Improved performance of inverted polymer solar cells by utilizing alcohol-soluble oligofluorenes as efficient cathode interlayers (Postprint)

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Full Text

Preamble

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Title and Authors

Improved Performance of Inverted Polymer Solar Cells by Utilizing Alcohol-Soluble Oligofluorenes as Efficient Cathode Interlayers

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Abstract

Two star-shaped oligofluorenes with hexakis(fluoren-2-yl)benzene as core have been designed and synthesized, namely Tn0 and Tn1. Diethylamino groups attached to the side chains of fluorene units enable alcohol solubility in both compounds, while additional hydrophobic n-hexyl chains are grafted onto the -extended fluorene arms of Tn1. Power conversion efficiencies (PCE) as high as 8.62% and 8.80% are achieved when utilizing Tn0 and Tn1 as cathode interlayers in inverted polymer solar cells, respectively. The work function of ITO is effectively decreased by introducing the interlayer, resulting in high open-circuit voltage (Voc) of the device. Additionally, the wetting properties of the interlayers can be tuned by modifying the oligofluorenes with -extended structure, and the more hydrophobic interlayer benefits device performance with enhanced short-circuit current density (Jsc) and fill factor (FF).

1. Introduction

Polymer solar cells (PSCs) have attracted extensive attention over the past decade due to their potential applications in flexible, low-cost, and large-area devices through solution processing [1e6]. The power conversion efficiency (PCE) of single-junction PSCs has grown rapidly [7e10]. The inverted device structure exhibits superior efficiency and stability compared with conventional counterparts [11e14]. Conventional structures typically consist of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) and easily oxidized low work function metal cathodes such as Ba and Ca [15e17]. Inverted structures avoid the acidic PEDOT:PSS and low work function metals, resulting in enhanced device stability. Inverted structures also take advantage of desired vertical phase separation with a composition gradient in the active layer [18,19], leading to significant performance improvement.

Since bare indium tin oxide (ITO) is not an ideal cathode due to its high work function that doesn’ t match the lowest unoccupied molecular orbital (LUMO) of the most commonly used acceptor fullerene, hindering effective electron extraction, it is critical to adjust the electrical properties of ITO and improve electron extraction capability. Interfacial modification has proven effective at reducing the work function of ITO and making it suitable for use as a cathode [20,21].

Numerous interlayer materials for PSCs have been investigated [22e26], including metal oxides [27e29], alkali-metal compounds [11,30], fullerene derivatives [31e33], self-assembled molecules (SAMs) [34,35], and alcohol-soluble conjugated or nonconjugated polymers [36,37]. For organic interlayers, specific functional groups such as amino [38], ammonium [39e41], diethanolamino [42], phosphonate [43], and amino oxide [44] are chosen to provide good solubility in methanol and avoid damage from the upper layer during spin-coating. Additionally, the polar groups generate interfacial dipoles, thus reducing the work function of the electrodes, which is considered an important reason for achieving high device performance [17,45].

Recently, some small molecules with well-defined structures have been applied as interlayers in inverted PSCs, achieving excellent device performances [7,8,46e50]. Small molecules with -conjugated structures are particularly attractive due to their easily adjustable conjugation length and precisely tunable properties through chemical structure modification. Compared with linear counterparts, star-shaped conjugated molecules usually exhibit additional advantages guaranteed by their unique structures [51]. Our previous research showed that hexakis(fluoren-2-yl)benzene (HFB) based molecules possess attractive properties such as excellent solubility, film-forming ability, and good thermal stability [52e54]. Additionally, they exhibit high optical transparency in the visible and near-infrared region due to their high energy gaps.

In this article, two star-shaped conjugated oligomers with HFB as core and fluorene as arms (namely Tn0 and Tn1) were designed and synthesized (shown in Scheme 1). Diethylamino groups were grafted onto the C-9 position of the fluorene arms. Tn1 possesses more -extended structures and additional n-hexyl chains in the inner fluorene arms. They were then utilized as electron-collecting interlayers in inverted PSCs. A blend of (6,6)-phenyl-C71-butyric acid methyl ester (PC71BM) and poly[4,8-bis(2-ethylhexyloxyl)-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) was chosen as the active layer to fabricate devices with the configuration of ITO/interlayer/PTB7:PC71BM/MoO3/Al (shown in Scheme 2). The devices achieved a maximum PCE of 8.80%, indicating that these star-shaped oligofluorenes are efficient electron-collecting interlayers in inverted PSCs.

2. Experimental Section

2.1. Materials Preparation

Unless otherwise indicated, all materials were obtained from commercial suppliers and used without further purification. Solvents for synthesis were purified by routine procedures and distilled under dry argon prior to use. The electron donor material PTB7 and electron acceptor PC71BM were purchased from 1-Material Chemscitech and American Dye Source Incorporated, respectively.

2.2. Measurements

^{1}H NMR and ^{13}C NMR spectra were measured on a Mercury-VX300 spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. EI mass spectra were measured on a ZAB 3FeHF mass spectrometer. MALDI-TOF mass spectra were performed on a Bruker

BIFLEX III TOF mass spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer.

Cyclic voltammetry (CV) was carried out in nitrogen-purged acetonitrile (oxidation scan) at room temperature with a CHI voltammetric analyzer. n-Bu PF (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consisted of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudoreference electrode with ferrocenium/ferrocene (Fc/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s^{1}. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. Ultraviolet photoelectron spectroscopy (UPS) was carried out in a Multifunctional X-ray Photoelectron Spectroscope (Kratos AXIS ULTRA DLD) using a He I (21.22 eV) discharge lamp.

The thicknesses of interlayer films were calculated from a combination of UV-vis absorption spectra and step profiler (Dektak150, Veeco). Tapping-mode AFM images were obtained using a scanning probe microscope (Dimension3100V, Veeco and SPM9700, Shimadzu). Contact angle measurements were performed on a video-based optical contact angle measuring instrument (OCA20, Dataphysics Corp.).

2.3. Device Fabrication

ITO-coated glass substrates were cleaned by sonication in detergent, deionized water, acetone, and isopropyl alcohol, then dried with a nitrogen stream followed by UV ozone treatment. The cathode interlayer was deposited by spin-coating from various concentration solutions of Tn0 or Tn1 in methanol at 1000 rpm for 1 min. Subsequently, a photoactive layer of PTB7/PC71BM (10:15, w/w) was spin-coated from chlorobenzene solution with 3% (v/v) 1,8-diiodooctane, resulting in an active layer thickness of 90 nm ± 10 nm. Finally, a 10 nm MoO layer and a 160 nm Al layer were evaporated in sequence through a shadow mask to define the active area of the devices (0.06 cm^2). The anode thickness was monitored during deposition using a crystal thickness monitor (Sycon). Device fabrication was carried out in a nitrogen atmosphere inside a glovebox. The J-V characteristics were recorded with a Keithley 236 source meter. The spectral response was measured with a commercial photomodulation spectroscopy setup (Oriel). A calibrated Si photodiode was used to determine the photosensitivity. PCE was measured under an AM 1.5G solar simulator, with the power of the sun simulation calibrated before measurement using a standard silicon solar cell.

2.4. Synthesis and Characterization

The star-shaped oligofluorenes were synthesized by a modified convergent core-creating approach (Scheme 1). The two key intermediates of 1,2-bis(oligofluoren-2-yl)ethyne were synthesized via palladium-catalyzed one-pot Sonagashira coupling and Suzuki coupling with bromohexyl chains on the fluorene units. The

HFB core was constructed through cobalt-catalyzed [2+2+2] cyclotrimerization reaction, then the bromohexyl groups were transformed to diethylamino groups by a simple nucleophilic substitution reaction to afford the final products Tn0 and Tn1 in high yield. Both Tn0 and Tn1 show good solubility in methanol but are almost insoluble in hexane, dichloromethane, and dichlorobenzene at ambient temperature. This solubility feature makes them easy to purify and suitable for fabricating PSCs via solution-processable methods.

Unless otherwise indicated, all starting materials were obtained from commercial suppliers and used without further purification. Solvents for synthesis were purified by routine procedures and distilled under dry argon prior to use. 2-iodo-9H-fluorene [55], 1,2-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)ethyne [52], and 2-(9,9-bis(6-bromohexyl)-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [56] were prepared according to literature procedures.

1,2-di(9H-fluoren-2-yl)ethyne (A1). To a mixture of 2-iodo-9H-fluorene (4.38 g, 15 mmol), CuI (0.15 g, 0.75 mmol), and Pd(PPh) (0.32 g, 0.45 mmol) were added degassed THF (75 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (13.5 mL). The mixture was stirred for 5 min under argon, then ethynyltrimethylsilane (1.05 mL, 7.4 mmol) and water (0.2 mL, 11 mmol) were quickly added. The mixture was sealed and stirred for 24 h at room temperature. The resulting mixture was poured into water and the solid was collected by filtration. The crude product was boiled three times in chloroform to remove by-products, then the pale yellow product was collected by filtration and used without further purification. MS (EI, m/z): [M] Calcd for C H : 354.1. Found: 354.2.

1,2-bis(9,9-bis(6-bromohexyl)-9H-fluoren-2-yl)ethyne (A2). 1,2-di(9H-fluoren-2-yl)ethyne (1.77 g, 5 mmol) was added batchwise to a mixture of aqueous sodium hydroxide (100 mL, 50%), tetrabutylammonium bromide (0.33 g, 1 mmol), and 1,6-dibromohexane (24.4 g, 100 mmol) at 75 °C. After 12 h, the mixture was cooled to room temperature. After extraction with CH Cl , the combined organic layers were washed successively with water, aqueous HCl (1 M), water, and brine, then dried over Na SO . After removal of the solvent and excess 1,6-dibromohexane under reduced pressure, the residue was purified by silica gel column chromatography using hexane/chloroform (3:1, v/v) as eluent to obtain the product as a white powder (yield: 53%). ^{1}H NMR (300 MHz, CDCl ,): 7.64-7.59 (m, 4H), 7.51-7.43 (m, 4H), 7.28-7.26 (m, 6H), 3.21 (t, J = 6.6 Hz, 8H), 1.92 (t, J = 8.1 Hz, 8H), 1.63-1.54 (m, 8H), 1.17-1.10 (m, 8H), 1.07-0.96 (m, 8H), 0.58-0.51 (m, 8H). ^{13}C NMR (75 MHz, CDCl ,): 150.87, 150.69, 141.63, 140.69, 130.95, 127.91, 127.33, 126.11, 123.06, 121.86, 120.34, 120.03, 90.83, 55.28, 40.52, 34.26, 32.91, 29.32, 28.05, 23.77. MS (MALDI-TOF, m/z): [M] Calcd for C H Br : 1006.2. Found: 1006.1.

1,2,3,4,5,6-hexakis(9,9-bis(6-bromohexyl)-9H-fluoren-2-yl)benzene (A3). To a mixture of 1,2-bis(9,9-bis(6-bromohexyl)-9H-fluoren-2-yl)ethyne (3.0 g, 3 mmol) and dicobaltoctacarbonyl (52 mg, 0.15 mmol) was added degassed 1,4-dioxane (60 mL). The solution was refluxed under argon for 24

h. The resulting mixture was poured into water and the solid was collected by filtration. The crude product was purified by column chromatography using hexane/chloroform (3:1, v/v) as eluent to obtain the product as a white powder (yield: 50%). ^{1}H NMR (300 MHz, CDCl ,): 7.71-7.69 (m, 12H), 7.58-7.54 (m, 12H), 7.36-7.34 (m, 18H), 3.29 (t, J = 6.9 Hz, 24H), 2.00 (t, J = 8.4 Hz, 24H), 1.71-1.61 (m, 24H), 1.24-1.13 (m, 24H), 1.10-1.03 (m, 24H), 0.64-0.58 (m, 24H). ^{13}C NMR (75 MHz, CDCl ,): 150.47, 149.24, 141.21, 140.09, 138.49, 129.68, 126.98, 126.78, 126.48, 122.79, 119.85, 118.01, 54.77, 40.57, 34.40, 33.12, 29.51, 28.09, 23.62. MS (MALDI-TOF, m/z): [M] calcd for C H Br : 3019.5, found: 3018.0.

1,2-bis(9 ,9 -bis(6-bromohexyl)-9,9-dihexyl-9H,9 H-[2,2 -bifluoren]-7-yl)ethyne (B1). To a mixture of 1,2-bis(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)ethyne (1.70 g, 2 mmol) and 2-(9,9-bis(6-bromohexyl)-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.10 g, 5 mmol) were added Pd(PPh) (0.15 g, 0.2 mmol) and K CO (1.38 g, 10 mmol) in THF (20 mL) and water (5 mL). The mixture was refluxed under argon for 24 h. The resulting mixture was poured into water and extracted with chloroform. The combined organic layer was washed with water and dried over Na SO . After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography using hexane/chloroform (1:3, v/v) as eluent to obtain the product (yield: 73%). ^{1}H NMR (300 MHz, CDCl ,): 7.73-7.65 (m, 8H), 7.60-7.51 (m, 12H), 7.27 (s, 6H), 3.19 (t, J = 6.9 Hz, 8H), 2.02-1.98 (m, 16H), 1.61-1.59 (m, 8H), 1.18-1.02 (m, 44H), 0.80-0.65 (m, 24H). ^{13}C NMR (75 MHz, CDCl ,): 152.08, 151.34, 150.80, 141.23, 141.01, 140.66, 139.93, 130.92, 127.38, 127.21, 126.49, 126.25, 123.06, 121.86, 121.50, 120.53, 120.28, 120.06, 91.11, 55.54, 55.29, 40.70, 40.47, 34.12, 32.85, 31.78, 29.97, 29.28, 27.98, 24.05, 23.83, 22.87, 14.35. MS (MALDI-TOF, m/z): Calcd for C H Br : 1670.7; Found: 1671.5.

1,2,3,4,5,6-hexakis(9 ,9 -bis(6-bromohexyl)-9,9-dihexyl-9H,9 H-[2,2 -bifluoren]-7-yl)benzene (B2). To a mixture of B1 (1.04 g, 0.6 mmol) and dicobaltoctacarbonyl (10 mg, 0.03 mmol) was added 1,4-dioxane (12 mL). The solution was refluxed under argon for 24 h. The resulting mixture was poured into water and the solid was collected by filtration. The crude product was purified by column chromatography using hexane/chloroform (3:1, v/v) as eluent to obtain the product as a white powder (yield: 62%). ^{1}H NMR (300 MHz, CDCl ,): 7.72-7.70 (m, 12H), 7.54-7.42 (m, 30H), 7.31-7.29 (m, 18H), 7.19-6.93 (m, 18H), 3.25-3.23 (m, 24H), 1.97-1.86 (m, 48H), 1.65-1.60 (m, 24H), 1.17 (br, 36H), 1.01 (br, 72H), 0.81-0.78 (m, 48H), 0.67 (br, 24H), 0.41 (br, 24H). ^{13}C NMR (75 MHz, CDCl ,): 151.54, 151.15, 150.76, 149.81, 141.33, 141.03, 140.48, 140.27, 140.01, 138.15, 129.64, 127.21, 127.13, 126.66, 126.28, 125.96, 123.00, 121.45, 121.25, 120.07, 119.96, 118.16, 55.19, 54.98, 40.77, 40.40, 34.11, 32.82, 31.79, 30.15, 29.24, 27.93, 23.76, 23.07, 22.93, 14.42. MS (MALDI-TOF, m/z): [M] Calcd for C H Br : 5015.0; Found: 5016.0.

1,2,3,4,5,6-hexakis[9,9-bis(6-(diethylamino)hexyl)-9H-fluoren-2-

yl]benzene (Tn0). To a mixture of A3 (0.77 g, 0.5 mmol) in DMF (10 mL) under Ar atmosphere, 3 mL of diethylamine was added in one portion. The reaction mixture was refluxed with vigorous stirring overnight. After cooling to room temperature, the mixture was poured into ice water and extracted with dichloromethane. The combined organic layer was washed with water and dried over Na SO . After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography using hexane/methanol/triethylamine (100:5:2, v/v/v) to afford Tn0 as a white solid (yield: 85%). ^{1}H NMR (300 MHz, CD OD,): 7.30-6.94 (m, 42H), 2.58-2.51 (m, 48H), 2.29-2.26 (m, 24H), 1.84 (br, 24H), 1.29-1.19 (m, 24H), 1.04-0.99 (m, 72H), 0.90 (br, 48H), 0.13 (br, 24H). ^{13}C NMR (75 MHz, CD OD,): 151.99, 150.37, 142.50, 141.64, 139.81, 131.03, 127.97, 127.82, 123.82, 120.73, 118.90, 55.98, 53.72, 41.61, 31.09, 28.33, 26.87, 24.70, 24.54; MS (MALDI-TOF, m/z): [M] Calcd for C H N : 2924.4; Found: 2924.8.

1,2,3,4,5,6-hexakis(9 ,9 -(6-(diethylamino)hexyl)-9,9-dihexyl-9H,9 H-[2,2 -bifluoren]-7-yl)benzene (Tn1). Tn1 was prepared using a similar procedure as for Tn0, from B2 and diethylamine. The crude product was purified by silica gel column chromatography using hexane/methanol/triethylamine (100:5:1, v/v/v), giving Tn1 as a light yellow solid (yield: 83%). ^{1}H NMR (300 MHz, CD OD,): 7.76-7.71 (m, 12H), 7.53-7.51 (m, 12H), 7.39-7.30 (m, 18H), 2.59-2.56 (m, 48H), 2.43-2.40 (m, 24H), 2.02 (br, 24H), 1.29 (br, 24H), 0.96 (br, 48H), 0.58 (br, 24H). ^{13}C NMR (75 MHz, CD OD,): 152.69, 152.52, 151.89, 151.03, 142.36, 142.02, 141.96, 141.76, 139.87, 134.83, 128.34, 126.71, 124.22, 122.22, 121.05, 56.43, 56.27, 53.45, 41.90, 41.56, 33.10, 33.00, 31.27, 30.68, 28.01, 26.07, 25.08, 24.93, 24.12, 15.19, 15.09. Yield: 86%. MS (MALDI-TOF, m/z): [M] Calcd for C H N O : 4917.9. Found: 4917.6.

3. Results and Discussion

3.1. Photophysical and Electrochemical Properties

UV/vis absorption spectra of Tn0 and Tn1 were recorded in methanol solution and in solid-state films. As shown in Figure 1: see original paper, the absorption spectra of Tn0 and Tn1 showed intense - * absorption bands, which progressively red-shifted from 313 to 340 nm with increasing chain length. The absorption spectra in film state exhibited only slight red-shifts. Due to the highly twisted backbone of the HFB core [52], the optical band gaps (E__g^opt) are calculated to be as high as 3.63 and 3.26 eV for Tn0 and Tn1, respectively. Both compounds possess optical transparency in the visible and near-infrared region.

Cyclic voltammetry (CV) was conducted to probe the electrochemical properties of Tn0 and Tn1, as shown in Figure 1: see original paper. From the onset of oxidation potentials, the highest occupied molecular orbital (HOMO) energy levels were determined to be -5.55 eV and -5.54 eV, respectively. The LUMO (lowest unoccupied molecular orbital) energy levels were -1.92 eV and -2.28 eV, respectively, which were calculated from HOMO and E_g^opt (Table 1).

3.2. UPS Analysis of the Interlayer on ITO

The interfacial properties of Tn0 and Tn1 were investigated by measuring the work function of ITO with and without the interlayer using ultraviolet photoelectron spectroscopy (UPS), as shown in Figure 2: see original paper. The work function of bare ITO was estimated to be -4.41 eV. After deposition of Tn0 and Tn1 on ITO substrates, the secondary electron cut-off shifted toward higher binding energies, and the work function was estimated to be -3.56 eV and -3.83 eV for Tn0- and Tn1-coated ITO substrates, respectively (Figure 2: see original paper). The interlayers with diethylamino groups are considered to generate dipoles at the interface, thus reducing the work function of the electrode. The vacuum level of Tn0-coated ITO shifted more than that of Tn1-coated ITO, indicating Tn0 possesses a larger dipole moment than Tn1. Tn0 and Tn1 have the same pendant diethylamino groups, while Tn1 has a -extended structure, which might result in smaller polarity. The decreased work functions of ITO allow them to form ohmic contacts with the fullerene acceptor, which is an important factor in obtaining high Voc in inverted PSCs. Additionally, the lowered work functions of ITO could increase the built-in potential, which is useful for electron collection and charge separation [17,45].

3.3. Device Performance

To evaluate the performance of Tn0 and Tn1 as cathode collecting interlayers in inverted PSCs, a blend of PC71BM and PTB7 was chosen as the active layer to fabricate devices with the configuration of ITO/interlayer/PTB7:PC71BM/MoO /Al (shown in Scheme 2). Due to the low conductivity of the organic interlayer, the thickness of the interlayer often significantly affects device performance [57]. Investigations on interlayer thickness were carried out using increasing concentrations of Tn0 and Tn1 in methanol, which were spin-coated onto pretreated ITO substrates at 1000 rpm for 1 min. The concentrations were 0.1, 0.4, and 1 mg/mL in methanol, yielding interlayer thicknesses of approximately 1 nm, 3 nm, and 6 nm, respectively. The current density-voltage (J-V) characteristics of the devices under AM 1.5G illumination (100 mW cm ^{2}) and in the dark are shown in Fig. S1, with detailed device parameters summarized in Table S1. Clearly, all devices with Tn0 and Tn1 as cathode interlayers show high PCEs, and device performance depends on interlayer thickness. For both materials, the optimized interlayer thickness was 3 nm. The best performances of the inverted PSCs benefited from remarkably high Voc, Jsc, and FF. The device with Tn1 as the cathode interlayer at 1 nm thickness showed relatively poor performance, attributed to its low fill factor (FF) and low Voc. For both interlayers, further increases in thickness led to inferior device performance with reduced Jsc, which can be attributed to decreased conductivity of the interlayers.

Devices were then fabricated with the optimized thickness for each interlayer.

Control devices with poly[(9,9-bis(3 -(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) as interlayer were also fabricated. The current density-voltage (J-V) characteristics of the devices are shown in [Figure 3: see original paper], and the Jsc, Voc, FF, and PCE data are summarized in .

The reference inverted PSC with bare ITO electrode showed quite low performance with a PCE of 1.18%. After inserting Tn0, Tn1, or PFN interlayer between the ITO electrode and active layer, the inverted PSCs exhibited remarkably enhanced performance with PCE values as high as 8.62%, 8.80%, and 8.46%, respectively. Owing to the interfacial dipole generated by the interlayers, the work function of ITO decreased and better matched the LUMO level of PC71BM. The interface formed ohmic contacts, thus Voc values increased from 0.25 V to 0.74 V for all devices. Additionally, compared with bare ITO, the introduction of interlayers increased the built-in potential and facilitated charge transport and collection, resulting in more balanced charge separation. The FF values increased remarkably from 33.46% to 71.19%, 71.70%, and 71.78%, respectively. The inverted PSCs with Tn0 or Tn1 as interlayer showed even better performance than the PFN-based device under the same conditions, revealing that Tn0 and Tn1 can be efficient cathode interlayers in inverted PSCs.

[Figure 4: see original paper] shows the external quantum efficiency (EQE) spectra of the inverted devices with Tn0 and Tn1 as interlayer. The EQE values remain above 50% over the range of 350-700 nm in both devices, indicating efficient photon-to-electron conversion. The Tn1-based devices showed slightly higher EQE values than Tn0-based devices between 530 and 670 nm, which agrees with Jsc values calculated from the EQE spectra and experimental measurements.

3.4. Wetting Properties of the Interlayers and AFM Analysis of the Active Layers

Tn1-based devices show better performance than Tn0-based devices, benefiting from slightly higher Jsc and FF. Our previous research indicated that the wetting properties of interlayers affect phase separation of the upper active layer in inverted devices [49,58,59], and morphological variation should be responsible for the diverse device performances. To understand this, surface wetting properties of Tn0- and Tn1-coated ITO substrates and surface morphologies of interlayer/active layers were investigated.

The wetting property of each interlayer was studied by measuring the water contact angle on the surface of Tn0- or Tn1-coated ITO substrates. Images of the water drops are shown in [Figure 5: see original paper]. The water contact angle for bare ITO is 24.5°, while for ITO/Tn0 surface it is 16.1°. In contrast, Tn1 exhibited obvious hydrophobic properties, with the water contact angle increasing to 73.8° for ITO/Tn1 surface. The hydrophobic property might be attributed to the -extended structure and additional n-hexyl chains in the inner fluorene arms. The variation tendencies in wetting properties correspond with molecular polarities, exhibiting a structure-property relationship.

Surface morphologies of different interlayers were examined by atomic force microscopy (AFM). As shown in Fig. S2, both surfaces were homogeneous and relatively smooth, indicating HFB-cored molecules possess good film-forming abilities. There were no significant differences in height or phase images between different interlayers. The root mean square (RMS) roughness for Tn0- and Tn1-coated surfaces are 3.24 and 3.06 nm, respectively. Since the roughness of different interlayers was similar, it could not be the reason for diverse device performance.

After spin-coating the PTB7:PC71BM active layer onto pretreated ITO substrates, the morphologies varied depending on different interlayers. As shown in [Figure 6: see original paper], the active layer deposited on hydrophobic Tn1 surface exhibited relatively lower roughness than that on Tn0 surface, and the active layer generated raised islands after deposition on hydrophilic Tn0 surface. The RMS roughness for PTB7:PC71BM on Tn0 and Tn1 surfaces is 2.03 and 1.44 nm, respectively. Additionally, the active layer coated on Tn1 surface showed obvious phase separation with proper domain size and continuous interpenetrating networks. The hydrophobic cathode surface would benefit intimate contact with the active layer, which could better spread out from chlorobenzene solution and consequently achieve better morphology.

The contact angle measurements and AFM images indicate that the wetting properties of the interlayers affect device performance to some extent, and the more hydrophobic surface induces better morphology of the active layer, resulting in enhanced Jsc and FF. Compared with Tn0, Tn1 possesses the same polar pendant group, but its more hydrophobic properties might be attributed to its -extended structure and additional n-hexyl chains in the inner fluorene arms. As our previous research suggested, backbone design is another important factor for realizing efficient interlayers in addition to polar groups.

4. Conclusions

In conclusion, we developed two star-shaped conjugated HFB oligomers, Tn0 and Tn1, and demonstrated that they are efficient interlayers in inverted devices. Owing to diethylamino polar groups, the interlayers generate interfacial dipoles and effectively reduce the work function of ITO. PCE values as high as 8.62% and 8.80% were achieved with Tn0 and Tn1, respectively. Additionally, the more hydrophobic Tn1 cathode benefited the morphology of the upper active layer, resulting in enhanced performance. The well-defined structure and processability in alcohol solution offer great opportunity for commercial use in solar cells. Our research reveals that not only modification of the electrode work function plays an important role in achieving high performance, but also adjustment of the electrode wetting property affects performance to some extent.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Appendix A. Supplementary Data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2015.12.025.

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