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Introduction

Bulk heterojunction polymer solar cells (PSCs) have attracted considerable attention because of their unique characteristics of being low cost, light weight, and having great potential for the realization of flexible devices and large-area solar energy conversion.¹⁻⁵ Typically, the PSCs adopt a basic architecture of a so-called "sandwich structure", that is, a blend active layer of a conjugated polymer donor and fullerene derivative acceptor sandwiched between the electron collecting cathode and the hole collecting anode. To maximize the performance of PSCs, numerous studies have been mainly focused on the design and synthesis of high-efficiency conjugated polymer donors and fullerene derivative acceptors as photovoltaic materials,6-11 and the maximum power conversion efficiency (PCE) of the conventional type of PSCs has been reported to be 8.37% by incorporating a thin layer of water/alcohol soluble conjugated polymer (WSCP) as the cathode interlayer.12a Chen and coworkers reported the highest PCE value of 7.5% for PSCs with

Pyridinium salt-based molecules as cathode interlayers for enhanced performance in polymer solar cells

Hua Ye,^a Xiaowen Hu,^a Zhixiong Jiang,^a Dongcheng Chen,^a Xin Liu,^a Han Nie,^a Shi-Jian Su,^{*a} Xiong Gong^b and Yong Cao^a

A series of water/alcohol-soluble small molecules based on electron-deficient pyridinium salts namely BTPS, BnPS and F8PS were successfully synthesized. Their photophysical and electrochemical properties were thoroughly studied. Due to its good film-forming ability, F8PS was employed as a cathode interlayer in an organic photovoltaic cell. Simultaneous enhancements in open-circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) were achieved, and the power conversion efficiency (PCE) was increased from 4.32% to 6.56% compared to the device based on the bare Al cathode. $V_{\rm oc}$ was significantly improved from 0.76 V to 0.94 V, and it is one of the best results reported in literature to date for polymer solar cells (PSCs) based on the active layer of poly [N-9'-heptadecanyl-2,7-carbazolealt-5,5-(4',7'- di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT):[6,6]-phenyl-C71-butyric acid methylester (PC₇₁BM). The greatly increased $V_{\rm oc}$ may be due to the interface dipoles generated by F8PS. It was also demonstrated that post treatment of the active layer with ethanol gave an improvement of the overall device efficiency from the initial 4.32% to 5.55%, compared to the device with the bare Al cathode. Therefore, the improvement in performance after pyridinium salt deposition may be due to a combination of the effects of ethanol treatment and the presence of the thin pyridinium salt layer. The good water/alcohol solubility, ideal HOMO/LUMO energy levels and the excellent electron transfer/ collection ability of the hydrophilic pyridinium salt derivatives makes them a promising family of electron transport materials for highly efficient PSCs.

> the simplest poly(3-hexylthiophene) (P3HT) as the donor and indene-C₆₀ bisadduct (ICBA) as the acceptor through using polyfluorene grafted with a crown ether intercalated with K⁺ (PFCn6:K⁺) as the electron transport layer (ETL) and Ca/Al as the cathode.^{12b} At the cathode interface, low work function metals, such as Ca and Ba, can be used to dramatically improve the performance of organic photovoltaics (OPVs) at the expense of the instability toward moisture and oxygen.13 Hence, expensive encapsulation processes are generally required to provide protection from the ambient conditions. Another alternative approach is to use air-stable high work-function metals (such as Al, Ag and Au) to improve the stability. Then, it is necessary to introduce an interfacial layer between the active layer and the metal cathode to minimize the energy barrier due to the high work-function metals.14 Therefore, interface modification is indispensable and critical to maximize carrier extraction and collection in high performance PSCs.

> WSCPs have been previously used in polymer light-emitting diodes (PLEDs) as the cathode interlayers.¹⁵ So far, nearly all of the WSCPs are conjugated polyelectrolytes, or their neutral precursors, with polar pendant groups on their side chains and the skeletons of the main chains are limited to polyfluorenes,¹⁶ polycarbazoles¹⁷ and polythiophenes.¹⁸ Furthermore, the inherent batch-to-batch variations of the polydispersity and

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[&]quot;State Key Laboratory of Luminescent Materials and Devices and Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou 510640, China. E-mail: mssjsu@scut.edu.cn

^bDepartment of Polymer Engineering, The University of Akron, 250 South Forge Street, Akron, Ohio 44325-0301, USA

molecular weight of the polymers restricts the practicality of these materials. In light of this, water/alcohol-soluble small molecules are more potential alternatives than their polymer counterparts.^{19,20} Wudl and coworkers^{19a} reported a water/ alcohol-soluble small molecule based on the commercially available pigment quinacridone which was employed as an ETL in OPVs with the active layer consisting of poly [*N*-9'-heptade-canyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothia-diazol)] (PCDTBT):[6,6]-phenyl-C₇₁-butyric acid methylester (PC₇₁BM),^{21a} and the addition of the quinacridone-based ETL improved the device efficiency from 4.3% to 5.2%. However, without exception, the polar groups were also limited and located at the terminal of the alkyl chain of the quinacridone-based molecule.^{19a}

Herein, a series of water/alcohol soluble small molecules based on electron-deficient pyridinium salt were designed and synthesized, and their photophysical and electrochemical properties were thoroughly studied. The electron-deficient pyridinium rings are positively charged and situated at the backbone of the molecules attached with the negatively charged halide ions, which is quite different from the previously reported WSCPs15-18 and other solution-processable electron transport materials.^{19,20} Recently, Kim and coworkers^{21b} reported three non-conjugated polyviologen derivatives with different alkyl chain lengths and counter anions as an interfacial layer in PSCs, and these PV derivatives showed potential performance for the devices based on the active layer of P3HT:[6,6]-phenyl-C₆₁-butyric acid methylester (PC₆₁BM). In contrast, the intensive electrophilicity of our pyridinium salts endows the excellent electron transfer and collection ability, and thus greatly improves the efficiency of the device. Furthermore, these pyridinium salts possess a well-defined structure and molecular weight, good film-forming ability and especially excellent solubility in polar solvents such as methanol, ethanol and water, which avoids intermixing between the active layer and the subsequently deposited interlayer, therefore allowing the fabrication of multilayer devices with orthogonal solvents by simple solution-process method of spin-coating. To our knowledge, this is the first report about an water/alcohol soluble cathode interlayer containing fully conjugated electrondeficient pyridinium salt for optoelectronic devices.

Experimental section

Measurement and characterization

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV-300 (300 MHz) with tetramethylsilane as an internal reference. UVvis absorption spectra were recorded on a HP 8453 spectrophotometer. Photoluminescence (PL) spectra were measured using a Jobin-Yvon spectrofluorometer. Cyclic voltammetry (CV) was performed on a CHI600D electrochemical workstation with a platinum working electrode and a platinum wire counter electrode at a scan rate of 50 mV s⁻¹ against a saturated calomel electrode (SCE) reference electrode with an argon saturated anhydrous solution of 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile. The film for the electrochemical measurements was coated from its ethanol solution.

Materials

All reagents were obtained from Sigma Aldrich Chemical Co., Alfa Aesar Chemical Co., Aladdin Chemical Co., and J&K Chemical Co. and they were used as received unless otherwise specified. All manipulations involving air-sensitive reagents were performed in the atmosphere of dry argon. The solvents (dichloromethane (DCM), tetrahydrofuran (THF) and toluene) were purified by routine procedures and were distilled under dry argon before being used. 1,4-Dibromo-2,5-bis-[2-(*tert*-butyldimethyl-silanyloxy)-ethyl]-benzene (1),^{22a} 2-pyridylzinc chloride,^{22b,c} and 4,7-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2yl)-benzo[1,2,5]thiadiazole (5)^{22d} were prepared according to the reference procedures.

2-{4-Bromo-2,5-bis-[2-(tert-butyl-dimethyl-silanyloxy)-ethyl]phenyl}-4,4,5,5-tetramethyl [1,3,2]dioxaborolane (2). To a solution of 1 (5.0 g, 8.73 mmol) in THF at -78 °C under argon, *n*butyllithium (20 mL, 32 mmol) was added dropwise and the mixture was stirred at -78 °C for 2 h. Then, 2-isopropoxy-4,4,5,5-tetramethyl-(1,3,2)-dioxaborolane (5.2 mL, 25.5 mmol) was added to the solution in one addition and the resulting mixture was stirred at -78 °C for 1 h and was allowed to warm to room temperature. Water was poured into the mixture to quench the reaction and the mixture was extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous magnesium sulfate. The precipitate was separated by filtration. The solvent was removed under reduced pressure and the residue went through a silica-gel column to give a yellow oil (4.13 g, 6.66 mmol) in 76.2% yield. ¹H NMR (300 MHz, CDCl₃), (ppm): 7.66 (s, 1H), 7.41 (s, 1H), 3.78–3.74 (m, 4H), 3.04 (t, 2H), 2.94 (t, 2H), 1.32 (s, 12H), 0.87 (s, 18H), -0.01 (s, 12H).

2-[2,5-Bis-[2-(tert-butyl-dimethyl-silanyloxy)-ethyl]-4-(4,4,5,5tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-pyridine (3). To the 2-pyridylzinc chloride solution (7.20 mmol) under argon, a solution of 2 (4.07 g, 6.56 mmol) in THF was added and then $Pd(PPh_3)_4$ (218 mg, 0.19 mmol) was added rapidly. The reaction mixture was stirred for 24 hours at reflux. After cooling to room temperature, water was poured into the mixture to quench the reaction and the mixture was extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous magnesium sulfate. The precipitate was separated by filtration. The solvent was removed under reduced pressure, and the residue went through a silica-gel column to give a yellow oil (1.58 g, 2.63 mmol) in 38.9% yield. ¹H NMR (300 MHz, CDCl₃), (ppm): 8.69 (d, 1H), 7.76-7.72 (m, 2H), 7.43 (d, 1H), 7.30-7.27 (m, 1H), 7.21 (s, 1H), 3.80-3.65 (dt, 4H), 3.13 (t, 2H), 2.92 (t, 2H), 1.35 (s, 12H), 0.88 (s, 9H), 0.82 (s, 9H), -0.01 (s, 6H), -0.02 (s, 6H). ¹³C NMR (CDCl₃, 75 MHz), (ppm): 160.22, 149.03, 143.49, 142.72, 138.80, 136.16, 133.45, 131.67, 124.11, 121.70, 83.48, 65.49, 64.38, 38.84, 36.10, 29.68, 25.96, 25.95, 24.85, 18.31, 18.27, -5.27, -5.41.

2-{2,5-Bis-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-4-pyridin-2-yl-phenyl}-5-bromo-pyridine (4). Compound 3 (0.54 g, 0.90 Paper

mmol), 2,5-dibromopyridine (441.8 mg, 1.8 mmol), 2 M K₂CO₃ (4 mL) and Pd(PPh₃)₄ (56 mg, 0.048 mmol) were dissolved in toluene : ethanol (15:3 mL) under argon atmosphere. The mixture was heated at 85 °C for 24 h. After cooling to room temperature, water was poured into the mixture and the mixture was extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous magnesium sulfate. The precipitate was separated by filtration. The solvent was removed under reduced pressure and the residue went through a silica-gel column to give a yellow solid (0.23 g, 0.37 mmol) in 40.7% yield. ¹H NMR (300 MHz, DMSO- d_6), (ppm): 8.78 (s, 1H), 8.66 (d, 1H), 8.18 (d, 1H), 7.91 (m, 1H), 7.59-7.53 (m, 2H), 7.40 (m, 1H), 7.34 (s, 2H), 3.63 (t, 4H), 2.92 (t, 4H), 0.74 (s, 18H), -0.14 (s, 12H). ¹³C NMR (CDCl₃, 75 MHz), (ppm): 158.20, 151.80, 150.24, 149.16, 140.90, 139.37, 138.84, 136.33, 134.85, 134.72, 132.44, 132.17, 125.45, 124.18, 121.89, 119.20, 64.32, 36.17, 25.91, 18.30, -5.40.

4,7-Bis-(6-{2,5-bis-[2-(tert-butyl-dimethyl-silanyloxy)-ethyl]-4pyridin-2-yl-phenyl}-pyridin-3-yl)-benzo[1,2,5]thiadiazole (8). Compound 4 (0.19 g, 0.30 mmol), compound 5 (58.2 mg, 0.15 mmol), 2 M K₂CO₃ (4 mL) and Pd(PPh₃)₄ (18 mg, 0.016 mmol) were dissolved in toluene : ethanol (10:2 mL) under argon atmosphere. The mixture was heated at 85 °C for 24 h. After cooling to room temperature, water was poured into the mixture and the mixture was extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous magnesium sulfate. The precipitate was separated by filtration. The solvent was removed under reduced pressure and the residue went through a silica-gel column to give a yellow-green solid (98.5 mg, 0.08 mmol) in 53.4% yield. ¹H NMR (300 MHz, CDCl₃), (ppm): 9.28 (d, 2H), 8.66 (d, 1H), 8.72 (d, 2H), 8.52 (m, 2H), 7.98 (s, 1H), 7.77 (t, 2H), 7.70-7.67 (m, 2H), 7.52-7.67 (m, 4H), 7.39 (s, 1H), 7.32-7.29 (m, 2H), 6.98 (s, 1H), 3.79 (td, 8H), 3.07 (td, 8H), 0.81 (s, 36H), -0.06 (s, 24H). ¹³C NMR (CDCl₃, 75 MHz), (ppm): 159.73, 154.00, 149.28, 149.12, 140.94, 140.19, 136.91, 136.26, 135.76, 134.86, 134.73, 132.44, 131.33, 130.99, 130.70, 128.12, 125.52, 124.18, 123.92, 121.86, 64.42, 36.34, 25.96, 18.34, -5.35.

1,3-Bis-(6-{2,5-bis-[2-(tert-butyl-dimethyl-silanyloxy)-ethyl]-4pyridin-2-yl-phenyl}-pyridin-3-yl)-benzene (9). 1,3-Bis-(4,4,5,5tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzene (6) was synthesized by following a similar procedure to 5.22d Compound 4 (0.16 g, 0.25 mmol), compound 6 (42 mg, 0.13 mmol), 2 M K₂CO₃ (4 mL) and Pd(PPh₃)₄ (17 mg, 0.015 mmol) were dissolved in toluene: ethanol (10:2 mL) under argon atmosphere. The mixture was heated at 85 °C for 24 h. After cooling to room temperature, water was poured into the mixture and the mixture was extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous magnesium sulfate. The precipitate was separated by filtration. The solvent was removed under reduced pressure and the residue went through a silica-gel column to give a pale yellow solid (86 mg, 0.073 mmol) in 58.7% yield. ¹H NMR (300 MHz, CDCl₃), (ppm): 9.02 (d, 2H), 8.73 (d, 2H), 8.06 (d, 2H), 7.91 (s, 1H), 7.86-7.58 (m, 7H), 7.50 (d, 2H), 7.43 (s, 2H), 7.38 (s, 2H), 7.35-7.29 (m, 2H), 3.77 (td, 8H), 3.02 (td, 8H), 0.80 (s, 36H), -0.07 (s, 24H). ¹³C NMR (CDCl₃, 75 MHz), (ppm): 159.70, 158.89, 149.20, 147.71,

140.77, 140.19, 138.81, 136.31, 134.79, 134.74, 132.37, 132.39, 132.34, 129.97, 126.87, 125.97, 124.21, 121.85, 64.44, 36.30, 25.95, 18.33, -5.34.

2,7-Bis-(6-{2,5-bis-[2-(tert-butyl-dimethyl-silanyloxy)-ethyl]-4pyridin-2-yl-phenyl}-pyridin-3-yl)-9,9-dioctyl-9H-fluorene (10). 2,7-Bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9,9-dioctyl-9H-fluorene (7) was synthesized by following a similar procedure to 2. Compound 4 (0.23 g, 0.37 mmol), compound 7 (114 mg, 0.18 mmol), 2 M K₂CO₃ (4 mL) and Pd(PPh₃)₄ (23 mg, 0.02 mmol) were dissolved in toluene : ethanol (15 : 3 mL) under argon atmosphere. The mixture was heated at 85 °C for 24 h. After cooling to room temperature, water was poured into the mixture and the mixture was extracted with ethyl acetate. The organic phase was washed with brine and dried over anhydrous magnesium sulfate. The precipitate was separated by filtration. The solvent was removed under reduced pressure, and the residue went through a silica-gel column to give a yellow-green solid (126.3 mg, 0.085 mmol) in 47.2% yield. ¹H NMR (300 MHz, CDCl₃), (ppm): 9.04 (s, 2H), 8.74 (d, 2H), 8.10 (m, 2H), 7.90 (d, 2H), 7.83 (m, 2H), 7.68 (d, 3H), 7.65 (s, 3H), 7.54 (m, 2H), 7.44 (s, 2H), 7.39 (s, 2H), 7.33 (m, 2H), 3.76 (td, 8H), 3.04 (td, 8H), 2.11 (m, 4H), 1.20–1.10 (m, 20H), 0.80 (s, 46H), -0.07 (s, 24H). ¹³C NMR (CDCl₃, 75 MHz), (ppm): 159.71, 158.26, 152.11, 149.20, 147.69, 140.72, 140.58, 140.29, 136.80, 136.32, 135.10, 134.82, 134.70, 132.42, 132.29, 126.14, 124.21, 124.08, 121.85, 121.56, 120.57, 64.43, 55.49, 40.43, 36.36, 31.75, 30.05, 29.23, 25.95, 23.94, 22.59, 18.33, 14.06, -5.35.

Cyclization of 8–10. To a solution of **8** (98.5 mg, 0.08 mmol) in 20 mL of acetonitrile, $SOCl_2$ (5 mL) was added and the mixture was stirred at room temperature for 3 hours. The resulting solution was evaporated. Washing from CH_2Cl_2 gave BTPS as an orange yellow solid. BnPS and F8PS were synthesized by following the similar procedure of BTPS giving pale yellow solids.

BTPS: yield: 31.0%. ¹H NMR (300 MHz, D_2O), (ppm): 9.75– 9.68 (m, 2H), 9.28–9.17 (m, 2H), 8.90–8.80 (m, 2H), 8.89–8.72 (m, 1H), 8.60 (m, 3H), 8.57–8.48 (m, 2H), 8.31 (s, 2H), 8.27 (s, 2H), 8.20 (m, 2H), 8.00–7.88 (m, 2H), 5.03 (m, 4H), 4.85 (m, 4H), 3.50 (m, 8H). Calcd $C_{46}H_{36}N_6Cl_4S$ 846.145, MALDI-TOF: 847.421.

BnPS: yield: 33.2%. ¹H NMR (300 MHz, D_2O), (ppm): 9.29 (s, 2H), 8.93 (d, 2H), 8.82 (d, 2H), 8.69 (s, 1H), 8.66 (s, 1H), 8.60-8.54 (m, 4H), 8.26 (s, 2H), 8.24 (m, 3H), 8.03-7.93 (m, 4H), 7.88-7.81 (m, 1H), 4.96 (t, 4H), 4.86 (t, 4H), 3.47 (m, 8H). Calcd $C_{46}H_{38}N_4Cl_4$ 788.182, MALDI-TOF: 789.492.

F8PS: yield: 30.0%. ¹H NMR (300 MHz, D_2O), (ppm): 9.21 (s, 2H), 8.84 (m, 4H), 8.58 (m, 6H), 8.22 (s, 4H), 8.04 (d, 2H), 7.94 (m, 4H), 7.82 (d, 2H), 4.92 (m, 8H), 3.44 (m, 8H), 2.10 (m, 4H), 0.99 (m, 20H), 0.60 (m, 10H). Calcd $C_{69}H_{74}N_4Cl_4$ 1100.464, MALDI-TOF: 1101.809.

Device fabrication and characterization

Patterned indium tin oxide (ITO)-coated glass substrates were used as the anode in the polymer solar cells. The substrates were cleaned by sonication in detergent, deionized water, acetone and isopropyl alcohol and dried in a nitrogen stream, followed by an oxygen plasma treatment. Then the surface of the ITO substrate was modified by spin-coating a 40 nm thin layer of poly(3,4-ethylenedioxy thiophene):poly(styrenesulfonic acid) (PEDOT:PSS) (Baytron PVPAI 4083), followed by baking at 140 °C for 10 minutes under ambient conditions. The substrates were then transferred into a nitrogen-filled glove box. An 80 nm thin active layer of PCDTBT:PC₇₁BM (1 : 4, w : w) was spin-coated from its solution in a solvent mixture of chlorobenzene and 1,2-dichlorobenzene (1 : 3, v : v) atop the PEDOT:PSS layer. Subsequently, the cathode interlayer was deposited by spin-casting from 0.5 mg mL⁻¹ pyridinium salt solution in ethanol. Finally, an 80 nm thin layer of aluminum was thermally deposited as the cathode through a shadow mask (defined active area of 0.16 cm²) in a chamber with a base pressure of <5 \times 10⁻⁴ Pa.

The cathode thickness was monitored upon deposition by using a crystal thickness monitor (Sycon). Profilometry (Veeco Dektak150) was used to determine the thickness of the organic films. Device fabrication was carried out in an N₂ atmosphere dry-box (Vacuum Atmosphere Co.). The current density-voltage (J-V) characteristics were recorded with a Keithley 236 source meter. The spectral response was measured with a commercial photomodulation spectroscopic setup (Oriel). A calibrated Si photodiode was used to determine the photosensitivity. PCE was measured under an AM1.5G solar simulator (Oriel model 91192). The power of the sun simulation was calibrated before the testing using a standard silicon solar cell.

Results and discussion

Synthesis and chemical characterization

The structures and the synthetic routes of the pyridinium salts are outlined in Scheme 1. To ensure sufficient water/alcohol solubility and film-forming ability of the resulting pyridinium salt-based materials, disubstituted derivatives containing four pyridinium groups on the two sides of benzo[1,2,5]thiadiazole (BT), benzene and fluorene, were designed and synthesized, respectively. Compound 1 was a pure white solid and was prepared according to the reference procedures.^{22a} Compound 2 was synthesized in 76.2% yield by reacting 1 with n-butyllithium at -78 °C under argon, followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and the crude product was purified through a silica-gel column to give a yellow oil. Negishi coupling reaction of compound 2 with freshly prepared 2-pyridylzinc chloride^{22b,c} in anhydrous THF gave compound 3 as a yellow oil in 38.9% yield. Key intermediates of compound 4, 8, 9 and 10 were obtained by a palladium-catalyzed Suzuki cross-coupling reaction in a yield between 40.0% and 60.0%. Hereafter, the electron-deficient pyridinium rings were obtained by an intramolecular cyclization by the reaction with thionyl chloride to provide the target molecules with low LUMO energy levels and a relatively planar structure for extended π -electron delocalization.^{22a} Finally, the products were precipitated from DCM. Their molecular structures were verified by ¹H NMR and MALDI-TOF. The obtained pyridinium salts were indeed soluble in highly polar solvents, such as water, methanol and ethanol, in which most of the active materials are



insoluble. Hence, the pyridinium salt would be a suitable candidate as a cathode modification layer by a simple solutionprocess method of spin-coating to fabricate multilayer PSC devices with orthogonal solvents.

Optical and electrochemical properties

In ethanol solution, BTPS exhibits one distinct absorption band at about 400 nm, which can be attributed to the π - π * transition of the conjugated molecular backbone (Fig. 1). Besides, it also exhibits one peak combined with a slight absorption band in the range of 280-350 nm that can be ascribed to the pyridiniumphenylene units. For BnPS, the distinct absorption band blueshifted to 365 nm owing to the weak conjugation of metasubstituted benzene compared to the para-substituted BT of BTPS. Due to the increased conjugation of fluorene in F8PS, the distinct absorption band shifted bathochromically to 410 nm. Compared with the absorption spectra in solution, bathochromic shifts were also observed for the absorption spectra recorded in thin solid film, which can probably be ascribed to the molecular aggregation. To gain more insight into the photophysical properties of the pyridinium salts, their PL spectra were also recorded in both ethanol solution and thin film. For BTPS in ethanol solution, the PL spectrum exhibits two peaks at 459 and 485 nm, respectively. In comparison, the PL spectrum in the thin film shifts to the longer wavelength of 553 nm. Such intense bathochromic shift relative to the spectrum in ethanol solution could be attributed to the strong aggregation induced by the excellent molecular planarity of BTPS. For BnPS, the PL spectra in ethanol solution and thin film show only one



Fig. 1 Normalized UV-vis absorption and PL spectra of the pyridinium salt derivatives in dilute ethanol solution (\bigcirc) and thin solid film state (\bigcirc).

emission band and peak at 422 and 438 nm, respectively. It is interesting to note that F8PS exhibits an extremely wide PL spectrum in both ethanol solution and thin film, which can be attributed to the intramolecular charge-transfer (ICT) interaction between the electron-donating fluorene and the electrondeficient pyridinium rings.

Electrochemical properties of the pyridinium salts were investigated by CV. Under the same experimental conditions, the redox potential $(E_{1/2})$ of ferrocene/ferrocenium (Fc/Fc⁺) was measured to be 0.42 V to the SCE reference electrode. Note that the redox potential of Fc/Fc⁺ has an absolute energy level of -4.80 eV to vacuum.^{23a,b} Thus, the HOMO and LUMO energy levels can be estimated according to the following equations: HOMO = $-e (E_{ox} + 4.38)$ (eV), LUMO = $-e (E_{red} + 4.38)$ (eV), where E_{ox} and E_{red} are the onset oxidation and reduction potential vs. SCE in the experimental conditions, respectively. As shown in Table 1, BTPS exhibited the highest onset reduction potential of -0.48 V owing to the additional electron-withdrawing ability of BT, hence, it showed the deepest LUMO energy levels of -3.90 eV according to the above-mentioned equations. In comparison, F8PS showed the lowest HOMO energy level of -6.07 eV and the highest LUMO energy level of -3.66 eV due to the large energy band gap (E_g) of fluorene. For BnPS, because of the poor conjugation of the *meta*-substituted benzene, its LUMO energy level is located between those of BTPS and F8PS. Furthermore, BnPS exhibited the lowest onset oxidation potential and thus the highest HOMO energy levels. Optical energy band gaps (E_g^{opt}) of the molecules were also estimated from the absorption edges of the UV-vis spectra of the thin films, the values of which are larger than those of the energy band gaps (E_g) calculated according to $E_g = |\text{HOMO}| - |\text{LUMO}|$. Anyway, such low LUMO energy levels of these pyridinium salts indicate that the pyridinium salts could be good electron transporting and collecting materials for PSCs.

Density functional theory calculations

To get further insight into the molecular orbitals of the pyridinium salts, density functional theory (DFT) calculations of the molecules were performed using the Gaussian suite of programs (Gaussian 03W). To obtain their HOMO and LUMO energy levels, molecular structure optimization (alkyl chains were omitted) and single-point energy calculations were performed at the B3LYP/6-31G(d) and B3LYP/6-311 + G(d, p) levels, respectively. As shown in Fig. 2, the HOMOs of BTPS, BnPS and F8PS are mainly located at the central arylene skeleton of BT, benzene and fluorene ring, respectively, as well as the two pyridine rings close to the central arylene rings. In comparison, the LUMOs of BnPS and F8PS reside along the two sides of the pyridinium rings, which is consistent with the intense electronaccepting behavior of the pyridinium rings and the electrically neutral benzene or electron-donating behaviour of fluorene. For BTPS, due to the electron affinity of BT, the LUMO is delocalized over the whole π -conjugation system since the whole molecule is electron-poor. The calculated HOMO and LUMO energy levels are demonstrated in Table 1. It can be clearly seen that the lowlying LUMO energy level can be obtained by introducing



Fig. 2 Calculated spatial distributions (DFT, B3LYP/6-31G(d)//B3LYP/6-311 + G(d, p), Gaussian 03W) of LUMOs (*Top*) and HOMOs (*Bottom*) of BTPS, BnPS and F8PS, respectively.

Table 1 Optical energy band gaps (E_g^{opt}) and electrochemical properties of the pyridinium salts									
Molecules	E_{g}^{opta} (eV)	$E_{\mathrm{ox}}\left(\mathbf{V}\right)$	$E_{\rm red}$ (V)	$E_{\rm HOMO}^{b}$ (eV)	E_{LUMO}^{c} (eV)	$E_{\rm g}^{\ \ d}$ (eV)	$HOMO^{e}$ (eV)	$LUMO^{e}$ (eV)	$E_{\rm g}^{\rm \ calcf}({\rm eV})$
BTPS	2.35	1.59	-0.48	-5.97	-3.90	2.07	-5.79	-3.49	2.30
BnPS	2.21	1.41	-0.60	-5.79	-3.78	2.01	-5.85	-3.33	2.52
F8PS	2.43	1.69	-0.72	-6.07	-3.66	2.41	-5.71	-3.31	2.40

^{*a*} Optical energy band gaps (E_g^{opt}) estimated from the absorption edges of the solid films. ^{*b*} Calculated according to HOMO = $-e(E_{ox} + 4.38)V$. ^{*c*} Calculated according to LUMO = $-e(E_{red} + 4.38)V$. ^{*d*} Calculated according to $E_g = |E_{HOMO}| - |E_{LUMO}|$. ^{*e*} Calculated from DFT, B3LYP/6-31G(d)//B3LYP/6-311 + G(d, p), Gaussian 03W. ^{*f*} Calculated according to $E_g^{cal} = |HOMO| - |LUMO|$. electron-deficient pyridinium rings. Although the experimental energy levels are somewhat different from the calculated ones, the tendency is consistent.

Cathode interlayer function in PSCs

Transparent and uniform film can be prepared on quartz plates by spin-casting from the ethanol solution of F8PS. Unfortunately, maybe due to the limited molecular weight and not having any flexible groups, both BTPS and BnPS could not form a uniform film by spin-coating. Therefore, only F8PS was introduced as a cathode interlayer in organic photovoltaics to investigate its electron extraction property. In this study, the PCDTBT:PC₇₁BM blend (1 : 4, w : w) was used as the active layer of PSCs with a general device configuration of ITO/PEDOT:PSS/ PCDTBT:PC₇₁BM/F8PS/Al. For comparison, control devices without any cathode interlayer were also fabricated under the same conditions.

Fig. 3a shows the current density-voltage (J-V) characteristics of the devices under 100 mW cm⁻² air mass 1.5 global (AM1.5G) irradiation. The resulting short circuit current (J_{sc}) , open circuit voltage (V_{oc}) , fill factor (FF) and PCE values, as determined from the *J*-*V* curves, are summarized in Table 2. It is interesting to note that the addition of the pyridinium salt F8PS as the cathode interlayer of the PSCs resulted in a significant improvement in V_{oc} (0.94 V), while it was only 0.76 V for the bare Al cathode device. Similarly, compared to the initial control device, the introduction of the pyridinium salt as the cathode interlayer led to increments in J_{sc} from 10.53 to 11.25 mA cm⁻², FF from 54% to 62%, and thus, contributing to an overall improvement in PCE from 4.32% to 6.56%.

Recently, Bazan *et al.* reported the post treatment of the preformed bulk heterojunction (BHJ) thin film with ethanol and the PCE increased from 3.9% to 5.1% due to the swelling by the



Fig. 3 Current density–voltage (*J*–*V*) characteristics (a) and external quantum efficiency (EQE) spectra (b) of the devices with various cathode interlayers in the configuration of ITO/PEDOT:PSS/PCDTBT:PC₇₁BM/interlayer/Al.

ethanol that changes the properties of the buried PEDOT:PSS/ BHJ interface.²⁴ To probe the possible effect of the solvent and pyridinium salt, a similar device, only differing in dripping the same volume of ethanol instead of F8PS solution atop of the active layer as solvent treatment procedure before Al deposition, was also fabricated for comparison. Ethanol was spin-coated onto the active layer under the same conditions (the volume of solution/solvent that was dropped on the active layer, wetting time, spin speed, spin time, etc.) taken for the devices containing the developed pyridinium salt. As shown by the filled circles in Fig. 3(a) and the data in Table 2, the ethanol-treated device showed an increased J_{sc} of 10.88 mA cm⁻², V_{oc} of 0.88 V and FF of 58%, and higher PCEs of 5.55%, compared to the device based on the bare Al cathode. As reported by Bazan et al., the wetting time was observed as the key factor that affects the device performance.²⁴ It is worth emphasizing that the wetting time for ethanol atop of the active layer was minimized to the limit of our operation in our experiments, and the performance enhancement was still impressive. However, all the values were not as high as for the device based on the pyridinium salt F8PS. Hence, it can be suspected that the improvement in performance after pyridinium salt deposition may be due to a combination of the effects of ethanol treatment and the presence of the thin pyridinium salt layer.18

To understand the improvement in device performance upon inserting the pyridinium salt cathode interlayer, the external quantum efficiency (EQE) spectra (see Fig. 3(b)) of the PSCs both with and without cathode interlayer were measured. For comparison, the ethanol-treated device was also measured. The integration of the EQE spectra of the three types of PSC devices indicates the different J_{sc} of the corresponding devices. The shapes of the EQE spectra of all the devices were almost identical across the entire wavelength range. Noting that the device with pyridinium salt layer exhibited significant elevation in EQE in the wavelength region of 380–620 nm which reveals a broad photoresponse from 300 to 750 nm, with a maximum value of 64% around 550 nm (Fig. 3b). The highest EQE value of the device with the pyridinium salt cathode interlayer was consistent with the highest J_{sc} and PCE.

To study the influence of the interfacial layer on the morphology of the underlying active layer, atomic force microscope (AFM) under the tapping mode was used to track the surface morphologies of the PCDTBT:PC71BM layer under an inert nitrogen atmosphere (Fig. 4). The surface of PCDTBT:PC71BM was relatively smooth and homogeneous, with a root-mean-square (rms) roughness of 0.57 nm (Fig. 4a). The ethanol-treated surface was slightly rougher (rms roughness = 0.77 nm) and remained homogeneous, as shown in Fig. 4b. The obvious minor changes to the surface topography suggest possible modification of the top metal contact.24 Deposition of the pyridinium salt on the PCDTBT:PC71BM active layer featured increased roughness from 0.57 to 0.68 nm. The increased roughness of the films of the ethanol-treated PCDTBT:PC71BM and the pyridinium salt-coated PCDTBT:PC71BM were beneficial for obtaining better contact with the top metal cathode, which is consistent with the increased Jsc and EQE observed for the corresponding solar cell devices.

Table 2	Summary of the device p	erformance of the BHJ PSC	in the configuration of IT	O/PEDOT:PSS/PCDTBT:PC	₇₁ BM/interlayer/Al
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Interlayer/cathode	$V_{\rm oc}$ (V)	$J_{ m sc}~({ m mA~cm^{-2}})$	FF (%)	PCE (%)	$R_{\rm sh} \left(\Omega \ {\rm cm}^2 \right)$	$R_{\rm s} \left(\Omega \ {\rm cm}^2 \right)$
None/Al	0.76	10.53	54	4.32	$6.3 imes10^4$	15
Ethanol/Al	0.88	10.88	58	5.55	7.7×10^4	9
F8PS/Al	0.94	11.25	62	6.56	$8.7 imes10^4$	7



Fig. 4 Tapping mode surface topographic atomic force microscope (AFM) images (5 μ m × 5 μ m) of the pristine PCDTBT:PC₇₁BM (1 : 4) film (a), the ethanol-treated PCDTBT:PC₇₁BM (1 : 4) film (b) and the PCDTBT:PC₇₁BM (1 : 4) film spin-coated with 5 nm of F8PS (c).

To gain an in-depth understanding of the improvement in device performance after using the pyridinium salt F8PS as the cathode interlayer, the J-V characteristics of the devices in dark conditions were measured and are shown in Fig. 5. In the regime from -2 to 2 V, the reverse and leakage current of the device with the cathode interlayer of pyridinium salt was significantly suppressed compared to that of the bare Al electrode device. It has been reported that the reduced reverse dark current contributed to the $V_{\rm oc}$ enhancement by incorporating WSCPs as the cathode interlayers in PSCs.^{25,26} In this case, in the regime from -2 to 0 V, the largely reduced reverse dark current density of the devices with F8PS as the cathode interlayer may also be beneficial to the greatly increased $V_{\rm oc}$ from 0.76 to 0.94 V compared to the bare Al cathode device. In the regime from 0 to 2 V, the device with the F8PS interlayer exhibits an onset voltage of about 0.6-0.7 V while it is only 0.3-0.4 V for the control device with no treatment, and the ethanol-treated device shows an onset voltage of about 0.5 V, implying that the built-in potential $(V_{\rm bi})$ across the device indeed



Fig. 5 Dark currents of the PCDTBT:PC₇₁BM-based solar cells with various cathode interlayers in the configuration of ITO/PEDOT:PSS/PCDTBT:PC₇₁BM/ interlayer/Al.

increases upon utilization of the F8PS cathode interlayer.12a Although the structural features of the pyridinium salt derivatives are different from the WSCPs, the interface dipoles could be induced by the pyridinium salt on the main chain which has been verified by Kim and coworkers who recently reported non-conjugated polyviologen derivatives as an interfacial layer between the active layer and Al cathode in PSCs and the work function of Al could be reduced upon being modified by the interface dipoles.21b Thus, the increased $V_{\rm bi}$, as well as $V_{\rm oc}$, could be attributed to the interface dipoles generated by F8PS, and the increased electric field could improve charge-transport properties, eliminate the build-up of space charge and reduce recombination loss,^{12a} leading to increased $J_{\rm sc}$ and FF.²⁷ Note that such a high $V_{\rm oc}$ value is one of the best results reported in literature to date for the PSCs based on the active layer of PCDTBT:PC71BM.12,16a,18,19a In addition, the shunt resistances $(R_{\rm sh})$ of the devices based on the bare Al, ethanol/Al, and pyridinium salt/Al, are 6.3, 7.2, and 8.7 Ω cm², respectively, which agrees well with the decreased leakage current and the increased $V_{\rm oc}$ in the devices. Moreover, the series resistances (R_s) of the ethanol-treated and the pyridinium salt-deposited devices are 9 and 7 Ω cm², respectively, which are lower than that of the control device $(15 \Omega \text{ cm}^2)$ based on the bare Al cathode, indicating better diode characteristics were obtained after simple ethanol treatment and deposition of the pyridinium salt as an ETL. As a result, the performance of the device incorporating pyridinium salt as the ETL can be improved, since good solar cells require high $R_{\rm sh}$ and low $R_{\rm s}$.^{18,26}

Conclusions

In summary, a series of water/alcohol-soluble small molecules based on pyridinium salt were successfully synthesized. By simply incorporating an ultra-thin layer of F8PS as the cathode interlayer between the active layer of PCDTBT:PC71BM and the metal cathode, simultaneous enhancements in $V_{\rm oc}$ (from 0.76 to 0.94 V), $J_{\rm sc}$ (from 10.53 to 11.25 mA cm⁻²) and FF (from 54 to 62%) could be achieved, giving a significantly increased PCE from the initial 4.32% to 6.56%. The high $V_{\rm oc}$ is one of the best results reported in literature to date for the PSCs based on the active layer of PCDTBT:PC71BM. Meanwhile, the overall device efficiency was improved from the initial 4.32% for the bare Al device to 5.55% for the device based on the ethanol-treated active layer. Therefore, the improvement in performance after pyridinium salt deposition may be due to the combination of the effects of ethanol treatment and the presence of electrondeficient pyridinium salt layer. Based on these results, the pyridinium salt derivatives would be a promising family of interfacial materials for highly efficient PSCs.

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