Supporting Information

Fluorene을 기본골격으로 한 공액형 고분자 전해질을 interlayer로 적용한 소자의 고분자태양전지의 광전효과

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Investigation of photovoltaic properties of polymer solar cells with fluorene-based polyelectrolytes as the interlayer

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Keywords*: polymer solar cell, fluorene-based polyelectrolyte, thiophene, cathode interlayer*.

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Experimental

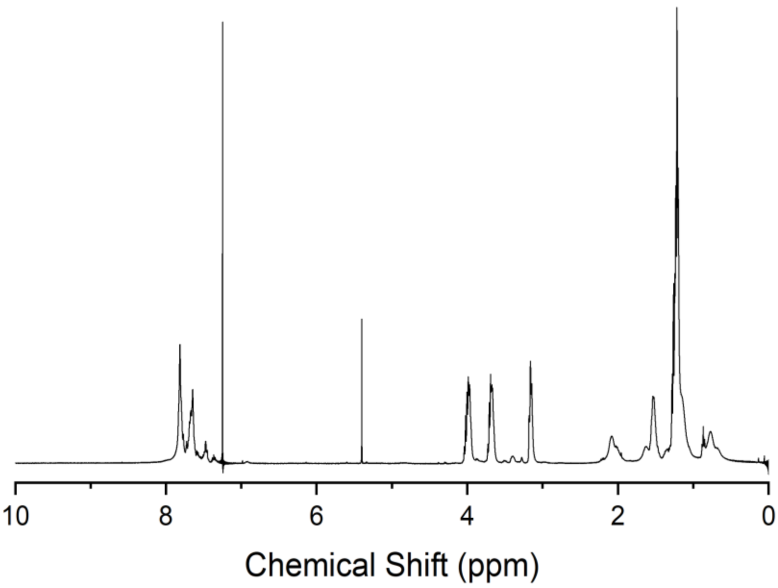
Materials

PTB7

(Poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-*b*:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl})) and $PC_{71}BM$ ([6,6]-phenyl C71 butyric acid methyl ester) were purchased from Derthon Co. The other material and solvent are commercial from Alfa Aesar or Sigma-Aldrich and used as received. 2,7-Dibromo-9,9-bis(6-bromohexyl)-9H-fluorene (1) [1–9] synthesized by according to the literature procedures.

Synthesis of PFB

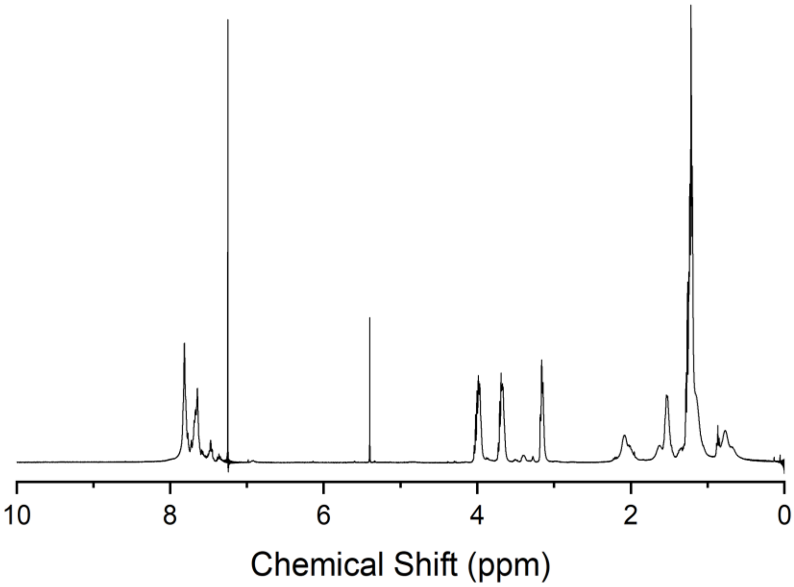
2,7-Dibromo-9,9-bis(6-bromohexyl)-9H-fluorene (0.2600 g, 0.4 mmol), 1,4-bis(4,4,5,5 -tetramethy-1,3,2-dioxaborolan-2-yl)benzene (0.132 g, 0.4 mmol), and tetrakis (triphenyl phosphine)-palladium(0) were dissolved in degassed toluene (3 mL) and aqueous 2M K_2CO_3 (3 mL). The solution was flushed with N_2, and then two drops of Aliquat 336 was added into the solution. The reaction was stirred for 24h at 90°C under a nitrogen atmosphere and poured into methanol. The precipitate was collected. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.30-8.09 (9H), 3.87-4.12 (4H), 3.57-3.79 (4H), 3.04-3.56 (4H), 1.83-2.34 (4H), 1.43-1.88 (4H), 0.55-1.00 (4H).



(^{1}H-NMR spectrum of PFB)

Synthesis of PFT

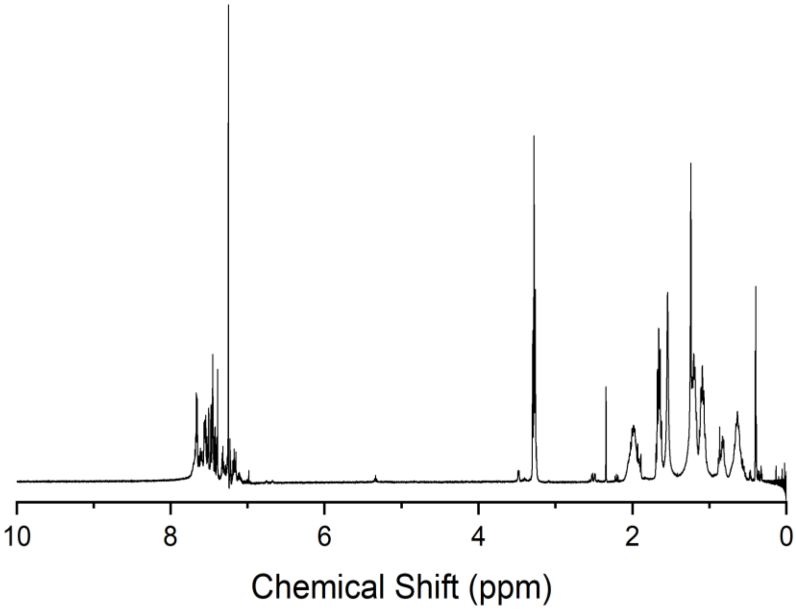
2,7-Dibromo-9,9-bis(6-bromohexyl)-9H-fluorene (0.2600 g, 0.4 mmol), 2,5-bis (trimethylstanny)thiophene (0.1639 g, 0.4 mmol), Tri(o-tolyl)phosphine (0.061 g, 0.2 mmol), and Bis(dibenzylideneace-tone)palladium(0) (0.0115 g, 0.02 mmol) were dissolved in degassed toluene (5 mL) and the reaction mixture was stirred 24hr at 100°C under a nitrogen atmosphere and poured into methanol. The precipitate was collected. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36-7.73 (6H), 6.98-7.24 (1H), 3.20-3.32 (4H), 1.85-2.13 (4H), 1.47-1.74 (8H), 1.03-1.15 (4H), 0.55-0.75 (4H)



(^{1}H-NMR spectrum of PFT)

Synthesis of PF2T

2,7-Dibromo-9,9-bis(6-bromohexyl)-9H-fluorene (0.2600 g, 0.4 mmol), 5,5'-bis (trimethylstannyl)-2,2'-bithiophene(0.1967 g, 0.4 mmol), tri(o-tolyl)phosphine (0.061 g, 0.2 mmol), and bis(dibenzylide-neacetone)palladium(0) (0.0115 g, 0.02 mmol) were dissolved in degassed toluene (5 mL) and follow same procedure with PFT polymer. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.74-7.94 (9H), 2.99-3.43 (4H), 1.80-2.43 (3H), 1.41-1.78 (6H), 0.94-1.39 (8H), 0.45-0.92 (3H)



(^{1}H-NMR spectrum of PF2T)

2.2.5. Synthesis of PFB-Br, PFT-Br, and PF2T-Br

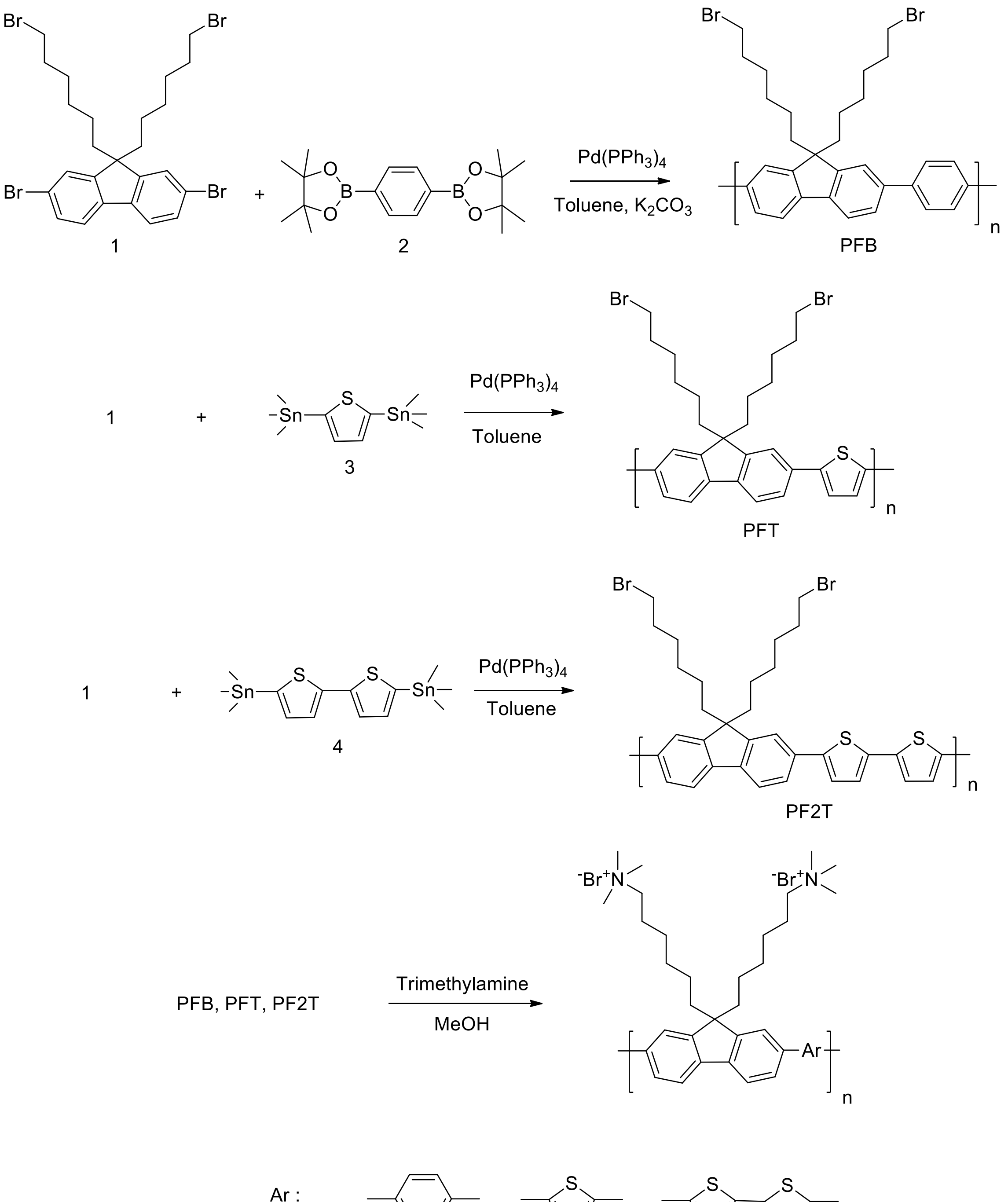
Each polymer was dissolved in 10 mL of trimethylamine, 1 M soln. in THF and stirred 72 hours at room temperature. The precipitate was filtered and collected.

Measurements. ^{1}H NMR spectra were measured by a JEOL JNM ECP 400 spectrometer. The work function of ZnO/**PFB**, ZnO/**PFT**, and ITO/**PF2T** were measured by Kelvin probe microscopy (KPM) measurements (KP technology Ltd. Model KP020). The work function of the samples was estimated by measuring the contact potential difference between the sample and a standard reference gold surface KPM tip with a work function of 5.1 eV. The thickness of the ZnO and the active layer was measured using an Alpha-Step IQ surface profiler (KLA-Tencor Co.). The current density-voltage measurements were performed under simulated light (AM 1.5G, 1.0 sun condition) from a 150 W Xe lamp, using a KEITHLEY Model 2400 source-measure unit. A calibrated Si reference cell with a KG5 filter certified by the National Institute of Advanced Industrial Science and Technology as used to confirm 1.0 sun condition. UV–visible spectra of solutions and films were recorded using a JASCO V-530. Cyclic voltammetry was performed by a CompactStat-Plus (Ivium technology) Scanning Potentiostat with a three-electrode cell in a solution of 0.1 M n-Bu_4NPF_6 (0.1 M) in acetonitrile at a scan rate of 100 mV/s. Pt coil was used as the counter, and a glassy carbon disk was used as the working electrode, and an Ag/AgCl electrode was used as the reference electrode. Before each measurement, the cell was deoxygenated with nitrogen. Non-modulated impedance spectra data were accumulated using an impedance analyzer (Ivium technology, CompactStat-Plus). A 50 mV perturbation was applied over a continuously applied bias, 0 ~ 1.0 V, in the frequency range between 1 Hz and 1.0 MHz under the dark condition with the device for a current density - voltage (J-V) characteristics. The incident photon-to-electron conversion efficiency (IPCE) spectra were measured by a 150 W Xe lamp (Abet Technology Model LS150), equipped with a monochromator (Oriel Cornerstone 130 1/8 m) and source-measure unit (KEITHLEY Model 2400). All the measurements were performed at room temperature under ambient conditions.

Fabrication of PSCs. The inverted OSCs with the device structure of [ITO/ZnO (25 nm) or ZnO/interlayer/PTB7: $PC_{71}BM$ (70 nm)/MoO_3 (3 nm)/Ag (100 nm)], ZnO stack solution was prepared by the sol-gel process, which contained zinc acetate dihydrate (0.3 g) and 0.075 mL of ethanolamine in 3 mL of methoxy ethanol and stirred for 12 hours at 60 °C. The solution spin-coated on the ITO substrate and cured at 200 °C for 10 min in the air atmosphere. Each interlayer thin film was spin-coated, as specified in table 1. The active layer of PTB7:$PC_{71}BM$ (obtained by dissolving 10 mg of PTB7 and 15 mg of $PC_{71}BM$ dissolved in 1 mL of chlorobenzene with 3% (v/v) 1,8-diiodooctane (DIO)) was prepared and filtered through a

0.45 μm membrane filter before spin coating. The active layer was spin-coated on ZnO/ITO substrate at 1800 rpm for 120 s in N_2. The MoO_3 and Ag were thermally evaporated through a shadow mask, with a device area of 0.12 cm^2 at 2 x 10^{-6} Torr.

Fabrication of Electron-Only Devices. Before spin coating, the $PC_{71}BM$ solution (15ml of $PC_{71}BM$ was dissolved in 1 mL of chlorobenzene with 3% (v/v) 1,8-diiodooctane (DIO)) was filtered through a 0.45 μm membrane filter. The $PC_{71}BM$ solution was spin-coated on the ITO/ZnO/with or without interlayer (3 nm) glass substrate. The Al layer was deposited with a thickness of 100 nm through a shadow mask with a device area of 0.12 cm^2.



Scheme S1. Synthesis of PFB-Br, PFT-Br, and PF2T-Br.

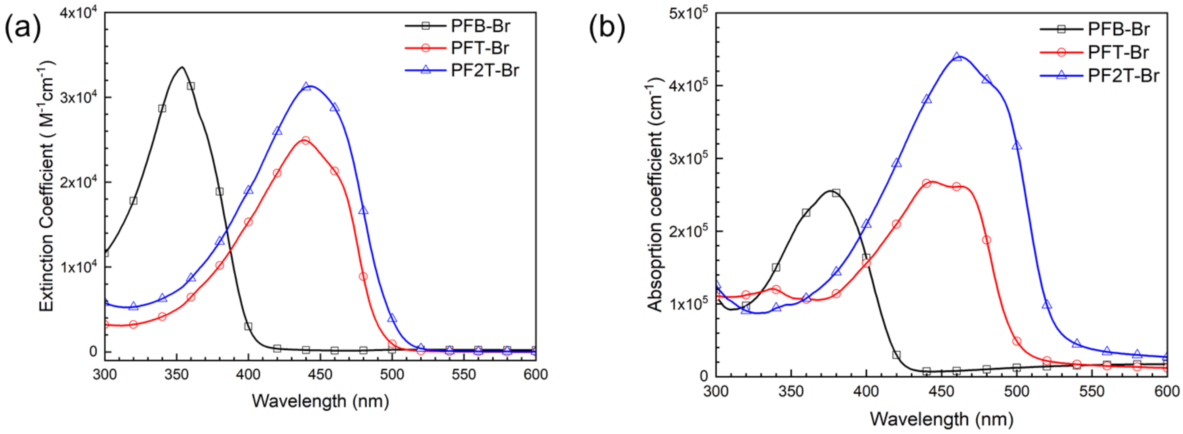


Figure S1. UV-Vis spectra of (a) solution and (b) film of **PFB-Br, PFT-Br and PF2T-Br**.

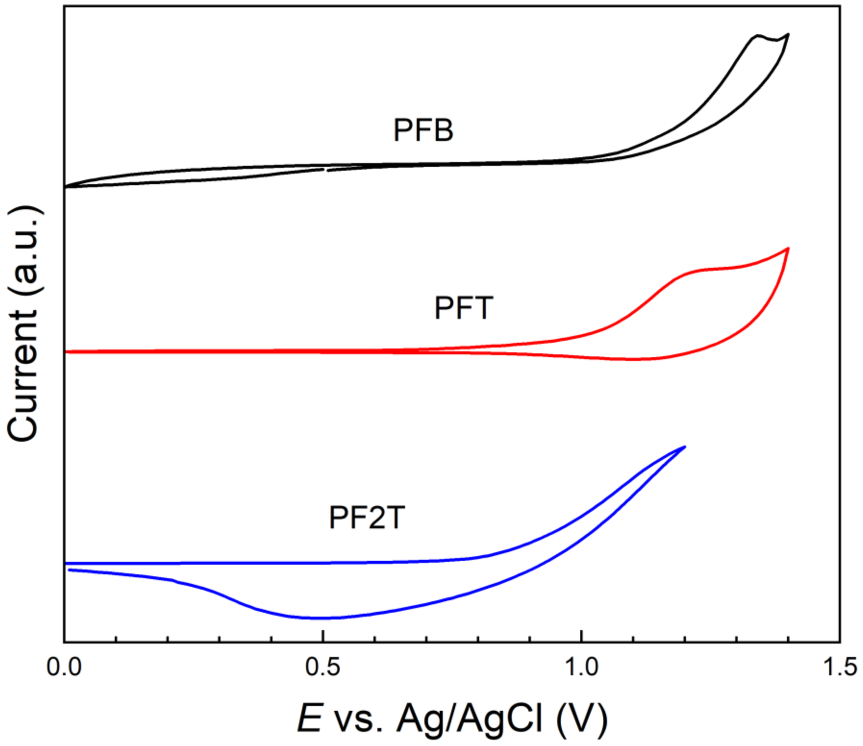


Figure S2. Cyclic voltammograms of PFB, PFT and PF2T.

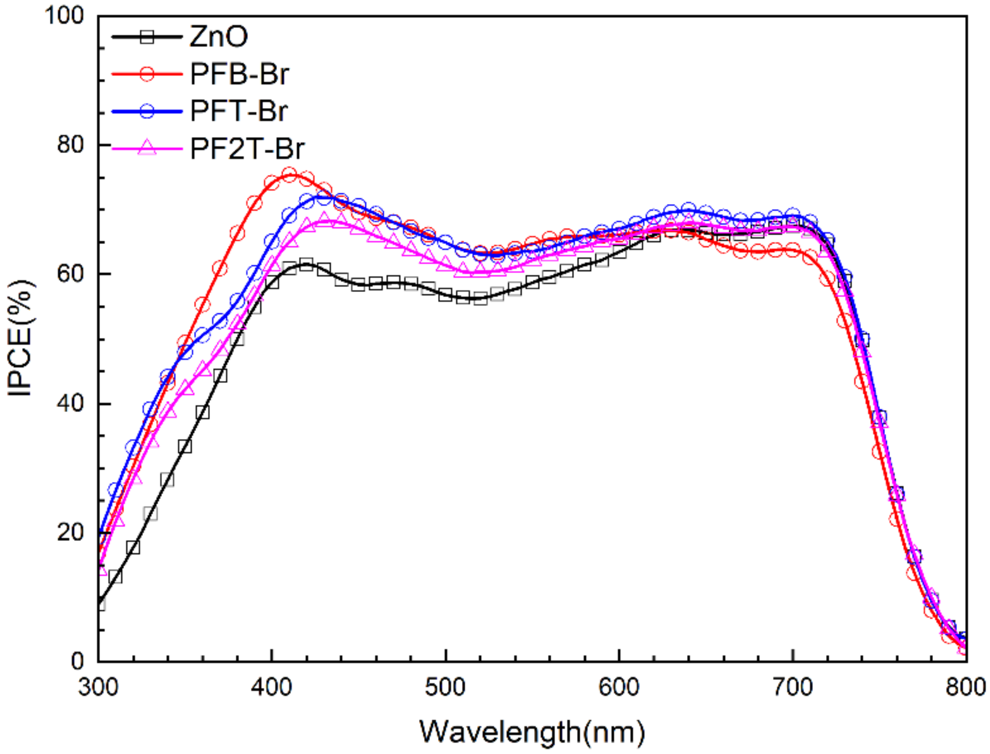


Figure S3. IPCE spectra of PSCs.

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