

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: <http://www.tandfonline.com/loi/gmcl20>

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To cite this article: Youn Hwan Kim, Mutia Anissa Marsya, Nadhila Sylvianti, Dong Geun Kim, Hee Lack Choi, Chan Young Park, Gun Dae Lee & Joo Hyun Kim (2018) Alcohol-soluble conjugated oligomers as the cathode interfacial layer in polymer solar cells, *Molecular Crystals and Liquid Crystals*, 660:1, 60-65, DOI: [10.1080/15421406.2018.1456050](https://doi.org/10.1080/15421406.2018.1456050)

To link to this article: <https://doi.org/10.1080/15421406.2018.1456050>



Published online: 02 May 2018.



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Alcohol-soluble conjugated oligomers as the cathode interfacial layer in polymer solar cells

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ABSTRACT

Two easily accessible fluorene-based conjugated oligo-electrolytes (COEs) **FTF-** and **FBF-NBr** have been developed as the cathode interfacial layer (CIL) in inverted type polymer solar cells (iPSCs). CILs are interpretative to improving the power conversion efficiency (PCE) and long-term stability of the polymer photovoltaic cell that utilizes a high work function cathode. Compared to the reference devices without interlayer, **FBF-** and **FTF-NBr** exhibit significant improvements of the device parameters by reducing the work function of indium thin oxide (ITO). Conjugated oligo-electrolytes in this work have low lying HOMO levels -5.54 eV for **FTF-NBr** and -5.77 eV for **FBF-NBr** which are beneficial to hole-blocking ability. The iPSCs with **FBF-** and **FTF-NBr** as the inter layer at the cathode side were fabricated to investigate the effect of CIL on the photovoltaic properties. As a result, the PCE of 7.89% with **FBF-NBr** and 8.05% with **FTF-NBr** as the CIL has been achieved. Thus, the results indicate that fluorene-based COEs are potential CIL materials for the iPSCs.

KEYWORDS

Cathode interfacial layer; fluorene-based conjugated oligomer; inverted polymer solar cell

1. Introduction

Polymer solar cells (PSCs) have attracted attention even if they have drawbacks such as low efficiency, and lack of long term stability because of several advantages such as flexible, lightweight, inexpensive processing cost. To improve the power conversion efficiency (PCE) of PSCs, new conjugated polymers and conjugated small molecules have been synthesized as donor materials [1–4]. These new materials have appropriate bandgap and good solubility in common organic solvent, resulting in high PCE. Especially, poly[4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-ethylhexyl-3-fluorothieno[3,4-b]thiophene-2-carboxylate-4,6-diyl] (PTB7) and its derivatives, which consist of thieno[3,4-b]thiophene and benzo[1,2-b:4,5-b']dithiophene units, are widely used in PSCs [5]. Alternatives of fullerene acceptor also have been developed because of low absorption in visible spectrum, limited energy level variability and high cost. The new acceptors should have a complementary absorption wavelength with the donor materials and be well soluble in common organic solvents to provide a good blending system [6–9]. As another

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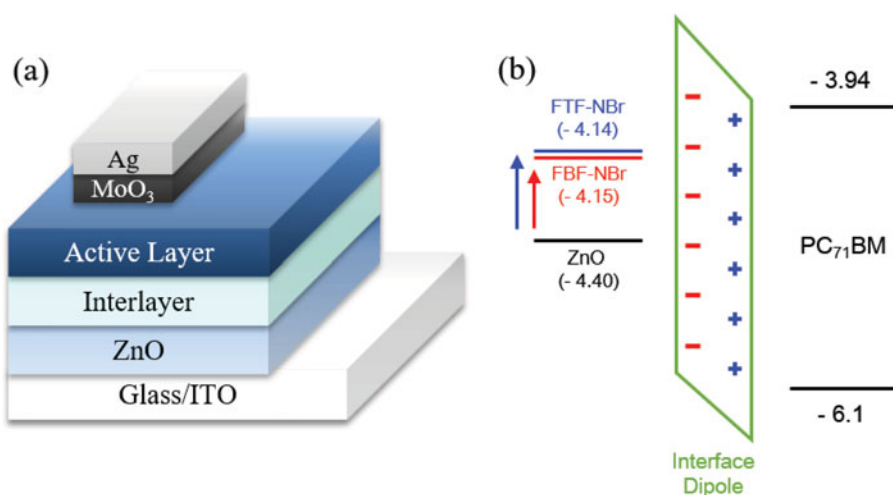
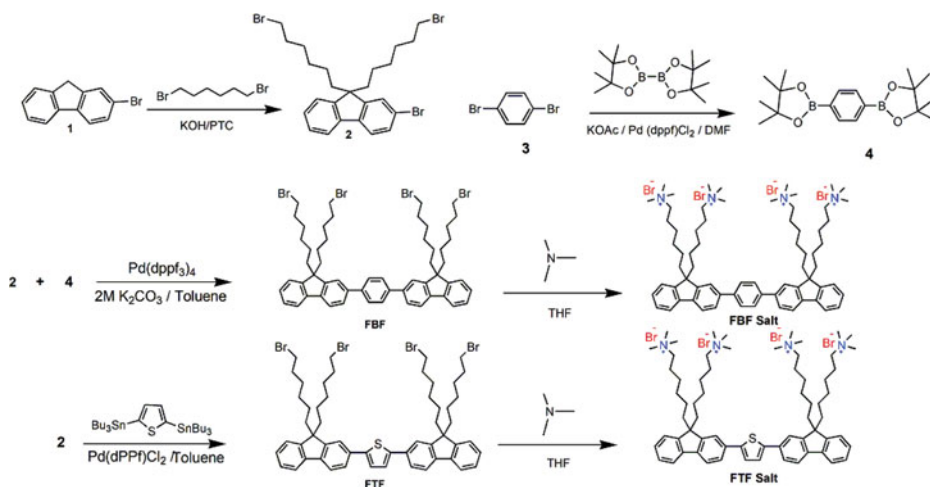


Figure 1. (a) Scheme of inverted PSCs structure. (b) Energy level diagram of ZnO, FBF-NBr, and FTF-NBr.

method for increasing the PCE is by introducing interfacial layer materials such as conjugated polymer or oligo-electrolytes [10–14].

In this article, we fabricated inverted PSCs (iPSCs) (as shown in Fig. 1(a)) with the cathode interlayer based on fluorene-based conjugated oligo-electrolytes (COEs), 6,6',6'',6'''-(1,4-phenylenebis(9H-fluorene-9,9,2-triyl))tetrakis(N,N,N-trimethylhexan-1-aminium) bromide (**FBF-NBr**) and 6,6',6'',6'''-(thiophene-2,5-diylbis(9H-fluorene-9,9,2-triyl))tetrakis(N,N,N-trimethylhexan-1-aminium) bromide (**FTF-NBr**) (Scheme 1). **FBF-NBr** and **FTF-NBr** have cationic quaternary ammonium pendants on the conjugated polymer backbone. Cationic quaternary ammonium pendants induce favorable interface dipole which means that the thin layer of COEs make efficient charge collection from the active layer to the cathode. As a result, short-circuit current (J_{sc}) improves due to favorable interface dipole, leading to an increase in PCE of device (Fig. 1(b)).



Scheme 1. Synthesis of conjugated oligomers (FBF- and FTF NBr).

2. Experimental

2.1. Materials

Chemicals were purchased from Alfa Aesar and were used as received unless otherwise described. PTB7 (Cat. No. OS0007) and PC₇₁BM (Cat No. nano-cPCBM-SF) were purchased from 1-materialCo. and nano-C, Inc., respectively.

2.1.1. Synthesis of 6,6',6'',6'''-(phenyl-2,5-diylbis(9H-fluorene-9,9,2-triyl))tetrakis(N,N,N-trimethylhexan-1-aminium) bromide (FBF-NBr)

This oligomer was synthesized by the Suzuki coupling reaction. The benzeneboronic ester (0.33 gr, 1 mmol), the 2-bromo-9,9-bis-(6-bromo-hexyl)-9H-fluorene (1.43 g, 2.5 mmol), 5% mol of tetrakis(triphenylphosphine) palladium [Pd(PPh₃)₄] (0.058 g, 0.050 mmol), and several drops of aliquat 336 in 20 mL of degassed 1:1 (by volume) mixed solvent of toluene and 2M K₂CO₃ aqueous was stirred for 72 hours at 110°C under the N₂. A portion of 100 mL of water was added the mixture and allowed to cool to room temperature. The mixture was extracted with methylene chloride (MC) and the extracted organic layer was dried over anhydrous MgSO₄. The organic solvent was removed by using a rotary evaporator. The crude product was purified by column chromatography on silica gel using MC/n-hexane. Then, the ionic FBF salt (FBF-NBr) was obtained by treating 2,5-bis-[9,9-bis-(6-bromo-hexyl)-9H-fluoren-2-yl]-benzene with trimethylamine in tetrahydrofuran (THF) for 6 days, followed by extraction with water. The water was then removed under reduced pressure. The trimer was dried in vacuum overnight and was obtained as a yellow solid. ¹H NMR (600 MHz, CD₃OD) δ 7.88~7.84 (m, 2H), 7.81~7.78 (d, J = 7.6 Hz, 1H), 7.79~7.75 (m, 2H), 7.72~7.66 (m, 2H), 7.48~7.40 (m, 1H), 3.24~3.16 (m, 4H), 3.02 (s, 18H), 2.23~2.03 (m, 4H), 1.61~1.46 (m, 4H), 1.19~1.08 (m, 8H), 0.72~0.56 (m, 4H).

2.1.2. Synthesis of 6,6',6'',6'''-(thiophene-2,5-diylbis(9H-fluorene-9,9,2-triyl))tetrakis(N,N,N-trimethylhexan-1-aminium) bromide (FTF-NBr)

A mixture of 2,5-bis-tributylstannanyl-thiophene (0.4 mmol) and 2-bromo-9,9-bis-(6-bromo-hexyl)-9H-fluorene (1 mmol) were dissolved in degassed toluene. [Pd(dppf)Cl₂] (22 mg) were added to the mixture as catalyst. The reaction mixture was stirred and heated to reflux for 48 h under N₂ atmosphere. A portion of 100 mL of water was added the mixture and allowed to cool to room temperature. The mixture was extracted with MC and the extracted organic layer was dried over anhydrous MgSO₄. The organic solvent was removed by using a rotary evaporator. The crude product was purified by recrystallization using methanol. Then, the ionic FTF salt (FTF-NBr) was obtained by treating 2,5-bis-[9,9-bis-(6-bromo-hexyl)-9H-fluoren-2-yl]-thiophene with trimethylamine in THF for 6 days, then the solvent was removed. The trimer was dried in vacuum overnight and was obtained as a red solid. ¹H NMR (600 MHz, CD₃OD) δ 7.78~7.71 (m, 2H), 7.69~7.67 (m, 1H), 7.44~7.27 (m, 4H), 3.19~3.08 (m, 4H), 2.99 (s, 18H), 2.16~1.98 (m, 4H), 1.47~1.42 (m, 4H), 1.18~1.02 (m, 8H), 0.59~0.52 (m, 4H).

2.2. Fabrication of PSCs

In the iPSCs with the structure of ITO/ZnO (40 nm)/FBF or FTF-NBr/active layer (PTB7:PC₇₁BM) (70 nm)/MoO₃ (10 nm)/Ag(100 nm) fabrication process, ITO-coated glass

substrates were washed by ultrasonic agitation in detergent, deionized water, methanol, acetone, and isopropanol respectively. After UV ozone treatment for 5 min, the ZnO layer was spin-cast on the pre-cleaned ITO at 2000 rpm for 1 min by using the sol-gel process. The sol-gel solution was prepared with zinc acetate dehydrate (0.164 g), and ethanalamine (0.05 ml) dissolved in 2-methoxyethanol (1 ml). The mixture was stirred at 60°C for overnight prior to carrying out the film deposition. The thin film of ZnO precursor was annealed at 200°C for 10 min in air. **FBF-** and **FTF-NBr** was dissolved in methanol to 1 mg/ml. The solution was spin cast on the ZnO layer at a speed of 4000 rpm for 1 min. The BHJ active layer was spin-cast in a N₂ filled glove box from the blend solution of PTB7: PC₇₁BM (1:1.5 weight ratio) in chlorobenzene with 3% v/v % 1,8-diiodooctane (DIO) at 1800 rpm for 120 s. Prior to spin coating, the active solution was filtered through a 0.2 μm membrane filter. Finally the MoO₃ and Ag layer were deposited sequentially at 2×10^{-6} Torr by thermal evaporation through a shadow mask with a device area of 0.13 cm².

2.3. Characterization

The current density–voltage of the solar cells were measured by KEITHLEY Model 2400 source-measure unit under 1.0 sun (100 mW/cm²) condition from a 150 W Xe lamp with an AM 1.5G filter. A calibrated Si reference cell with a KG5 filter certified by National Institute of Advanced Industrial Science and Technology was used to confirm 1.0 sun condition. Kelvin probe microscopy (KPM) measurements (KP technology Ltd. Model KP020) were performed to confirm the work function of the cathode with or without interlayer, which are estimated by the contact potential difference between the sample and the KP tip. The KP tip work function was calibrated by a standard gold with a work function of 5.1 eV. A thin film of interlayer (ca. 5 nm) was prepared by spin-coating from the solution in methanol (MeOH) on the surface of the ZnO under ambient condition to measure contact potential difference by KPM and investigate the effective work function of interlayer coated substrate.

3. Results and discussion

Prior to the device fabrication, optical and electro chemical properties of oligomers were investigated by UV-vis absorption spectroscopy and cyclic voltammetry (CV). As shown in Fig. 2(a), **FBF-** and **FTF-NBr** solutions in methanol showed an absorption maximum

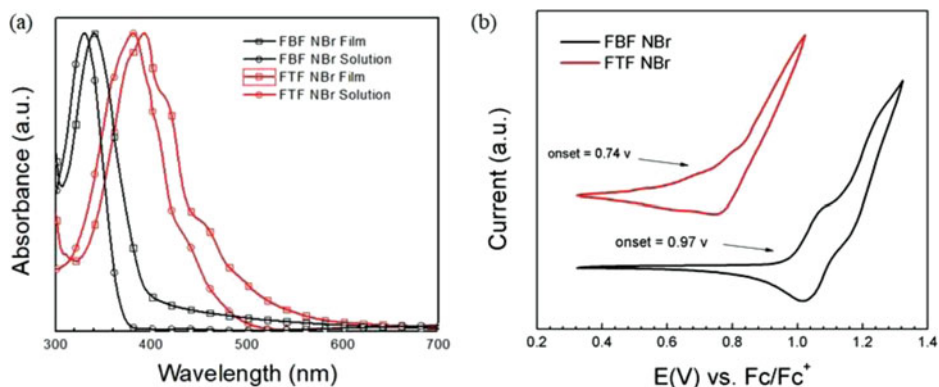


Figure 2. (a) UV-vis absorption spectra in solution and film of **FBF-** and **FTF NBr**. (b) CV spectra of **FBF-** and **FTF NBr**.

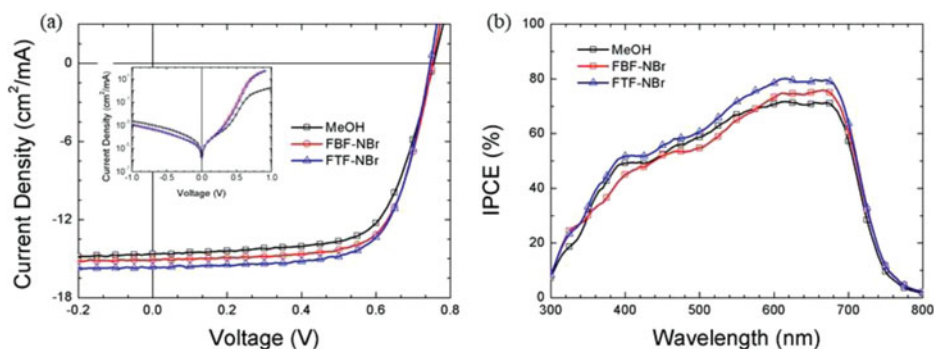


Figure 3. (a) Current density–voltage curves of PSCs under AM 1.5G simulated illumination with an intensity of 100 mW/cm² (inset: under the dark condition). (b) IPCE spectra of the devices with and without cathode interfacial layer.

($\lambda_{\text{abs,max}}$) at 381 and 330 nm, respectively. As for the thin film of COEs, $\lambda_{\text{abs,max}}$ are red-shifted than those of solutions, which appeared at 392 and 340 nm for **FBF-NBr** and **FTF-NBr**, respectively. The HOMO and LUMO levels of for the oligomers were obtained from the onset of the oxidation and reduction potential of cyclic voltammograms, which were obtained in 0.1 M of Bu₄NPF₄ in an acetonitrile solution. The HOMO energy level of **FBF-NBr** and **FTF-NBr** were calculated to be -5.54 and -5.77 eV, respectively. The LUMO energy level of the **FBF-NBr** and **FTF-NBr** were estimated to be -3.29 and -3.19 , respectively.

We fabricated iPSCs with device structure of ITO/ZnO/**FBF** or **FTF NBr**/active layer (PTB7:PC₇₁BM)/MoO₃/Ag. The current density-voltage (J-V) characteristics were measured under an AM 1.5G simulated illumination with a 100 mW/cm² and the dark condition showed in Fig. 3(a). The J_{sc} of the device with ZnO/**FBF-NBr** and **FTF-NBr** exhibit 15.08 and 15.64 mA/cm² respectively, which are higher than the device based on ITO/ZnO (14.65 mA/cm²). However, the fill factor (FF) of the devices with CILs are almost identical to that of the reference device. The device with **FTF-NBr** as the CIL shows the PCE of 8.05% and the PCE of the device with **FBF-NBr** also has a higher than reference device. It is indicating that the **FBF-NBr** and **FTF-NBr** layer induce favorable interface dipole between ZnO and active layer. Comparing the **FBF-NBr** and **FTF-NBr** layer, the J_{sc} of the **FTF-NBr** is measured higher because the **FTF-NBr** has a thiophene ring, which acts as an electron donor, it makes better electron collection efficiency than that of **FBF-NBr**. The incident photon-to-current efficiency (IPCE) spectra of the devices are presented in Fig. 3(b). The IPCE values of the **FTF-NBr** device is higher than those of the other devices. IPCE results are well correlate with the J_{sc} of the devices.

Table 1. Photovoltaic performances of devices with and without cathode interfacial layer.

Buffer layer	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	Work Function (eV)
ZnO/ MeOH	14.65 (14.36)	0.76 (0.76)	66.6 (67.8)	7.41 (7.34)	−4.40
ZnO/ FBF-NBr	15.08 (15.24)	0.75 (0.75)	69.7 (68.5)	7.89 (7.84)	−4.15
ZnO/ FTF-NBr	15.64 (15.49)	0.75 (0.76)	68.6 (67.9)	8.05 (7.94)	−4.14

Kelvin Probe Microscopy (KPM) was used to investigate the work function of ZnO and oligomer coated ZnO layer. The work function of **FBF-** and **FTF-NBr** coated ZnO are measured to be -4.14 and -4.15 eV, which are higher than that of ZnO (-4.4 eV) (Table 1) due to formation of favorable interface dipole. Even though, **FBF-NBr** coated ZnO is almost identical to that of **FTF-NBr** the work function, the performances of the device with **FTF-NBr** are better than those of the device based **FBF-NBr**. This is presumably due to that **FTF-NBr** has electron rich thiophene ring.

4. Conclusion

We have successfully synthesized and characterized two easily accessible **FBF-** and **FTF-NBr** as the CIL in iPSCs. The J_{sc} of the device with ZnO/**FBF-** and **FTF-NBr** exhibit 15.08, 15.64 mA/cm² respectively, which are higher than the device based on ZnO/MeOH (14.65 mA/cm²). Accordingly, the PCE of the device with **FBF-** and **FTF-NBr** exhibit 7.89%, and 8.05% respectively, which are higher than the device with ZnO/MeOH (7.44%) due to formation of favorable interface dipole. These results demonstrate that introducing COE is a good strategy for obtain high photovoltaic performances of device.

Funding

This research work was supported by a grant of Pukyong National University (year 2017).

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