ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

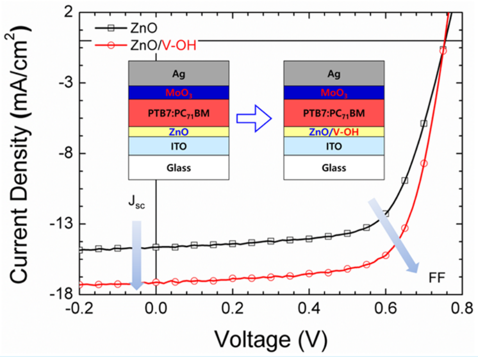
A Simple Approach to Fabricate an Efficient Inverted Polymer Solar Cell with a Novel Small Molecular Electrolyte as the Cathode Buffer Layer

Youn Hwan Kim,[†] Nadhila Sylvianti,[†] Mutia Anissa Marsya,[†] Juyun Park,[‡] Yong-Cheol Kang,[‡] Doo Kyung Moon,[§] and Joo Hyun Kim*,[†]

[†]Department of Polymer Engineering, Pukyong National University, Busan 48547, Korea
[‡]Department of Chemistry, Pukyong National University, Busan 48513, Korea
[§]Department of Materials Chemistry and Engineering, Konkuk University, Seoul 05029, Korea

Supporting Information

ABSTRACT: A novel small-molecule electrolyte, 1,1′-bis(4-hydroxypropyl)-[4,4′-bipyridine]-1,1′-diium bromide (V-OH), containing a mixture of PTB7:$PC_{71}BM$ has been designed and synthesized as a cathode buffer layer for inverted polymer solar cells (iPSCs). The molecular structure of this new compound comprises a viologen skeleton with hydroxyl group terminals. While the viologen unit is responsible for generating a favorable interface dipole, the two terminal hydroxyl groups of V-OH may generate a synergy effect in the magnitude of the interface dipole. Consequently, the devices containing the V-OH interlayer exhibited a power conversion efficiency (PCE) of 9.13% (short circuit current = 17.13 mA/cm^2, open circuit voltage = 0.75 V, fill factor = 71.1%). The PCE of the devices with V-OH exhibited better long-term stability compared to that of the devices without V-OH. Thus, we found that it is possible to enhance the efficiency of PSCs by a simple approach without the need for complicated methods of device fabrication.



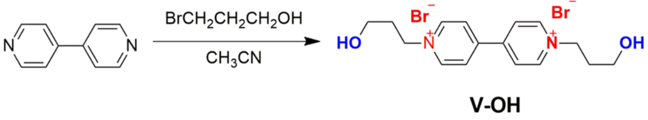
KEYWORDS: *electrolyte, inverted polymer solar cell, cathode buffer layer, work function, viologen*

INTRODUCTION

Flexible polymer solar cells (PSCs) have attracted much attention due to their potential applications as clean energy sources and the possibility of their large-area fabrication.[1−4] There has been a rapid improvement in the power conversion efficiencies (PCEs) of PSCs. 10% or more of PCE has been reported, and such a value has been achieved because of tremendous advancements being made in the development of efficient conjugated materials, including polymers and oligomers,[5−8] and electrode interface engineering.[9] Charge collection at the electrode interfaces is considered the most crucial factor responsible for creating efficient devices. Interlayers made of alcohol/water-soluble conjugated polymer electrolytes (CPEs),[10−19] nonconjugated polymers,[20−25] alcohol/water-soluble conjugated[26−30] or nonconjugated small molecules,[31−35] and polar solvent treatments[36−40] have been used to attempt to improve the PCEs of the devices. When a thin film of these materials is present as an interlayer in the cathode interface, it dramatically improves the performance of the PSC. It has been reported that ionic end groups in side chains on the conjugated polymer backbone induce favorable interface dipoles, which in turn cause a reduction of the cathode work function.[29,30] Nonconjugated polymers or small molecules[31−40] can reduce the work function of the cathode owing to the formation of a favorable interface dipole. When compared to polymeric materials, small molecules have several advantages, such as a high degree of purity and ease of synthesis. In addition, small molecules do not have batch-to-batch variations or broad molecular weight distributions.

In this research, a nonconjugated small-molecule organic electrolyte, 1,1′-bis(4-hydroxypropyl)-[4,4′-bipyridine]-1,1′-diium bromide (V-OH), was synthesized based on viologen derivatives. The molecular structure also consists of two terminal polar hydroxyl groups, as shown in Scheme 1. Viologen derivatives are used as the materials for electrochromic devices. These have high electron affinity, low lying reduction potential, and are highly soluble in polar protic solvents such as water and alcohol. Thus, viologen derivatives

Scheme 1. Synthesis and Chemical Structure of V-OH



Received: July 15, 2016
Accepted: November 15, 2016
Published: November 15, 2016

DOI: 10.1021/acsami.6b08628
ACS Appl. Mater. Interfaces 2016, 8, 32992−32997

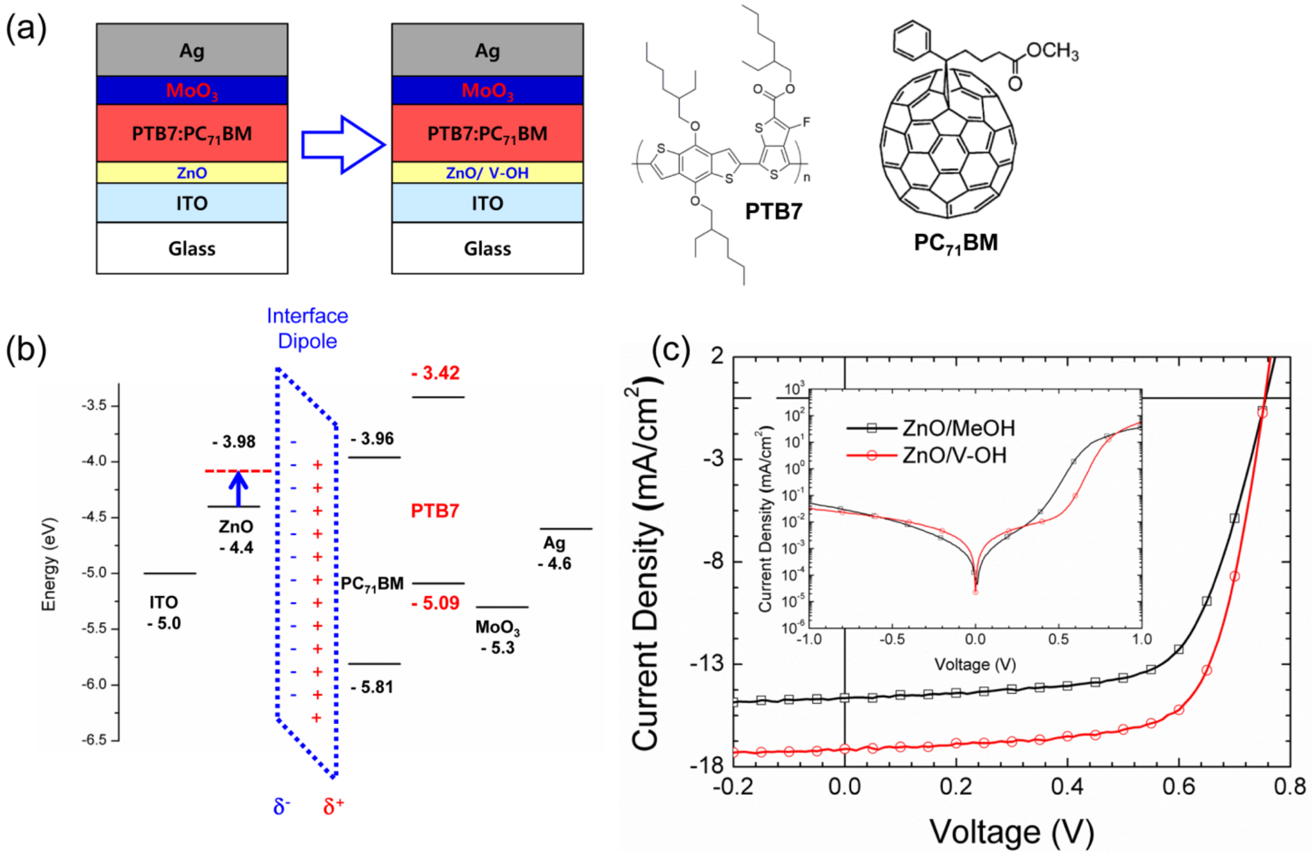


Figure 1. (a) Device structures in the research and chemical structure of PTB7 and $PC_{71}BM$. (b) Energy level diagram of electrodes PTB7 and $PC_{71}BM$. (c) Current density−voltage curves of iPSCs under illumination (inset: in the dark condition).

Table 1. Performances of iPSCs Showing the Best PCE[a]

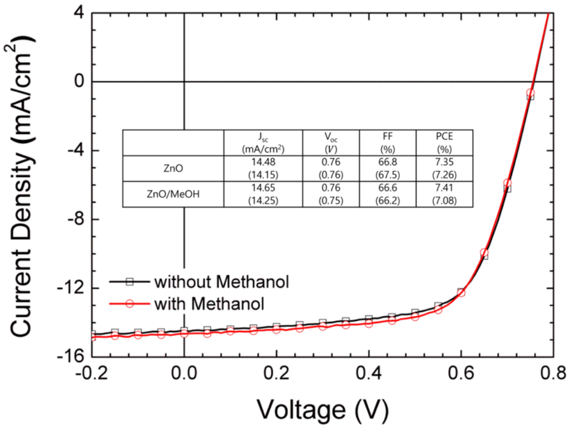
buffer layer	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)	R_s (Ω cm^2)	R_{sh} (kΩ cm^2)
ZnO/MeOH	14.65 (14.25 ± 0.40)	0.76 (0.75 ± 0.005)	66.6 (66.2 ± 0.45)	7.41 (7.29 ± 0.11)	5.9	0.37
ZnO/V-OH	17.13 (16.81 ± 0.18)	0.75 (0.75 ± 0.004)	71.1 (70.9 ± 0.66)	9.13 (8.96 ± 0.11)	3.4	0.31

[a] The averages and deviations (20 for ZnO/MeOH and 30 devices for ZnO/V-OH are averaged, respectively) are summarized in parentheses. Series (R_s) and shunt resistance (R_{sh}) are estimated from the device having the best PCE.

enable the fabrication of multilayer devices via orthogonal solubility in the processing solvents. In addition, the thin layer of V-OH used in this study was found to generate favorable interface dipoles on the quaternary ammonium bromide of the viologen unit, which is widely used as a cathode interlayer material.[19−21] In addition, it was found that the magnitude of the interface dipole could be increased by the presence of two terminal hydroxyl groups of V-OH. To investigate the effect of the V-OH as a cathode buffer layer on the properties of PSCs, inverted-type PSCs (iPSCs) with a device structure of ITO/ZnO/V-OH/PTB7:$PC_{71}BM$(1:1.5)/MoO_3/Ag (shown in Figure 1a) have been fabricated. The presence of thin V-OH layer between the ZnO layer and the active layer in the device improves the PCE from 7.41 to 9.13%, resulting in a relative enhancement of 23.2%. Although the open circuit voltage (V_{oc}) of the device with V-OH was similar to that of the reference device, the short circuit current (J_{sc}) and fill factor (FF) were much higher than the reference device. Significantly, enhancement in the PCE of the device without V-OH is thought to occur mainly due to the increase in the J_{sc}. In addition, the thin layer of V-OH facilitates charge collection from the active layer to the ZnO layer due to its favorable interface dipole, which indicates the formation of an Ohmic contact.

RESULTS AND DISCUSSION

iPSCs with or without V-OH have been fabricated to investigate the effect of V-OH on the efficiency of PSCs. The current density vs voltage relationship and the photovoltaic parameters of the iPSCs with the structure of ITO/ZnO/with or without V-OH/PTB7:$PC_{71}BM$/MoO_3/Ag are shown in Figure 1c and Table 1. It has been reported that there is a positive effect on the performance of conventional PSCs following polar solvent treatment at the cathode interface.[31−35] To remove any possible synergistic effect due to the interlayer processing solvent (methanol), the ZnO layer in the device was treated with methanol. The J_{sc} of the methanol-treated device slightly increased from 14.48 to 14.65 mA/cm^2, while the V_{oc} remained almost identical, as shown in Figure 2. This indicates that methanol does not significantly affect the performance of the iPSCs in this study; however, methanol reduces defects on the ZnO surface. The J_{sc} of the devices with V-OH is 17.13 mA/cm^2, which is a dramatic improvement over the device without the V-OH layer (14.65 mA/cm^2). The FF of the



	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
ZnO	14.48 (14.15)	0.76 (0.76)	66.8 (67.5)	7.35 (7.26)
ZnO/MeOH	14.65 (14.25)	0.76 (0.75)	66.6 (66.2)	7.41 (7.08)

Figure 2. Current density–voltage relationship and photovoltaic performances of the device based on ZnO and MeOH-treated ZnO.

devices containing V-OH also increased from 66.6 to 71.1%. The device with V-OH as the buffer layer showed the highest PCE of 9.13%, indicating that the V-OH layer induces a favorable interface dipole between the ZnO layer and the active layer. The enhancement of the PCE of the device with V-OH mainly results from enhancement of the J_{sc}. The work function of ZnO with V-OH from the Kelvin probe microcopy (KPM) measurements is 3.98 eV, which is smaller than that of methanol-treated ZnO (4.4 eV) and indicates the formation of a favorable interface dipole. We performed the ultraviolet photoelectron spectroscopy (UPS) experiments (see Figure S1) to cross check the interface dipole formation at the surface of the ZnO layer. The work function of ZnO/V-OH is 3.61 eV, which is smaller than that of methanol-treated ZnO (4.31 eV). According to the UPS results, the reduction of ZnO work function by introducing the thin layer of V-OH has been confirmed. It is crucial that the Ohmic contact at the interface has a high J_{sc}, and subsequently, the J_{sc} value is strongly associated with the change in the work function. Herein, the J_{sc} improvement indicates the formation of an Ohmic contact. Interestingly, the V_{oc} of the device with V-OH is almost same as that of the reference device. Even though the interlayer modifies the surface potential of the ZnO layer, it hardly affects the V_{oc} of the device. Similar features have been reported in the literature.[34,35] However, the shunt resistance (R_{sh}) of the device with V-OH is slightly smaller than that of the reference device. Thus, the device with V-OH has estimated smaller series resistance (R_s) and larger FF values.

The effect of V-OH on electron collection and transport property was investigated by the space charge limited current (SCLC) study of the electron-only device with the structure of ITO/ZnO with or without V-OH/PC$_{71}$BM/Al. The energy level diagram under flat band condition is shown as an inset in Figure 3. The energy gap between the LUMO level of PC$_{71}$BM and the work function of ZnO (cathode) layer and the HOMO level of PC$_{71}$BM and the Al (anode) layer were 0.44 and 2.01 eV, respectively. Thus, the major carriers in the device were found to be electrons under forward bias. The energy gap between the PC$_{71}$BM layer and the ZnO layer is reduced from 0.47 to 0.02 eV. Thus, the turn-on voltage of the device with V-OH was 0.4 V, which is considerably smaller than that of the device without V-OH (1.7 V).[41−43] Above the built-in voltage (inset of Figure 3), the current density and $V-V_{bi}$ (voltage−built in voltage) exhibit SCLC characteristics. This is expressed by the Mott−Gurney law:[44]

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{L^3}$$

where J is the current density, μ is the charge mobility, V is the voltage, $\varepsilon_0\varepsilon_r$ is the permittivity of the PC$_{71}$BM layer, and L is

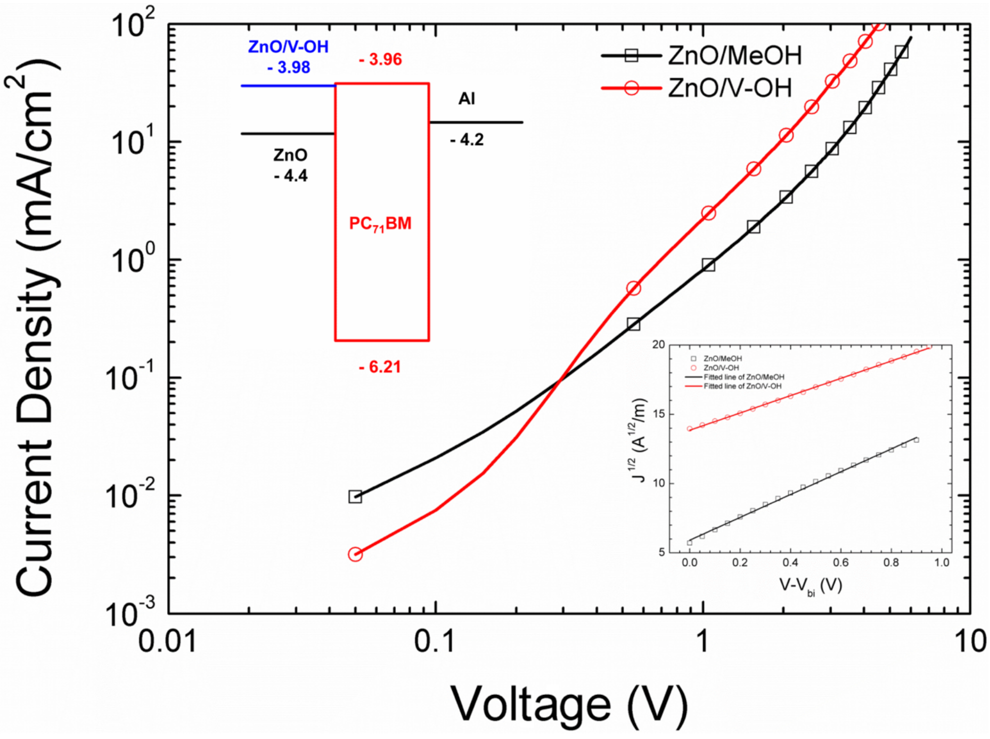


Figure 3. Current density as a function of voltage curves of the electron-only device with a fitted line (V, applied voltage; V_{bi}, built-in voltage).

the thickness of the $PC_{71}BM$ layer. The current density vs voltage relationship of the device agrees well with Mott–Gurney Law ($\varepsilon_r = 3.9$).[45] The electron mobility of the device with V-OH was found to be 1.82×10^{-7} m^2 V^{-1} s^{-1}, which is lower than that of the device without V-OH (3.17×10^{-7} m^2 V^{-1} s^{-1}). Interestingly, V-OH hardly affects the electron mobility of the device. Significantly, the magnitude of current density above the built-in voltage of the device with V-OH is higher than that of the device without V-OH, implying that the contact resistance at the cathode is decreased by the V-OH layer.

Surface morphology and wetting property of the devices were determined using AFM and water contact angle measurements, respectively. The surface roughness of the ZnO surface with V-OH (Figure 4b) is comparable to that of the surface without V-OH (Figure 4a), the former being 1.61 nm and the latter being 1.44 nm. The presence of the V-OH layer made the ZnO surface more hydrophilic compared to the bare ZnO surface due to the intrinsic property of the material.[19] The incident photon-to-current efficiency (IPCE) curves (Figure 5) showed very good correlation with the J_{sc} data of the devices under 1.0 sun simulated illumination. The devices were then placed in a glovebox filled with N_2 gas without passivation. After 125 days, the device with and without V-OH maintained 88 and 79%, respectively, of its initial PCE. The PCE of iPSC with V-OH showed a better stability.

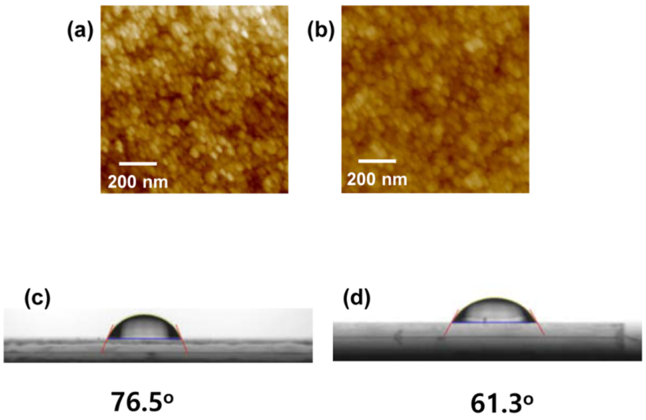


Figure 4. AFM images of (a) ZnO without V-OH and (b) ZnO with the V-OH surface. Static water contact angle data of (c) ZnO without V-OH and (d) ZnO with the V-OH surface.

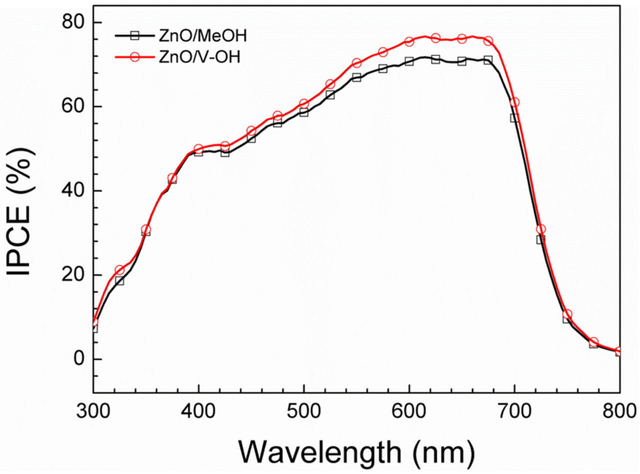


Figure 5. IPCE spectra of the devices based on methanol-treated ZnO and V-OH-coated ZnO.

CONCLUSION

A new alcohol/water-soluble small molecular electrolyte viologen derivative with two polar hydroxyl groups at the end of the molecule V-OH was successfully synthesized. The presence of the V-OH layer leads to a high J_{sc} in solar cells. This is due to the formation of a favorable interface dipole. As a result, the PCE of the devices with V-OH as the cathode interlayer showed the highest PCE of 9.13% (J_{sc} = 17.13 mA/cm^2, V_{oc} = 0.75 V, FF = 71.1%). This research provides an approach to fabricate efficient PSCs without complicated deign and synthesis of compounds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b08628.

> Experimental details, including materials, synthesis, measurements, fabrication of PSCs and electron-only devices, and UPS results (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: jkim@pknu.ac.kr.

ORCID

Joo Hyun Kim: 0000-0002-1507-1640

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the New & Renewable Energy Core Technology Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (Grant 20153010140030) and Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant 201603930154).

REFERENCES

(1) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions. *Science* **1995**, *270*, 1789–1791.

(2) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. Hybrid Nanorod-Polymer Solar Cells. *Science* **2002**, *295*, 2425–2427.

(3) Gunes, S.; Neugebauer, H.; Sariciftci, N. S. Conjugated Polymer-Based Organic Solar Cells. *Chem. Rev.* **2007**, *107*, 1324–1338.

(4) Lu, L.; Zheng, T.; Wu, Q.; Schneider, A. M.; Zhao, D.; Yu, L. Recent Advances in Bulk Heterojunction Polymer Solar Cells. *Chem. Rev.* **2015**, *115*, 12666–12731.

(5) Vohra, V.; Kawashima, K.; Kakara, T.; Koganezawa, T.; Osaka, I.; Takimiya, K.; Murata, H. Efficient Inverted Polymer Solar Cells Employing Favourable Molecular Orientation. *Nat. Photonics* **2015**, *9*, 403–408.

(6) Kan, B.; Li, M.; Zhang, Q.; Liu, F.; Wan, X.; Wang, Y.; Ni, W.; Long, G.; Yang, X.; Feng, H.; Zuo, Y.; Zhang, M.; Huang, F.; Cao, Y.; Russell, T. P.; Chen, Y. A Series of Simple Oligomer-like Small Molecules Based on Oligothiophenes for Solution-Processed Solar Cells with High Efficiency. *J. Am. Chem. Soc.* **2015**, *137*, 3886–3893.

(7) Song, H.-J.; Kim, D.-H.; Lee, E.-J.; Moon, D.-K. Conjugated Polymers Consisting of Quinacridone and Quinoxaline as Donor Materials for Organic Photovoltaics: Orientation and Charge Transfer Properties of Polymers Formed by Phenyl Structures with a Quinoxaline Derivative. *J. Mater. Chem. A* **2013**, *1*, 6010−6020.

(8) Song, H.-J.; Kim, D.-H.; Lee, E.-J.; Haw, J. R.; Moon, D.-K. Correlation of Intramolecular Charge Transfer and Orientation Properties among Quinacridone and Acceptor Units, *Sol. Sol. Energy Mater. Sol. Cells* **2014**, *123*, 112−121.

(9) Kan, B.; Li, M.; Zhang, Q.; Liu, F.; Wan, X.; Wang, Y.; Ni, W.; Long, G.; Yang, X.; Feng, H.; Zuo, Y.; Zhang, M.; Huang, F.; Cao, Y.; Russell, T. P.; Chen, Y. A Series of Simple Oligomer-like Small Molecules Based on Oligothiophenes for Solution-Processed Solar Cells with High Efficiency. *J. Am. Chem. Soc.* **2015**, *137*, 3886−3893.

(10) Liang, Y.; Xu, Z.; Xia, J. B.; Tsai, S. T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. For the Bright Future—Bulk Heterojunction Polymer Solar Cells with Power Conversion Efficiency of 7.4%. *Adv. Mater.* **2010**, *22*, E135−E138.

(11) He, Z.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. Enhanced Power-Conversion Efficiency in Polymer Solar Cells Using an Inverted Device Structure. *Nat. Photonics* **2012**, *6*, 593−597.

(12) Choi, H.; Park, J. S.; Jeong, E.; Kim, G. W.; Lee, B. R.; Kim, S. O.; Song, M. H.; Woo, H. Y.; Kim, J. Y. Combination of Titanium Oxide and a Conjugated Polyelectrolyte for High-Performance Inverted-Type Organic Optoelectronic Devices. *Adv. Mater.* **2011**, *23*, 2759−2763.

(13) 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.

(14) Ma, W.; Iyer, P. K.; Gong, X.; Liu, B.; Moses, D.; Bazan, G. C.; Heeger, A. J. Water/Methanol-Soluble Conjugated Copolymer as an Electron-Transport Layer in Polymer Light-Emitting Diodes. *Adv. Mater.* **2005**, *17*, 274−277.

(15) Jin, Y.; Bazan, G. C.; Heeger, A. J.; Kim, J. Y.; Lee, K. Improved Electron Injection in Polymer Light-Emitting Diodes Using Anionic Conjugated Polyelectrolyte. *Appl. Phys. Lett.* **2008**, *93*, 123304.

(16) Zhu, X.; Xie, Y.; Li, X.; Qiao, X.; Wang, L.; Tu, G. Anionic Conjugated Polyelectrolyte−Wetting Properties with an Emission Layer and Free Ion Migration When Serving as a Cathode Interface Layer in Polymer Light Emitting Diodes (PLEDs). *J. Mater. Chem.* **2012**, *22*, 15490−15494.

(17) Fang, J.; Wallikewitz, B. H.; Gao, F.; Tu, G.; Muller, C.; Pace, G.; Friend, R. H.; Huck, W. T. S. Conjugated Zwitterionic Polyelectrolyte as the Charge Injection Layer for High-Performance Polymer Light-Emitting Diodes. *J. Am. Chem. Soc.* **2011**, *133*, 683−685.

(18) Huang, F.; Zhang, Y.; Liu, M. S.; Jen, A. K. Y. Electron-Rich Alcohol-Soluble Neutral Conjugated Polymers as Highly Efficient Electron-Injecting Materials for Polymer Light-Emitting Diodes. *Adv. Funct. Mater.* **2009**, *19*, 2457−2466.

(19) Wu, H.; Huang, F.; Mo, Y.; Yang, W.; Wang, D.; Peng, J.; Cao, Y. Efficient Electron Injection from a Bilayer Cathode Consisting of Aluminum and Alcohol-/Water-Soluble Conjugated Polymer. *Adv. Mater.* **2004**, *16*, 1826−1830.

(20) Jo, M. Y.; Ha, Y. E.; Kim, J. H. Polyviologen Derivatives as an Interfacial Layer in Polymer Solar Cells. *Sol. Sol. Energy Mater. Sol. Cells* **2012**, *107*, 1−8.

(21) Jo, M. Y.; Ha, Y. E.; Kim, J. H. Interfacial Layer Material Derived from Dialkylviologen and Sol−Gel Chemistry for Polymer Solar Cells. *Org. Electron.* **2013**, *14*, 995−1001.

(22) Lim, G. E.; Ha, Y. E.; Jo, M. Y.; Park, J.; Kang, Y. C.; Kim, J. H. Nonconjugated Anionic Polyelectrolyte as an Interfacial Layer for the Organic Optoelectronic Devices. *ACS Appl. Mater. Interfaces* **2013**, *5*, 6508−6513.

(23) Wang, H.; Zhang, W.; Xu, C.; Bi, X.; Chen, B.; Yang, S. Efficiency Enhancement of Polymer Solar Cells by Applying Poly(vinylpyrrolidone) as a Cathode Buffer Layer via Spin Coating or Self-Assembly. *ACS Appl. Mater. Interfaces* **2013**, *5*, 26−34.

(24) Zhang, F.; Ceder, M.; Inganas, O. Enhancing the Photovoltage of Polymer Solar Cells by Using a Modified Cathode. *Adv. Mater.* **2007**, *19*, 1835−1838.

(25) Ha, Y. E.; Lim, G. E.; Jo, M. Y.; Park, J.; Kang, Y. C.; Moon, S. J.; Kim, J. H. Enhancing the Efficiency of Opto-Electronic Devices by the Cathode Modification. *J. Mater. Chem. C* **2014**, *2*, 3820−3825.

(26) Liu, X.; Xu, R.; Duan, C.; Huang, F.; Cao, Y. Non-Conjugated Water/Alcohol Soluble Polymers with Different Oxidation States of Sulfide as Cathode Interlayers for High-Performance Polymer Solar Cells. *J. Mater. Chem. C* **2016**, *4*, 4288−4295.

(27) Xu, W.; Kan, Z.; Ye, T.; Zhao, L.; Lai, W.-Y.; Xia, R.; Lanzani, G.; Keivanidis, P. E.; Huang, W. Well-Defined Star-Shaped Conjugated Macroelectrolytes as Efficient Electron-Collecting Interlayer for Inverted Polymer Solar Cells. *ACS Appl. Mater. Interfaces* **2015**, *7*, 452−459.

(28) Wang, Z.; Li, Z.; Xu, X.; Li, Y.; Li, K.; Peng, Q. Stimuli-Directing Self-Organized 3D Liquid-Crystalline Nanostructures: From Materials Design to Photonic Applications. *Adv. Funct. Mater.* **2016**, *26*, 10−28.

(29) Do, T. T.; Hong, H. S.; Ha, Y. E.; Lim, G. E.; Won, Y. S.; Kim, J. H. Investigation of the Effect of Conjugated Oligoelectrolyte as a Cathode buffer layer on the Photovoltaic Properties. *Synth. Met.* **2014**, *198*, 122−130.

(30) Zhang, K.; Zhong, C.; Liu, S.; Mu, C.; Li, Z.; Yan, H.; Huang, F.; Cao, Y. Highly Efficient Inverted Polymer Solar Cells Based on a Crosslinkable Water-/Alcohol-Soluble Conjugated Polymer Interlayer. *ACS Appl. Mater. Interfaces* **2014**, *6*, 10429−10435.

(31) Do, T. T.; Hong, H. S.; Ha, Y. E.; Yoo, S. I.; Won, Y. S.; Moon, M.-J.; Kim, J. H. Synthesis and Characterization of Conjugated Oligoelectrolytes Based on Fluorene and Carbazole Derivative and Application of Polymer Solar Cell as a Cathode Buffer Layer. *Macromol. Res.* **2015**, *23*, 367−376.

(32) Guo, S.; Ning, J.; Körstgens, V.; Yao, Y.; Herzig, E. M.; Roth, S. V.; Müller-Buschbaum, P. The Effect of Fluorination in Manipulating the Nanomorphology in PTB7:$PC_{71}BM$ Bulk Heterojunction Systems. *Adv. Energy Mater.* **2015**, *5*, 1401315.

(33) Min, C.; Shi, C.; Zhang, W.; Jiu, T.; Chen, J.; Ma, D.; Fang, J. A Small-Molecule Zwitterionic Electrolyte Without a π-Delocalized Unit as a Charge-Injection Layer for High-Performance PLEDs. *Angew. Chem., Int. Ed.* **2013**, *52*, 3417−3420.

(34) Liu, Z.; Ouyang, X.; Peng, R.; Bai, Y.; Mi, D.; Jiang, W.; Facchetti, A.; Ge, Z. Efficient Polymer Solar Cells Based on the Synergy Effect of a Novel Non-Conjugated Small-Molecule Electrolyte and Polar Solvent. *J. Mater. Chem. A* **2016**, *4*, 2530−2536.

(35) Ouyang, X.; Peng, R.; Ai, L.; Zhang, X.; Ge, Z. Efficient Polymer Solar Cells Employing a Non-conjugated Small-molecule Electrolyte. *Nat. Photonics* **2015**, *9*, 520−524.

(36) Li, X.; Zhang, W.; Wang, X.; Wu, Y.; Gao, F.; Fang, J. Critical Role of the External Bias in Improving the Performance of Polymer Solar cells with a Small Molecule Electrolyte Interlayer. *J. Mater. Chem. A* **2015**, *3*, 504−508.

(37) Seo, J. H.; Gutacker, A.; Sun, Y. M.; Wu, H. B.; 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.

(38) 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.

(39) Zhou, H. Q.; Zhang, Y.; Seifter, 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.

(40) Tan, Z.-K.; Vaynzof, Y.; Credgington, D.; Li, C.; Casford, M. T. L.; Sepe, A.; Huettner, S.; Nikolka, M.; Paulus, F.; Yang, L.; Sirringhaus, H.; Greenham, N. C.; Friend, R. H. In-Situ Switching from Barrier-Limited to Ohmic Anodes for Efficient Organic Optoelectronics. *Adv. Funct. Mater.* **2014**, *24*, 3051−3058.

(41) 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.

(42) Guo, S.; Cao, B.; Wang, W.; Moulin, J.-F.; Muller-Buschbaum, P. Effect of Alcohol Treatment on the Performance of PTB7:$PC_{71}BM$ Bulk Heterojunction Solar Cells. *ACS Appl. Mater. Interfaces* **2015**, *7*, 4641−4649.

(43) Parker, I. D. Carrier Tunneling and Device Characteristics in Polymer Light-Emitting Diodes. *J. Appl. Phys.* **1994**, *75*, 1656−1666.

(44) Bagui, A.; Iyer, S. S. K. Increase in Hole Mobility in Poly(3-hexylthiophene-2,5-diyl) Films Annealed Under Electric Field During the Solvent Drying Step. *Org. Electron.* **2014**, *15*, 1387−1395.

(45) Mihailetchi, V. D.; van Duren, J. K.; Blom, P. W.; Hummelen, J. C.; Janssen, R. A.; Kroon, J. M.; Rispens, M. T.; Verhees, W. J. H.; Wienk, M. M. Electron Transport in a Methanofullerene. *Adv. Funct. Mater.* **2003**, *13*, 43−46.

DOI: 10.1021/acsami.6b08628
ACS Appl. Mater. Interfaces 2016, 8, 32992−32997