

# Organic Photovoltaic Cells with Stable Top Metal Electrodes Modified with Polyethylenimine

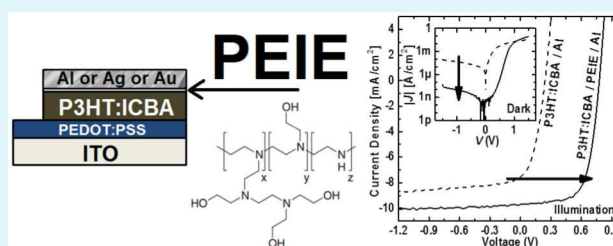
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## Supporting Information

**ABSTRACT:** Efficient organic photovoltaic cells (OPV) often contain highly reactive low-work-function calcium electron-collecting electrodes. In this work, efficient OPV are demonstrated in which calcium electrodes were avoided by depositing a thin layer of the amine-containing nonconjugated polymer, polyethylenimine (PEIE), between the photoactive organic semiconductor layer and stable metal electrodes such as aluminum, silver, or gold. Devices with structure ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/poly(3-hexylthiophene):indene- $C_{60}$ -bis-adduct (P3HT:ICBA)/PEIE/Al demonstrated overall photovoltaic device performance comparable to devices containing calcium electron-collecting electrodes, ITO/PEDOT:PSS/P3HT:ICBA/Ca/Al, with open-circuit voltage of  $775 \pm 6$  mV, short-circuit current density of  $9.1 \pm 0.5$  mA cm<sup>-2</sup>, fill factor of  $0.65 \pm 0.01$ , and power conversion efficiency of  $4.6 \pm 0.3\%$ , averaged over 5 devices at 1 sun.

**KEYWORDS:** polymer solar cells, interlayers, water-/alcohol-soluble polymers, low-work-function electrodes, polyethylenimine



Highly efficient organic photovoltaic devices (OPV) often incorporate calcium electrodes, typically deposited prior to a more air-stable capping metal, such as aluminum or silver.<sup>1</sup> Although the use of calcium leads to OPV that demonstrate high fill factor (FF) and open-circuit voltage ( $V_{OC}$ ) values, its air instability and the consequent reduction in device lifetime could preclude such devices from reaching commercialization. Additionally, the lower reflectance of calcium compared to aluminum and silver results in less photons being absorbed in the photoactive layer during the second pass after reflection from the top metal electrode, diminishing the short-circuit current density ( $J_{SC}$ ).<sup>2-4</sup> For these reasons, it is important to develop OPV that exhibit superior photovoltaic device performance in the absence of calcium.

One approach toward replacing calcium has been the development of so-called inverted geometry OPV where the photoactive layer and other functional layers are deposited on top of the low-work-function electron-collecting electrode, thereby masking it from air.<sup>5</sup> Tin-doped indium oxide (ITO) coated with a variety of materials, including metal oxides, polymers, and inorganic salts, has successfully served as the electron-collecting electrode in inverted geometry OPV. Another approach toward the elimination of calcium in OPV has been the development of interfacial modifiers that can be deposited on top of the photoactive layers and underneath air-stable metals that act as the electron-collecting electrodes. Of particular interest are solution-processable polymeric modifiers. Significant research efforts have been put into the development of such interfacial modifiers.<sup>6-15</sup> Poly(ethylene oxide) was one

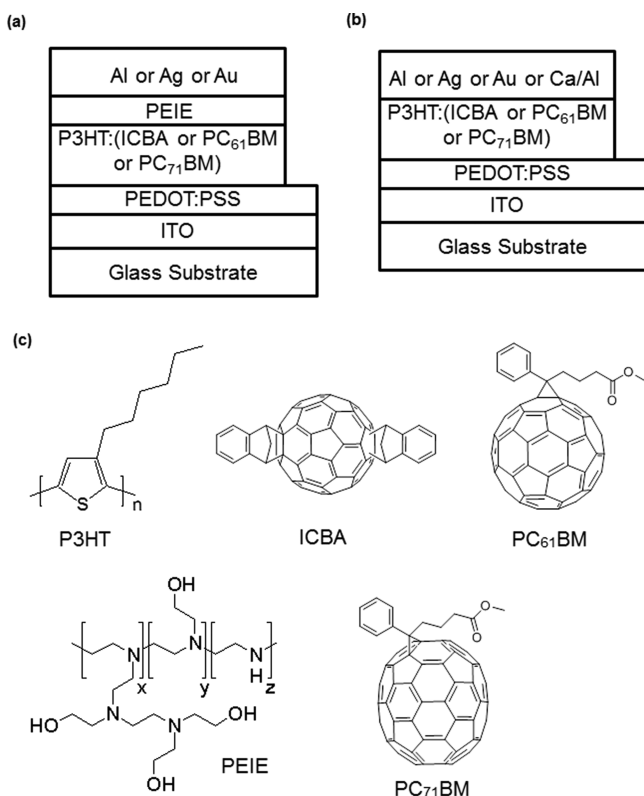
of the first polymeric cathode modifiers demonstrated in OPV.<sup>14</sup> It was shown to enhance  $V_{OC}$  when placed between the photoactive layer of APFO-5:PCBM and the aluminum electrode. In addition, the ionic conjugated polyelectrolyte copolymer PF2/6-*b*-P3TMAHT has been shown to enhance the performance parameters in PCDTBT:PC<sub>71</sub>BM devices with an aluminum electrode.<sup>6</sup> Recently, PFN led to improved performance parameters in conventional geometry OPV using low bandgap materials systems.<sup>15</sup>

We have previously demonstrated that ethoxylated polyethylenimine (PEIE) can substantially reduce the work function of a wide variety of materials, including metals, metal oxides, and conducting polymers.<sup>16</sup> Spin-coating PEIE onto the surface of various conductive materials to produce electron-collecting electrodes directly lent itself toward the fabrication of inverted geometry OPV, where other layers were processed upon the polymer-modified low-work-function electrode surfaces. In this work, we show that the low-work-function interface can also be produced by reversing the order of deposition, i.e., by depositing conductors on top of PEIE, facilitating the development of conventional geometry OPV devices, as shown in Figure 1. As a result, various electrode metals such as aluminum and silver, as well as the high-work-function metal gold, were used to obtain devices of the structure ITO/

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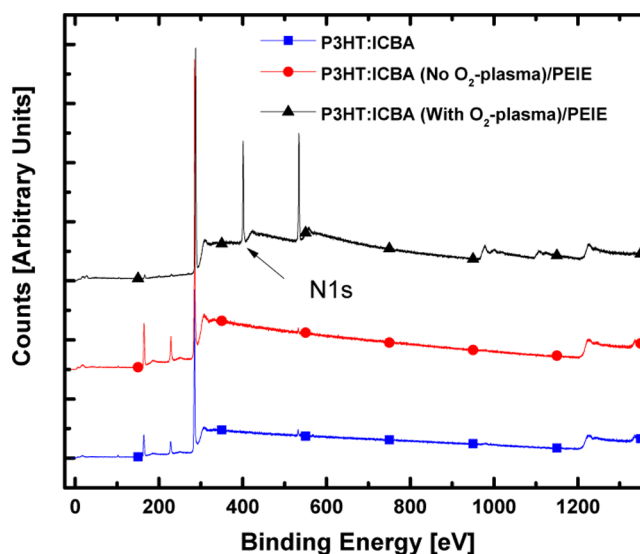


**Figure 1.** (a) Device structure of solar cells with PEIE interfacial modification. (b) Device structure of solar cells without PEIE interfacial modification. (c) Chemical structures of materials used in this study.

PEDOT:PSS/P3HT:ICBA/PEIE/Al or Ag or Au, with efficient electron collection.

To produce the solar cells (detailed fabrication procedures are included in the Supporting Information), patterned ITO-coated glass slides were first solvent cleaned and oxygen plasma-treated. The slides were then spin-coated with PEDOT:PSS and thermally annealed in air. After transfer to a nitrogen-filled glovebox, various photoactive layers including P3HT:ICBA, P3HT:PC<sub>61</sub>BM, and P3HT:PC<sub>71</sub>BM, were spin-coated on top of the ITO/PEDOT:PSS slides. After slow drying of the films in covered glass Petri dishes, the films were removed from the glovebox and exposed to a very brief flash of oxygen plasma in order to make the active layer surface hydrophilic. A diluted solution of PEIE was then spin-coated on the photoactive layers in air, followed by a final anneal step inside the glovebox. Various stable top electrode metals, such as aluminum, silver, and gold were then thermally evaporated on top of the films, thereby completing device fabrication.

The deposition of PEIE from 2-methoxyethanol on the hydrophobic surface of P3HT:ICBA required surface treatment, such as a brief flash of oxygen plasma, to turn the surface hydrophilic. Figure 2 shows XPS surveys conducted on the surface of P3HT:ICBA on which PEIE was not spun, on which PEIE was spun without plasma treatment, and on which PEIE was spun with prior plasma treatment. The emergence of the N 1s peak confirms the presence of PEIE on the surface. Nitrogen is an appropriate identifier element because it is not present in the chemical structures of either P3HT or ICBA. As shown in Figure 2, N 1s is only observed when PEIE was spun on the plasma-treated P3HT:ICBA surface. Results of solar cells with

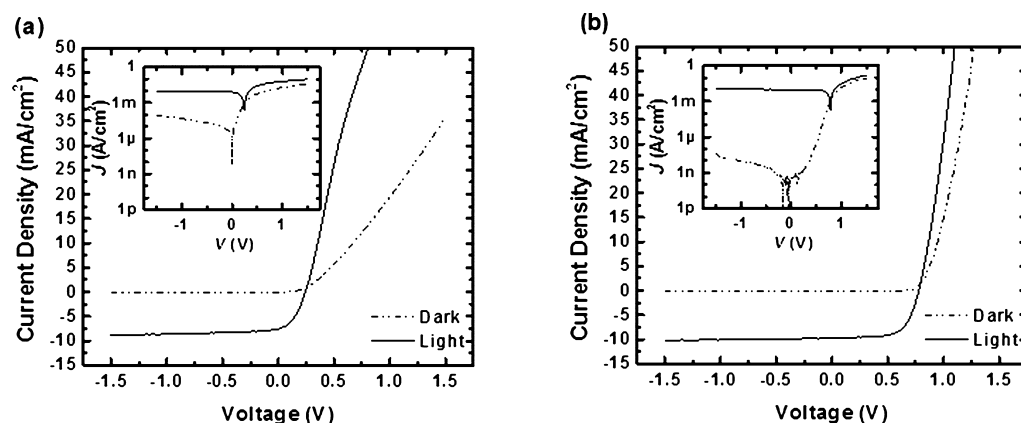


**Figure 2.** XPS spectra taken from the surface of P3HT:ICBA without PEIE, when PEIE is spin-coated on top of P3HT:ICBA without surface treatment, or when PEIE is spin-coated on top of P3HT:ICBA with a brief flash of O<sub>2</sub>-plasma.

different metals modified by PEIE for electron collection are shown as follows.

A study of the performance of solar cells with both P3HT:ICBA and P3HT:PCBM as the active layers with aluminum electron-collecting electrodes is first presented. ICBA is widely used in OPV because it yields higher  $V_{OC}$  as compared to PCBM, when blended with P3HT.<sup>17</sup> It has previously been shown that OPV devices based on P3HT:PC<sub>61</sub>BM with the structure ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM/Al demonstrated a high fill factor (FF) of 68% without using calcium or other interfacial modifiers by thermally annealing completed devices after the aluminum top metal electrode deposition for 30 min at 150 °C.<sup>18</sup> However, P3HT:ICBA-based OPV devices with the analogous structure ITO/PEDOT:PSS/P3HT:ICBA/Al, demonstrated poor FF when the devices were either thermally annealed at 150 °C for 10 min before aluminum top electrode deposition (“pre-annealing”; FF = 0.41 ± 0.01) or after (“post-annealing”; FF = 0.55 ± 0.01). Representative  $J-V$  characteristics of these devices are shown in Figure S1 in the Supporting Information. The devices exhibited poor rectification in the dark and inflection in the curves under illumination. This illustrates the poor electron collection of the aluminum electrode in devices using P3HT:ICBA active layers.

Figure 3 shows representative  $J-V$  characteristics for devices with the structure ITO/PEDOT:PSS/P3HT:ICBA/PEIE/Al in which PEIE was spin-coated on the oxygen-plasma treated P3HT:ICBA photoactive layer prior to deposition of aluminum as the electron-collecting top metal electrode. The presence of PEIE substantially improves the photovoltaic performance over devices with the structure ITO/PEDOT:PSS/P3HT:ICBA/Al. Note that for these reference devices not containing PEIE, the photoactive layer was not subjected to the flash of oxygen plasma (the effects of subjecting the photoactive layer to a flash of oxygen-plasma on device performance are shown in Figure S2 in the Supporting Information). Devices containing PEIE/Al electrodes showed  $V_{OC} = 775 \pm 6$  mV,  $J_{SC} = 9.1 \pm 0.5$  mA cm<sup>-2</sup>, FF = 0.65 ± 0.01, and PCE = 4.6 ± 0.3%, averaged over 5 devices. The PCE in this case was comparable to that attained



**Figure 3.** Representative  $J$ - $V$  characteristics (a) for a reference device with structure ITO/PEDOT:PSS/P3HT:ICBA/Al and (b) for a device with structure ITO/PEDOT:PSS/P3HT:ICBA/PEIE/Al. The insets show the  $J$ - $V$  characteristics on a semilogarithmic scale.

when using calcium electron-collecting top metal electrodes with the structure ITO/PEDOT:PSS/P3HT:ICBA/Ca/Al (see Figure S3 in the Supporting Information and Table 1). Note

**Table 1. OPV Performance Statistics under Simulated 100 mW cm<sup>-2</sup> AM 1.5 G Illumination for P3HT-Based Bulk Heterojunction Devices with a 200 nm Thick Photoactive Layer<sup>a</sup>**

acceptor/electrode (no. of devices data is averaged over)	$V_{OC}$ (mV)	$J_{SC}$ (mA cm <sup>-2</sup> )	FF	PCE (%)
ICBA/Al (10)	246 ± 14	7.5 ± 0.3	0.41 ± 0.01	0.8 ± 0.1
ICBA/PEIE/Al (5)	775 ± 6	9.1 ± 0.5	0.65 ± 0.01	4.6 ± 0.3
ICBA/(solvent)/Al (10)	428 ± 29	6.3 ± 0.2	0.51 ± 0.02	1.4 ± 0.2
PC <sub>61</sub> BM/Al (5)	105 ± 18	5.4 ± 0.5	0.29 ± 0.01	0.2 ± 0.1
PC <sub>61</sub> BM/PEIE/Al (5)	551 ± 5	7.3 ± 0.1	0.56 ± 0.01	2.2 ± 0.1
PC <sub>71</sub> BM/Al (4)	200 ± 34	5.8 ± 0.1	0.34 ± 0.01	0.4 ± 0.1
PC <sub>71</sub> BM/PEIE/Al (10)	607 ± 3	7.9 ± 0.2	0.68 ± 0.01	3.3 ± 0.1
ICBA/Ag (10)	446 ± 27	7.9 ± 0.3	0.38 ± 0.01	1.4 ± 0.1
ICBA/PEIE/Ag (4)	762 ± 5	9.4 ± 0.2	0.63 ± 0.01	4.5 ± 0.2
ICBA/Au (10)	277 ± 5	7.1 ± 0.3	0.42 ± 0.01	0.8 ± 0.1
ICBA/PEIE/Au (9)	733 ± 8	7.5 ± 0.3	0.64 ± 0.01	3.5 ± 0.1
ICBA/Ca/Al (5)	822 ± 4	8.0 ± 0.1	0.71 ± 0.01	4.6 ± 0.1

<sup>a</sup>All data shown is for devices that were thermally annealed prior to the metal deposition.

that the  $V_{OC}$  obtained in the case of PEIE/Al electrodes was lower than that for devices with Ca/Al electrodes. However, the higher reflectivity of aluminum provided a greater  $J_{SC}$  compared with the use of calcium, due to the second pass contribution after light reflects back into the photoactive layer from the metal electrode, compensating for the lower  $V_{OC}$  value.

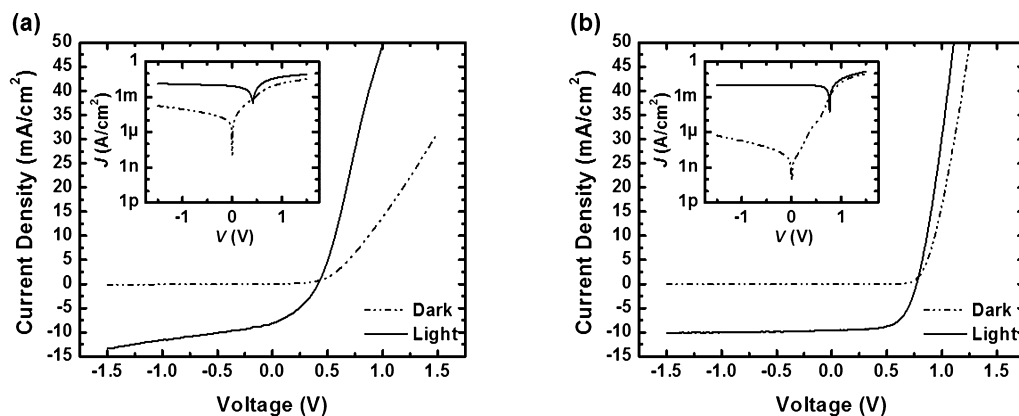
Representative  $J$ - $V$  characteristics for a control device where the solvent alone, not containing any PEIE, was spin-coated above the oxygen-plasma treated photoactive layer with device structure ITO/PEDOT:PSS/P3HT:ICBA (2-methoxyethanol)/Al, are shown in Figure S4 in the Supporting Information, confirming that PEIE plays a critical role in the device performance improvement. There is a slight improvement in  $V_{OC}$  and FF for devices with structure ITO/PEDOT:PSS/P3HT:ICBA (2-methoxyethanol)/Al as compared to devices

ITO/PEDOT:PSS/P3HT:ICBA/Al. A number of recent studies have demonstrated OPV device improvements by means of a so-called solvent treatment, where a polar solvent is spin-coated on the photoactive layer prior to top metal electrode deposition.<sup>19–25</sup> These studies have postulated a number of reasons leading to device improvement upon spin-coating the polar solvent on top of the photoactive layer, including the passivation of surface traps leading to reduced charge recombination, an increase in hole mobility leading to more balanced charge transport, and a more favorable morphology for charge extraction. Some of the studies specifically ruled out changes in the active layer morphology upon solvent treatment. Regardless, most significant solvent treatment effects are seen specifically in low bandgap polymer systems. The gains of the solvent treatment on its own in the case for P3HT:ICBA were minimal and necessitated the addition of PEIE in the solvent for substantial device performance improvements.

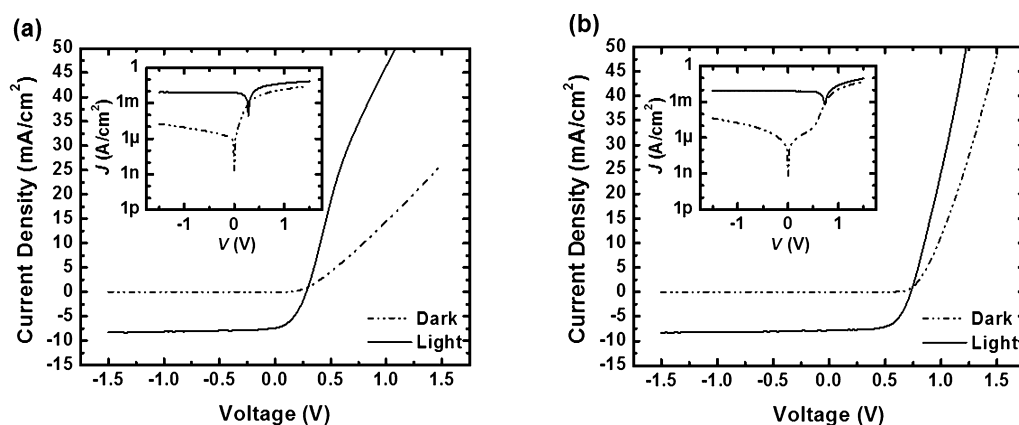
It is also important to note that the PEIE solution spin-coated on top of the photoactive layers to improve the electron-collecting contacts was more dilute than that used in our previous studies when PEIE was directly coated on top of various conductors.<sup>16</sup> Using the more concentrated PEIE solution (0.4 wt %) in the conventional geometry architecture resulted in poor performance, as illustrated in Figure S5 in the Supporting Information.

Because PEIE was used to modify the electron-collecting interface in OPV devices, it was instructive to demonstrate its effectiveness for a variety of acceptor materials. Therefore, OPV were also fabricated using the fullerene-derivatives PC<sub>61</sub>BM and PC<sub>71</sub>BM, by the same approach. These fullerene derivatives have a larger electron affinity than ICBA.<sup>26</sup> Figures S6 and S7 in the Supporting Information show representative  $J$ - $V$  characteristics for devices with the structure ITO/PEDOT:PSS/P3HT:(PC<sub>61</sub>BM or PC<sub>71</sub>BM)/PEIE/Al. A substantial improvement in performance over devices with the structure ITO/PEDOT:PSS/P3HT:(PC<sub>61</sub>BM or PC<sub>71</sub>BM)/Al was observed, both for cells with PC<sub>61</sub>BM and PC<sub>71</sub>BM acceptors, after inserting PEIE prior to the aluminum metal deposition (Table 1), indicating broad applicability of the method.

In addition to using the electrode modifier PEIE with aluminum, it was also applied in conjunction with silver top electrodes. Silver is more air-stable than aluminum and possesses a higher reflectance above 400 nm, which should further enhance the second-pass current contribution.<sup>27</sup> Figure



**Figure 4.** Representative  $J$ - $V$  characteristics (a) for a reference device with structure ITO/PEDOT:PSS/P3HT:ICBA/Ag and (b) for a device with structure ITO/PEDOT:PSS/P3HT:ICBA/PEIE/Ag. The insets show the  $J$ - $V$  characteristics on a semilogarithmic scale.



**Figure 5.** Representative  $J$ - $V$  characteristics (a) for a reference device with structure ITO/PEDOT:PSS/P3HT:ICBA/Au and (b) for a device with structure ITO/PEDOT:PSS/P3HT:ICBA/PEIE/Au. The insets show the  $J$ - $V$  characteristics on a semilogarithmic scale.

4 displays representative device  $J$ - $V$  curves for (a) reference devices with the structure ITO/PEDOT:PSS/P3HT:ICBA/Ag (b) ITO/PEDOT:PSS/P3HT:ICBA/PEIE/Ag. In this case again, there was a substantial enhancement in the open-circuit voltage ( $446 \pm 27$  mV to  $762 \pm 5$  mV) as well as the fill factor ( $0.38 \pm 0.01$  to  $0.63 \pm 0.01$ ) after PEIE incorporation (Table 1). Indeed, the greater reflectance of silver was indicated by the higher  $J_{SC}$  ( $9.4 \pm 0.2$  mA cm<sup>-2</sup>) as compared to the case where aluminum electrodes were used.<sup>3</sup>

To demonstrate the versatility of the method, we also repeated experiments using gold electrodes to show that devices could be fabricated with high-work-function metals acting as the top metal electron-collecting electrode. Representative  $J$ - $V$  characteristics of devices with structure ITO/PEDOT:PSS/P3HT:ICBA/Au and ITO/PEDOT:PSS/P3HT:ICBA/PEIE/Au are shown in Figure 5. Surprisingly, the reference devices ITO/PEDOT:PSS/P3HT:ICBA/Au also acted as diodes despite the expectation that the similar work functions of PEDOT:PSS and Au would result in an insufficient built-in electric field. It is likely that the work function of gold was somewhat lower than that of PEDOT:PSS in this case, for reasons such as surface contamination, as described previously.<sup>28</sup> Nonetheless, enhancements were seen in  $V_{OC}$ ,  $J_{SC}$ , and FF for the case of ITO/PEDOT:PSS/P3HT:ICBA/PEIE/Au as shown in Table 1.

Although the objective of the study was to use PEIE to facilitate electron collection by stable metal electrodes, the effects of the PEIE underlayer in conjunction with calcium

electrodes were also studied. The device performance improvement of the structure ITO/PEDOT:PSS/P3HT:ICBA/PEIE/Ca/Al is shown in the representative  $J$ - $V$  curves in Figure S8 in the Supporting Information.

When PEIE is spin-coated on top of conductors, it reduces their work function by the formation of a surface dipole.<sup>16</sup> Similarly, we attribute the improvement in device performance for devices with structure ITO/PEDOT:PSS/P3HT:ICBA/PEIE/Al or Ag or Au as compared to devices without PEIE with device structures ITO/PEDOT:PSS/P3HT:ICBA/Al or Ag or Au, to the formation of surface dipoles that arise because of a partial electron transfer from the amine groups of PEIE to the respective metals deposited on them. The surface dipoles, with a slight negative charge toward the metals and the corresponding positive charge toward the active layer, result in the lowering of the vacuum level of the metals. The vacuum level shift is the source of the metal work function reduction, allowing the formation of a low-work-function contact between ICBA and the respective metals.

The results of a recent report<sup>29</sup> also allow us to infer that such a work function reduction could lead to improved OPV device performance by means of decreased surface recombination of holes in P3HT at the PEIE/metal interface, as a result of increased band bending. This hypothesis could be appropriate since studies<sup>26</sup> have shown that P3HT preferentially segregates toward the top of the P3HT:ICBA film, which is the surface where PEIE was deposited in the experiments described here.

The photoactive layer morphology of bulk heterojunction solar cells generally depends on a number of factors, including the solvent from which the film is spin-coated, the underlying substrate including any surface treatments, spin coating speed and other parameters, and film drying time. These parameters were kept uniform across all devices studied. The only difference introduced in the test devices was a very brief flash of oxygen plasma and the spin-coating of PEIE from 2-methoxyethanol solvent, followed by the typical thermal annealing conducted on P3HT-based films. We do not anticipate any significant changes to active layer morphology resulting from the momentary plasma exposure. On the basis of the insolubility of P3HT and ICBA in 2-methoxyethanol, again no change in photoactive layer morphology is expected. The only difference that could rise may result from the thermal annealing process of P3HT:ICBA with and without the presence of PEIE on top. It is possible that the anneal step might cause some degree of migration of PEIE into the photoactive layer.

In conclusion, the deposition of aluminum, silver, or gold on top of PEIE yields low-work-function electrodes in OPV cells with a conventional geometry. Spin-coating PEIE on the P3HT:ICBA photoactive layer prior to the top metal deposition in OPV was found to significantly improve electron collection for devices with the structure ITO/PEDOT:PSS/P3HT:ICBA/PEIE/Al or Ag or Au as compared to the reference devices without PEIE (ITO/PEDOT:PSS/P3HT:ICBA/Al or Ag or Au). Device performance improvements were consequently seen in  $V_{OC}$ ,  $J_{SC}$ , and FF for aluminum, silver, and gold metal electrodes, as well as with different acceptor materials including PC<sub>61</sub>BM, PC<sub>71</sub>BM, and ICBA. We assign the improvement of the contact to a reduction in the work function of the metal at the interface by a vacuum level shift due to a surface dipole caused by the partial electron transfer from the amine-groups in PEIE to the metal. We infer that the process is identical to that studied previously in devices in which the order of deposition of an amine-containing polymer and a conductor is reversed. The results are particularly significant for ICBA, which does not form an Ohmic contact with aluminum, as evidenced by the low fill factor in OPV devices where aluminum is directly deposited on the photoactive layer, regardless of the annealing sequence with respect to metal deposition, thereby necessitating the presence of a low-work-function metal such as calcium. These developments reduce the reliance on calcium for efficient devices and open up the possibilities of novel device structures including conventional geometry tandem OPV and modules. The results show that the method, by which the work function of air-stable electrodes is significantly reduced by amine-containing polymers such as PEIE, is independent of the order of deposition of the surface modifier and the conductor.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Detailed device fabrication procedures and supplementary solar cell current density - voltage curves and device performance data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Zhang, M.; Guo, X.; Zhang, S.; Hou, J. Synergistic Effect of Fluorination on Molecular Energy Level Modulation in Highly Efficient Photovoltaic Polymers. *Adv. Mater.* **2014**, *26*, 1118–1123.
- (2) Hadipour, A.; Cheyng, D.; Heremans, P.; Rand, B. P. Electrode Considerations for the Optical Enhancement of Organic Bulk Heterojunction Solar Cells. *Adv. Energy Mater.* **2011**, *1*, 930–935.
- (3) Pandey, A. K.; Shaw, P. E.; Samuel, I. D. W.; Nunzi, J.-M. Effect of Metal Cathode Reflectance on the Exciton-Dissociation Efficiency in Heterojunction Organic Solar Cells. *Appl. Phys. Lett.* **2009**, *94*, 103303.
- (4) Potsavage, W. J.; Sharma, A.; Kippelen, B. Critical Interfaces in Organic Solar Cells and Their Influence on the Open-Circuit Voltage. *Acc. Chem. Res.* **2009**, *42*, 1758–1767.
- (5) Şahin, Y.; Alem, S.; de Bettignies, R.; Nunzi, J.-M. Development of Air Stable Polymer Solar Cells Using an Inverted Gold on Top Anode Structure. *Thin Solid Films* **2005**, *476*, 340–343.
- (6) Seo, J. H.; Gutacker, A.; Sun, Y.; Wu, H.; Huang, F.; Cao, Y.; Scherf, U.; Heeger, A. J.; Bazan, G. C. Improved High-Efficiency Organic Solar Cells via Incorporation of a Conjugated Polyelectrolyte Interlayer. *J. Am. Chem. Soc.* **2011**, *133*, 8416–8419.
- (7) Luo, J.; Wu, H.; He, C.; Li, A.; Yang, W.; Cao, Y. Enhanced Open-Circuit Voltage in Polymer Solar Cells. *Appl. Phys. Lett.* **2009**, *95*, 043301.
- (8) Na, S.-I.; Oh, S.-H.; Kim, S.-S.; Kim, D.-Y. Efficient Organic Solar Cells with Polyfluorene Derivatives as a Cathode Interfacial Layer. *Org. Electron.* **2009**, *10*, 496–500.
- (9) Zhao, Y.; Xie, Z.; Qin, C.; Qu, Y.; Geng, Y.; Wang, L. Enhanced Charge Collection in Polymer Photovoltaic Cells by Using an Ethanol-Soluble Conjugated Polyfluorene as Cathode Buffer Layer. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 604–608.
- (10) He, C.; Zhong, C.; Wu, H.; Yang, R.; Yang, W.; Huang, F.; Bazan, G. C.; Cao, Y. Origin of the Enhanced Open-Circuit Voltage in Polymer Solar Cells via Interfacial Modification Using Conjugated Polyelectrolytes. *J. Mater. Chem.* **2010**, *20*, 2617–2622.
- (11) Oh, S.-H.; Na, S.-I.; Jo, J.; Lim, B.; Vak, D.; Kim, D.-Y. Water-Soluble Polyfluorenes as an Interfacial Layer Leading to Cathode-Independent High Performance of Organic Solar Cells. *Adv. Funct. Mater.* **2010**, *20*, 1977–1983.
- (12) He, Z.; Zhang, C.; Xu, X.; Zhang, L.; Huang, L.; Chen, J.; Wu, H.; Cao, Y. Largely Enhanced Efficiency with a PFN/Al Bilayer Cathode in High Efficiency Bulk Heterojunction Photovoltaic Cells with a Low Bandgap Polycarbazole Donor. *Adv. Mater.* **2011**, *23*, 3086–3089.
- (13) Jung, J. W.; Jo, J. W.; Jo, W. H. Enhanced Performance and Air Stability of Polymer Solar Cells by Formation of a Self-Assembled Buffer Layer from Fullerene-End-Capped Poly(ethylene glycol). *Adv. Mater.* **2011**, *23*, 1782–1787.
- (14) Zhang, F.; Ceder, M.; Inganäs, O. Enhancing the Photovoltage of Polymer Solar Cells by Using a Modified Cathode. *Adv. Mater.* **2007**, *19*, 1835–1838.
- (15) He, Z.; Zhong, C.; Huang, X.; Wong, W.-Y.; Wu, H.; Chen, L.; Su, S.; Cao, Y. Simultaneous Enhancement of Open-Circuit Voltage, Short-Circuit Current Density, and Fill Factor in Polymer Solar Cells. *Adv. Mater.* **2011**, *23*, 4636–4643.
- (16) Zhou, Y.; Fuentes-Hernandez, C.; Shim, J.; Meyer, J.; Giordano, A. J.; Li, H.; Winget, P.; Papadopoulos, T.; Cheun, H.; Kim, J.; Fenoll,

M.; Dindar, A.; Haske, W.; Najafabadi, E.; Khan, T. M.; Sojoudi, H.; Barlow, S.; Graham, S.; Bredas, J. L.; Marder, S. R.; Kahn, A.; Kippelen, B. A Universal Method to Produce Low Work Function Electrodes for Organic Electronics. *Science* **2012**, *336*, 327–332.

(17) Zhao, G.; He, Y.; Li, Y. 6.5% Efficiency of Polymer Solar Cells Based on Poly(3-hexylthiophene) and Indene-C<sub>60</sub> Bisadduct by Device Optimization. *Adv. Mater.* **2010**, *22*, 4355–4358.

(18) Ma, W. L.; Yang, C. Y.; Gong, X.; Lee, K.; Heeger, A. J. Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology. *Adv. Funct. Mater.* **2005**, *15*, 1617–1622.

(19) Zhou, H.; Zhang, Y.; Seifert, J.; Collins, S. D.; Luo, C.; Bazan, G. C.; Nguyen, T.-Q.; Heeger, A. J. High-Efficiency Polymer Solar Cells Enhanced by Solvent Treatment. *Adv. Mater.* **2013**, *25*, 1646–1652.

(20) Yang, B.-W.; Tsai, M.-Y.; Cheng, W.-H.; Chen, J.-S.; Hsu, S. L.-C.; Chou, W.-Y. Synergistic Amplification of Short-Circuit Current for Organic Solar Cells via Modulation of P3HT:PCBM Spatial Distribution with Solvent Treatment. *J. Phys. Chem. C* **2013**, *117*, 14472–14478.

(21) Wang, Y.; Liu, Y.; Chen, S.; Peng, R.; Ge, Z. Significant Enhancement of Polymer Solar Cell Performance via Side-Chain Engineering and Simple Solvent Treatment. *Chem. Mater.* **2013**, *25*, 3196–3204.

(22) Synooka, O.; Kretschmer, F.; Hager, M. D.; Schubert, U.; Gobsch, G.; Hoppe, H. Impact of Methanol Top-Casting or Washing on the Polymer Solar Cell Performance. *Proc. SPIE* **2013**, *8811*, 881117.

(23) Kai, Z.; Zhicheng, H.; Chunhui, D.; Lei, Y.; Fei, H.; Yong, C. The Effect of Methanol Treatment on the Performance of Polymer Solar Cells. *Nanotechnology* **2013**, *24*, 484003.

(24) Nam, S.; Jang, J.; Cha, H.; Hwang, J.; An, T. K.; Park, S.; Park, C. E. Effects of Direct Solvent Exposure on the Nanoscale Morphologies and Electrical Characteristics of PCBM-Based Transistors and Photovoltaics. *J. Mater. Chem.* **2012**, *22*, 5543–5549.

(25) Liu, X.; Wen, W.; Bazan, G. C. Post-Deposition Treatment of an Arylated-Carbazole Conjugated Polymer for Solar Cell Fabrication. *Adv. Mater.* **2012**, *24*, 4505–4510.

(26) Guan, Z.-L.; Kim, J. B.; Loo, Y.-L.; Kahn, A. Electronic Structure of the Poly(3-hexylthiophene):Indene-C<sub>60</sub> Bisadduct Bulk Heterojunction. *J. Appl. Phys.* **2011**, *110*, 043719.

(27) Dobrowolski, J. A. Coatings and Filters. In *Handbook of Optics*; Driscoll, W. G.; Vaughan, W., Eds.; McGraw-Hill: New York, 1978; p 92.

(28) Wan, A.; Hwang, J.; Amy, F.; Kahn, A. Impact of Electrode Contamination on the Alpha-NPD/Au Hole Injection Barrier. *Org. Electron.* **2005**, *6*, 47–54.

(29) Knesting, K. M.; Ju, H.; Schlenker, C. W.; Giordano, A. J.; Garcia, A.; Smith, O. N. L.; Olson, D. C.; Marder, S. R.; Ginger, D. S. ITO Interface Modifiers Can Improve VOC in Polymer Solar Cells and Suppress Surface Recombination. *J. Phys. Chem. Lett.* **2013**, *4*, 4038–4044.