were used as monomers for the 3F polymer, and a dark green solid was obtained as a product (112 mg, 72%). ¹H NMR (500 MHz, CDCl₃): δ (ppm), 8.48-7.46 (m, 3H), 7.05-4.92 (m, 2H), 3.15-0.85 (br, 98H). For the 4F polymer, the compound **2** (68 mg, 0.13 mmol) and **4** (150 mg, 0.13 mmol) were used as monomers, and a dark green solid was obtained as a product (120 mg, 76%). ¹H NMR (500 MHz, CDCl₃): δ (ppm), 8.50-7.42 (m, 2H), 6.91-4.90 (m, 2H), 3.15-0.85 (br, 98H).

Characterization

The chemical structures of polymers were identified by ¹H NMR (Avance DPX-500) using *d*-chloroform (CDCl₃) as solvent and tetramethylsilane as internal reference. Molecular weight and distribution of polymers were measured by GPC (Waters) with a refractive index detector (Waters 2414) at 80 °C. *o*-Dichlorobenzene was used as an eluent, and the molecular weight of polymers were calibrated by polystyrene standards. The optical absorption spectra were obtained by an UV–Vis spectrophotometer (Lambda 25, Perkin Elmer). Cyclic voltammetry were conducted on a potentiostat/galvanostat (VMP 3, Biologic) in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile. Pt wires

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(Bioanalytical System Inc.) were used as both counter and working electrodes, and silver/silver ion (Ag in 0.1 M AgNO₃ solution, Bioanalytical System Inc.) was used as a reference electrode. The HOMO energy levels of polymers were calculated by using the equation: HOMO (V) = $-[E_{\text{ox}} - E_{1/2}(\text{ferrocene}) + 4.8]$, where E_{ox} is the onset oxidation potential of the polymer and $E_{1/2}(\text{ferrocene})$ is the onset oxidation potential of ferrocene vs. Ag/Ag⁺. DFT calculations at the B3LYP/6-31G(d,p) level were carried out on Gaussian 09.

Device fabrication and testing

Bottom-gate/top-contact OFETs were fabricated using heavily doped Si wafer as the bottom gate electrode with 300 nm of SiO₂ layer as the gate dielectric. The substrate was cleaned in acetone and isopropanol, and dried in an oven at 150 °C. The device was treated with UV ozone for 15 min, and then the SiO₂ layer was treated with octadecyltrimethoxysilane. The polymer films were spin-cast at 1000 rpm and annealed at a 150 °C for 20 min. Finally, the 40 nm thick gold top contact was thermally evaporated in vacuum through a shadow mask. The field effect mobilities were extracted from the saturation regime using the relationship $\mu_{\text{sat}} = (2I_{\text{DS}}L)/(WC(V_{\text{G}} - V_{\text{th}})^2)$, where I_{DS} denotes the saturation drain current, W is channel width ($W = 1$ mm), L is channel length ($L = 50$ μm), C is the capacitance ($C_i = 10.8$ nF·cm⁻²) of SiO₂ dielectric, V_{G} is the gate bias, and V_{th} is the threshold voltage. The inverted solar cells were fabricated with a device configuration of ITO/ZnO/PEIE/polymer:PC₇₁BM/MoO₃/Ag. ZnO layer with 30 nm thickness was spin-coated onto the ITO-coated glass from a ZnO precursor solution (zinc acetate dihydrate in 2-methoxyethanol and ethanolamine). After thermal annealing at 200 °C for 1 h, thin layer of PEIE was spin coated onto the ZnO film from dilute PEIE solution (0.4 wt% in 2-methoxyethanol) at 5000 rpm for 1 min and dried at 100 °C for 10 min. It should be noted here that the PEIE layer in the device lowers the work function of ZnO by the dipole

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formation and also improves physical contact between ZnO and active layer.³ The active layers were then spin-coated from the blend solution. MoO₃ (8 nm) and Ag (150 nm) were thermally evaporated on the top of the active layer under vacuum ($<10^{-6}$ Torr). The film thickness of the active layer was measured by atomic force microscopy (Nano Xpert II, EM4SYS). The effective area of the cell was ca. 0.1 cm². The current density–voltage (J – V) characteristics were measured with a Keithley 4200 source-meter under AM 1.5G (100 mW cm⁻²) simulated by a Newport-Oriel solar simulator. The light intensity was calibrated using a NREL-certified photodiode prior to each measurement. The EQE was measured using a lock-in amplifier with a current preamplifier (K3100, Mac Science Co.) at short circuit current state under illumination of monochromatic light. The morphologies of polymer:PC₇₁BM blend films were observed by a TEM (JEM-1010, JEOL). The SCLC J – V curves were obtained in the dark using hole-only devices (ITO/PEDOT:PSS/polymer:PC₇₁BM/Au), and hole mobilities were calculated using the Mott-Gurney square law, $J = (9/8)\epsilon_0\epsilon_r\mu(V^2/L^3)$, where ϵ_0 is vacuum permittivity, ϵ_r is the dielectric constant of polymer, μ is the charge carrier mobility, V is the effective applied voltage, and L is the thickness of the film. GIWAXS measurements were conducted at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea.

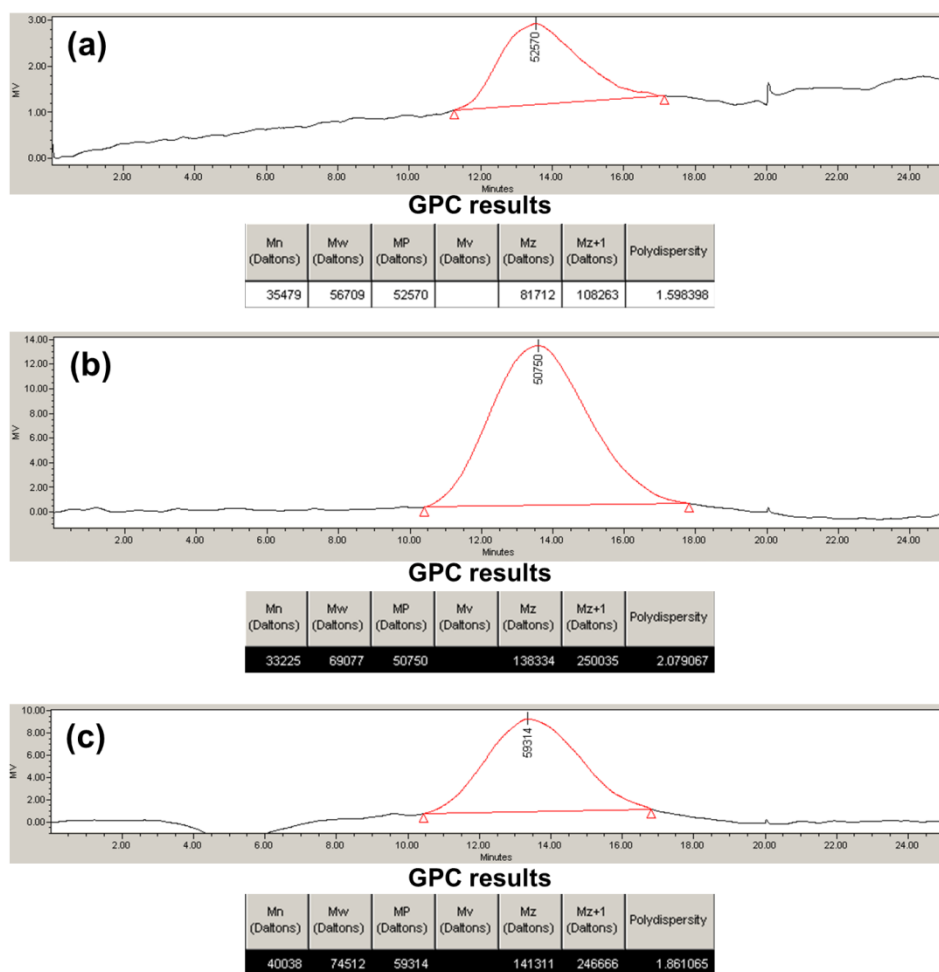


Figure S1 GPC traces of (a) 2F, (b) 3F and (c) 4F eluted with *o*-dichlorobenzene at 80 °C.

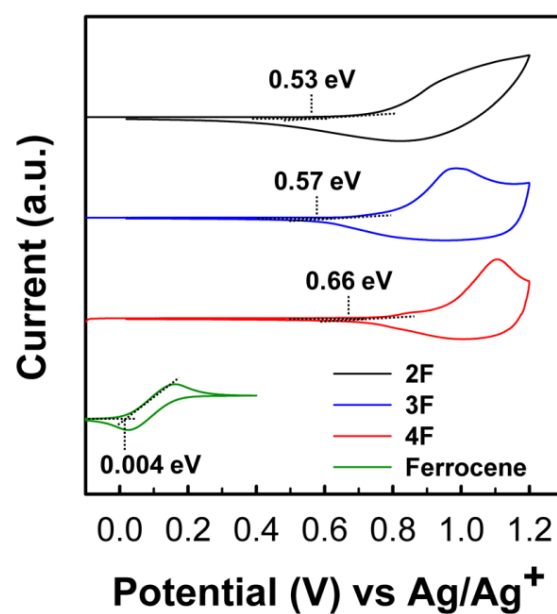


Figure S2 Cyclic voltammograms of polymers.

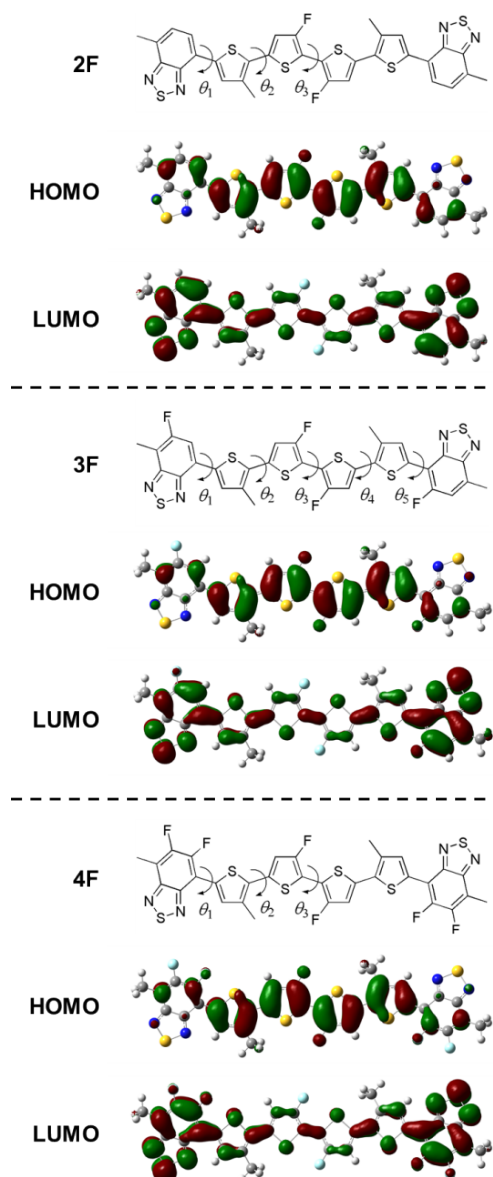


Figure S3 Chemical structure of repeating units for simulation, and the HOMO and LUMO orbital distributions as calculated at the B3LYP/6-31G(d,p) level.

Table S1 Torsion angles and energy levels of repeating units calculated by DFT.

Polymer	θ_1 [Deg]	θ_2 [Deg]	θ_3 [Deg]	θ_4 [Deg]	θ_5 [Deg]	HOMO [eV]	LUMO [eV]
2F	2.08	-8.99	0.48			-4.85	-2.63
3F	1.36	-8.81	-0.41	7.79	-0.17	-4.89	-2.71
4F	0.21	11.01	0.46			-4.94	-2.75

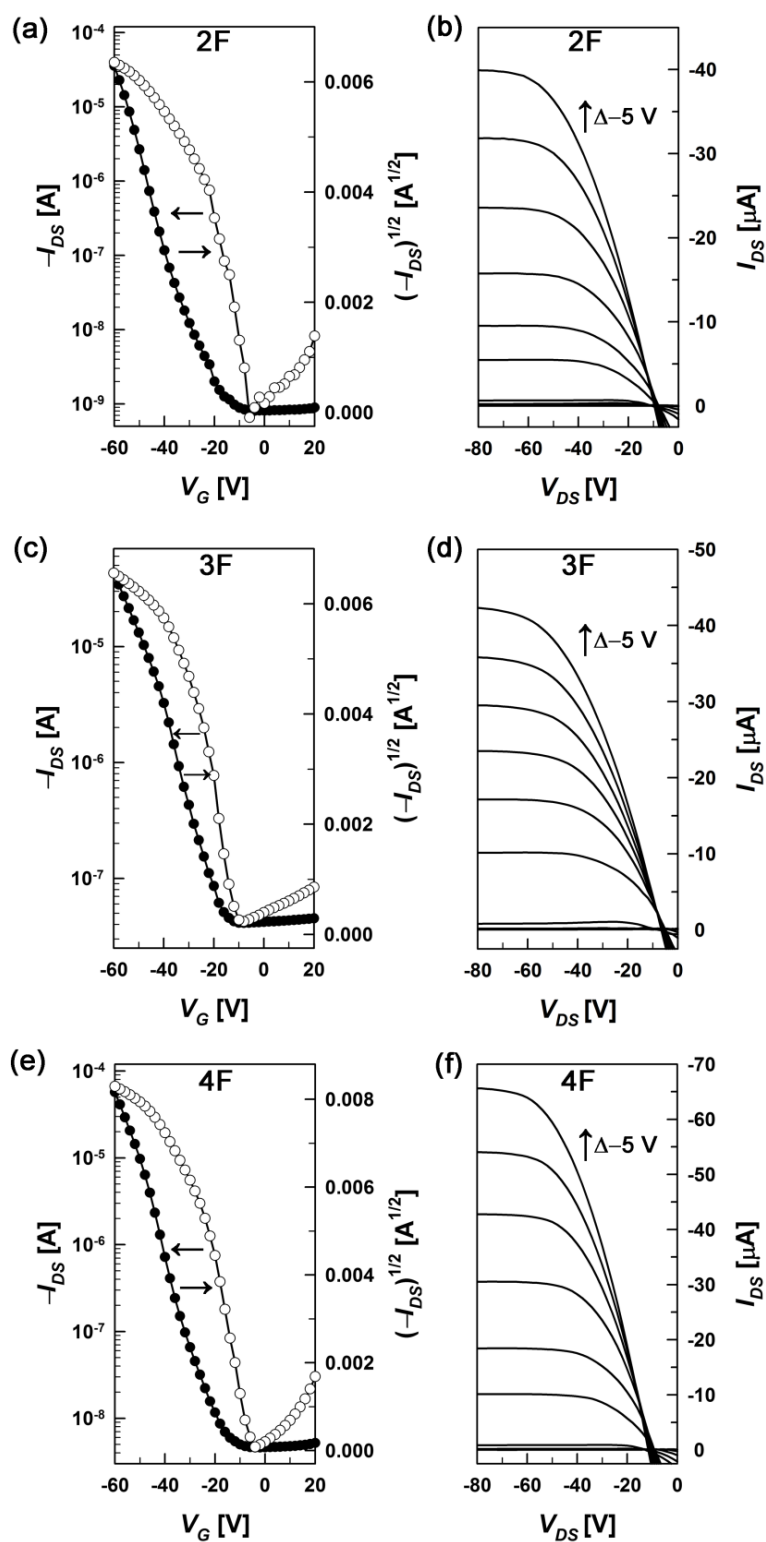


Figure S4 (Left column, a, c and e) OFET transfer curves and (right column, b, d and f) output curves for a transistor fabricated from 150 °C annealed polymers at $V_{DS} = 60$ V ($L = 50$ μ m, $W = 1.0$ mm). The gate voltage changes from -60 to 20 V with an interval of 5 V.

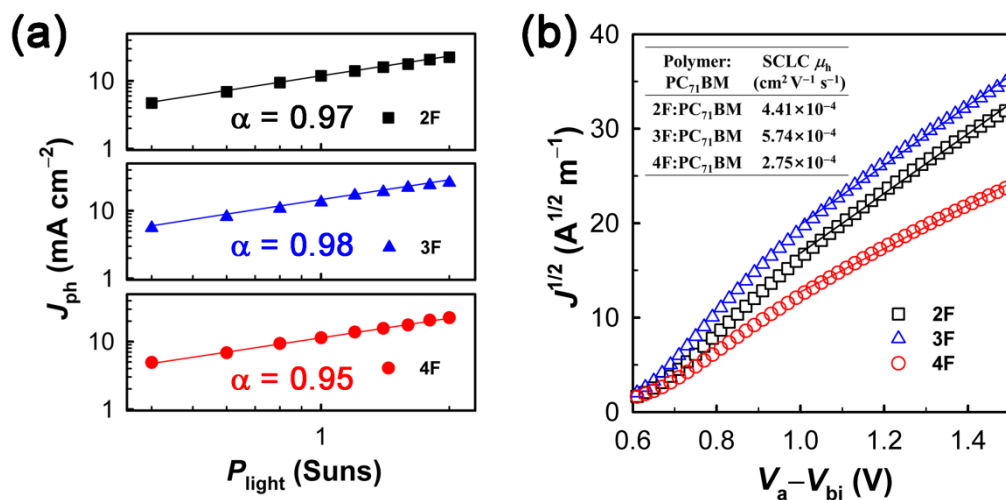


Figure S5 (a) A plot of relative J_{ph} vs. light intensity as measured at $V = 0$ V; (b) dark J - V characteristics of polymer:PC₇₁BM blends with hole-only device, where the solid lines represent the best linear fit of the data points.

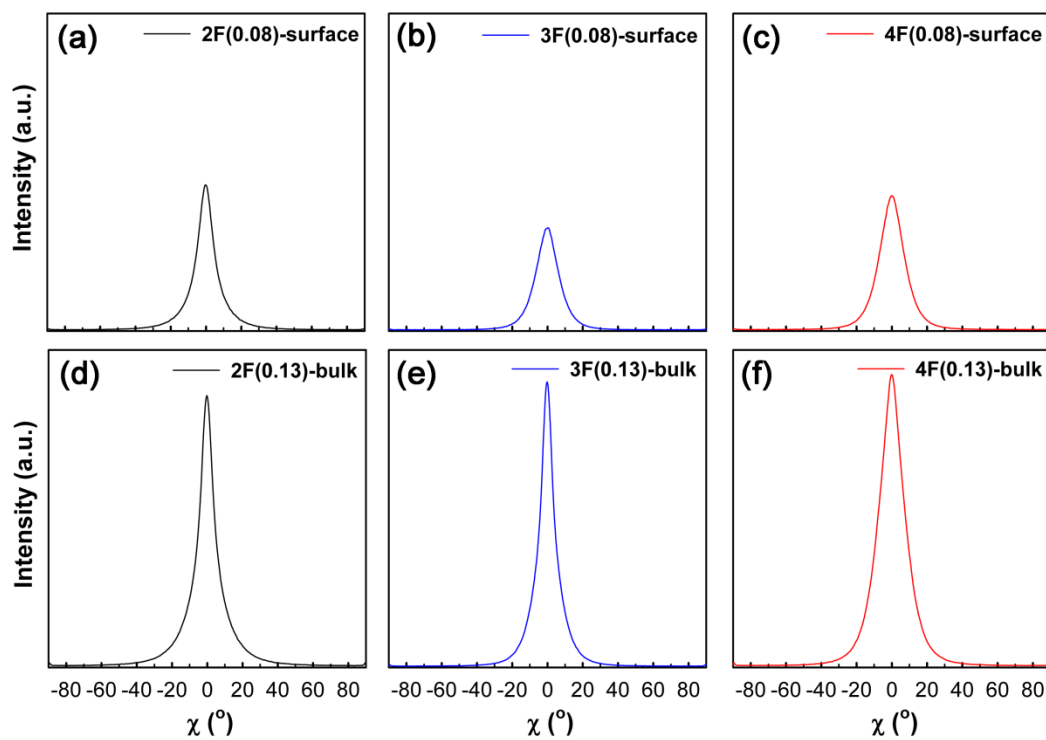


Figure S6 Azimuthal angle scans of the (100) reflection from (a, d) 2F, (b, e) 3F and (c, f) 4F polymer films with different incident angles ($\alpha_i = 0.08$ and 0.13°).

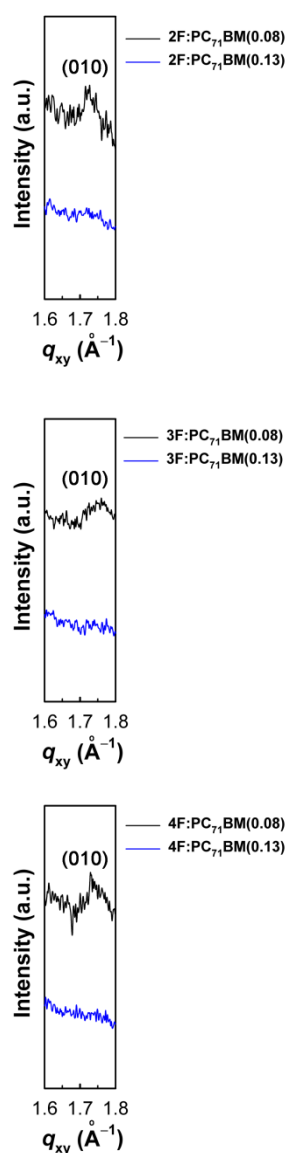


Figure S7 q_{xy} scans of GIWAXS at two different incident angles ($\alpha_i = 0.08$ and 0.13°) in the range between 1.6° and 1.8° from polymer:PC₇₁BM(1:1.5 w/w) blend films processed from DCB containing 2 vol% of CN.

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