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# Enhanced Performance in Bulk Heterojunction Polymer Solar Cell Using Water Soluble Conjugated Polymer

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We have synthesized water-soluble polymer, poly[(9,9-bis((6'-(*N*,*N*,*N*-trimethylammonium)hexyl)-2,7-fluorene))-alt-bisphenylfumaronitrile]dibromide (AHF-alt-PFN), the polymer typically obtained by the Suzuki type of polymerization reaction and shows good solubility in methanol. Bulk heterojunction polymer solar cells (BHJ-PSCs) fabricated by using water soluble conjugated polymer and positive (Cs<sup>+</sup>) and negative (F<sup>-</sup>, CO<sub>3</sub><sup>-</sup>) charge ions doping as an interfacial layer for poly(3-hexylthiophene):phenyl-C61 butyric acid methyl ester (P3HT:PCBM). We have achieved an enhancement of the short circuit density and power conversion efficiency in solar cell by introducing poly(AHF-alt-PFN) layer between the active layer and the cathode metal. The device with poly(AHF-alt-PRN) layer containing F<sup>-</sup>, CO<sub>3</sub><sup>2-</sup> showed a short circuit current density more 1.3, 2.3 times higher than those of the device without poly(AHF-alt-PFN) + ion layer. We explain the better performance in solar cell with poly(AHF-alt-PFN) have but also to the decrease of the electron barrier near cathode by the addition of the negative ions.

Keywords: Water-Soluble Polymer, Polymer Solar Cell, Bulk Hetero Junction.

# **1. INTRODUCTION**

Organic and polymeric materials have generated great interest over the past decade for their potential application in flat panel display and photovoltaic cell as well. Among the organic photovoltaic cells, the bulkheterojuction polymer solar cell (BHJ-SC) where the light absorbing active layer is consists of a blend of electron donating conjugated polymer (*p*-type) and electron accepting fullerene (*n*-type) is one of the promising candidates for next generation of solar cell due to its simple solution processing with largearea, low cost, and flexible possibility.<sup>1–4</sup>

Many efforts have been made in BHJ-SC for higher power conversion efficiency (PCE), mostly trying to synthesize the low-band gap donor polymers by designing novel copolymers with various electron rich and poor

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units for a better internal charge transfer (ICT).<sup>5,6</sup> This ICT causes broadening of the light-absorbing wavelength range (i.e., lowering the band gap) and increase of short circuit current  $(J_{sc})$  and thus the PCE as well. Recently, PCE of over 7% have been achieved by using low band gap copolymers with controlled morphology of the active polymer blends.<sup>7,8</sup> Water-soluble polymers could also be promising candidates as efficient interfacial layer materials for highly efficient inverted PSCs because they can provide solution processing capabilities and avoid intermixing between the underlying water/alcohol-soluble interlayer and the subsequently deposited organic soluble active layer, which is very beneficial for the future development of all-solution processed or roll-to-roll processed PSCs.9 In this work, we have fabricated highly efficiency polymer solar cells from water soluble conjugated polymer (poly[(9,9-bis(6-trimetylammonomhexyl)

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fluorine-alt-diphenylfumaronitrile)]) (Poly(AHF-alt-PFN)) by using it as a ultra thin electron transport layer on the top of commercially available active layer, poly(3-hexyl-thiophene)-2,5-diyl (P3HT): $\{6\}$ -1-(3-(methoxycarbonyl) propyl)- $\{5\}$ -1-phenyl-[6,6]-C<sub>61</sub> (PCBM). For the second time, we have fabricated highly efficiency polymer solar cell from ions dispersed water soluble conjugated polymer, (Poly(AHF-alt-PFN)).

## 2. EXPERIMENTAL DESCRIPTION

### 2.1. Synthesis of Water Soluble Polymer

# 2.1.1. Synthesis of 2,7-Dibromo-9,9-Bis (6"-bromohexyl)-Fluorene

9.72 g of 2,7-dibromofluorene and 0.96 g of tetrabutylammoniumbromide were dissolved in 100 mL of 1,6dibromohexane and 30 mL of a 45% KOH solution was then injected under nitrogen. The solution was stirred at 75 °C for 1 h. The reaction mixture was extracted with 300 mL dichloromethane and the resulting solution was evaporated. The reaction mixture was distilled under vacuum, to remove the 1,6-dibromohexane. The reaction mixture was purified by column chromatography using hexane and dichloromethane.(Yield 70%) <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ 7.56–7.43 (*m*, 6 H), 3.30 (*t*, 4 H), 1.92 (*t*, 4 H), 1.67 (*t*, 4 H), 1.20 (*m*, 4 H), 1.08 (*m*, 4 H), 0.58 (*m*, 4 H).

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## 2.1.2. Synthesis of 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-3-yl)-9,9-(6-dibromohexyl)-Fluroene

2,7-Dibromo-9,9-bis(6"-bromohexyl)-fluorene and bis (pinacolato)diboron (3 g) were dissolved in 1,4-dioxane and PdCl<sub>2</sub>(dppf) was then injected under nitrogen. The solution was stirred at 85 °C for 16 h. The reaction mixture was extracted with dichloromethane and water. The organic layer was dried with MgSO<sub>4</sub> and concentrated under reduced pressure. The reaction mixture was purified by column chromatography using hexane and dichloromethane. The final product was a white solid, produced in 40% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ 7.82 (*d*, 2 H), 7.74 (*s*, 2 H), 7.72 (*d*, 2 H), 3.27 (*t*, 4 H), 1.98 (*m*, 4 H), 1.62 (*m*, 4 H), 1.33 (*s*, 24 H), 1.20 (*m*, 4 H), 1.15 (*m*, 4 H), 0.55 (*m*, 4 H).

#### 2.1.3. Synthesis of Bis(4-bromophenyl)Fumaronitrile

A two-neck flask was charged with 4-bromophenylacetonitrile (2.45) and iodine (3.172) in dry ether (50 mL) and cooled to -78 °C. A solution of sodium methoxide (1.38 g) in methanol (10 mL) was added into the reaction solution at -78 °C under a nitrogen atmosphere. The reaction mixture was gradually warmed to 0 °C for 4 h. The reaction was quenched with a 3% aqueous solution of hydrochloric acid. The solution was filtered to isolate the solid, which was rinsed with methanol to remove the ionic residues. The product was recrystallized from methylene chloride as a white solid (Yield 80%). <sup>1</sup>H NMR (DMSO, 400 MHz):  $\delta$ 7.47 (*d*, 4 H), 7.32 (*d*, 4 H).

## 2.1.4. Synthesis of Poly[2-(4-(9,9-bis(6-bromohexyl)-7-methyl-9H-fluoren-2-yl)phenyl)-3-p-Tolylfumaronitrile

2,7-Dibromo-9,9-bis(6"-bromohexyl)-fluorene (0.74 g), Bis(4-bromophenyl)fumaronitrile (0.38 g), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg) were dissolved in 40 mL of THF under nitrogen and 20 mL 2 M Na<sub>2</sub>CO<sub>3</sub> was added. The mixture was refluxed at 80 °C for 72 h, and then precipitated into methanol. The polymer was filtered and washed with methanol and acetone, and then dried under vacuum. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ 7.91–7.64 (*m*, 14 H), 3.20 (*m*, 4 H), 1.98–1.62 (*m*, 8 H), 1.33 (*s*, 4 H), 1.20 (*m*, 4H.), 1.15 (*m*, 4 H), 0.55 (*m*, 4 H).

# 2.1.5. Synthesis of Poly[(9,9-bis((6'-(N,N,Ntrimethylammonium)hexyl)-2,7-fluorene))-altbisphenylfumaronitrile)]Dibromide

30% aqueous solution of trimethylamine (5 mL) was added dropwise to a solution of the Polymer (60 mg) in THF (50 mL) at room temperature. The mixture was stirred at room temperature for 24 h. After removing most of the solvent, acetone was added to precipitate polymer (Poly(AHF-alt-PFN). <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 400 MHz):  $\delta$ 7.98 (*m*, 8H), 7.79 (*m*, 6H), 3.18 (*m*, 4 H), 3.00 (*m*, 18 H), 2.21 (*m*, 4 H), 1.62 (*m*, 4 H), 1.33 (*s*, 24 H), 1.20 (*m*, 4 H), 1.15 (*m*, 4 H), 0.56 (*m*, 4 H).

#### 2.2. Fabrication of the Polymer Solar Cells

PEDOT:PSS ( $\sim 40$  nm) was used for all the devices as a hole transport layer which was spun on the cleaned indium tin oxide (ITO) anode and annealed at 100 °C for 10 min. The light-absorbing active layer ( $\sim 80$  nm), also used for all the test devices, was prepared by spin coating onto the PEDOT:PSS film from a blend of P<sub>3</sub>HT and  $PC_{60}BM$  (P3HT:PC60BM = 1:0.7 by weight) in a cosolvent (CB:DCB = 1:1) and then annealed at 120 °C for 10 min. As an electron transport layer, the synthesized poly(AHF-alt-PFN) were dissolved in methanol spun with 2000 rpm for 40 sec onto the active polymer blend film followed by annealing at 100 °C for 10 min. This leads to ultrathin layers for poly(AHF-alt-PFN) with a thickness of around 5 nm that was estimated from extrapolation approximation.<sup>10</sup> Finally, Al was vacuum evaporatied with an evaporation rate of 0.1 nm/sec. A vacuum pressure of  $2 \times 10^{-6}$  Torr was maintained during all of the vacuum deposition. Their thickness was 150 nm. The PSCs device structures in this study are summarized as follows:

Device 1: A/active layer/C,

Device 2: A/active layer/poly(AHF-alt-PFN)/C

- Device 3: A/active layer/poly(AHF-alt-PFN)+Cs<sup>+</sup>/ C
- Device 4: A/active layer/poly(AHF-alt-PFN) +  $F^{-}/C$
- Device 5: A/active layer/poly(AHF-alt-PFN) +  $CO_3^{2-}/C$

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Where, the A and B denote anode (ITO/PEDOT:PSS) and cathode (Al), respectively.

### 3. RESULTS AND DISCUSSION

The molecular structures of water soluble polymer (poly(AHF-alt-PRN)) are shown in Figure 1 and the polymer typically obtained by the Suzuki type of polymerization reaction and shows good solubility in methanol. IP of poly(AHF-alt-PFN) was measured by cyclic voltammogram and the band gaps  $(E_a)$  were estimated from absorbance measurement (Shimadzu UV-160 PC). Figure 2 shows the UV absorption for poly(AHF-alt-PFN) as a solid film. The band gap energy of the polymer was estimated from the absorption spectrum and was found to be 496 nm (2.5 eV). The electrochemical behavior of the polymer was investigated by cyclic voltammetry (CV) and outlined in Figure 3. The onset potential for oxidation was observed to be 0.6 V. On the other hand,  $E_{g}$  was estimated from UV<sub>onset</sub> and calculated from  $E_A = I_P - E_g$ . According to the equation,  $I_P = ([E_{onset}]^{ox} + 4.8)$  eV, where  $[E_{onset}]^{ox}$ was the onset potential for the oxidation of polymer, the HOMO and LUMO of the polymer were estimated to be 5.4 and 3.7 eV.

J-V characteristics of the fabricated BHJ-SC were recorded from Keithley 2400 source meter under 100 mW/cm<sup>2</sup> white light illumination. All devices have shown the characteristics of short circuit current density  $(J_{\rm sc})$ , open circuit voltage  $(V_{\rm OC})$ , fill factor (FF) and power conversion efficiency (PCE). Figure 3 shows J-V characteristics of these solar cells and the results are summarized in Table I. As can be seen from Table I, the short circuit currents and efficiencies are significantly increased when poly(AHF-alt-PFN)+ions are introduced in the solar cells (device 2-5) compared to that of the device without poly(AHF-alt-PFN) (device 1).  $J_{sc}$  of device 5 is  $8.49\ mA/cm^2$  which is corresponding to 32% increase compared to that of the device 1 (6.41 mA/cm<sup>2</sup>) while PCE of device 5 (2.3%) increases about 100% than the device 1 (1.01%).

The improvement of photovoltaic performance with water soluble polymer implies that poly(AHF-alt-PFN) ultrathin layers (~5 nm) help for electron injection and transport from the active layer to cathode. We have



Figure 1. Molecular structure of poly(AHF-alt-PFN).

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Figure 2. Optical and electro chemical properties. (a) UV-Vis absorption spectra, (b) cyclic voltammogram.

proposed that the counter ion attracts the electron from the active layer and that the water soluble polymer layer is thin enough for electron tunneling. As a result, the better performance in solar cells with poly(AHF-alt-PFN) + ion layer was due not only to the increase of electron mobility



**Figure 3.** J-V characteristics of polymer solar cells.

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Table I.	Summary performance of the PSCs devices.			
	$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}~({ m V})$	FF (%)	PEC (%)
Device 1	6.41	0.36	39	1.01
Device 2	6.27	0.42	47	1.48
Device 3	7.00	0.46	54	1.50
Device 4	7.89	0.49	51	2.00
Device 5	8.49	0.49	52	2.30

soluble polymer and ions could be useful for the enhancement of polymer solar cell performance.

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in poly(AHF-alt-PFN) but also to the decrease of electron barrier near cathode by the addition of the negative ions.

## 4. CONCLUSION

We have fabricated efficiency solar cell from metal ions dispersed water soluble conjugated polymer, Poly(AHFalt-PFN), which is used as an electron transport layer on the top of commercially available active layer, P3HT:PCBM. The device with Poly(AHF-alt-PFN) layer containing  $F^-$  and  $CO_3^{2-}$  (device 4, 5) showed a better performance in  $J_{\rm sc}$  and thus in PCE increased up to 100% compared to that of the solar cell without water soluble polymer. We explain the better performance in solar cell with Poly(AHF-alt-PFN) + ion layer was due not only to the increase of electron mobility in Poly(AHF-alt-PFN) layer but also to the decrease of electron barrier near cathode by the addition of the negative ions. This result implies that further modifications of the ETL, with various water ology t (2007) erial College London