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Water-Soluble Polyfluorenes as an Interfacial Layer Leading to Cathode-Independent High Performance of Organic Solar Cells

By *Seung-Hwan Oh, Seok-In Na, Jang Jo, Bogyu Lim, Doojin Vak,* and *Dong-Yu Kim**

Novel poly[(9,9-bis((6′-(*N,N,N*-trimethylammonium)hexyl)-2,7-fluorene)-*alt*-(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9-fluorene)) dibromide (WPF-6-oxy-F) and poly[(9,9-bis((6′-(*N,N,N*-trimethylammonium)hexyl)-2,7-fluorene)-*alt*-(9,9-bis(2-(2-methoxyethoxy)ethyl)-fluorene)] dibromide (WPF-oxy-F) compounds are developed and the use of these water-soluble polymers as an interfacial layer for low-cost poly(3-hexylthiophene):phenyl-C_{61} butyric acid methyl ester (P3HT:PCBM) organic solar cells (OSCs) is investigated. When WPF-oxy-F or WPF-6-oxy-F is simply inserted between the active layer and the cathode as an interfacial dipole layer by spin-coating water-soluble polyfluorenes, the open-circuit voltage (V_{oc}), fill factor (FF), and power-conversion efficiency (PCE) of photovoltaic cells with high work-function metal cathodes, such as Al, Ag, Au, and Cu, dramatically increases. For example, when WPF-6-oxy-F is used with Al, Ag, Au, or Cu, regardless of the work-function of the metal cathode, the V_{oc} is 0.64, 0.64, 0.58, and 0.63 V, respectively, approaching the original value of the P3HT:PCBM system because of the formation of large interfacial dipoles through a reduction of the metal work-function. In particular, introducing WPF-6-oxy-F into a low-cost Cu cathode dramatically enhanced the device efficiency from 0.8% to 3.36%.

1. Introduction

Organic solar cells (OSCs) based on conjugated polymers have attracted considerable attention because of the low-cost fabrication and flexible device applications.[1] This has encouraged intensive research in recent years and the performance of organic cells has been rapidly improved by molecular engineering,[2] novel device architectures,[3] and advancement in processing techniques based on the morphological evolution of the active layers.[4] Concurrently, fabrication techniques for large-area devices have become a very important issue in this field. Most high-performance devices have thus far been fabricated using a spin-coating process, which is not scalable. Recently, scalable printing and coating methods[5–8] have been reported as fabrication methods for the active layer of OSCs. Although efficient OSCs have been fabricated by scalable methods, high performance of these devices could only be achieved by adopting a vacuum evaporation method for the construction of low work-function metal cathodes. For the low-cost mass production of OSCs, it is very important to achieve air-stable and/or printable metal electrodes, such as Ag and Au ink. In order to use air-stable noble metals several problems should be solved. One is the poor performance of OSCs with noble metal cathodes, as they show a decreased open-circuit voltage (V_{oc})[9] because of the higher work-function. The other problem is the high cost of these noble metals, which is a stumbling block on the commercial scale. The use of a low-cost metal as a cathode could significantly reduce the cost of OSCs. Among all low-cost metals, Cu could be a good candidate as a cathode in OSCs. However, Cu is not suitable as a cathode material because of its high work-function, which also reduces the V_{oc} of OSCs.

Using OSCs with an inverted structure has been shown to be one of the solutions for the decreased V_{oc} when a high work-function metal cathode is used.[10] Another promising solution to the problem is the introduction of interfacial layers between the active layer and the metal electrode.[11]

In OSCs based on a P3HT:PCBM blend, charge extraction is affected by the work-function of the metal cathode.[9] In order to achieve a high performance, the interface between the electrode

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and the photoactive layer should be in ohmic contact to minimize the contact resistance and to maximize the V_{oc},[9a,b] which has been achieved using thermally deposited LiF.[9c] Recently, Yip et al.[11] reported that OSCs with self-assembled monolayers (SAMs) as the interfacial dipole layers showed a dramatic enhancement in the V_{oc} and the fill factor (FF). Water-soluble polymers could also be good candidates for the interfacial layer materials in OSCs because they can prevent damage to the underlying organic soluble active layer, and have solution-processing capabilities. These polymers also possess either ionic or polar groups that can reduce the work-function of the cathode through favorable interface dipoles. A typical water-soluble polymer, poly(ethylene oxide) (PEO), has been inserted between the active layer and the Al cathode, and the V_{oc}, FF, and short-circuit current (J_{sc}) of this particular solar cell were all improved because of the internal electric field.[12] However, the insulating properties of PEO could also be disadvantageous.

The present study reports the synthesis of novel poly[(9,9-bis((6′-(N,N,N-trimethylammonium)hexyl)-2,7-fluorene)-alt-(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-9-fluorene)) dibromide (WPF-6-oxy-F), as shown in Scheme 1, and we demonstrate highly efficient P3HT:PCBM OSCs with both air-stable high work-function metal cathodes and novel water-soluble polymers as interfacial layers. Compared to previously studied interfacial dipole materials,[11,12] WPF-oxy-F[13] and WPF-6-oxy-F as the interfacial layer have several advantages. First, the conjugated main chain of this water-soluble polymer can provide good conductivity. Second, cationic ammonium ions, mobile ions, and ethylene oxide side groups induce large interfacial dipoles between the active layer and the high work-function metal cathodes. These water-soluble polymers are also advantageous because they do not damage the underlying organic soluble polymer film. When either WPF-oxy-F or WPF-6-oxy-F was simply inserted between the active layer and the cathode as an interfacial dipole layer by spin-coating, it dramatically increased the V_{oc}, FF, and power-conversion efficiency (PCE) of photovoltaic cells even with high work-function metal cathodes, such as Al, Ag, Au, and Cu. In particular, when WPF-6-oxy-F was used with Al, Ag, Au, and Cu, regardless of the work-function of the metal cathode, a V_{oc} of 0.64, 0.64, 0.58, and

0.63 V, respectively was observed, approaching the original value of the P3HT:PCBM system, and the PCE was 3.89%, 3.69%, 2.60%, and 3.36%, respectively. Especially, we successfully completed the first demonstration of a significant improvement in performance ($V_{oc} = 0.63$ V, $J_{sc} = 8.72$ mA cm^{-2}, FF = 61%, and PCE = 3.36%) using a low-cost Cu cathode with WPF-6-oxy-F. This approach provides an effective way to achieve both highly efficient and low-cost OSCs. The use of Cu as a cathode, which is the first demonstration in OSCs, could be an important step toward the realization of low-cost OSCs.

2. Result and Discussion

The synthesis of water-soluble polyfluorene (WPF-6-oxy-F) is shown in Scheme 1. The compounds 1[14], 2,[13] and 4[15] were prepared according to a previously published process. The neutral polymer PF-6-oxy-F was synthesized from the corresponding monomer via a Suzuki-coupling reaction, see Experimental.

Figure 1 shows the three materials used as the interfacial layer (Fig. 1a) and the overall device structure (Fig. 1b). The structure of each device was as follows: indium tin oxide (ITO)/poly-(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS (30nm))/P3HT:PCBM (90nm)/interfacial layer (3nm)/metal cathode (50nm). All devices were fabricated from the same batch.

The photocurrent density–voltage (J–V) characteristics of each device are shown in Figure 2 and Table 1. The V_{oc} of the devices with only Al, Ag, Au, or Cu cathodes (without an interfacial layer) were 0.53 V, 0.33 V, 0.22 V, and 0.27 V, respectively. In the case of the Al cathode, the V_{oc} was higher than for the other metal cathodes because of a small interface barrier between the lowest occupied molecular orbital (LUMO) of PCBM (4.3 eV) and the work-function of Al.[9a,16] However, devices with Ag, Au, or Cu cathodes showed a low V_{oc} owing to the mismatch between the work-function of these metals and the LUMO of PCBM. The transport of electrons from the active layer to the metal cathode was not efficient in these devices because of the Schottky-barrier effect caused by the high contact resistance between the high work-function cathode and the LUMO of PCBM.[11a] With an interfacial layer of
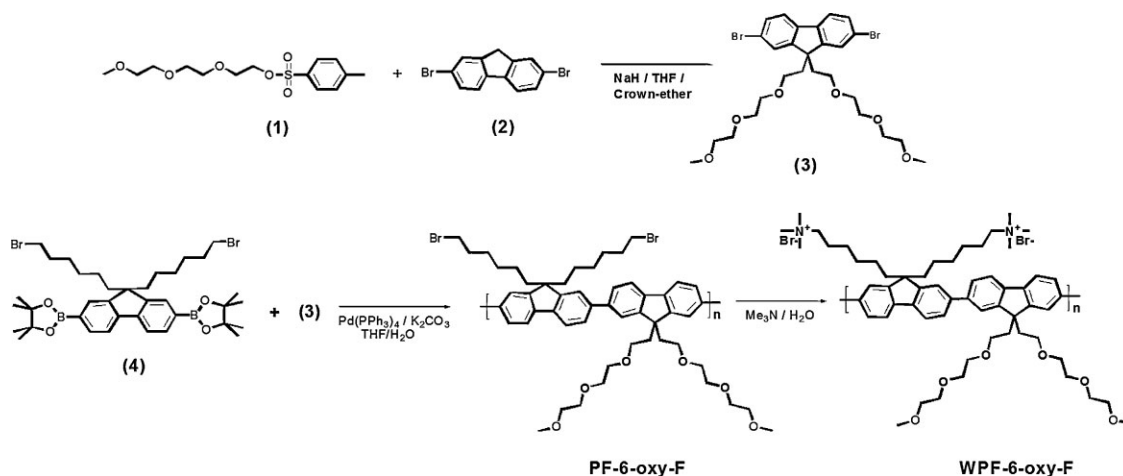

Scheme 1. Synthetic scheme for the water-soluble polyfluorene (WPF-6-oxy-F).

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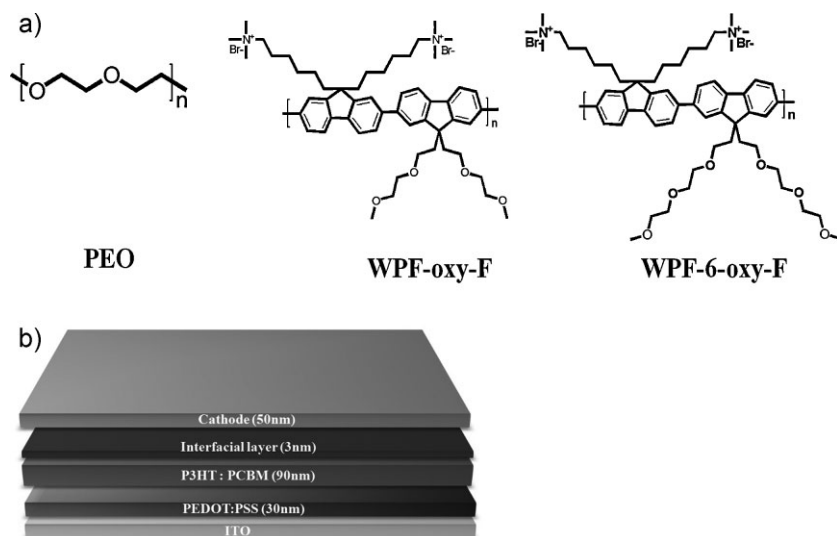
Figure 1. a) Structure of the materials used for the interfacial layer. b) Structure of the organic solar cells.

polyethylene oxide (PEO), the V_{oc}, FF, and J_{sc} improved only slightly owing to the insulating properties of PEO. However, when WPF-oxy-F and WPF-6-oxy-F were used as the interfacial layers with various metal cathodes, the V_{oc}, FF, and J_{sc} dramatically

improved. This enhancement resulted from lowering the work-function of the cathodes because of an interfacial dipole between the interfacial layers and the cathodes,[11,12,17] which was induced between the two amine ionic salts and the ethylene oxide side groups. The dipole moment itself lies at the 9-position of WPF-oxy-F and WPF-6-oxy-F which leads to an interfacial dipole interaction between the metal cathode and the ionic groups of the interfacial layer[13] Therefore, at cathodes with an interfacial layer attached, the ohmic contact to the electron being transported from the active layer to the cathode is more favorable.[18] As shown in Figure 2 and Table 1, the V_{oc} of devices with Al, Ag, Au, and Cu cathodes and a WPF-oxy-F layer increased by 90, 270, 270, and 220 mV, respectively. However, using a cathode with WPF-oxy-F was not sufficient to approach the original V_{oc} of traditional OSCs based on P3HT:PCBM (ca. 0.65 V). The V_{oc} of devices with high work-function cathodes using WPF-6-oxy-F, which has longer ethylene oxide units that can induce a larger interfacial dipole compared to WPF-oxy-F, as an interfacial layer, was dramatically improved. Although a large energy barrier between the work-function and the LUMO of PCBM is created
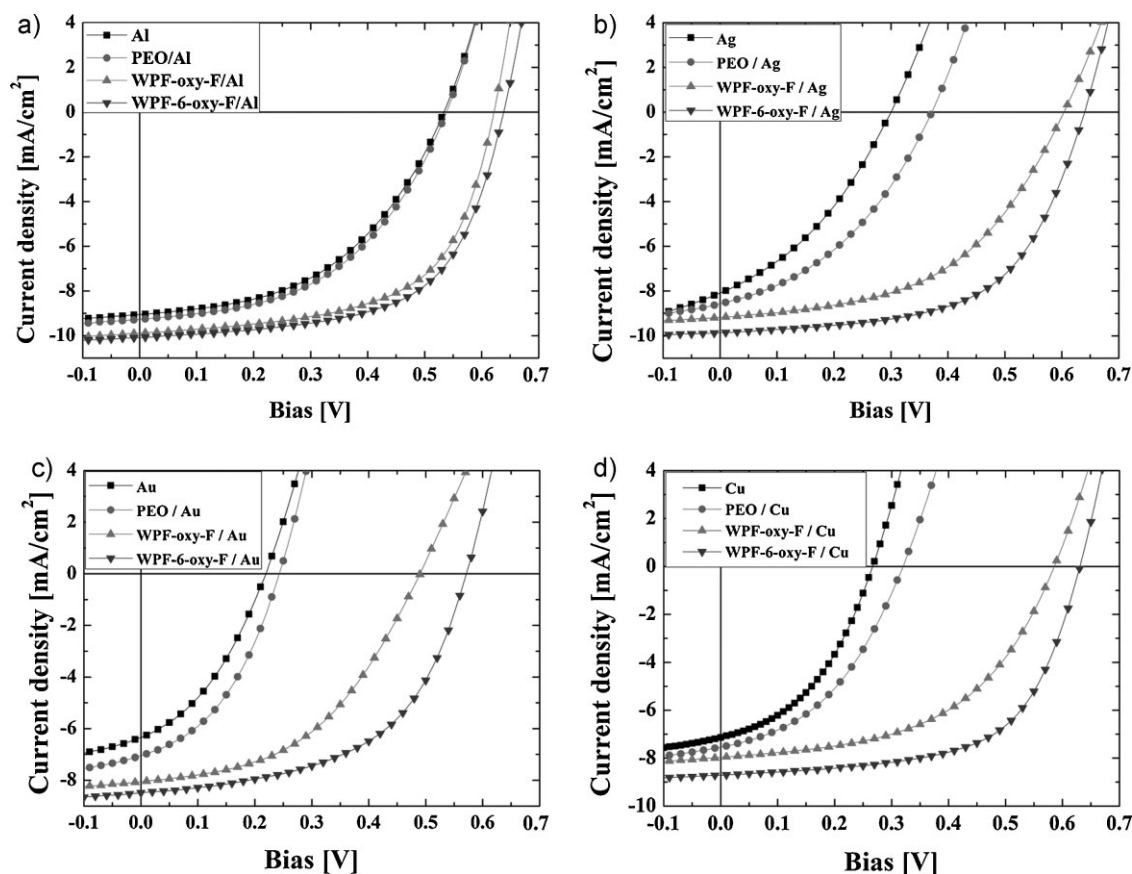

Figure 2. J–V curves of organic solar cells with or without interfacial layer and a) Al, b) Ag, c) Au, and d) Cu cathodes.

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Table 1. Summary of performance of the devices with different metal cathodes, with or without interfacial layer.

Cathode	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	R_{sh} [k$\Omega \cdot$ cm^2]	R_s [$\Omega \cdot$ cm^2]
Al	0.53	9.04	48	2.30	164.74	2.46
PEO/Al	0.54	9.26	48	2.41	187.61	2.22
WPF-oxy-F/Al	0.62	9.89	59	3.67	300.31	1.92
WPF-6-oxy-F/Al	0.64	10.08	60	3.89	571.42	1.80
Ag	0.33	8.08	36	0.86	0.54	7.57
PEO/Ag	0.37	8.56	40	1.25	2.39	4.05
WPF-oxy-F/Ag	0.60	9.17	50	2.77	48.03	3.26
WPF-6-oxy-F/Ag	0.64	9.86	58	3.69	126.42	2.45
Au	0.22	6.34	37	0.51	1.18	23.84
PEO/Au	0.24	7.04	41	0.70	1.98	12.11
WPF-oxy-F/Au	0.49	8.05	46	1.84	45.16	3.57
WPF-6-oxy-F/Au	0.58	8.48	52	2.60	189.75	3.31
Cu	0.27	7.14	41	0.80	1.86	8.20
PEO/Cu	0.32	7.54	42	1.01	6.36	4.35
WPF-oxy-F/Cu	0.59	7.97	51	2.39	217.39	2.65
WPF-6-oxy-F/Cu	0.63	8.72	61	3.36	358.42	2.19

when using Au as the cathode, the V_{oc} and PCE of WPF-6-oxy-F-modified devices using Au were 0.58 V and 2.6%, respectively. In particular, when high work-function Ag and Cu were used as the cathode, the V_{oc} and PCE of these devices using WPF-6-oxy-F as the interfacial layer were 0.64 and 0.63 V, and 3.69% and 3.36%, respectively, which is comparable to the maximum V_{oc} of a traditional P3HT:PCBM system.

To investigate and compare the effect of these interfacial layers on the work-function of each metal, the effective work-function of each metal with different interfacial layers was measured using a Kelvin-probe system under N_2 atmosphere. This technique is an effective tool to investigate the possible shift of the vacuum level at the interface or a change of work-function induced by the formation of dipoles.[19] Figure 3 shows the effective work-functions of metal
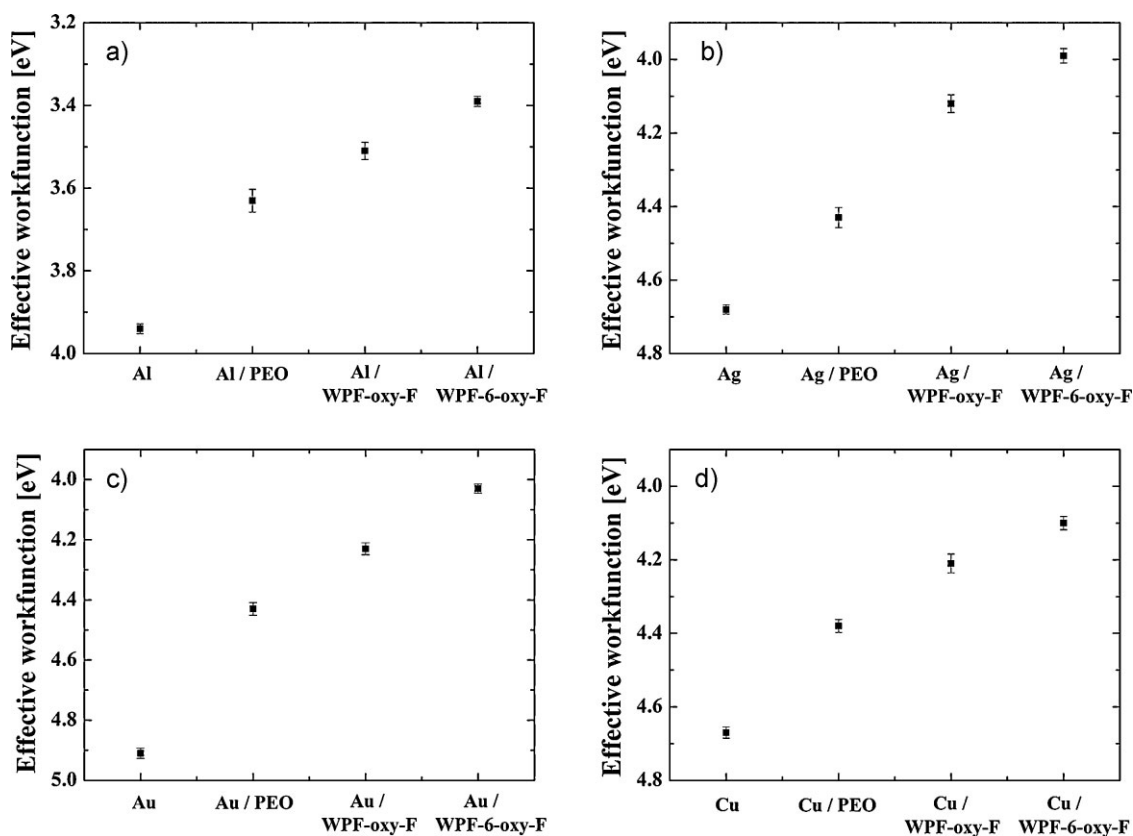
Figure 3. The effective work-function of the metals in devices with interfacial layers for a) Al, b) Ag, c) Au, and d) Cu measured with a Kelvin probe under N_2.

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Table 2. Work-function values of metal with various interfacial layers measured by a Kelvin probe under N_2.

Work-function of	metal only [eV]	with PEO [eV]	with WPF-oxy-F [eV]	with WPF-6-oxy-F [eV]
Al	3.94 ± 0.012	3.63 ± 0.027	3.51 ± 0.020	3.39 ± 0.012
Ag	4.68 ± 0.012	4.43 ± 0.027	4.12 ± 0.024	3.99 ± 0.019
Au	4.91 ± 0.016	4.43 ± 0.020	4.23 ± 0.019	4.03 ± 0.014
Cu	4.67 ± 0.015	4.38 ± 0.017	4.21 ± 0.025	4.10 ± 0.018

cathodes with interfacial layers. The work-functions of Al, Ag, Au, and Cu were 3.9,[20a] 4.6, 4.9, and 4.6 eV, respectively.[20b] The work-functions of the metal cathodes were reduced, depending on the interfacial layers, in the following order: PEO < WPF-oxy-F < WPF-6-oxy-F. The work-functions of Al, Ag, Au, and Cu with PEO, WPF-oxy-F, and WPF-6-oxy-F interfacial layers are summarized in Table 2. Introducing proper interfacial layers is reported to reduce the work-function by the formation of interfacial dipoles between the metal and the organic interfacial layer[21] or a conjugated polyelectrolyte.[22]

As a result, the series resistance (R_s) and shunt resistance (R_{sh}) were affected by the reduced metal work-functions caused by the interfacial layers. The R_s and R_{sh} were calculated from the inverse slope near V_{oc} and 0 V, respectively, in the dark J–V curves.[11,17] As seen in Figure 4 and Table 1, large R_s values and small R_{sh} values were observed in devices without interfacial dipole layers because of poor diode characteristics. However, the R_s was reduced in the devices with PEO, WPF-oxy-F, and WPF-6-oxy-F interfacial layers because of the formation of favorable interfacial dipoles. In addition, interfacial dipole layers reduced the device leakage currents because the interfacial layer prevents physical damage to the metal cathodes during thermal deposition and reduces the recombination of holes and electrons near the metal cathodes.[23] In particular, the R_s values of Al, Ag, Au, and Cu devices with WPF-6-oxy-F were reduced by 65%, 67%, 84%, and 73%, respectively, as calculated from the inverse slope near the V_{oc}. In addition, the R_{sh} of devices with WPF-6-oxy-F increased by one to two orders of magnitude at negative voltages. Thus, the efficiency (e.g., the improved V_{oc} and FF) of OSCs with WPF-6-oxy-F was higher than for devices with other interfacial layer materials, because of better electron transport and collection through the reduction of the metal work-functions by large interfacial dipoles.
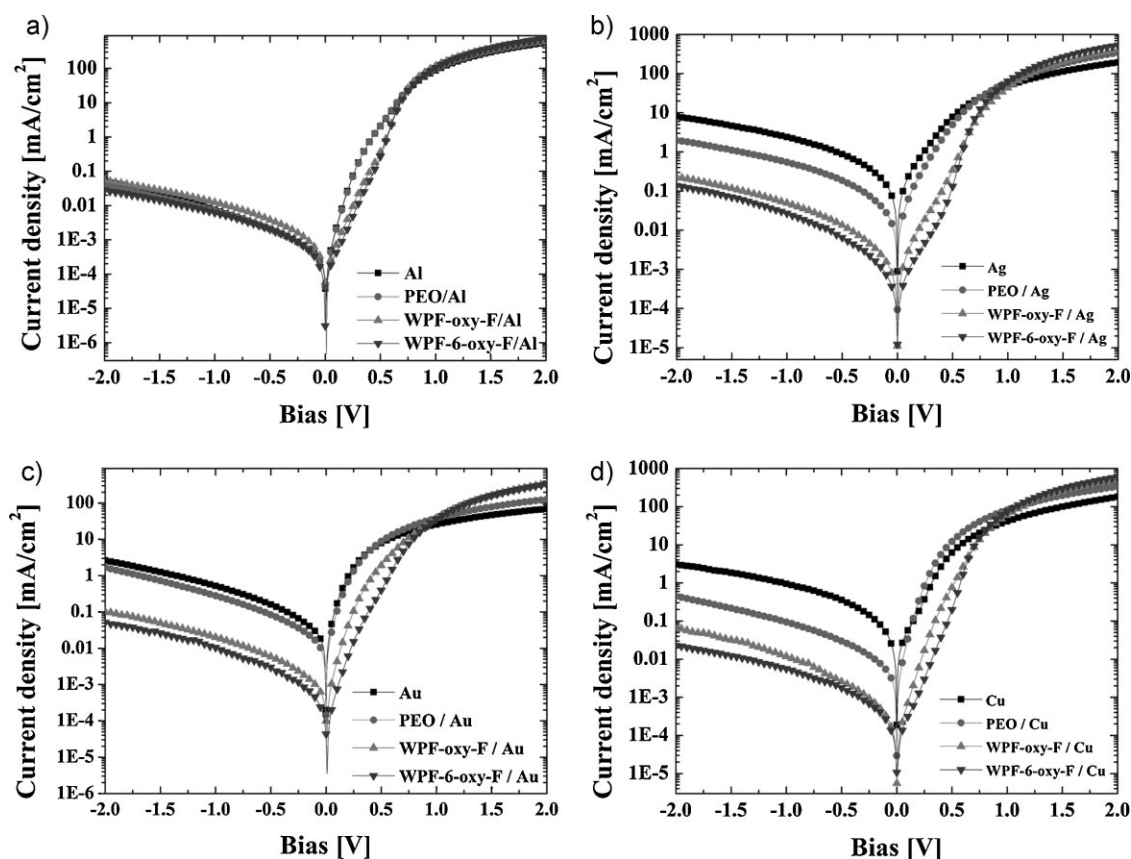
Figure 4. Dark J–V characteristics of organic solar cells with or without interfacial layers and a) Al, b) Ag, c) Au, and d) Cu cathodes.

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3. Conclusions

Novel water-soluble polyfluorene derivatives containing mobile bromide ions and ethylene oxide units were developed. These materials were used as interfacial dipole layers for low-cost and highly efficient OSCs with high work-function metal cathodes. The efficiency of OSCs with water-soluble polyfluorenes inserted between the active layer and the metal cathode was dramatically enhanced because of the formation of interfacial dipoles. WPF-6-oxy-F was the most successful polymer for enhancing the OSC performance for all the metal cathodes that were investigated (Al, Ag, Au, and Cu). In particular, introducing WPF-6-oxy-F into devices using low-cost Cu as the cathode dramatically enhanced the device efficiency from 0.8% to 3.36%. High-performance OSCs using a Cu electrode have not been reported so far. These water-soluble polyfluorene interfacial layers fabricated using solution processing could be very useful for the development of low-cost and highly efficient OSCs, particularly when using solution-processable noble metal electrodes.

4. Experimental

Synthesis of 2,7-dibromo-9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene (4): 24 g of sodium hydride (NaH) was dissolved in 50 mL of tetrahydrofuran (THF). The solution was cooled to 0 °C and then a solution of 5 g of 2,7-dibromofluorene in 30 mL of THF was slowly injected under nitrogen atmosphere. After the solution was stirred at room temperature for 1 h, 5 g of (2-(2-(2-methoxyethoxy)ethoxy)ethoxy)*p*-toluenesulfonate was injected under nitrogen. The solution was stirred at room temperature for 2 h. The reaction mixture was extracted with 300 mL of ether, and the resulting solution was evaporated. The reaction mixture was purified by column chromatography using hexane and ethyl acetate (hexane/ethyl acetate = 2:1) as the eluent ($R_f = 0.11$). The final product was a yellowish oil, produced in 70% yield. ^{1}H-NMR (300 MHz; CDCl$_3$; Me$_4$Si): δ [ppm]: 7.81 (d, $J = 8.0$ Hz, 2H, fluorene), 7.50 (dd, $J = 8.0$ and 1.65 Hz, 2H, fluorene), 7.35 (d, $J = 8.0$ Hz, 2H, fluorene), 3.61 (m, 4H, $-$CH$_2$O$-$), 3.51 (m, 4H, $-$OCH$_2-$), 3.34 (s, 6H, $-$OCH$_3$), 3.39 (m, 4H, $-$CH$_2$O$-$), 3.21 (m, 4H, $-$OCH$_2-$), 2.7 (t, $J = 7$ Hz, 4H; $-$CH$_2-$), 2.3 (t, $J = 7$ Hz, 4H; $-$CH$_2-$). ^{13}C-NMR (300 MHz; CDCl$_3$; Me$_4$Si): δ [ppm]: 39.46, 51.88, 58.96, 68.63, 70.03, 70.52, 70.70, 71.87, 121.26, 121.60, 126.67, 130.64, 138.44, 150.93. Anal. calcd. for C$_{52}$H$_{66}$Br$_6$O$_6$: C 49.31, H 5.25; found: C 49.26, H 5.23.

Synthesis of Poly[(9,9-bis(6-bromohexyl)-fluorene]-alt-(9,9-bis(2-(2-(2-methoxyethoxy) ethoxy)ethyl)-fluorene)](PF-6-oxy-F): 0.74 g of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-(6-dibromohexyl)-fluorene, 0.61 g of 2,7-dibromo-9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene and 60 mL THF were placed in a two-neck flask under a nitrogen atmosphere. Then, 20 mL of 2 M K$_2$CO$_3$ solution was injected, and 1 mol% of Pd(PPh3)4 was added to the solution. The solution was refluxed for 3 days. The reaction mixture was slowly cooled to room temperature and poured into a mixture of 250 mL of methanol and water (methanol: water = 4:1). The precipitate was collected, redissolved in chloroform and reprecipitated several times by adding methanol. The resulting polymer (number-average molecular weight (M_n) of 20 000, as determined by gel-permeation chromatography) was a yellowish powder. (Yield 70%). ^{1}H-NMR (300 MHz; CDCl$_3$; Me4Si): δ [ppm]: 7.75 (br, 6H, fluorene), 7.71 (br, 6H, fluorene), 3.52 (br, 4H, $-$CH$_2$Br), 3.45 (br, 8H $-$OCH$_2-$) 3.31 (br, 6H, $-$OCH$_3$), 3.27 (br, 4H, $-$OCH$_2-$), 2.93 (br, 4H, $-$CH$_2$O$-$), 2.59 (br, 4H, $-$OCH$_2-$), 2.18 (br, 8H, $-$CH$_2-$), 1.70 (br, 4H, $-$CH$_2-$), 1.24 (br, 8H, $-$CH$_2-$), 0.81 (br, 4H, $-$CH$_2-$). Anal. Calc. for C$_{52}$H$_{66}$Br$_2$O$_6$: C 66.13, H 7.06; found: C 67.17, H 7.52.

Synthesis of Poly[(9,9-bis(6-bromohexyl)-fluorene]-alt-(9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene)]: Dibromide (WPF-6-oxy-F): 0.25 g of PF-6-oxy-F was dissolved in 100 mL of THF. To the solution was added 5 mL of trimethylamine solution, which was then stirred at room temperature for 24 h. The solubility of the ionic polymer is lower in THF and precipitation occurred during this period. 20 mL of water was added to the solution in order to dissolve the precipitate. The solution was evaporated and the residue was redissolved in methanol. The ionic polymer was precipitated from ether and a yellow powder resulted. Yield 88%. ^{1}H-NMR (300 MHz; CD$_3$OD; Me$_4$Si): δ [ppm]: 7.87 (br, 6H, fluorene), 7.75 (br, 6H, fluorene), 3.39 (br, 4H, -CH$_2$N-), 3.34 (br, 8H, -OCH$_2$-), 3.21 (br, 4H, -OCH$_2$-), 3.17 (br, 6H, $-$OCH$_3$), 2.95 (br, 18H, $-$NCH$_3$), 2.91 (br, 4H, $-$CH$_2$O$-$), 2.56 (br, 4H, $-$OCH$_2-$), 2.22 (br, 8H, $-$CH$_2-$), 1.53 (br, 4H, $-$CH$_2-$), 1.17 (br, 8H, $-$CH$_2-$), 0.72 (br, 4H, $-$CH$_2-$). Anal. Calcd. for C$_{58}$H$_{84}$Br$_2$N$_2$O$_6$: C 66.11, H 7.95, N 2.30; found: C 65.67, H 7.79, N 2.41.

Device Fabrication: The water-soluble polyfluorenes were used as an interfacial dipole layer in OSCs. The structure of the devices was ITO/PEDOT:PSS (30 nm)/P3HT:PCBM (90 nm)/water-soluble polyfluorene (3 nm)/metal cathode (50 nm). The glass substrate, pre-coated with indium-tin-oxide (ITO, Samsung Corning Co, Ltd) having a sheet resistance of around 10 Ω sq^{-1} as cleaned in an ultrasonic bath sequentially with acetone, detergent, and deionized water, followed by 2-propanol, and dried at 120 °C in an oven. The surface was cleaned by UV-ozone treatment. The hole-injecting layer PEDOT:PSS (Baytron P VPAI 4083) was spin coated on the ITO at a thickness of 30 nm and baked at 120 °C for 10 min on a hot plate under air. A solution of 30 mg of P3HT (Rieke Metal) and 15 mg of PCBM (Nano-C) in 2 mL of chlorobenzene was spin-coated on the PEDOT:PSS layers to obtain a thickness of 90 nm, and was subsequently baked at 110 °C for 10 min under N$_2$. A 0.1 wt% solution of PEO or 0.2 wt% solution of WPF-oxy-F or WPF-6-oxy-F in methanol was spin coated on the P3HT:PCBM layer as an interfacial dipole layer. Al, Ag, Au, or Cu was deposited as the cathode through a shadow mask by thermal evaporation at a base pressure of 1×10^{-6} Torr. The photoactive area was defined by the shadow mask (4.64 mm^2). For comparison devices without interfacial layers were also fabricated using experimental procedures identical to those for devices with interfacial layers.

Device Characterization: Photocurrent–voltage (J–V) measurements were performed using a Keithley 4200 instrument under 100 mA cm^{-2} illumination from a 1-KW Oriel solar simulator with an AM 1.5 G filter in a N$_2$-filled glove box. A calibrated silicon reference solar cell with a KG5 filter certified by the National Renewable Energy Laboratory (NREL) was used to confirm the measurement conditions. All the device performance data in this manuscript represent the average for a minimum of 20 devices.

Kelvin Probe Measurements: The glass substrate (Corning Eagle 2000) was cleaned in an ultrasonic bath sequentially with acetone, detergent, and deionized water, followed by 2-propanol, and dried at 120 °C in oven. Al, Ag, Au, or Cu was deposited on the glass substrate by thermal evaporation at a base pressure of 1×10^{-6} Torr. A 0.1 wt% solution of PEO or 0.2 wt% solution of WPF-oxy-F or WPF-6-oxy-F in methanol was spin coated on each metal (Al, Ag, Au, or Cu) in a N$_2$-filled glove box. The contact potential difference (CPD) of each sample was detected by a Kelvin probe (KP 6500 Digital Kelvin probe, McAllister Technical Services. Co. Ltd) under N$_2$. The CPD was calibrated to highly ordered pyrolytic graphite (HOPG) at -4.58 ± 0.03 eV.

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