

# *N*-Acylidithieno[3,2-*b*:2',3'-*d*]pyrrole-Based Low-Band-Gap Conjugated Polymer Solar Cells with Amine-Modified [6,6]-Phenyl-C61-butyric Acid Ester Cathode Interlayers

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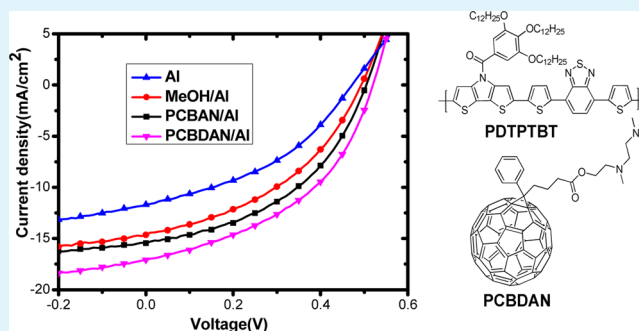
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## S Supporting Information

**ABSTRACT:** Efficient low-band-gap polymers are one key component for constructing tandem solar cells with other higher-band-gap materials to harvest wide absorption of the solar spectrum. The *N*-acylidithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) building block is used for making low-band-gap polymers. It is attractive because of its strong donating ability and relatively low highest-occupied-molecular-orbital level in comparison with the *N*-alkyl DTP building block. However, additional solubilizing groups on the accepting units are needed for soluble donor–acceptor polymers based on the *N*-alkanoyl DTP building block. Combining *N*-benzoyl DTP with a 4,7-dithieno-2,1,3-benzothiadiazole building block, a polymer with a low band gap of 1.44 eV, delivers a high short-circuit current of 17.1 mA/cm<sup>2</sup> and a power conversion efficiency of 3.95%, which are the highest for the devices with DTP-containing materials. Herein, an alcohol-soluble diamine-modified fullerene cathode interfacial layer improved the device efficiency significantly more than the mono-amine analogue.

**KEYWORDS:** polymer solar cells, low-band-gap polymers, *N*-acylidithienopyrrole, amine-modified fullerene, interfacial materials



## INTRODUCTION

Polymer solar cells have attracted broad interest in academic and industry settings as renewable energy sources because of their unique advantages of being light weight and flexible and of having a low cost of fabrication.<sup>1</sup> The highest efficiency solar cells that have been recently reported are tandem solar cells with a power conversion efficiency (PCE) of 10.6 %<sup>2</sup> and single inverted solar cells with an alcohol-soluble conjugated-polymer cathode interfacial layer or a fullerene-modified ZnO cathode interlayer with a PCE of 9.2 and 9.35%, respectively.<sup>3</sup> Tandem solar cells provide an effective way to harvest a broader spectrum of solar radiation by combining two or more solar cells with different absorption profiles to achieve higher PCE values.<sup>2,5–7</sup> Other ways to harvest wide light absorption include the use of a ternary blend composed of two donors with different but complementary absorption properties to the solar spectrum<sup>8–10</sup> as well as reflective tandem solar cells.<sup>11</sup>

One of the significant features of the record tandem solar cell is the novel low-band-gap polymer.<sup>2</sup> There are very few highly efficient low-band-gap polymers (<1.5 eV), and most of them

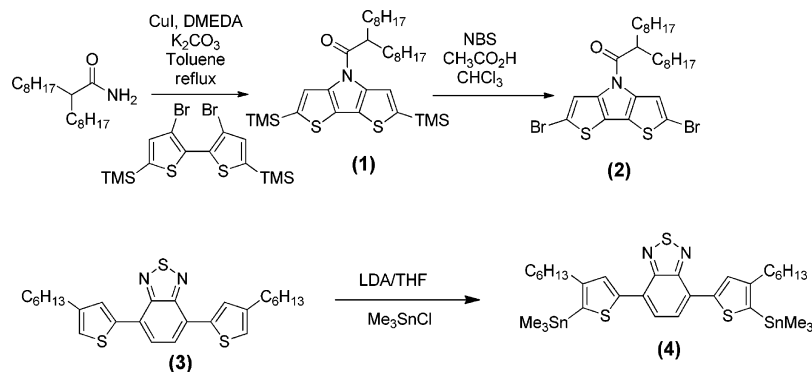
have strong electron-accepting building blocks.<sup>5–7,12–16</sup> As the band gaps of the donor materials become low, the requirements for high-efficiency devices will not be easily achieved. For example, suitable highest-occupied-molecular-orbital (HOMO) and lowest-unoccupied-molecular-orbital (LUMO) levels and high mobility along with sufficient solubility are needed.<sup>17–20</sup> Therefore, the design and synthesis of new materials with low band gaps remains of great importance.

Among the various donor moieties used in donor–acceptor (D–A) polymers, dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) has attracted attention previously. DTP is a fused bithiophene with a bridging nitrogen that is strongly electron-donating and planar. This leads to materials with low band gaps and high mobilities.<sup>21–34</sup> However, DTP-based materials suffer from high HOMO levels and thus low open-circuit voltages ( $V_{oc}$ ) and low PCEs. Recently, *N*-acyl-substituted DTPs were

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Scheme 1. Synthesis of *N*-Alkanoyldithieno[3,2-*b*:2',3'-*d*]pyrrole- and 2,1,3-Benzothiadiazole-Based Monomers

reported, and the introduced carbonyl group was shown to lower the HOMO level.<sup>35</sup> Rasmussen and co-workers have also reported *N*-acyldithieno[3,2-*b*:2',3'-*d*]pyrrole-based oligomeric models to demonstrate further the extent of HOMO energy modulation.<sup>36</sup> Thus, we chose to incorporate this building block into the polymers reported in this work. Changing from *N*-alkanoyl- to *N*-benzoyl-substituted DTP, a polymer with a band gap of 1.44 eV, gives a PCE of 3.95% with the help of an alcohol-soluble fullerene cathode interlayer.

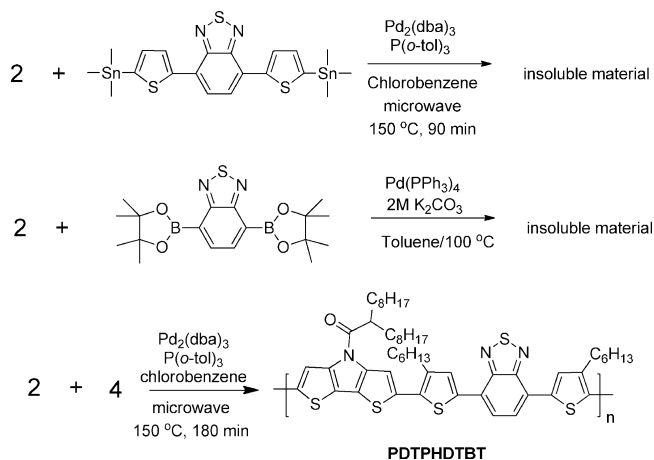
The cathode interfacial material, is one of the key components for the record single-junction solar cell.<sup>3,4</sup> Poly[(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctyl-fluorene)] (PFN) has previously been used as an electron-injection layer for organic light-emitting diodes<sup>37–39</sup> and more recently has been applied to polymer solar cells.<sup>3,37–46</sup> Many different organic cathode interlayers have been reported recently.<sup>47–65</sup> The interfacial dipole formation between an amine and a metal electrode, n-doping of conducting fullerenes, and hole traps accumulation at the electron-collecting electrode are claimed to be the main reasons for the improvement in device performance.<sup>37–65</sup> Recently, we reported two new amine group-modified PCBM derivatives, [6,6]-phenyl-C<sub>61</sub>-butyric acid 2-((2-(dimethylamino)ethyl)-(methyl)amino)-ethyl ester (PCBDAN) and [6,6]-phenyl-C<sub>61</sub>-butyric acid 2-((2-(trimethylammonium)ethyl)-(dimethyl)ammonium)ethyl ester diiodonium, and these cathode interlayers improved the device performance significantly in high-efficiency PSCs.<sup>66</sup> In this work, the diamine-modified interlayer PCBDAN improved the efficiency of low-band-gap polymer solar cells from 2.21 to 3.95%, which is better than a new mono-amine-modified interlayer, [6,6]-phenyl-C<sub>61</sub>-butyric acid dimethylaminoethyl ester (PCBAN), that improved the efficiency to 3.49%. The PCE of 3.95% with a short-circuit current ( $J_{sc}$ ) of 17.1 mA/cm<sup>2</sup> are the highest with DTP materials-based solar cells.<sup>21–34</sup>

## RESULTS AND DISCUSSION

Both *N*-alkanoyl and *N*-benzoyl DTP building blocks were prepared, and polymers from both building blocks were evaluated in solar cells.

***N*-Alkanoyl DTP Building-Block-Based Polymers.** The *N*-alkanoyl DTP monomer **2** was made according to a literature,<sup>35</sup> and the synthetic route is shown in Scheme 1. Polymerization of this electron-donating monomer with two electron-accepting monomers, 4,7-bis(S-(trimethylstannyl)-thiophen-2-yl)-2,1,3-benzothiadiazole and 4,7-bis(4,4,5,5-tetra-methyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole, were

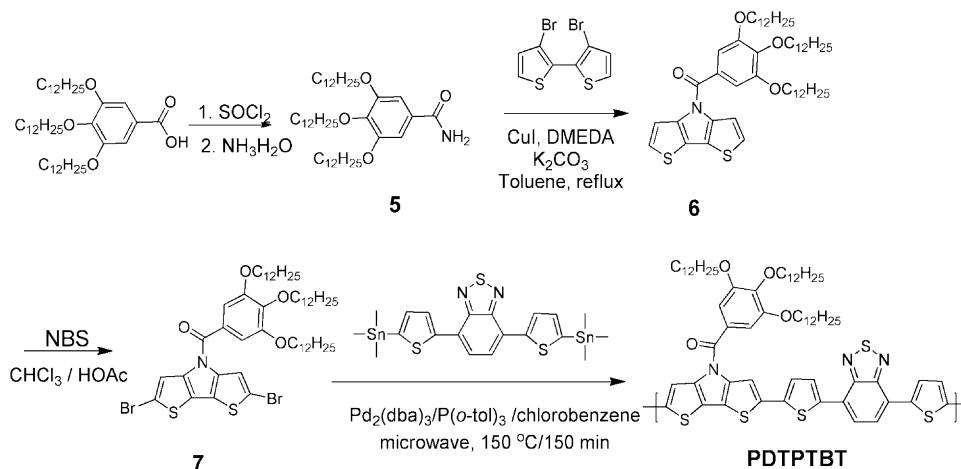
attempted by a Stille coupling reaction and a Suzuki coupling polymerization respectively (Scheme 2). Unfortunately, the

Scheme 2. Materials Based on the *N*-Alkanoyldithieno[3,2-*b*:2',3'-*d*]pyrrole Building Block

resulting materials were not soluble even when the monomer feed ratios for both reactions were changed to 1:1.1. The unbalanced monomer feed ratios should have given low molecular weights for better solubility. To improve the solubility of *N*-alkanoyl DTP-based polymers, a hexyl group was introduced on each thiophene of the accepting unit, and a polymer, PDTPHTBT, was obtained as a soluble material (Scheme 2). Photoelectron spectroscopy in air (PESA) was used to estimate the HOMO level of the polymer.<sup>67–69</sup> PESA has been more often used for estimating the HOMO levels of organic semiconductors in solid state directly, and it provides a simple method in addition to electrochemical methods that usually need an oxygen- and moisture-free environment. The HOMO level of the polymer was measured as 5.00 eV with PESA (see the Supporting Information). From the onset of its UV–vis absorption (see the Supporting Information), the band gap was estimated to be 1.52 eV. The LUMO was thus calculated to be 3.48 eV. The moderate band gap and suitable HOMO and LUMO offsets with PCBM encouraged us to explore its application as a donor material in polymer solar cells. The device structure for evaluating the material was ITO/PEDOT-PSS/PDTPHTBT:PC<sub>61</sub>BM/Ca/Al, where PEDOT:PSS and PC<sub>61</sub>BM represent poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (Baytron-P 4083, Bayer AG) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester,

**Table 1.** Performance of Devices ITO/PEDOT–PSS/PDTPHTBT:PC<sub>61</sub>BM/Ca/Al

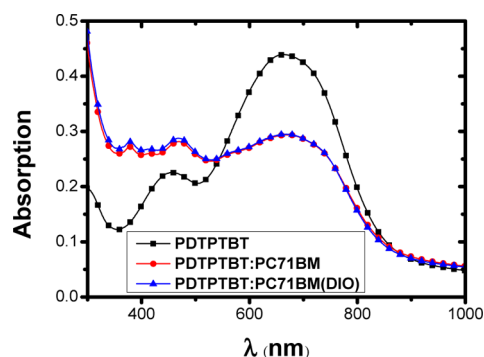
PDTPHTBT:PC <sub>61</sub> BM (by weight)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)	PCE % average (five devices)
1:1	0.60	5.13	37.1	1.14	1.02
1:2	0.58	3.36	35.5	0.69	0.59
1:3	0.52	3.36	32.6	0.57	0.48

**Scheme 3.** Synthesis of *N*-Benzoyldithieno[3,2-*b*:2',3'-*d*]pyrrole-Based Monomer and Polymer PDTPPTBT

respectively. The device performance is listed in Table 1. A relatively high open-circuit voltage,  $V_{oc}$  (0.60 V), and a reasonable PCE (1.14%) were obtained. The  $V_{oc}$  is the highest among the DTP-based materials.<sup>21–34</sup> However, the short-circuit current,  $J_{sc}$  (5.13 mA/cm<sup>2</sup>), and fill factor, FF (37.1%), are relatively low. The introduced hexyl side chains on the accepting units may weaken the intermolecular interaction, lower the charge-transport mobilities, and result in high  $V_{oc}$  but low PCE values.<sup>70</sup> A similar phenomena was found previously with a polyfluorene copolymer having an octylphenyl side chain on the same electron-accepting unit, which delivered a high  $V_{oc}$  of 1.15 V but a relatively low PCE.<sup>71</sup>

It was reported that the introduction of a fraction of short-branch side chains onto long side chain polyfluorenes can form denser films that exhibited both higher charge-carrier mobility and higher photoluminescence efficiency.<sup>72</sup> Our strategy here is to keep the accepting building block unalkylated to increase the interchain interaction and to introduce bulky solubilizing side chain on the donating monomer to maintain the solubility. Thus, monomer 7 was made according to Scheme 3.

***N*-Benzoyl DTP Building-Block-Based Polymer.** The *N*-benzoyl DTP monomer 7 was obtained similarly to the *N*-alkanoyl DTP monomer 2. The polymer, PDTPPTBT, was synthesized through the Stille coupling reaction of monomer 7 with 4,7-bis-(5-(trimethylstannyl)-thiophen-2-yl)-2,1,3-benzothiadiazole, as shown in Scheme 3. The polymer is soluble in common solvents such as chloroform, chlorobenzene, and dichlorobenzene (DCB). The number averaged molecular weight is 21.6 k, with a polydispersity index (PDI) of 1.51, measured by gel-permeation chromatography (GPC). The thermal stability of the polymer was investigated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The polymer shows good thermal stability with 5% weight loss at 389 °C (see the Supporting Information). No thermal-phase transition was detected by differential scanning calorimeter (DSC) from –60 to 300 °C, indicating an amorphous structure. The UV–vis absorption spectrum of the polymer film is shown in Figure 1. From its onset, a band

**Figure 1.** UV–vis absorption spectra of films for pure PDTPPTBT and its blends with PC<sub>71</sub>BM with and without DIO.

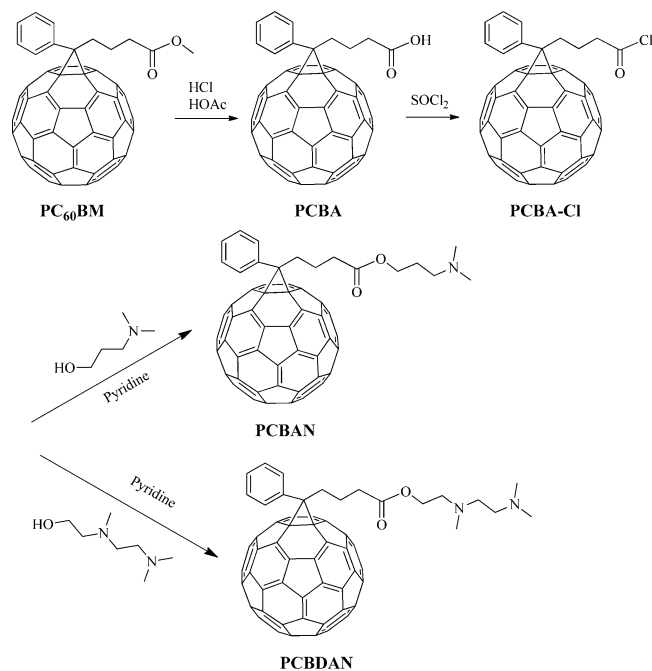
gap of 1.44 eV was estimated. The HOMO level was measured with PESA to be 5.00 eV. This HOMO level is slightly lower than that for a similar polymer that has exactly the same structure except that no carbonyl group is present on the DTP unit (4.9 eV).<sup>30</sup> Although it is hard to directly compare these two values, the literature on other polymers showed that a small HOMO level shift towards lower energy did exist with a carbonyl group.<sup>73</sup>

PDTPPTBT was also evaluated as a donor in polymer solar cells using the same device structure, ITO/PEDOT–PSS/PDTPPTBT:PC<sub>61</sub>BM/Ca/Al. The device performance is summarized in Table 2. A PCE of around 2.0% was obtained for donor-to-acceptor weight ratios of 1:1 and 1:2. The  $J_{sc}$  and FF are now significantly improved compared with the devices on the hexyl-substituted polymer PDTPHTBT.

To explore further the potential of the polymer in solar cells, PC<sub>71</sub>BM was used as an acceptor because it absorbs light in the high-energy range, as can be seen in Figure 1. Amine-modified fullerene cathode interlayers were also evaluated in the low-band-gap polymer solar cells. The interlayers PCBAN and PCBDAN<sup>66</sup> were synthesized via the route shown in Scheme 4.

**Table 2. Performance of Devices ITO/PEDOT–PSS/PDTPBT:PC<sub>61</sub>BM/Ca/Al**

PDTPBT:PC <sub>61</sub> BM (by weight)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)	PCE % average (five devices)
1:1	0.56	7.91	44.9	1.99	1.90
1:2	0.52	8.57	45.0	2.01	1.93
1:3	0.50	7.19	41.8	1.50	1.41

**Scheme 4. Synthesis of [6,6]-Phenyl-C<sub>61</sub>-butyric Acid Dimethylaminoethyl Ester (PCBAN) and PCBDAN**

The device structure ITO/PEDOT–PSS/PDTPBT:PC<sub>71</sub>BM/interlayer/Al was used. Table 3 summarizes the device performance with and without the interlayers. Devices prepared using a methanol treatment only, where methanol was spin-coated onto the blend films, were also prepared for comparison. 1,8-Diiodooctane (DIO) has also been used as a solvent additive in the active layer to improve device performance.<sup>74</sup> DIO (0.5%) in the blend of PDTPBT:PC<sub>71</sub>BM gave the best device, with improved parameters such as V<sub>oc</sub>, J<sub>sc</sub>, FF, R<sub>s</sub>, and R<sub>sh</sub> as well as the highest PCE of 2.21%, which is 20% higher than the control device without DIO. The addition of DIO did not red shift the absorption of the blend film, as shown in Figure 1. This

**Table 3. Performance of Devices ITO/PEDOT–PSS/PDTPBT:PC<sub>71</sub>BM (1:1 wt)/Interlayer/Al**

interlayer	DIO (%)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)	PCE % average (ten devices)	R <sub>sh</sub> (kΩ cm <sup>2</sup> ) <sup>a</sup>	R <sub>s</sub> (Ω cm <sup>2</sup> ) <sup>b</sup>
none	no	0.46	11.2	36.2	1.86	1.78	3.01	17.6
none	0.5	0.47	11.7	40.4	2.21	2.11	3.33	16.0
none	1	0.49	10.5	37.8	1.95	1.82	3.16	16.3
none	2	0.49	7.73	43.7	1.66	1.54	2.67	17.3
MeOH	0.5	0.49	14.6	41.9	3.01	2.93	5.08	3.33
PCBAN	0.5	0.50	15.4	45.1	3.49	3.37	5.11	2.86
PCBDAN	0.5	0.52	17.1	44.4	3.95	3.81	5.36	1.94

<sup>a</sup>Shunt resistance, R<sub>sh</sub>, was measured from dark currents from slopes at 0 V <sup>b</sup>Series resistance, R<sub>s</sub>, was measured from dark currents from slopes at 2 V.

optimized conditions with DIO as an additive were used to study the effects of the methanol treatment and fullerene interlayers. Methanol treatment improved all of the parameters such as V<sub>oc</sub>, J<sub>sc</sub>, FF, and PCE, the PCBAN interlayer further enhanced all of the parameters, and the most significant improvement was achieved with a PCBDAN interlayer. With a PCBDAN interlayer, V<sub>oc</sub> increased from 0.47 to 0.52 V, FF increased from 40.4 to 44.4%, R<sub>s</sub> reduced from 16.0 to 1.94 Ω cm<sup>2</sup>, R<sub>sh</sub> increased from 3.33 to 5.36 kΩ cm<sup>2</sup>, J<sub>sc</sub> increased from 11.7 to 17.1 mA/cm<sup>2</sup> (which is extraordinarily high), and the PCE increased from 2.21 to 3.95%. To the best of our knowledge, the PCE and J<sub>sc</sub> values are the highest among devices based on the DTP-containing materials,<sup>27–34</sup> showing that both the low-band-gap polymer and the PCBDAN interlayer are promising for application in PSCs.

The hole mobilities of the pure polymer film and the blend with or without interlayer modification processed with 0.5% DIO were approximated using space-charge-limited current-voltage measurements of hole-only devices,<sup>75</sup> and the results are summarized in Table 4. The hole mobility increased from

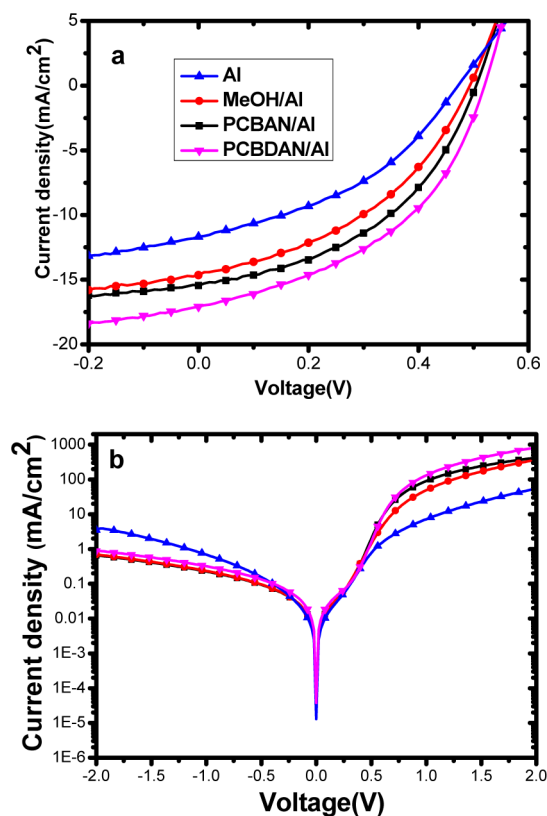
**Table 4. Hole Mobilities of the Devices ITO/PEDOT–PSS (38 nm)/Polymer Film (95 nm)/with or without Interlayer/MoO<sub>3</sub> (10 nm)/Ag (100 nm)**

films	interlayer	hole mobility (cm <sup>2</sup> /(V s))
PDTPBT	none	9.01 × 10 <sup>-5</sup>
PDTPBT:PC <sub>71</sub> BM	none	2.06 × 10 <sup>-4</sup>
PDTPBT:PC <sub>71</sub> BM	MeOH	2.87 × 10 <sup>-4</sup>
PDTPBT:PC <sub>71</sub> BM	PCBAN	4.87 × 10 <sup>-4</sup>
PDTPBT:PC <sub>71</sub> BM	PCBDAN	8.70 × 10 <sup>-4</sup>

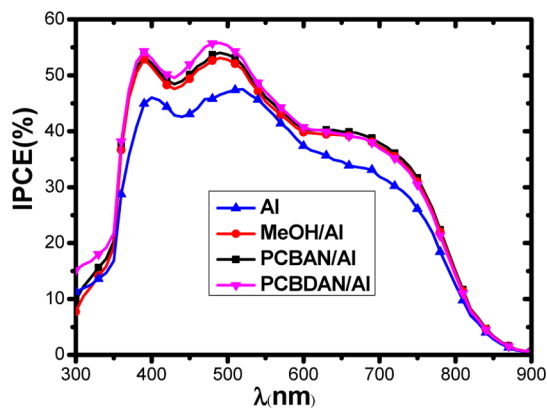
9.01 × 10<sup>-5</sup> cm<sup>2</sup>/(V s) for the pure polymer film to 8.70 × 10<sup>-4</sup> cm<sup>2</sup>/(V s) with PCBDAN interlayer. The sequence of the hole mobility matches the increase of the efficiency of the devices. It was reported that the electron mobility remains similar but the hole mobility increases with the interlayer modification.<sup>45,49</sup> The increased hole mobility could balance the charge transport and reduce the build-up of space charges and charge recombination, improving the device efficiency.

To understand the effects of the interfacial modification, four types of devices were compared that were all based on an active layer with 0.5% DIO additive. The current density versus voltage characteristics under illumination and dark are shown in Figure 2, and the incident photon to current efficiency (IPCE) is shown in Figure 3. From the dark currents in Figure 2b, it is evident that the built-in potentials are slightly increased and the leak currents reduced with the interfacial treatments. It has been reported that the amines or methanol treatment could





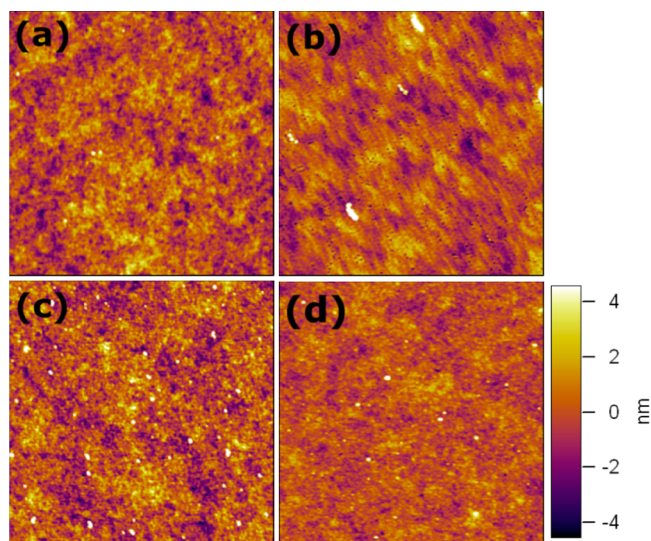
**Figure 2.** Current density versus voltage characteristics of devices ITO/PEDOT-PSS/PDTPBT:PC<sub>71</sub>BM/interlayer/Al under AM 1.5G (a) and dark (b).



**Figure 3.** IPCE of devices ITO/PEDOT-PSS/PDTPBT:PC<sub>71</sub>BM/interlayer/Al.

form surface dipoles or interfacial dipoles with Al and help electron collection from the Al cathode.<sup>3,37–56,76,77</sup> Interfacial dipoles could also work in the cells produced here. The topography and surface roughness of the films were studied by atomic force microscopy and are shown in Figure 4. The root-mean-square (rms) roughness of the blend film changed from 1.12 to 0.76 nm after the methanol treatment, whereas the coating of PCBAN and PCBDAN made it a little bit rougher (0.98 and 0.84 nm, respectively) than the methanol treatment, which probably indicates some coverage of the of the interlayers on top of the active layer.

We note that the  $V_{oc}$  for the PDTPBT:PC<sub>71</sub>BM-based device with the highest PCE of 3.95% is 0.52 V. This  $V_{oc}$  is not significantly higher than solar cells based on an analogue



**Figure 4.** Surface morphology AFM images: (a) without interlayer, (b) with methanol treatment, (c) with PCBAN interlayer, and (d) with PCBDAN. The scan area is  $5 \times 5 \mu\text{m}^2$ , and the scan rate is 0.86 Hz.

polymer without the carbonyl group.<sup>30</sup> In that polymer-based solar cell, the  $V_{oc}$  varies from 0.394 to 0.511 V, depending on processing solvents and polymer/PCBM ratio in the active blend.<sup>30</sup> The  $V_{oc}$  is 0.436 V when DCB was used.<sup>30</sup> In our devices, we always used DCB as the solvent, and the  $V_{oc}$  varies from 0.46 to 0.56 V, depending on the donor/acceptor ratio, interlayers, cathodes, and the amount of the processing additive DIO.  $V_{oc}$  usually relates to the HOMO level of donor polymers. However, there are many factors that could determine the  $V_{oc}$ . For example, it was reported that strong intermolecular interaction in donor materials could result in a lower  $V_{oc}$  but a high  $J_{sc}$ .<sup>70</sup> Our *N*-alkanoyl-substituted DTP materials have solubility issues, whereas the *N*-alkyl analogues in the literature are soluble.<sup>25</sup> This may indicate that *N*-acyl-substituted materials have stronger intermolecular interaction and thus  $V_{oc}$  is not enhanced significantly if the lower of HOMO level does exist with the carbonyl group. Of course, charge mobility, morphology, charge recombination, and other factors could all affect the  $V_{oc}$ . However, the  $J_{sc}$  is relatively high, but FF is still low. The factors affecting the FF could be complicated, but the low  $V_{oc}$  could be one of the reasons.<sup>78</sup> Further molecular engineering such as the introduction of electron-withdrawing atoms or groups and side-chain modification could bring down the HOMO level further to enhance the  $V_{oc}$  and the overall performance.

## CONCLUSIONS

By modifying the side-chain structure of the *N*-acyldithieno-[3,2-*b*:2',3'-*d*]pyrrole-based polymers, we obtained a soluble polymer with a band gap of 1.44 eV that gave a PCE of 3.95 % and a very high  $J_{sc}$  of 17.1 mA/cm<sup>2</sup>. Therefore, *N*-acyldithieno-[3,2-*b*:2',3'-*d*]pyrrole could become one of the donor building blocks that form highly efficient low-band-gap photovoltaic materials and has great potential for application in tandem solar cells. In addition, the diamine-modified fullerene PCBDAN could be used as the cathode interlayer in various active blends in general. Because of its structural similarity with the acceptor PCBM, some other interesting properties could be expected, and this work is in progress.

## EXPERIMENTAL SECTION

**Materials.** 3,4,5-Tris(dodecyloxy)benzoic acid,<sup>79</sup> 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)-2,1,3-benzothiadiazole,<sup>80,81</sup> 4,7-bis(4-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (3),<sup>82</sup> PCBA,<sup>83</sup> PCBA-Cl,<sup>83</sup> and PCBDAN<sup>66</sup> were synthesized according to literature methods.

***N*-(2-Octyldecanoyl)-2,6-bis(trimethylsilyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (1).** The compound was synthesized using a modified procedure described in the literature.<sup>35</sup> To a 100 mL round-bottomed flask were added potassium carbonate (15.0 mmol, 2.07 g), *N,N'*-dimethylethylenediamine (DEMDA, 0.22 mL, 2.0 mmol), and copper(I) iodide (0.50 mmol, 95 mg). Then toluene (20 mL) was injected under an argon atmosphere. The mixture was stirred for about 30 min, and then 2-octyldecanamide (6.00 mmol, 1.70 g) was added followed by 3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (5.00 mmol, 2.34 g). The mixture was heated and stirred for 24 h just below reflux temperature and then was cooled to room temperature. The mixture was quenched with water and extracted with hexane. The organic layers were combined, dried, and purified by column chromatography (petroleum eluent) to give the product (1.04 g, yield 38.0%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 7.90 (s, 1H), 7.24 (s, 1H), 3.35–3.29 (m, 1H), 1.92–1.84 (m, 2H), 1.68–1.61 (m, 2H), 1.39–1.34 (m, 4H), 1.28–1.21 (m, 20H), 0.84 (t, *J* = 7.0 Hz, 6H), 0.36 (s, 18H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ): 173.36, 146.36, 143.11, 140.96, 140.37, 127.31, 126.26, 124.10, 120.87, 45.11, 32.11, 32.03, 30.06, 29.66, 29.46, 27.71, 22.84, 14.29, 0.12 ppm.

**2,6-Dibromo-*N*-(2-octyldecanoyl)-dithieno[3,2-*b*:2',3'-*d*]pyrrole (2).** To a solution of compound 1 (2.018 g, 3.42 mmol) in 30 mL of CHCl<sub>3</sub>/AcOH (1:1 v/v) was added NBS (1.25 g, 7.01 mmol) portion by portion at 0 °C under an argon atmosphere. The mixture was stirred for about 3 h. To this, 30 mL of water was added, the mixture was extracted with DCM three times, and the organic layers were combined and washed with water, dried over anhydrous magnesium sulphate, and purified by column chromatography (eluent petroleum) to give a white solid. The yield was 97%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.80 (s, 1H), 7.24 (s, 1H), 3.19–3.12 (m, 1H), 1.86–1.80 (m, 2H), 1.66–1.53 (m, 2H), 1.30–1.20 (m, 24H), 0.84 (t, *J* = 6.8 Hz, 6H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 173.07, 140.29, 137.54, 121.20, 118.59, 111.80, 45.03, 32.06, 32.00, 29.95, 29.54, 29.41, 27.31, 22.85, 14.31 ppm. HRMS calcd for C<sub>26</sub>H<sub>37</sub>Br<sub>2</sub>NOS<sub>2</sub>, 603.0658; found, 603.0655.

**4,7-Bis(4-hexyl-5-(trimethylstannyl)thiophen-2-yl)-2,1,3-benzothiadiazole (4).** Ten milliliters of anhydrous THF was added into a 100 mL round-bottomed flask under an argon atmosphere, and the mixture was cooled to –78 °C. LDA (3.0 equiv, 20.28 mmol) was added, and the solution was stirred for 30 min. Compound 3 (1.00 eq, 6.67 mmol, 3.17 g) was added in one portion, and the mixture was stirred for 1 h, then warmed to room temperature, stirred for 30 min, and cooled to –78 °C again. Trimethylchlorostannane (4.00 equiv, 27.0 mmol) was added dropwise, and the solution was stirred for 30 min at this temperature. The solution was warmed to room temperature and was kept stirring for 3 h. The mixture was quenched with water and extracted with ethyl acetate, washed with an aqueous potassium fluoride solution, and dried over anhydrous magnesium sulphate, and the solvents were removed under reduced pressure. The crude grease was recrystallized from ethanol, and solid was obtained (yield 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.06 (s, 2 H), 7.80 (s, 2 H), 2.66 (t, *J* = 8.0 Hz, 4 H), 1.68 (m, 4 H), 1.40–1.29 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 6 H), 0.42 (s, 18 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 152.88, 151.23, 144.75, 134.72, 130.13, 126.04, 125.86, 33.25, 32.39, 32.02, 29.60, 22.86, 14.32, –7.58 ppm.

**3,4,5-Tris(dodecyloxy)benzamide (5).** To a 150 mL round-bottomed flask were added 3,4,5-tris(dodecyloxy)benzoic acid (25.0 mmol, 16.88 g) and 50 mL of thionyl chloride. The mixture was stirred at room temperature overnight. The excess thionyl chloride was distilled off under vacuum to give the acyl chloride. The acyl chloride was dissolved in 25 mL of dry acetonitrile, and 50 mL of an aqueous ammonium hydroxide solution (25 %) was added dropwise at 0 °C. The mixture was stirred for 2 h and was then extracted with ethyl acetate (300 mL). The organic phase was washed with an aqueous

sodium hydroxide solution and dried over magnesium sulphate, and the solvents were removed under reduced pressure. The white solid product was obtained after recrystallization with ethyl acetate and petroleum ether (15.0 g, 89.0%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 6.98 (s, 2 H), 5.89 (b, 1 H), 5.47 (b, 1 H), 3.99–3.96 (m, 6 H), 1.81–1.67 (m, 6 H), 1.46–1.40 (m, 6 H), 1.28–1.24 (m, 48 H), 0.86 (t, *J* = 8.0 Hz, 9 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 169.53, 153.28, 141.87, 128.37, 106.39, 73.74, 72.08, 69.61, 32.14, 30.53, 29.96, 29.94, 29.91, 29.87, 29.85, 29.79, 29.60, 29.58, 26.29, 22.90, 14.32 ppm.

***N*-(3,4,5-Tris(dodecyloxy)benzoyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (6).** To a 100 mL round-bottomed flask under an argon atmosphere were added potassium carbonate (18.0 mmol, 2.48 g), DMEDA (1.20 mmol, 106 mg), copper(I) iodide (1.20 mmol, 229 mg), and then 20 mL of dry toluene by injection. The mixture was stirred for 30 min, and 3,4,5-tris(dodecyloxy)benzamide (6.60 mmol, 4.45 g) was added followed by 3,3'-dibromo-2,2'-bithiophene (6.00 mmol, 1.94 g). The reaction mixture was heated to just below reflux for 24 h and was then cooled to room temperature, quenched with water, and extracted with hexane. The combined organic layers were dried over magnesium sulphate and purified by column chromatography with petroleum ether to give the product (1.76 g, 35%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.10 (d, *J* = 6.0 Hz, 2 H), 6.92 (d, *J* = 6.0 Hz, 2 H), 6.91 (s, 2 H), 4.05 (t, *J* = 6.8 Hz, 2 H), 3.92 (t, *J* = 6.4 Hz, 4 H), 1.80–1.73 (m, 6 H), 1.51–1.18 (m, 54 H), 0.88–0.84 (m, 9 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 166.92, 153.43, 143.21, 141.62, 128.84, 124.20, 121.56, 116.68, 107.40, 73.87, 69.47, 32.17, 32.15, 30.58, 29.99, 29.97, 29.93, 29.91, 29.88, 29.84, 29.83, 29.62, 29.58, 29.44, 26.32, 26.24, 22.93, 22.92, 14.34 ppm.

**2,6-Dibromo-*N*-(3,4,5-tris(dodecyloxy)benzoyl)dithieno[3,2-*b*:2',3'-*d*]pyrrole (7).** Solid NBS (4.27 mmol, 0.76 g) was added slowly to a solution of compound 6 (2.03 mmol, 1.70 g) in 30 mL of CHCl<sub>3</sub>/AcOH (1:1) at 0 °C under an argon atmosphere. The mixture was stirred for 3 h, and 30 mL of water was added. The aqueous layer was extracted with dichloromethane three times, and the combined organic layers were washed with water, dried over anhydrous magnesium sulphate, and purified by column chromatography (petroleum ether) to give a white solid (1.04 g, yield 52%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 6.95 (s, 2 H), 6.87 (s, 2 H), 4.06 (t, *J* = 6.4 Hz, 2 H), 3.94 (t, *J* = 6.4 Hz, 4 H), 1.81–1.73 (m, 6 H), 1.51–1.16 (m, 54 H), 0.88–0.84 (m, 9 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 166.46, 153.51, 142.19, 140.01, 127.77, 121.11, 119.50, 111.48, 107.63, 73.92, 69.58, 32.17, 32.15, 30.56, 30.05, 29.98, 29.97, 29.96, 29.92, 29.88, 29.84, 29.81, 29.74, 29.62, 29.59, 29.56, 29.41, 26.30, 26.24, 22.92, 14.35 ppm. HRMS calcd for C<sub>51</sub>H<sub>79</sub>Br<sub>2</sub>NOS<sub>2</sub>, 993.3786; found, 993.3795.

**PDTPTBT.** Compound 7 (497 mg, 0.500 mmol), 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)-2,1,3-benzothiadiazole (313 mg, 0.500 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (11.5 mg, 5 mol %), and P(*o*-tol)<sub>3</sub> (15.2 mg, 10 mol %) were added to a 5 mL microwave reaction vial. The vial was transferred to a glove box and sealed after chlorobenzene (3 mL) was added. The vial was then placed into a microwave reactor and heated at 150 °C for 150 min with stirring. The end-capping reagent 2-tributyltinthiophene (19 mg, 10 mol %) was added and heated at 150 °C for 15 min in the microwave reactor. Finally, bromobenzene (11.8 mg, 15 mol %) was added, and the vial was heated for 15 min at 150 °C in the microwave reactor again to complete the reaction. After cooling to room temperature, the mixture was precipitated into a mixture of methanol (250 mL) and hydrochloric acid (25 mL). The polymer was filtered off and dried under vacuum. The polymer was washed via Soxhlet extraction with methanol, acetone, ethyl acetate, and then petroleum ether. The polymer was collected and dried under vacuum to yield a black solid (528 mg, 93%). GPC (in chloroform): *M*<sub>w</sub> = 32 700; PDI = 1.51. <sup>1</sup>H NMR (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 150 °C, δ): 7.17 (br, 10 H), 4.27 (br, 6 H), 1.98 (br, 6 H), 1.37 (br, 54 H), 0.96 (br, 9 H).

**PDTPTBT.** The synthesis procedure is similar to that for PDTPTBT except that the reaction time is 180 min. The yield was 60%. GPC (in chloroform): *M*<sub>w</sub> = 27 600; PDI = 1.84. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.5–8.1 (br), 3.35 (s), 2.5–3.0 (br), 0.5–2.1 (m).



**PCBAN.** A solution of PCBA-Cl (0.10 g, 0.098 mmol), 3-(dimethylamino)-1-propanol (0.041 g, 0.39 mmol), and pyridine (0.3 mL) in dry toluene (30 mL) was stirred at room temperature for 24 h. After removal of the solvent under reduced pressure, the residue was purified by neutral aluminum oxide column chromatography using chloroform as the eluent to give a brown solid PCBAN (0.09 g, 93%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 1.75–1.85 (m, 2H), 2.14–2.28 (m, 8H), 2.25–2.35 (m, 2H), 2.49 (t, 2H,  $J = 6.0$  Hz), 2.85–2.93 (m, 2H), 4.12 (t, 2H,  $J = 6.0$  Hz), 7.41–7.48 (m, 1H), 7.49–7.58 (m, 2H), 7.93 (d, 2H,  $J = 8.0$  Hz).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 22.6, 27.1, 33.9, 34.3, 45.6, 52.1, 56.4, 63.1, 80.1, 128.4, 128.6, 132.3, 136.9, 137.7, 138.2, 140.9, 141.2, 142.28, 142.30, 142.35, 142.4, 143.09, 143.15, 143.19, 143.29, 143.9, 144.2, 144.6, 144.7, 144.82, 144.85, 144.95, 145.20, 145.25, 145.31, 145.36, 146.0, 148.0, 149.0, 173.2. MALDI-TOF-MS: calcd for  $\text{C}_{76}\text{H}_{23}\text{NO}_2$ , 981.2; found  $[\text{M} + \text{H}]^+$ , 981.8.

**Instrumentation.**  $^1\text{H NMR}$  and  $^{13}\text{C NMR}$  spectra were measured on a Bruker DMX-400 spectrometer or a Bruker BioSpin Av500 with chloroform-*d* or  $\text{C}_2\text{D}_2\text{Cl}_4$  as the solvents. For  $^1\text{H NMR}$ ,  $\text{CDCl}_3$  ( $\delta = 7.24$  ppm) and  $\text{C}_2\text{D}_2\text{Cl}_4$  ( $\delta = 6.00$  ppm) were used as internal standards, and data are reported as follows: chemical shift, integration, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet, and *br* = broad), and coupling constant (Hz). For  $^{13}\text{C NMR}$ ,  $\text{CDCl}_3$  ( $\delta = 77.23$  ppm) was used as an internal standard, and spectra were obtained with complete proton decoupling. High-resolution mass spectra were obtained either with a Thermo Scientific Q Exactive FTMS employing an ASAP probe or with a Bruker autoflex III MALDI TOF/TOF MALDI mass spectrometer. Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen flow rate of  $30\text{ mL}/\text{min}$ . Differential scanning calorimetry (DSC) was conducted on a Mettler Toledo DSC821e analyzer. Molecular weights of the polymers were measured by gel-permeation chromatography (GPC) using a Waters 2695 separations module with a Waters 2414 refractive index detector and a Waters 2996 photodiode array detector, a series of four Polymer Laboratories PLGel columns ( $3 \times 5\ \mu\text{m}$  Mixed-C and  $1 \times 3\ \mu\text{m}$  Mixed-E), and Empower Pro software. The molecular weights were calibrated with narrow polydispersity polystyrene standards (Polymer Laboratories EasiCal, MW from 264 to 256 000), and molecular weights are reported as polystyrene equivalents based on the refractive index detector using chloroform as the eluent at a rate of  $1.0\text{ mL}/\text{min}$  at  $30^\circ\text{C}$ . UV-vis spectra were measured with a Hewlett Packard Model 8453 UV-vis spectrophotometer. The HOMO levels of the films were measured by photo-electron spectroscopy in air (PESA) with a Riken Keiki AC2. A light density of  $5\text{ nW}$  was used. The roughness analysis and atomic force microscopy (AFM) images were carried out on MFD-3D AFM instrument. The thickness of the active layer was determined by an Ambios Tech. XP-2 profilometer. Current density-voltage (*J*-*V*) characteristics of the devices were measured using a Keithley 2410 source meter unit. Solar-cell performance was measured under an Air Mass 1.5 Global (AM 1.5 G) Oriel solar simulator fitted with a 1000 W Xe lamp that was filtered to give an output of  $100\text{ mW}/\text{cm}^2$  in a glove box. The incident photon to current efficiency (IPCE) spectra were measured using an Oriel 150 W Xe lamp coupled to a monochromator and an optical fibre. The IPCE was calibrated with a standard, unfiltered Si cell.

**Devices Fabrication.** Two device structures were used: ITO/PEDOT:PSS(38 nm)/polymer:PC<sub>61</sub>BM (95 nm)/Ca(20 nm)/Al(100 nm) or ITO/PEDOT:PSS(38 nm)/polymer:PC<sub>71</sub>BM (95 nm)/with or without interlayer/Al(100 nm). ITO substrates were cleaned with a neutral detergent solution, deionized water, acetone, and isopropyl alcohol sequentially. They were then treated with UV/ozone at  $30^\circ\text{C}$  for 10 min. The PEDOT:PSS layer (about 38 nm) was spin-coated onto the substrates and annealed at  $150^\circ\text{C}$  for 10 min in air. After that, the devices were transferred to a glove box where the active layers were spin-coated at 700 rpm for 90 s onto the PEDOT:PSS layer from blend solutions of the polymers and fullerene derivatives in dichlorobenzene. Before evaporation of 100 nm of Al at a pressure below  $2 \times 10^{-6}$  Pa, 20 nm Ca was thermally deposited. In the case of the methanol treatment or interlayer modification, methanol or

PCBAN and PCBDAN solutions (0.1 mg/mL in methanol with a trace amount of acetic acid) was spin-coated at 3000 rpm for 30 s on top of the active layer, and no calcium was evaporated. For the hole-only device, a layer of 10 nm  $\text{MoO}_3$  was thermally evaporated onto the active layer at a rate of  $0.2\ \text{\AA}/\text{s}$  followed by a layer of 100 nm silver at  $3\ \text{\AA}/\text{s}$  at a pressure below  $2 \times 10^{-6}$  Pa. A mask defined the active area of the solar-cell device as  $10\text{ mm}^2$ .

## ■ ASSOCIATED CONTENT

### Supporting Information

NMR and MS of the compounds, PESA of the two polymers, TGA and DSC graphs of PDTPTBT, *J*-*V* curves of the hole-only devices, and detail optimization of devices with Al as the cathode. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789–1791.
- (2) You, J. B.; Dou, L. T.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, H. C.; Gao, J.; Li, G.; Yang, Y. *Nat. Commun.* **2013**, *4*, 1446.
- (3) He, Z.; Zhong, Z.; Su, S.; Xu, M.; Wu, H.; Cao, Y. *Nat. Photon.* **2012**, *6*, 591–595.
- (4) Liao, S. H.; Jhuo, H. J.; Cheng, Y. S.; Chen, S. A. *Adv. Mater.* **2013**, *25*, 4766–4771.
- (5) Hadipour, A.; Boer, B.; Wildeman, J.; Kooistra, F. B.; Hummelen, J. C.; Turbiez, M. G. R.; Wienk, M. M.; Janssen, R. A. J.; Blom, P. W. M. *Adv. Funct. Mater.* **2006**, *16*, 1897–1903.
- (6) Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T. Q.; Dante, M.; Heeger, A. J. *Science* **2007**, *317*, 222–225.
- (7) Dou, L. T.; You, J. B.; Yang, J.; Chen, C. C.; He, Y. J.; Murase, S.; Moriarty, T.; Emery, K.; Li, G.; Yang, Y. *Nat. Photon.* **2012**, *6*, 180–185.
- (8) Yang, L. Q.; Zhou, H. X.; Price, S. C.; You, W. J. *Am. Chem. Soc.* **2012**, *134*, 5432–5435.
- (9) Khlyabich, P. P.; Burkhart, B.; Thompson, B. C. *J. Am. Chem. Soc.* **2012**, *134*, 9074–9077.
- (10) Singh, T. B.; Chen, X.; Wong, W. W. H.; Ehlig, T.; Kempainen, P.; Chen, M.; Watkins, S. E.; Winzenberg, K. N.; Holdcroft, S.; Jones, D. J.; Holmes, A. B. *Appl. Phys. A* **2012**, *108*, S15–S20.
- (11) Tvingstedt, K.; Andersson, V.; Zhang, F.; Inganäs, O. *Appl. Phys. Lett.* **2007**, *91*, 123514-1–123514-3.

- (12) Dou, L.; Chen, C. C.; Yoshimura, K.; Ohya, K.; Chang, W. H.; Gao, J.; Liu, Y.; Richard, E.; Yang, Y. *Macromolecules* **2013**, *46*, 3384–3390.
- (13) Huo, L.; Hou, J.; Chen, H. Y.; Zhang, S.; Jiang, Y.; Chen, T. L.; Yang, Y. *Macromolecules* **2009**, *42*, 6564–6571.
- (14) Wang, E.; Ma, Z.; Zhang, Z.; Vandewal, K.; Henriksson, P.; Inganas, O.; Zhang, F.; Andersson, M. R. *J. Am. Chem. Soc.* **2011**, *133*, 14244–14247.
- (15) Jung, J. W.; Jo, J. W.; Liu, F.; Russell, T. P.; Jo, W. H. *Chem. Commun.* **2012**, *48*, 6933–6935.
- (16) Yiu, A. T.; Beaujuge, P. M.; Lee, O. P.; Woo, C. H.; Toney, M. F.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2012**, *134*, 2180–2185.
- (17) Cheng, Y. J.; Yang, S. H.; Hsu, C. S. *Chem. Rev.* **2009**, *109*, 5868–5923.
- (18) Chen, H. Y.; Hou, J. H.; Zhang, S. Q.; Liang, Y. Y.; Yang, G. W.; Yang, Y.; Yu, L. P.; Wu, Y.; Li, G. *Nat. Photon.* **2009**, *3*, 649–653.
- (19) Zhou, H.; Yang, L.; You, W. *Macromolecules* **2012**, *45*, 607–632.
- (20) Duan, C. H.; Huang, F.; Cao, Y. *J. Mater. Chem.* **2012**, *22*, 10416–10434.
- (21) Rasmussen, S. C.; Evenson, S. J. *Prog. Polym. Sci.* [Online early access]. DOI: 10.1016/j.progpolymsci.2013.04.004. Published Online: April 30, 2013.
- (22) Ogawa, K.; Rasmussen, S. C. *J. Org. Chem.* **2003**, *68*, 2921–2928.
- (23) Ogawa, K.; Rasmussen, S. C. *Macromolecules* **2006**, *39*, 1771–1778.
- (24) Evenson, S. J.; Mumm, M. J.; Pokhodnya, K. I.; Rasmussen, S. C. *Macromolecules* **2011**, *44*, 835–841.
- (25) Zhou, E.; Nakamura, M.; Nishizawa, T.; Zhang, Y.; Wei, Q. S.; Tajima, K.; Yang, C. H.; Hashimoto, K. *Macromolecules* **2008**, *41*, 8302–8305.
- (26) Zhou, E.; Yamakawa, S.; Tajima, K.; Yang, C. H.; Hashimoto, K. *Chem. Mater.* **2009**, *21*, 4055–4061.
- (27) Zhou, E.; Wei, Q. S.; Yamakawa, S. P.; Zhang, Y.; Tajima, K.; Yang, C. H.; Hashimoto, K. *Macromolecules* **2010**, *43*, 821–826.
- (28) Zhou, E.; Cong, J.; Tajima, K.; Yang, C.; Hashimoto, K. *Macromol. Chem. Phys.* **2011**, *212*, 305–310.
- (29) Steckler, T. T.; Zhang, X.; Hwang, J.; Marder, S. R.; Reynold, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 2824–2826.
- (30) Zhang, X.; Steckler, T. T.; Dasari, R. R.; Ohira, S.; Reynolds, J. R.; Marder, S. R. *J. Mater. Chem.* **2010**, *20*, 123–134.
- (31) Yue, W.; Zhao, Y.; Shao, S.; Tian, H.; Xie, Z.; Geng, Y.; Wang, F. *J. Mater. Chem.* **2009**, *19*, 2199–2206.
- (32) Zhang, W.; Li, J.; Zou, L.; Zhang, B.; Qin, J. G.; Lu, Z. S.; Poon, Y. F.; Chan-Park, M. B.; Li, C. M. *Macromolecules* **2008**, *41*, 8953–8955.
- (33) Liu, J.; Zhang, R.; Sauve, G.; Kowalewski, T.; McCullough, R. D. *J. Am. Chem. Soc.* **2008**, *130*, 13167–13176.
- (34) Liu, J.; Zhang, R.; Osaka, I.; Mishra, S.; Javier, A. E.; Smilgies, D. M.; Kowalewski, T.; McCullough, R. D. *Adv. Funct. Mater.* **2009**, *19*, 3427–3434.
- (35) Evenson, S. J.; Rasmussen, S. C. *Org. Lett.* **2010**, *12*, 4054–4057.
- (36) Evenson, S. J.; Pappenfus, T. M.; Delgado, M. C. R.; Radke-Wohlers, K. R.; Navarrete, J. T. L.; Rasmussen, S. C. *Phys. Chem. Chem. Phys.* **2012**, *14*, 6101–6111.
- (37) Huang, F.; Wu, H.; Wang, D.; Yang, W.; Cao, Y. *Chem. Mater.* **2004**, *16*, 708–716.
- (38) Huang, F.; Hou, L.; Wu, H.; Wang, X.; Shen, H.; Cao, W.; Yang, W.; Cao, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9845–9853.
- (39) Huang, F.; Wu, H.; Cao, Y. *Chem. Soc. Rev.* **2010**, *39*, 2500–2521.
- (40) Duan, C. H.; Zhang, K.; Zhong, C. M.; Huang, F.; Cao, Y. *Chem. Soc. Rev.* [Online early access]. DOI: 10.1039/C3CS60200A. Published Online: Aug 30, 2013.
- (41) Luo, J.; Wu, H.; He, C.; Li, A.; Yang, W.; Cao, Y. *Appl. Phys. Lett.* **2009**, *95*, 043301-1–043301-3.
- (42) He, C.; Zhong, C.; Wu, H.; Yang, R.; Yang, W.; Huang, F.; Bazan, G. C.; Cao, Y. *J. Mater. Chem.* **2010**, *20*, 2617–2622.
- (43) Zhang, L.; He, C.; Chen, J.; Yuan, P.; Huang, L.; Zhang, C.; Cai, W.; Liu, Z.; Cao, Y. *Macromolecules* **2010**, *43*, 9771–9778.
- (44) He, Z.; Zhang, C.; Xu, X.; Zhang, L.; Huang, L.; Chen, J. W.; Wu, H. B.; Cao, Y. *Adv. Mater.* **2011**, *23*, 3086–3089.
- (45) He, Z. C.; Zhong, C. M.; Huang, X.; Wong, W.; Wu, H. B.; Chen, L. W.; Su, S. J.; Cao, Y. *Adv. Mater.* **2011**, *23*, 4636–4643.
- (46) Wang, X. C.; Jiang, P.; Chen, Y.; Luo, H.; Zhang, Z. G.; Wang, H. Q.; Li, X. Y.; Yu, G.; Li, Y. F. *Macromolecules* **2013**, *46*, 4805–4812.
- (47) Seo, J. H.; Gutacker, A.; Sun, Y.; Wu, H.; Huang, F.; Cao, Y.; Scherf, U.; Heeger, A. J.; Bazan, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 8416–8419.
- (48) Chen, Y.; Jiang, Z.; Gao, M.; Watkins, S. E.; Lu, P.; Wang, H.; Chen, X. *Appl. Phys. Lett.* **2012**, *100*, 203304-1–203304-5.
- (49) Lv, M. L.; Li, S. S.; Jasieniak, J. J.; Hou, J. H.; Zhu, J.; Tan, Z. A.; Watkins, S. E.; Li, Y. F.; Chen, X. W. *Adv. Mater.* [Online early access]. DOI: 10.1002/adma.201302726. Published Online: Oct 7, 2013.
- (50) Liao, S. H.; Li, Y. L.; Jen, T. H.; Cheng, Y. S.; Chen, S. A. *J. Am. Chem. Soc.* **2012**, *134*, 14271–14274.
- (51) Duan, C. H.; Zhong, C. M.; Liu, C. C.; Huang, F.; Cao, Y. *Chem. Mater.* **2012**, *24*, 1682–1689.
- (52) Duan, C. H.; Cai, W. Z.; Hsu, B. B. Y.; Zhong, C. M.; Zhang, K.; Liu, C. C.; Hu, Z. C.; Huang, F.; Bazan, G. C.; Heeger, A. J.; Cao, Y. *Energy Environ. Sci.* **2013**, *6*, 3022–3044.
- (53) Tang, Z.; Andersson, L. M.; George, Z.; Vandewal, K.; Tvingstedt, K.; Heriksson, P.; Kroon, R.; Andersson, M. R.; Inganas, O. *Adv. Mater.* **2012**, *24*, 554–558.
- (54) Oh, S. H.; Na, S. I.; Jo, J.; Lim, B.; Vak, D.; Kim, D. Y. *Adv. Funct. Mater.* **2010**, *20*, 1977–1983.
- (55) Zhou, Y. H.; Fuentes-Hernandez, C.; Shim, J.; Meyer, J.; Giordano, A. J.; Li, H.; Winget, P.; Papadopoulos, T.; Cheun, H.; Kim, J.; Fenoll, M.; Dindar, A.; Haske, W.; Najafabadi, E.; Khan, T. M.; Sojoudi, H.; Barlow, S.; Graham, S.; Br; am, J.; Marder, S. R.; Kahn, A.; Kippelen, B. *Science* **2012**, *336*, 327–332.
- (56) Kang, H.; Hong, S.; Lee, J.; Lee, K. *Adv. Mater.* **2012**, *24*, 3005–3009.
- (57) Wei, Q.; Nishizawa, T.; Tajima, K.; Hashimoto, K. *Adv. Mater.* **2008**, *20*, 2211–2216.
- (58) Tada, A.; Geng, Y. F.; Wei, Q. S.; Hashimoto, K.; Tajima, K. *Nat. Mater.* **2011**, *10*, 450–455.
- (59) Hau, S. K.; Yip, H.; Acton, O.; Baek, N. S.; Ma, H.; Jen, A. K. Y. *J. Mater. Chem.* **2008**, *18*, 5113–5119.
- (60) Li, C.; Chueh, C.; Yip, H.; O'Malley, K. M.; Chen, W.; Jen, A. K. Y. *J. Mater. Chem.* **2012**, *22*, 8574–8578.
- (61) O'Malley, K. M.; Li, C.; Yip, H.; Jen, A. K. Y. *Adv. Energy Mater.* **2012**, *2*, 82–86.
- (62) Li, C. Z.; Chueh, C. C.; Yip, H. L.; Ding, F.; Li, X.; Jen, A. K. Y. *Adv. Mater.* **2013**, *25*, 2457–2461.
- (63) Duan, C. H.; Zhang, K.; Guan, X.; Zhong, C. M.; Xie, H. M.; Huang, F.; Chen, J. W.; Peng, J. B.; Cao, Y. *Chem. Sci.* **2013**, *4*, 1298–1307.
- (64) Mei, Q.; Li, C. H.; Gong, X.; Lu, H.; Jin, E. Q.; Du, C.; Lu, Z.; Jiang, L.; Meng, X. Y.; Wang, C. R.; Bo, Z. S. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8076–8080.
- (65) Zhang, Z. G.; Li, H.; Qi, B. Y.; Chi, D.; Jin, Z. W.; Qi, Z.; Hou, J. H.; Li, Y. F.; Wang, J. Z. *J. Mater. Chem. A* **2013**, *1*, 9624–9629.
- (66) Li, S. S.; Lei, M.; Lv, M. L.; Watkins, S. E.; Tan, Z. A.; Zhu, J.; Hou, J. H.; Chen, X. W.; Li, Y. F. *Adv. Energy Mater.* [Online early access]. DOI: 10.1002/aenm.201300425. Published Online: July 23, 2013.
- (67) Pu, Y. J.; Higashidate, M.; Nakayama, K. I.; Kido, J. *J. Mater. Chem.* **2008**, *18*, 4183–4188.
- (68) Keyworth, C. W.; Chan, K. L.; Labram, J. G.; Anthopoulos, T. D.; Watkins, S. E.; Mckiernan, M.; White, A. J. P.; Holmes, A. B.; Williams, C. K. *J. Mater. Chem.* **2011**, *21*, 11800–11814.
- (69) Bronstein, H.; Chen, Z. Y.; Ashraf, R. S.; Zhang, W. M.; Du, J. P.; Durrant, J. R.; Tuladhar, P. S.; Song, K.; Watkins, S. E.; Geerts, Y.; Wienk, M. M.; Janssen, R. A. J.; Anthopoulos, T.; Siringhaus, H.; Heeney, M.; McCulloch, I. *J. Am. Chem. Soc.* **2011**, *133*, 3272–3275.



- (70) Perez, M. D.; Borek, C.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2009**, *131*, 9281–9286.
- (71) Chen, X.; Schulz, G. L.; Han, X.; Zhou, Z.; Holdcroft, S. J. *Phys. Chem. C* **2009**, *113*, 8505–8512.
- (72) Yap, B. Y.; Xia, R.; Campoy-Quiles, M.; Staverinou, P. N.; Bradley, D. D. C. *Nat. Mater.* **2008**, *7*, 376–380.
- (73) Zhang, Z. G.; Zhang, S.; Min, J.; Cui, C.; Geng, H.; Shuai, Z.; Li, Y. *Macromolecules* **2012**, *45*, 2312–2320.
- (74) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497–500.
- (75) Blom, W. M.; Vissenberg, M. C. J. M. *Mater. Sci. Eng.* **2000**, *27*, 53–94.
- (76) Zhou, H.; Zhang, Y.; Seifert, J.; Collins, S. D.; Luo, C.; D.; Bazan, G. C.; Nguyen, T. Q.; Heeger, A. J. *Adv. Mater.* **2013**, *25*, 1646–1652.
- (77) Wang, Q.; Zhou, Y.; Zheng, H.; Shi, J.; Li, C.; Su, C. Q.; Wang, L.; Luo, C.; Hu, D.; Pei, J.; Wang, J.; Peng, J.; Cao, Y. *Org. Electron.* **2011**, *12*, 1858–1863.
- (78) Qi, B. Y.; Wang, J. Z. *Phys. Chem. Chem. Phys.* **2013**, *15*, 8972–8982.
- (79) Terazzi, E.; Torelli, S.; Bernardinelli, G.; Rivera, J. P.; Bénech, J. M.; Bourgogne, C.; Donnio, B.; Guillon, D.; Imbert, D.; Bünzil, J. C.; Pinto, A.; Jeannerat, D.; Piguet, C. *J. Am. Chem. Soc.* **2005**, *127*, 888–903.
- (80) Kim, J.-J.; Choi, H.; Lee, J. W.; Kang, M. S.; Song, K.; Kang, S. O.; Ko, J. *J. Mater. Chem.* **2008**, *18*, 5223–5229.
- (81) Lee, K.-H.; Lee, H. J.; Kuramoto, K.; Tanaka, Y.; Morino, K.; Sudo, A.; Okauchi, T.; Tsuge, A.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 3543–3549.
- (82) Hou, Q.; Zhou, Q. M.; Zhang, Y.; Yang, W.; Yang, R. Q.; Cao, Y. *Macromolecules* **2004**, *37*, 6299–6305.
- (83) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532–538.