Electronic Supplementary Information

Small-molecule electrolytes with diverse ionic functionality as the cathode buffer layer for polymer solar cells

Mijin Jeong[a], Doo Kyung Moon[b], Hyun Sung Kim[*,c], Joo Hyun Kim[*,a]

[a]Department of Polymer Engineering, Pukyong National University, Busan 48513, Korea

[b]Division of Chemical Engineering, Konkuk University, Seoul 05029, Korea

[c]Department of Chemistry, Pukyong National University, Busan 48513, Korea

Keywords: Small-molecule electrolyte, number of ionic functionality, cathode interlayer, polymer solar cell

1. Experimental

1.1. Materials and Measurements.

Poly([2,6′-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,3-b]dithiophene]{3-fluoro-2[(2-ethylhexyl) carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7-Th) and $PC_{71}BM$ ([6,6]-phenyl C71 butyric acid methyl ester) were purchased from Derthon optoelectronic materials science technology Co. LTD. Other chemicals were purchased from Alfa Aesar and Sigma-Aldrich. They were used as received unless otherwise described. The thickness of the ZnO and the active layer were determined using an Alpha-Step IQ surface profiler (KLA-Tencor Co.). X-ray photoelectron spectroscopy (XPS) studies were carried out using Al Ka X-ray line (15 kV, 300 W) (Thermo Electron Co., MultiLab 2000). The data was acquired in the hybrid mode. Atomic force microscopy (AFM) images were obtained from a Bruker (NanoScope V) AFM in the tapping mode. Kelvin probe microscopy (KPM) measurements (KP technology Ltd. Model KP020) were conducted on the ZnO layers, with and without interlayer, and the work function of the samples were estimated by measuring the contact potential difference between the sample and the KPM tip at ambient condition. The KPM tip was calibrated against a standard reference gold surface, with a work function of 5.1 eV. Details are as below;

The KP Technology Ambient Kelvin Probe System performs measurements of CPD (contact potential difference) between Sample and Tip. This value is NOT the WF (work function) value of a sample. This value must be calculated by first determining the WF value of the Tip being used. The following instructs the user on the method used to determine this manually.

If we assume the value you received from performing a single-point measurement of the Gold reference sample is 400 mV.

WF of Tip = WF of Gold – CPD

WF of Tip = 5100 meV – 400 mV

WF of Tip = 4700 meV

We now know the WF of the tip so we can place any sample underneath the Kelvin Probe and give the exact WF value of that sample. Remove the Gold Reference Sample from the sample holder and place your sample onto the sample holder, ensure that the sample is ground with the conductive tape supplied. Measure the CPD between the tip and the sample. We already know the WF of the tip, so we use the following equation to calculate the WF of the sample: Let us assume the CPD value of the sample you have just measured is 250 mV.

WF of Sample = WF of Tip + CPD

WF of Sample = 4700 meV + 250 mV

WF of Sample = 4950 meV

The current density-voltage measurements were performed under simulated light (AM 1.5G, 1.0 sun condition, Peccell Technology, Model PEC-L01) equipped with a 150 W Xe lamp and a KEITHLEY Model 2400 source-measure unit. The 91150-KG5 Reference Cell and Meter (National Institute of Advanced Industrial Science and Technology) was used to verify 1.0 sun light condition. Non-modulated impedance spectra data were accumulated using an impedance analyzer (IVIUM technologies COMPACTSTAT). A 50 mV voltage perturbation was applied over a constant 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 monochromator (Oriel Cornerstone 130 1/8 m) and source-measure unit (KEITHLEY Model 2400). All the measurements were performed at room temperature under ambient condition.

1.2. Synthesis

Synthesis of (N,N'-(1,2-phenylenebis(methylene))bis(N,N-diethylethanaminium) bromide) (2EBr).

A mixture of 1,2-bis(bromomethyl)benzene (0.528 g, 2 mmol), and triethylamine (0.455 g, 4.5 mmol) in toluene was stirred at 50 °C for 12 hours. After cooling down to room temperature, white precipitates (**2EBr**) were filtered and washed with copious amount of toluene and diethyl ether (yield = 85.7%). ^{1}H NMR (600 MHz, D_2O, ppm) δ 7.57 ~ 7.56 (d, 2H), 7.48~4.46 (t, 2H), 4.49 (s, 4H), 3.31~3.27 (m, 12H), 1.29~1.26 (t, 18H). ^{13}C NMR (150 MHz, CD_3OD, ppm) δ 132.54, 130.80, 127.85, 59.22, 55.20, 8.76. Anal. Calcd. For $C_{20}H_{38}Br_2N_2$: C, 51.51; H, 8.21; N, 6.01. Found: C, 51.42; H, 8.11; N, 5.87.

Synthesis of ((benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(triphenylphosphonium) bromide) (4PBr) A mixture of 1,2,4,5-tetrakis(bromomethyl)benzene (0.900 g, 2 mmol), and triphenylphosphine (2.229 g, 8.5 mmol) in acetonitrile was stirred at 70 °C for 12 hours. After cooling down to room temperature, white precipitates (**4PBr**) were filtered and washed with copious amount of acetonitrile and diethyl ether (yield = 82.5%). ^{1}H NMR (400 MHz, DMSO-D$_6$, ppm) δ 7.97~7.92 (t, 12H), 7.78~7.70 (t, 24H), 7.52~7.46 (d, 24H), 6.70 (s, 2H), 4.28 (s, 8H). ^{13}C NMR (150 MHz, DMSO-D$_6$, ppm) δ 135.56, 133.84, 130.53, 130.40, 128.92, 128.22, 35.90. Anal. Calcd. For $C_{82}H_{70}Br_4P_4$: C, 65.71; H, 4.71. Found: C, 65.53; H, 4.62.

1.3. Fabrication of PSCs. In order to fabricate the inverted type organic photovoltaic (OPV) with the device structure: [ITO/ZnO (25 nm) with or without interlayer/active layer (PTB7-Th:PC$_{71}$BM, 70 nm)/MoO$_3$ (3 nm)/Ag (100 nm)], a ZnO layer was deposited on an ITO substrate by the sol-gel process. Zinc acetate dihydrate (0.1 g) and 0.025 mL of ethanolamine were dissolved in 1 mL of methoxyethanol and stirred for 12 hours at 60 °C. A thin film of ZnO sol-gel precursor was spin coated at 4000 rpm for 60 s then cured at 200 °C for 10 min. Interlayer was spin-cast from the solution in methanol (1 mg/mL) and the thickness of the interlayer was controlled by the spic coating speed. The active layer was spin-cast from a mixture of PTB7-Th and PC$_{71}$BM (obtained by dissolving 10 mg of PTB7-Th and 15 mg of PC$_{71}$BM in 1 mL of chlorobenzene with 3% (v/v) 1,8-diiodooctane (DIO)) and rotated at 1800 rpm for 120 s. The active solution was filtered through a 0.45 μm membrane filter before spin coating. Successive layers of MoO$_3$ and Ag were thermally evaporated through a shadow mask, with a device area of 0.09 cm^2 at 2 x 10^{-6} Torr.

1.4. Fabrication of electron-only devices. Electron-only devices with the structure: [ITO/ZnO (25 nm) with or without interlayer/PC$_{71}$BM (60 nm)/Al (100 nm)], have been fabricated to investigate the electron mobility.

Table S1. Photovoltaic parameters of PSCs based on ZnO/interlayer. The averages (10 devices) are shown in parentheses.

ETL	Thickness of interlayer (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF* (%)	*PCE* (%)
ZnO/2EBr	3	19.5 (19.4±0.1)	0.77 (0.77±0.00)	62.8 (62.6±0.36)	9.37 (9.32±0.04)
ZnO/2EBr	3	19.9 (19.7±0.2)	0.78 (0.78±0.00)	60.4 (59.6±0.75)	9.36 (9.14±0.21)
ZnO/2EBr	5	19.7 (19.6±0.2)	0.80 (0.80±0.00)	61.1 (60.4±0.78)	9.56 (9.41±0.21)
ZnO/2EBr	9	19.0 (18.9±0.1)	0.81 (0.81±0.00)	60.0 (59.9±0.32)	9.25 (9.15±0.09)
ZnO/4PBr	3	20.1 (20.0±0.2)	0.79 (0.79±0.00)	62.9 (62.4±0.67)	9.90 (9.77±0.18)
ZnO/4PBr	5	20.2 (20.1±0.2)	0.79 (0.79±0.00)	66.6 (65.2±1.38)	10.63 (10.29±0.34)
ZnO/4PBr	8	19.8 (19.6±0.2)	0.79 (0.79±0.00)	65.1 (64.7±0.53)	10.15 (10.01±0.20)
ZnO/4PBr	12	19.1 (19.1±0.1)	0.80 (0.80±0.00)	65.1 (63.5±1.35)	9.94 (9.70±0.20)

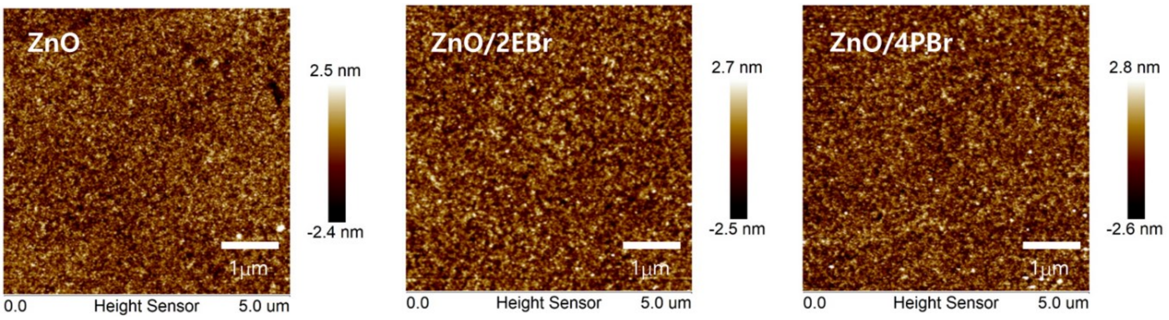

Figure S1. AFM images of ZnO, ZnO/2EBr and ZnO/4PBr.