

# Polyviologen derivatives as an interfacial layer in polymer solar cells

Mi Young Jo, Ye Eun Ha, Joo Hyun Kim\*

Department of Polymer Engineering, Pukyong National University, Yongdang-Dong, Nam-Gu, Busan 608-739, Korea

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## ABSTRACT

To apply as an interfacial layer for solution processible polymer solar cells (PSCs) based on poly(3-hexylthiophene): [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (P3HT:PCBM), novel poly(1,1'-dibutyl-4,4'-bipyridinium dibromide) (PV4), poly(1,1'-didodecyl-4,4'-bipyridinium dibromide) (PV12), and poly(1,1'-triethylenedioxy-4,4'-bipyridinium di-p-toluenesulfonate) (PV-OTs) are synthesized. These polyviologen (PV) derivatives have different alkyl chain length and counter anion. From the ultraviolet spectroscopy (UPS) study, the reduction of the work function of Al are observed by the formation of interface dipole, which is induced by the thin film of PV derivatives. The power conversion efficiency (PCE) of conventional type PSC based on PV4 and PV12 with a structure of ITO/PEDOT:PSS/P3HT:PCBM/PV layer/Al are 2.22 and 2.71%, respectively. In particular, the PCE of PSC with PV-OTs reaches 3.30%. The  $J_{sc}$  and  $V_{oc}$  are  $-9.51 \text{ mA/cm}^2$  and 0.60 V, which are dramatically improved than those of the devices based on PV4 and PV12. This is due to different contact property between active layer and Al, which is controlled by the alkyl chain length and counter anion of PV derivatives. The series resistance ( $R_s$ ) of the device with PV-OTs is  $3.05 \text{ (ohm cm}^2\text{)}$ , which is smaller than that of the device without PV and with PV4 and PV12. The performances of PSC with PV derivatives as a interfacial layer are strongly related with both contact property and formation of interface dipole. The work function of ITO is also reduced by the thin layer of PV derivatives. Inverted type PSCs with a structure of ITO/PV layer/P3HT:PCBM/WO<sub>3</sub>/Ag show typical rectification and pretty good photovoltaic property, while the device without PV layer shows very weak photovoltaic property and does not show diode characteristics.

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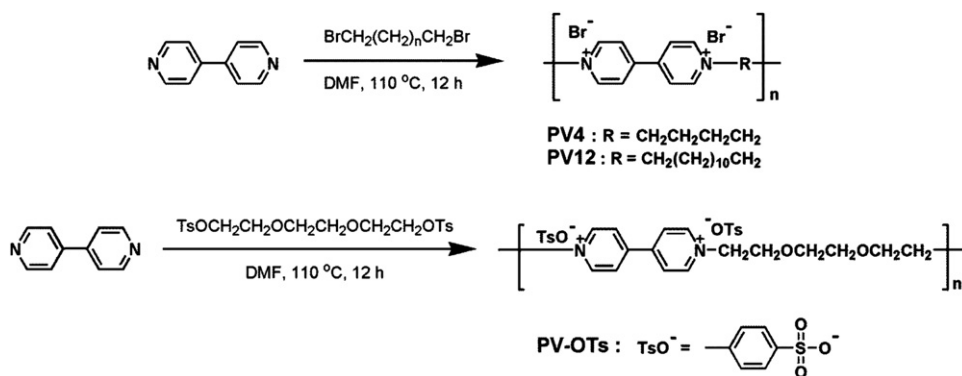
## 1. Introduction

Recently, the bulk hetero-junction (BHJ) type polymer solar cells (PSCs) have been attracting attention because of the possibility of their application in flexible devices and low fabrication cost [1–3]. The BHJ type PSCs based on regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) [4–6] have demonstrated their power conversion efficiencies (PCEs) up to 2.0 to 5.0%. Intensive researches have been encouraged by aforementioned advantages and thus the performances of the PSCs have been rapidly improved by the molecular engineering [7–11] and device engineering [12–15]. Meanwhile, large area devices have become a very important issue in the field of PSCs. To fabricate large area PSCs, solution process such as printing methods and spray coating have been reported [16–20]. Hole transporting layer (HTL) between ITO and active layer are very important to get highly efficient devices. The solution processible poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [21–24], crosslinkable arylamine derivatives [25–29], and NiO [30] have been developed for HTL. For a

cathode side, highly efficient devices are then achieved by introducing low work function metal electrode such as Ca. However, low work function metals are very sensitive to oxygen or moisture under the ambient condition. The utilization of relatively high work function metals such as Al or Ag appears to be unavoidable although the devices based on Al or Ag show poor performances. One of the potential methods to improve performances of the PSCs is introducing a buffer layer between the active layer and metal electrode. The buffer layer minimizes contact resistance and maximizes open circuit voltage. The introduction of very thin layer of LiF [31–33] improves performances of PSCs. Poly(ethylene oxide) [34],  $\pi$ -conjugated polymer electrolytes (CPEs), [35–37] or alcohol-soluble neutral conjugated polymers [38] have been reported for buffer layer for PSCs. These polymers have either ionic salts or polar groups, which are soluble in protic solvents and induce interface dipoles between active layer and cathode. As a result, the open circuit voltage ( $V_{oc}$ ), fill factor (FF), and short circuit current ( $J_{sc}$ ) of PSCs with these polymers as interfacial layers are improved because of the reduction of work function of metal and contact resistance. The interface dipoles are induced by the cationic, anionic salts, or polar groups on the side chain. Solution processible *n*-type metal oxide such as TiO<sub>x</sub> [39] and ZnO [40] have been tested for buffer layer. There is a long-term problem in PSCs. One of the alternate

\* Corresponding author. Tel.: +82 51 629 6452.

E-mail address: [jkim@pknu.ac.kr](mailto:jkim@pknu.ac.kr) (J. Hyun Kim).



**Scheme 1.** Structures and synthesis of polyviologen derivatives [11].

strategies to overcome this problem is to fabricate PEDOT:PSS free inverted type PSCs with a structure of ITO/Electron transporting layer (ETL)/active layer/HTL/Ag [41–44]. In this case, metal oxides such as TiO<sub>x</sub>, ZnO, WO<sub>3</sub>, and MoO<sub>3</sub> are used as ETL or HTL. Inverted type PSCs have many advantages such as air stable, low cost, non-toxic, and highly transparent. All the polar polymeric materials mentioned before can be used as ETL in both conventional and inverted type PSCs.

Viologen derivatives are well known as electrochromic materials [45], which show very high electron affinity, high-lying reduction potential, and good solubility in water or alcoholic aqueous solvent. This is because viologen has two pyridinium salts. We take advantages of solubility in alcoholic aqueous solvent and high electron affinity of viologen moiety. In this paper, we report characteristics of non-conjugated novel polyviologen (PV) derivatives (as shown in Scheme 1) and demonstrate PSCs based on these PV derivatives as an interfacial layers. To the best of our knowledge, poly-electrolytes containing viologen have never been tested for PSCs before. As for CPEs, it is well known that the work function of metal cathode can be reduced by the formation of interface dipole, which is induced by the salts on the end of side chains. The structural features of PV derivatives are somewhat different from CPEs. Pyridinium salts of PV derivatives are on the main chain and main chain of PV derivatives are not fully conjugated, while salts of CPEs are on the terminal of side chains and main chain of CPEs are fully conjugated. However, it is expected that interface dipole can be induced by PV derivatives and the performances of PSCs with PV derivatives as an interfacial layer are improved.

## 2. Experimental

### 2.1. Materials

Chemicals were purchased from Aldrich Chemical Co. and Alfa Aesar and were used as received unless otherwise described. Regioregular P3HT (Cat. no. 4002-EE) and PCBM (Cat. no. nano-PCBM-BF) were purchased from Rieke Metals Inc. and nano-C, Inc., respectively.

### 2.2. Synthesis of polyviologen derivatives

#### 2.2.1. Synthesis of poly(1,1'-dibutyl-4,4'-bipyridinium dibromide) (PV4)

A solution of 1,4-dibromobutane (0.69 g, 3.2 mmol) and 4,4'-bipyridyl (0.50 g, 3.2 mmol) in 2 mL of *N,N*-dimethylformamide (DMF) was stirred for 12 h at 110 °C. After cooling the reaction mixture to room temperature, solid precipitates were collected by filtration and washed with 50 mL of *n*-hexane and 50 mL of MC,

successively. The solid product was dried under the vacuum. The yield of light yellow solid was 82.1% (0.98 g). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, ppm): δ 9.18–9.15 (Br, 4H), 8.60–8.56 (Br, 4H), 4.85–4.81 (Br, N<sup>+</sup>–CH<sub>2</sub>–, 4H), 2.31–2.25 (Br, –CH<sub>2</sub>–, 4H). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O, ppm): δ 151.47, 146.78, 128.55, 62.29, 28.60. Anal. Calcd. for C<sub>28</sub>H<sub>26</sub>Br<sub>4</sub>N<sub>4</sub>: C, 45.56; H, 3.55; N, 7.59; Br, 43.30. Found: C, 47.51; H, 4.19; N, 7.99.

#### 2.2.2. Synthesis of poly(1,1'-didodecyl-4,4'-bipyridinium dibromide) (PV12)

A solution of 1,4-dibromododecane (1.05 g, 3.2 mmol) and 4,4'-bipyridyl (0.50 g, 3.2 mmol) in 2 mL of DMF was stirred for 12 h at 110 °C. After cooling the reaction mixture to room temperature, solid particles were collected by filtration and washed with 50 mL of *n*-hexane and 50 mL of MC. The light yellow solid product was dried under the vacuum. The yield of light yellow solid was 81.5% (1.27 g). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, ppm): δ 9.15–9.12 (Br, 4H), 8.59–8.56 (Br, 4H), 4.77–4.72 (Br, N<sup>+</sup>–CH<sub>2</sub>–, 4H), 2.15–2.06 (Br, –CH<sub>2</sub>–, 4H), 1.42–1.26 (Br, –CH<sub>2</sub>–, 16H). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O, ppm): δ 151.12, 146.61, 128.18, 63.46, 31.80, 29.78, 29.67, 29.28, 26.47. Anal. Calcd. for C<sub>44</sub>H<sub>58</sub>Br<sub>4</sub>N<sub>4</sub>: C, 54.90; H, 6.07; N, 5.82; Br, 33.20. Found: C, 55.97; H, 7.23; N, 6.11.

#### 2.2.3. Synthesis of poly(1,1'-triethylenedioxy-4,4'-bipyridinium di-*p*-toluenesulfonate) (PV-OTs)

A solution of triethylene glycol di(*p*-toluenesulfonate) (1.47 g, 3.2 mmol) and 4,4'-bipyridyl (0.50 g, 3.2 mmol) in 2 mL of DMF was stirred for 12 h at 110 °C. After cooling to room temperature, the reaction mixture was dropped into 100 mL of MC and filtered to obtain polymer. The solid product was dried under the vacuum. The yield of light yellow solid was 72.3% (1.46 g). MS [M<sup>+</sup>], *m/z* 361. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, ppm): δ 7.38–7.34 (Br, 4H), 7.02–6.98 (Br, 4H), 4.76–4.66 (Br, 4H), 3.97–3.89 (Br, 4H), 3.62–3.53 (Br, 4H). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O, ppm): δ 165.98, 146.93, 142.94, 141.28, 130.45, 127.57, 126.50, 70.96, 38.03, 32.52, 21.58. Anal. Calcd. for C<sub>60</sub>H<sub>62</sub>N<sub>4</sub>O<sub>16</sub>S<sub>4</sub>: C, 58.90; H, 5.11; N, 4.58; O, 20.92; S, 10.48. Found: C, 57.11; H, 4.32; N, 5.23; S, 11.16.

### 2.3. Measurements

<sup>1</sup>H NMR spectra of PV derivatives were recorded with a JEOL JNM ECP-400 spectrometer. UV–visible spectrum of the polymer solutions 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 lithium trifluoromethanesulfonate (0.1 M) in  $\gamma$ -butyrolactone water at a scan rate of 100 mV/s. Pt wire was used as the counter and working electrode, and the standard calomel electrode (SCE) was used as the reference electrode. Prior to each measurement,

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