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# Simultaneous Enhancement of Solar Cell Efficiency and Photostability via Chemical Tuning of Electron Donating Units in Diketopyrrolopyrrole-Based Push–Pull Type Polymers

Tae In Ryu,<sup>†</sup> Youngwoon Yoon,<sup>§</sup> Ji-Hoon Kim,<sup>||</sup> Do-Hoon Hwang,<sup>||</sup> Min Jae Ko,<sup>§</sup> Doh-Kwon Lee,<sup>§</sup> Jin Young Kim,<sup>§</sup> Honggon Kim,<sup>§</sup> Nam-Gyu Park,<sup>\*,†,‡</sup> Bongsoo Kim,<sup>\*,§</sup> and Hae Jung Son<sup>\*,§</sup>

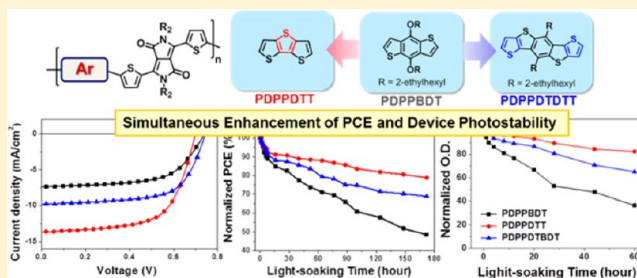
<sup>†</sup>School of Chemical Engineering and <sup>‡</sup>Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea

<sup>§</sup>Photoelectronic Hybrid Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

<sup>||</sup>Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Korea

## S Supporting Information

**ABSTRACT:** We synthesized a series of push–pull-type copolymers by copolymerizing an electron-deficient diketopyrrolopyrrole with three electron-donating benzodithiophene (BDT) moieties. PDPPDTT, which incorporated a dithienothiophene (DTT), showed a higher power conversion efficiency (PCE) of 6.11% compared to 3.31% for the BDT-based polymer (PDPPBDT). PDPPDTBDT, which incorporated a dithienobenzodithiophene (DTBDT), also exhibited superior performance, with a PCE of 4.75% although this value was lower than that obtained for PDPPDTT. The presence of the DTT unit in the polymer backbone lowered the energy bandgap of the polymer and induced an optimal morphology in the polymer:PC<sub>71</sub>BM blend film, resulting in higher charge carrier generation. Furthermore, the effectively delocalized frontier orbitals of PDPPDTT enhanced intermolecular interactions between the polymer chains by favoring effective  $\pi$ – $\pi$  stacking, which facilitated charge carrier transport. By contrast, PDPPDTBDT unexpectedly showed a low-crystallinity thin film despite its backbone planarity, which reduced the performance relative to that of PDPPDTT. Importantly, PDPPDTT exhibited significantly better device stability compared to the other polymers in a light soaking test due to the much higher photochemical stability of PDPPDTT. We demonstrated a systematic approach to simultaneously increasing the photovoltaic performances and device stability, and we explored the basis for the structure–property relationship that accompanied such improvements.



## INTRODUCTION

Over the past decade, bulk heterojunction polymer solar cells (BHJ PSCs) prepared using conjugated polymers as an electron donor and fullerene derivatives (e.g., [6,6]-phenyl C<sub>71</sub>-butyric acid methyl ester, PC<sub>71</sub>BM) as an electron acceptor have been extensively studied,<sup>1</sup> and power conversion efficiencies (PCEs) have reached values of ~9% for single cells<sup>2</sup> and ~10% for tandem cells.<sup>3</sup> A lot of conjugated polymers have been developed to achieve high photovoltaic properties, and design strategies relevant to organic photovoltaic devices to achieve a high PCE in BHJ solar cells have been set. Further advancements in the efficiency of a PSC will require developments of new conjugated polymers that satisfy several important criteria, including<sup>4,5</sup> (i) efficient light harvesting to increase the short-circuit current ( $J_{sc}$ ), (ii) a lowest unoccupied molecular orbital (LUMO) energy level in the polymer should be at least 0.3 eV higher than that of the acceptor to provide a driving force for efficient charge separation at the polymer/acceptor interface, (iii) energy offsets between the highest occupied molecular orbital (HOMO) level of the conjugated polymer and the LUMO level of the fullerene derivative should be sufficient to support a high open-circuit voltage ( $V_{oc}$ ), (iv)

morphology in the BHJ polymer blend should be optimal and include a nanoscale interpenetrating network to achieve a high interfacial area and efficient charge separation and transport, and (v) charge carrier mobilities should be high to increase charge collection and thus  $J_{sc}$  by reducing charge recombination. Apart from these points, the polymer must be easily processed and reproducibly synthesized for commercialization of a solar cell device at a low cost.<sup>6</sup>

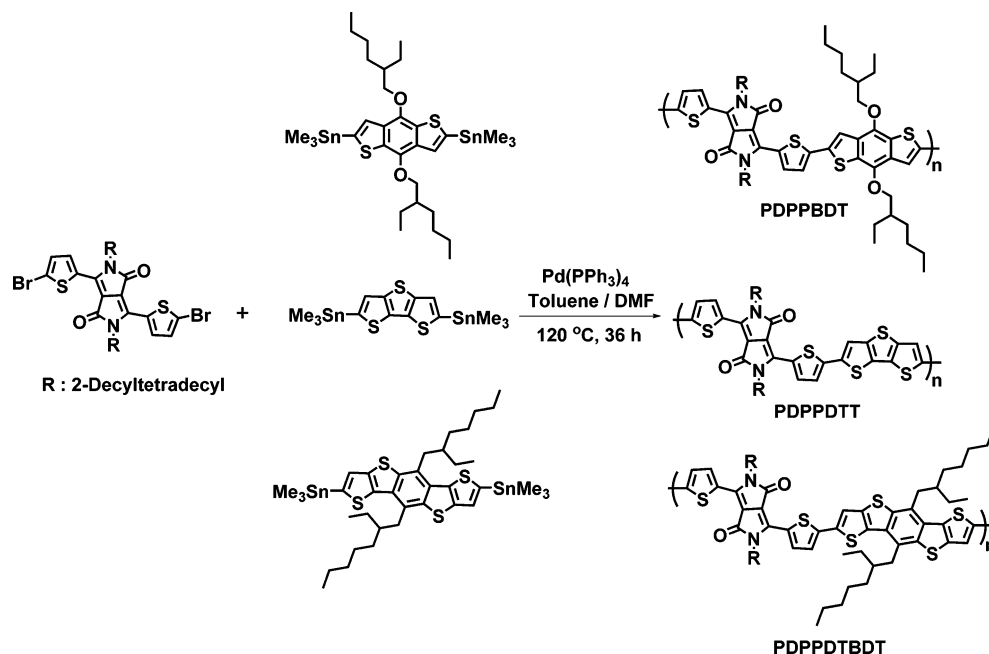
One of the most reliable approaches to prepare conjugated polymers for high-efficiency PSCs has involved synthesizing push–pull-type alternating copolymers composed of electron-donating and electron-accepting conjugated units. In general, aromatic compounds with a high electron density are used as the electron-donating unit, and electron-deficient aromatic compounds functionalized with electron-withdrawing groups are employed as the electron-accepting units. Mono- or oligo-heteroaromatic compounds are typical examples of electron-donating units.<sup>7</sup> 4,8-Dialkoxybenzo[1,2-*b*:4,5-*b'*]dithiophene

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Scheme 1. Synthesis of PDPPBDT, PDPPDTT, and PDPPDTBDT



(BDT) has been utilized extensively as an electron donor unit over the past several years.<sup>8</sup> Several copolymers consisting of BDTs and various electron-accepting units such as thieno[3,4-*b*]thiophene (TT),<sup>9</sup> 4,7-dithiophene-2-yl-2,1,3-benzothiadiazole (DTBT),<sup>10</sup> thienopyrrole-4,6-dione (TPD),<sup>11</sup> benzotriazole (BTZ),<sup>12</sup> etc., have been synthesized. These copolymers displayed good physical properties for PSC applications, such as deep HOMO energy levels, high charge carrier mobilities, and good thermal stabilities in comparison with traditional thiophene-based polymers. Recently, conjugated polymers based on the 5-alkylthiophene-2-yl-substituted counterpart of BDT (BDTT) were shown to further improve the performances of the PSC prepared using this electron-donating polymer (PCE > 8%),<sup>13</sup> and a variety of polymers that incorporated BDTT have been prepared.<sup>14</sup> Despite the notable performances of the BDT-based polymers, however, our understanding of their structural effects on the solar cell properties tends to be phenomenological. It is important to systematically tune the chemical structures of BDT and to study the interplay between the structure and the solar cell parameters. Such insights would contribute to the construction of more concrete design guidelines for the future development of new polymer solar cells.

Here, we synthesized a series of push–pull-type alternating copolymers that employ BDT moieties as the electron-donating unit. Diketopyrrolopyrrole (DPP) was employed as the accepting unit because the DPP effectively increased the charge carrier mobility and controlled the energy bandgap of the conjugated polymer.<sup>15</sup> The first polymer was a copolymer of DPP and BDT (PDPPBDT) as shown in Scheme 1. The second polymer was designed by replacing a fused phenyl ring in the BDT unit with a thiophene ring, resulting in a copolymer of DPP and dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT) (PDPPDTT). Because thiophene has a lower aromaticity and a higher electron density compared with benzene, the thiophene-based polymer was expected to have a lower energy bandgap compared with its corresponding benzene-based counterpart.<sup>16</sup> Furthermore, thiophene is generally better than

benzene at improving the stability of the polymer because the electronegative sulfur moiety can stabilize the aromatic system.<sup>17</sup> The third polymer designed here was a dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (DTBDT)-based polymer prepared by annulating two thiophene rings at the BDT terminals. The incorporation of fused ring aromatic architectures into the polymer backbone is typically beneficial for preparing high-performance solar cells because their rigid and planar  $\pi$ -conjugated skeletons increase the charge carrier mobility.<sup>18</sup> The 2-ethylhexyloxy group of the BDT was substituted with a weaker electron-donating 2-ethylhexyl group in DTBDT because it has been reported that the presence of strong electron-donating groups can decrease the stability of acene compounds such as DTBDT.<sup>19</sup>

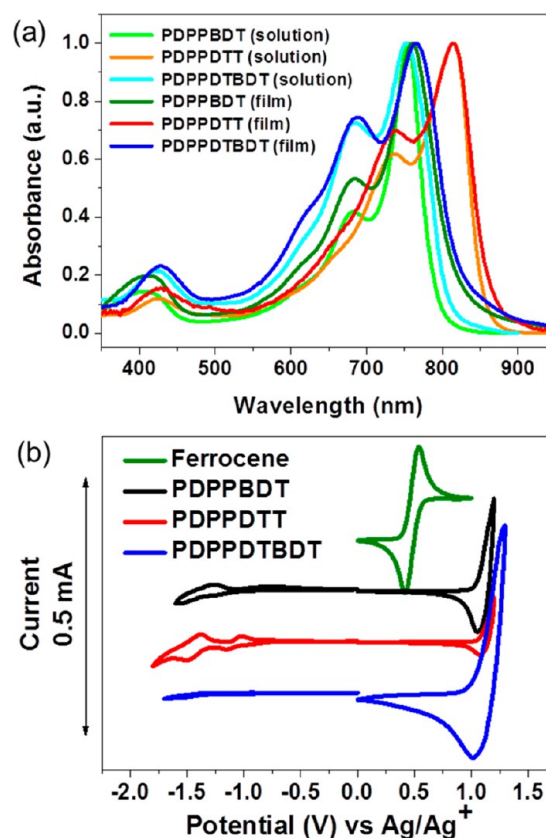
This paper describes the synthesis and photovoltaic properties of the DPP- and BDT-based polymers and examines how chemically tuning the BDT's molecular structure in the polymer can influence the solar cell properties and device stability. Among the polymers tested, PDPPDTT achieved the best performance with a 6.11% PCE. The incorporation of DTT into the polymer simultaneously improved light absorption across the near-IR range and the  $\pi$ – $\pi$  intermolecular interactions of the polymer by introducing more delocalized  $\pi$ -orbitals into the polymer backbone. The morphological properties of the polymer:PC<sub>71</sub>BM blend film were significantly improved relative to those of PDPPBDT. Importantly, the introduction of DTT in place of the BDT or DTBDT units in the polymer significantly improved the polymer's photochemical stability, which increased the long-term stability of the PDPPDTT-based solar cells in a light soaking test under air.

## RESULTS AND DISCUSSION

**Polymer Synthesis.** The synthetic routes to the polymers PDPPBDT, PDPPDTT, and PDPPDTBDT are illustrated in Scheme 1. The syntheses of 2,5-diethylhexyl-3,6-bis(5-bromothiophene-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP), 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]-

dithiophene (BDT), 2,6-bis(trimethyltin)dithieno[3,2-*b*:2',3'-*d'*]thiophene (DTT), and 2,7-bis(trimethyltin)-5,10-bis(2-hexyldecyl)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (DTBDT) were performed according to procedures reported previously.<sup>20</sup> The polymers were synthesized via a palladium-catalyzed Stille coupling reaction. After polymerization, the polymers were collected by precipitation in methanol and purified by performing successive Soxhlet extractions with methanol and hexane to remove the byproducts and oligomers. The <sup>1</sup>H NMR spectrum provided the number of aromatic and aliphatic protons present, estimated based on integration over the peaks. These values were consistent with the expected values based on the repeating unit present in the copolymers. The resulting copolymers displayed good solubility in common organic solvents, such as chloroform, toluene, chlorobenzene, and *o*-dichlorobenzene, although the solubility of PDPPDTT was slightly lower compared with the other two polymers. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using 1,2-dichlorobenzene (DCB) as the eluent and polystyrene as the standard. The polymers gave molecular weights of 122, 43, and 29 kg/mol, with polydispersity indices (PDIs) of 5.6, 1.5, and 2.6 for PDPPBDT, PDPPDTT, and PDPPDTBDT, respectively. The molecular weight of PDPPBDT was much higher than those of the other polymers because the high solubility of DPPBDT probably improved the efficiency of the polymerization reaction compared with PDPPDTT and PDPPDTBDT. The thermal properties of the polymers were investigated by differential scanning calorimetry (DSC), conducted at a heating rate of 10 °C/min under a nitrogen atmosphere. The DSC results obtained from PDPPBDT (Figure S1, in Supporting Information) exhibited an endotherm at 220 °C, but both PDPPDTT and PDPPDTBDT showed no apparent thermal transitions up to 270 °C. Thermogravimetric analysis (TGA) of the polymers was measured under a nitrogen flow (Figure S2). The 5% weight loss temperature (*T*<sub>d</sub>) values of PDPPDTT and PDPPDTBDT were 388 and 380 °C, respectively, which were ~100 °C higher than the value obtained from PDPPBDT, suggesting better thermal stability in the polymers that lacked an alkoxy substitution.

**Optical and Electrochemical Properties.** The UV–vis absorption spectra of the polymers measured both in a toluene solution and in a thin film are shown in Figure 1a, and the characteristics of the optical properties are summarized in Table 1. All polymer spectra featured two absorption bands: one in the range 350–450 nm, which was assigned to localized  $\pi$ – $\pi^*$  transitions, and the other band with a vibronic shoulder in the range 650–900 nm, which corresponded to intramolecular charge transfer (ICT) between the acceptor (DPP) and electron donor (BDT, DTT, or DTBDT) units. The absorption features of PDPPBDT and PDPPDTBDT in the solid spectra were similar to the features of the corresponding solution spectra, with 10–30 nm red-shifts in the absorption onset points, indicating enhanced molecular planarity of the polymer chain due to intermolecular  $\pi$ – $\pi$  interactions in the solid state. The onsets of the thin film absorptions were used to estimate the optical bandgaps of the polymers and are summarized in Table 1. The energy bandgap of PDPPDTT (1.43 eV) was reduced by 0.08 eV relative to that of PDPPBDT (1.51 eV). The low aromaticity of DTT compared with BDT effectively induced PDPPDTT to form a quinoid structure, which reduced the energy bandgap.<sup>21</sup> Cyclic voltammetry (CV) was used to



**Figure 1.** (a) UV–vis absorption spectra of PDPPBDT, PDPPDTT, and PDPPDTBDT in toluene solutions and thin films. (b) Cyclic voltammogram of PDPPBDT, PDPPDTT, and PDPPDTBDT.

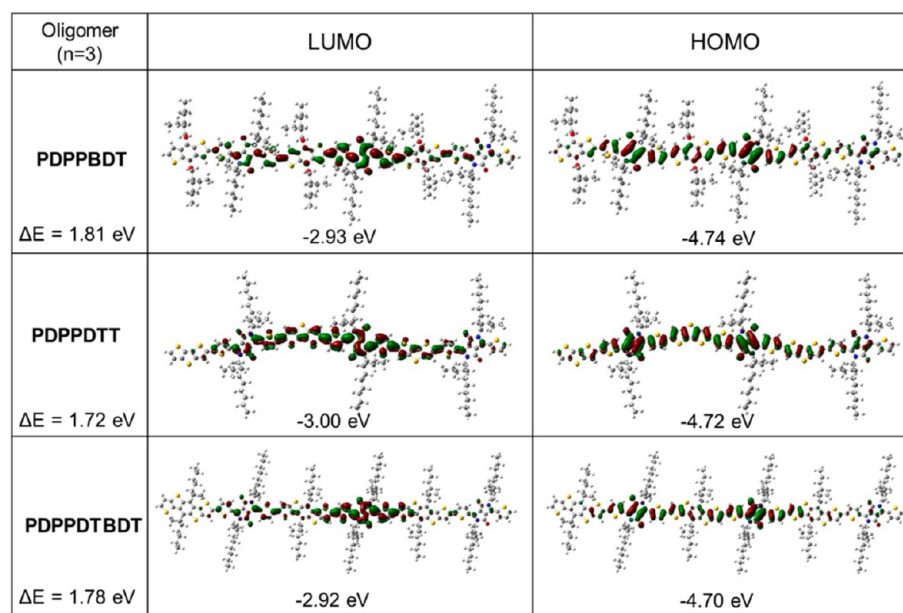
examine the electrochemical properties and to determine the energy levels of the polymers.<sup>22</sup> Figure 2b shows the CV curves, and the results of the electrochemical measurements are summarized in Table 1. The HOMO energy levels decreased slightly in the order: PDPPBDT, PDPPDTT, and PDPPDTBDT, and the LUMO energy level of PDPPDTT (−3.59 eV) was ~0.2 eV lower than the levels of PDPPBDT (−3.39 eV) and PDPPDTBDT (−3.35 eV). The energy bandgaps obtained from the CV measurements were consistently larger than the measured optical bandgaps by an offset of  $\Delta E = 0.36$ – $0.5$  eV. This difference reflects the fact that the optical bandgap is the energy difference between the ground and excited states, whereas the redox potentials correspond to the energy needed for electron addition or extraction, for which Coulombic attraction should be accounted for.<sup>23</sup>

**Theoretical Calculations.** The electronic structures and HOMO/LUMO energy levels of the polymers were compared by performing density functional theory (DFT) calculations using Gaussian 09 at the B3LYP level with a 6-31G(d) basis set.<sup>24</sup> A trimer of each polymer which included a 2-butyloctyl side chain on the DPP unit was used as a model compound. As shown in Figure 2, both the HOMOs and LUMOs of the polymers were delocalized over the electron-donating (BDT, DTT, or DTBDT) and electron accepting (DPP) units. The HOMO was predominantly aromatic in character, and the LUMO mainly displayed a quinoid character. The calculated LUMO values increased in the order PDPPDTT, PDPPBDT, and PDPPDTBDT, whereas the HOMOs followed the trend PDPPBDT < PDPPDTT < PDPPDTBDT, consistent with the



Table 1. Optical and Electrochemical Properties of PDPPBDT, PDPPD TT, and PDPPDTBDT

polymers	UV–vis absorption data				electrochemical data		
	solution		film		film		
	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (nm)	$\lambda_{\text{onset}}$ (nm)	$E_{\text{g}}^{\text{opt}}$ (eV)	HOMO (eV)	LUMO (eV)	$E_{\text{g}}^{\text{CV}}$ (eV)
PDPPBDT	754	760	823	1.51	−5.37	−3.39	1.98
PDPPD TT	814	814	865	1.43	−5.36	−3.59	1.77
PDPPDTBDT	752	764	826	1.50	−5.35	−3.35	2.0



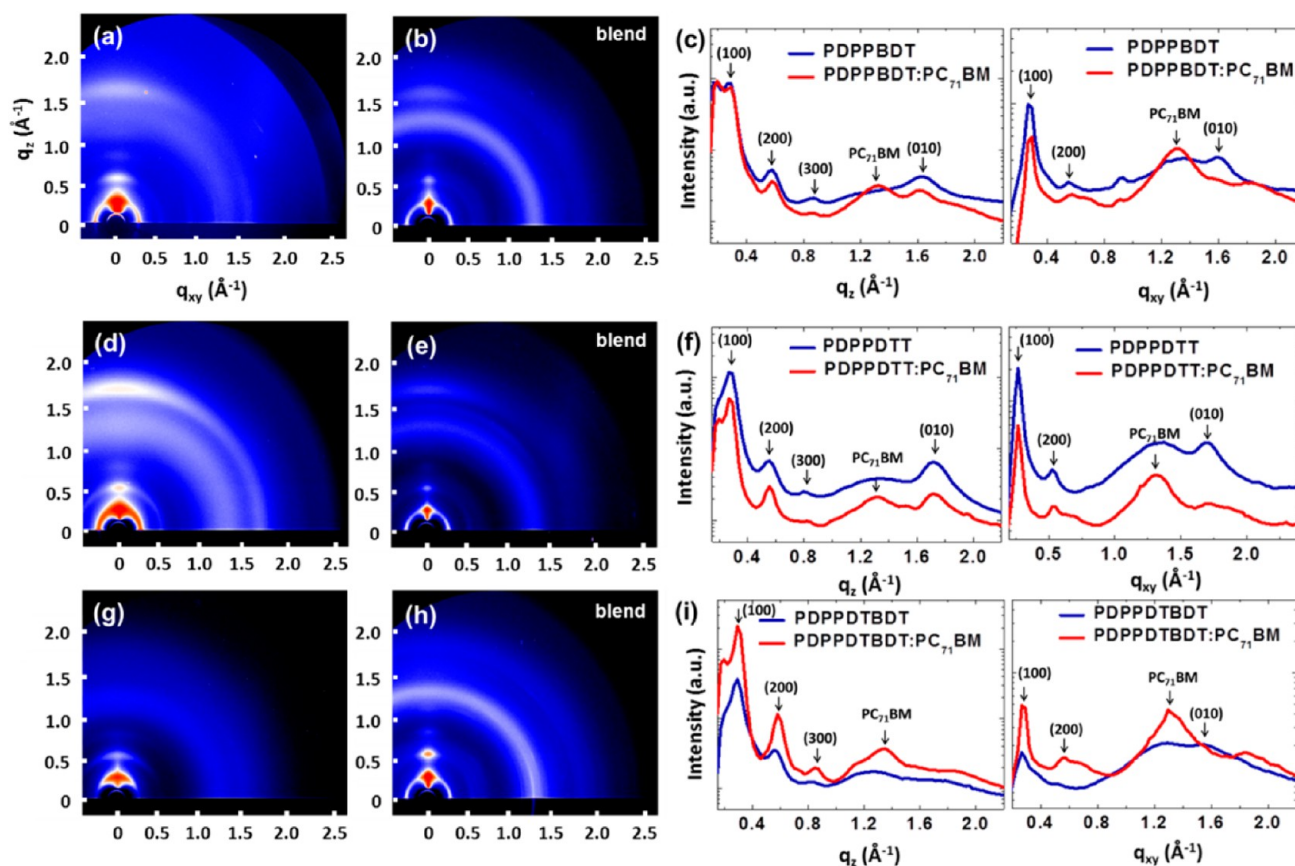
**Figure 2.** HOMO/LUMO energy levels and frontier molecular orbitals obtained from DFT calculations on the oligomers ( $n = 3$ ) of PDPPBDT, PDPPD TT, and PDPPDTBDT with optimized geometries.  $\Delta E$  is an energy bandgap of the oligomers estimated from difference between the HOMO and LUMO values.

CV results. Figure S3 illustrates the dihedral angles of the optimized oligomers. In comparison with PDPPDTBDT, PDPPBDT and PDPPD TT polymers displayed larger absolute dihedral angle values between neighboring aromatic rings in the oligomer, indicating more planar structures in the PDPPDTBDT due to the large aromatic DTBDT system. Notably, both the HOMO and LUMO were more effectively distributed over the trimer backbone in PDPPD TT than in PDPPBDT or PDPPDTBDT, suggesting that the effective conjugation length of PDPPD TT was longer than that of the other two polymers. This result was consistent with the fact that PDPPD TT displayed the lowest energy bandgap among the polymers examined.

**Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) Studies.** Structural information, such as the molecular ordering and the intermolecular distances within the pure polymers and the polymer:PC<sub>71</sub>BM blend films, were investigated by GIWAXS. Figure 3 shows 2D GIWAXS images and in-plane and out-of-plane line cuts, and Table 2 summarizes the characteristic peak and  $d$ -spacing values. The component of the scattering vector parallel to the substrate plane is given by  $q_{xy}$  and  $q_z$  is the component perpendicular to the substrate plane. In the pure polymer films, PDPPBDT and PDPPD TT showed semicrystalline properties whereas the PDPPDTBDT film was less crystalline. PDPPBDT and PDPPD TT exhibited discernible (010) and (100) peaks along the  $q_z$  direction due to the  $\pi$ – $\pi$  stacking and lamellar structures of the polymer, respectively. The diffraction patterns

revealed that crystallites in both PDPPBDT and PDPPD TT assumed random orientations without a significant preference for edge-on or face-on orientations on the substrate. The lamellar distances ( $d$ ) of the polymers were calculated based on the peaks at  $0.29 \text{ \AA}^{-1}$  for PDPPBDT,  $0.27 \text{ \AA}^{-1}$  for PDPPD TT, and  $0.29 \text{ \AA}^{-1}$  for PDPPDTBDT. These distances were 21.7, 23.7, and 21.7  $\text{\AA}$ , respectively. The longer lamellar distance in PDPPD TT most likely arose from the molecular conformation of the polymer backbone. In Figure S4, the linear shaped backbones of PDPPBDT and PDPPDTBDT would have a smaller chain separation distance in the lamellar structure compared with the relatively wavy backbone in PDPPD TT, which formed a less compact structure.<sup>25</sup> The reflection peak for PDPPD TT at  $q_z = 1.71 \text{ \AA}^{-1}$  corresponding to the  $\pi$ – $\pi$  stacking interactions was slightly shifted from  $q_z = 1.61 \text{ \AA}^{-1}$  in PDPPBDT, indicating that the  $\pi$ – $\pi$  stacking distance was higher in PDPPBDT (3.9  $\text{\AA}$ ) than in PDPPD TT (3.7  $\text{\AA}$ ). The  $\pi$ – $\pi$  stacking distance in PDPPD TT is one of the smallest  $\pi$ – $\pi$  stacking distances for conjugated polymers observed until date.<sup>26</sup> Compared with PDPPBDT and PDPPD TT, PDPPDTBDT displayed a very weak  $\pi$ – $\pi$  stacking peak at  $\sim 1.55 \text{ \AA}^{-1}$  ( $d = 4.0 \text{ \AA}$ ) in the in-plane scan. This suggested that  $\pi$ – $\pi$  stacking structures were not well-formed in the PDPPDTBDT film and the crystallites of the polymer were predominantly edge-on in character.

The GIWAXS patterns of the PDPPBDT and PDPPD TT blend films (Figure 3) were similar to those observed in the pure polymers, and a diffraction halo peak associated with the



**Figure 3.** GIWAXS images of polymer films of (a) PDPPBDT, (d) PDPPDTT and (g) PDPPDTBDT and polymer:PC<sub>71</sub>BM blend films of (b) PDPPBDT, (e) PDPPDTT, and (h) PDPPDTBDT. Out-of-plane and in-plane line cuts of pristine polymer films and polymer:PC<sub>71</sub>BM blend films for (c) DPPBDT, (f) DPPDTT, and (i) DPPDTBDT.

**Table 2.** GIWAXS Diffraction Peaks and *d*-Spacing of Pristine Polymers and Polymer:PC<sub>71</sub>BM Blended Films

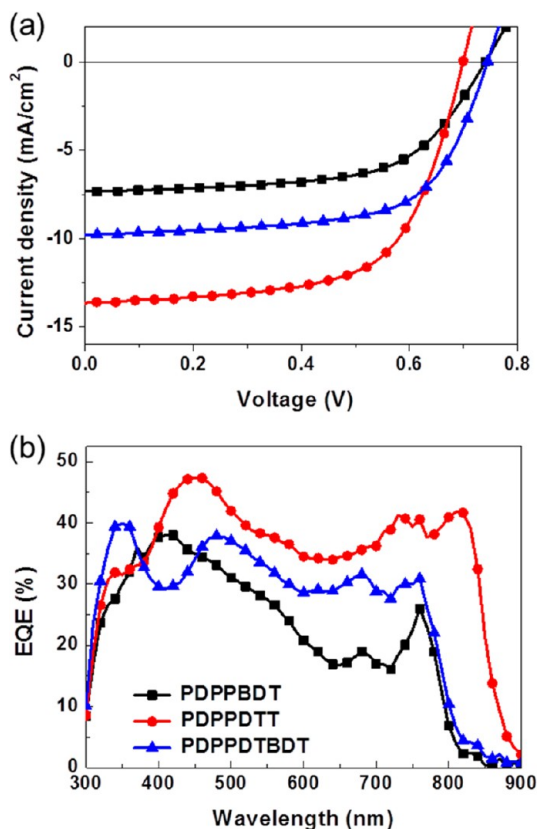
film	<i>q</i> (Å <sup>−1</sup> ) ( <i>d</i> -spacing (Å))	
	(100)	(010)
PDPPBDT	0.29 (21.7)	1.61 (3.9)
PDPPDTT	0.27 (23.7)	1.71 (3.7)
PDPPDTBDT	0.29 (21.7)	1.55 (4.0)
PDPPBDT:PC <sub>71</sub> BM	0.29 (21.7)	1.61 (3.9)
PDPPDTT:PC <sub>71</sub> BM	0.27 (23.7)	1.71 (3.7)
PDPPDTBDT:PC <sub>71</sub> BM	0.29 (21.7)	not observed

PC<sub>71</sub>BM amorphous phase was observed near 1.33 Å<sup>−1</sup>.<sup>27</sup> The crystallinity of the blend PDPPDTBDT film was enhanced compared to the amorphous structure of the pure polymer film, and thus, the (100) peak associated with a lamellar structure at 0.29 Å<sup>−1</sup> in the out-of plane direction became more pronounced compared with the corresponding peak in the pure polymer film. It should be noted that a reflection pattern arising from  $\pi$ – $\pi$  stacking in the PDPPDTBDT film was not detected, although the overall crystallinity of the polymer increased in the blend film. The peak positions characteristic of the polymer packing structures of each polymer remained nearly unchanged upon blending with PC<sub>71</sub>BM, suggesting that the lamellar and  $\pi$ – $\pi$  stacking distances of the polymers were not significantly influenced by the presence of the blended PC<sub>71</sub>BM molecules. The results point to several important conclusions regarding the relation between the chemical structure of the electron-donating unit in the polymer and

the polymer's packing structure: the replacement of the BDT unit with DTBDT in PDPPBDT did not improve the crystallinity or  $\pi$ – $\pi$  stacking of the polymer even though DTBDT had a larger aromatic size and an enhanced polymer backbone planarity. Instead, the incorporation of DTT into the polymer backbone promoted effective  $\pi$ – $\pi$  stacking and decreased the  $\pi$ – $\pi$  stacking distance from 3.9 Å in PDPPBDT to 3.7 Å in PDPPDTT. This result was obtained, in part, as a result of the reduced steric hindrance in DTT compared with BDT which includes a bulky 2-ethylhexyloxy chain. The docking of a small electron-donating unit into a large electron-accepting unit in push–pull-type polymers has been reported to enhance interchain  $\pi$ – $\pi$  stacking.<sup>25c</sup> The improved ordered structure in PDPPDTT could be explained in terms of the frontier orbital distribution of the polymer as illustrated in Figure 2. As mentioned earlier, the HOMO of the PDPPDTT oligomer was more effectively delocalized over the oligomer backbone than the HOMO of PDPPBDT; however, the HOMO of PDPPDTBDT was not well developed over the DTBDT unit. As a result, PDPPDTT was expected to display the strongest intermolecular interactions due to the large  $\pi$ -orbital overlap between the polymer chains due to the presence of relatively well-developed frontier orbitals along the polymer backbone, which increased the effectiveness of  $\pi$ – $\pi$  stacking.<sup>28</sup>

**Photovoltaic Properties of the Polymers.** The photovoltaic properties of the prepared polymers were examined by fabricating bulk heterojunction solar cells with a device structure of ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM/TiO<sub>2</sub>/Al. The photoactive layer was fabricated by spin-casting a solution

of the polymer:PC<sub>71</sub>BM mixtures dissolved in a chlorobenzene (CB):1,8-diiodooctane (DIO) (97:3 vol %) cosolvent. The optimized polymer:PC<sub>71</sub>BM ratios that gave the best solar cell performances were 1:2, 1:1.5, and 1:2 for PDPPBDT, PDPPDTT, and PDPPDTBDT, respectively. The photovoltaic performances of the prepared solar cell devices were investigated under simulated AM 1.5G 1 sun illumination (100 mW/cm<sup>2</sup>). The current density–voltage (*J*–*V*) curves obtained from the solar cell devices are shown in Figure 4, and



**Figure 4.** (a) *J*–*V* curves and (b) EQE spectra of the polymer:PC<sub>71</sub>BM solar cells.

**Table 3.** Photovoltaic Parameters of the Polymer Solar Cells

active layer		$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
PDPPBDT:PC <sub>71</sub> BM (1:2)	best	0.741	7.33	0.61	3.31
	ave	0.742	7.12	0.62	3.28
PDPPDTT:PC <sub>71</sub> BM (1:1.5)	best	0.70	13.64	0.64	6.11
	ave	0.70	13.47	0.63	5.94
PDPPDTBDT:PC <sub>71</sub> BM (1:2)	best	0.745	9.80	0.65	4.75
	ave	0.743	9.71	0.65	4.69

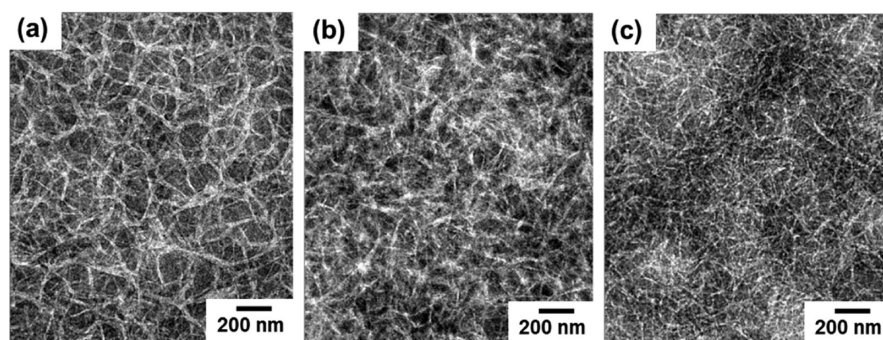
the characteristic solar cell data are summarized in Table 3. PDPPDTT showed the best solar cell performance with the highest measured PCE value of 6.11%, a  $J_{sc}$  of 13.64 mA/cm<sup>2</sup>, a fill factor (FF) of 0.64, and a  $V_{oc}$  of 0.70 V. PDPPDTT was followed by PDPPDTBDT, which achieved a PCE of 4.75% with a  $J_{sc}$  of 9.80 mA/cm<sup>2</sup>, a FF of 0.65, and a  $V_{oc}$  of 0.745 V. PDPPBDT showed the lowest PCE of 3.31%, mainly due to a

low  $J_{sc}$  value of 7.33 mA/cm<sup>2</sup>. Figure 4b shows the external quantum efficiency (EQE) spectra of the polymer solar cell devices. The EQE spectra of the polymers reflected the absorption properties of each polymer, and thus, PDPPDTT exhibited EQE values exceeding 40% over the range of 400–900 nm. By contrast, the EQEs of PDPPDTBDT and PDPPBDT fell below 5% over the range of 800–900 nm. An important factor that contributed to the enhanced  $J_{sc}$  in PDPPDTT was the polymer's photon absorption over the near-IR range due to the reduced energy bandgap. The EQEs of PDPPBDT within the range of 600–800 nm in which photons are most strongly absorbed by the polymer were lower than those measured in the other two polymers. This result indicated that charge carrier generation as a result of photon absorption by PDPPBDT was not efficient and PDPPBDT showed the lowest  $J_{sc}$  among the polymers tested (see below details).

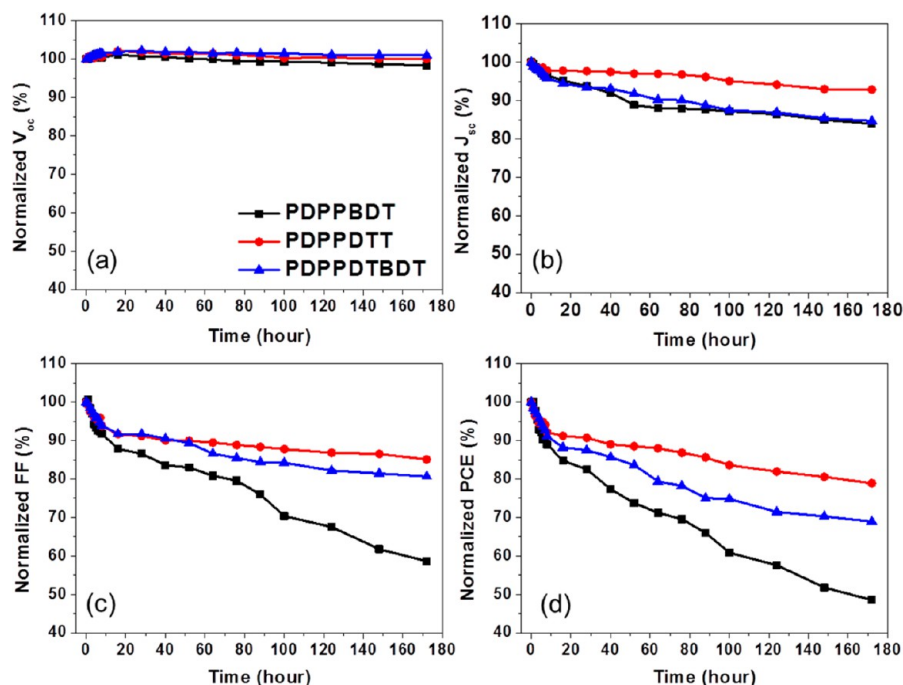
The structural factors underlying the good performance of the PDPPDTT polymer were investigated by performing a series of experiments and morphological studies. Figure 5 shows the transmission electron microscopy (TEM) images of the polymer:PC<sub>71</sub>BM blend films prepared under the conditions used to fabricate the solar cell device. The TEM image of the PDPPDTT blend film showed clear fibril structures of 30–40 nm in width due to polymer aggregation. Figures 5b and 5c show that the PDPPBDT and PDPPDTBDT films formed finer and better dispersed fibrous structures with widths on a 10 nm scale. These polymers were also more miscible with PC<sub>71</sub>BM. The TEM images of the polymer blend films offered an explanation for the solar cell and EQE properties: The widths of the fibrils in the PDPPBDT film which exceed the exciton diffusion length (10 nm)<sup>29</sup> may reduce the probability that excitons generated in the polymer reach the polymer/PC<sub>71</sub>BM interface and dissociate into charge carriers. This hypothesis is consistent with the observed EQE drop over the range of 600–800 nm (see the EQE spectrum of PDPPBDT in Figure 4b) associated with photon absorption by PDPPBDT and the low  $J_{sc}$  value of the PDPPBDT solar cell. By contrast, the narrow fibrous structures which were well-dispersed with the PC<sub>71</sub>BM in the PDPPDTT and PDPPDTBDT blend films favored charge carrier generation and increased the photocurrent densities of the solar cell device. The high FFs in the PDPPDTT and PDPPDTBDT solar cells were expected to arise from the improved morphologies of the polymer films. The high  $J_{sc}$  of PDPPDTT (13.64 mA/cm<sup>2</sup>) compared to 9.8 mA/cm<sup>2</sup> of PDPPDTBDT may have originated from the good crystallinity of the PDPPDTT film, which featured a small interchain  $\pi$ – $\pi$  stacking distance that promoted charge carrier transport in the solar cell.<sup>30</sup> This hypothesis was supported by the observation that the hole mobility in the PDPPDTT blend film ( $6.0 \times 10^{-5}$  cm<sup>2</sup> V<sup>−1</sup> s<sup>−1</sup>) was better than that of the PDPPDTBDT blend film ( $9.3 \times 10^{-6}$  cm<sup>2</sup> V<sup>−1</sup> s<sup>−1</sup>). Despite the semicrystalline properties of PDPPBDT, the lowest hole mobility was observed in the PDPPBDT blend film ( $2.3 \times 10^{-6}$  cm<sup>2</sup> V<sup>−1</sup> s<sup>−1</sup>). The low hole mobility most likely arose from the more sparsely dispersed polymer network in the film, which reduced charge carrier transport.

The excellent performance of the PDPPDTT film originated from the polymer's molecular structure. As described in the previous section, the presence of DTT in the polymer structure delocalized the polymer's frontier orbitals along the polymer backbone to a greater extent than was obtained in the PDPPBDT and PDPPDTBDT films. Delocalization favored





**Figure 5.** TEM images of the polymer:PC<sub>71</sub>BM blend films prepared from the polymers of (a) PDPPBDT, (b) PDPPD TT, and (c) PDPPDTBDT.



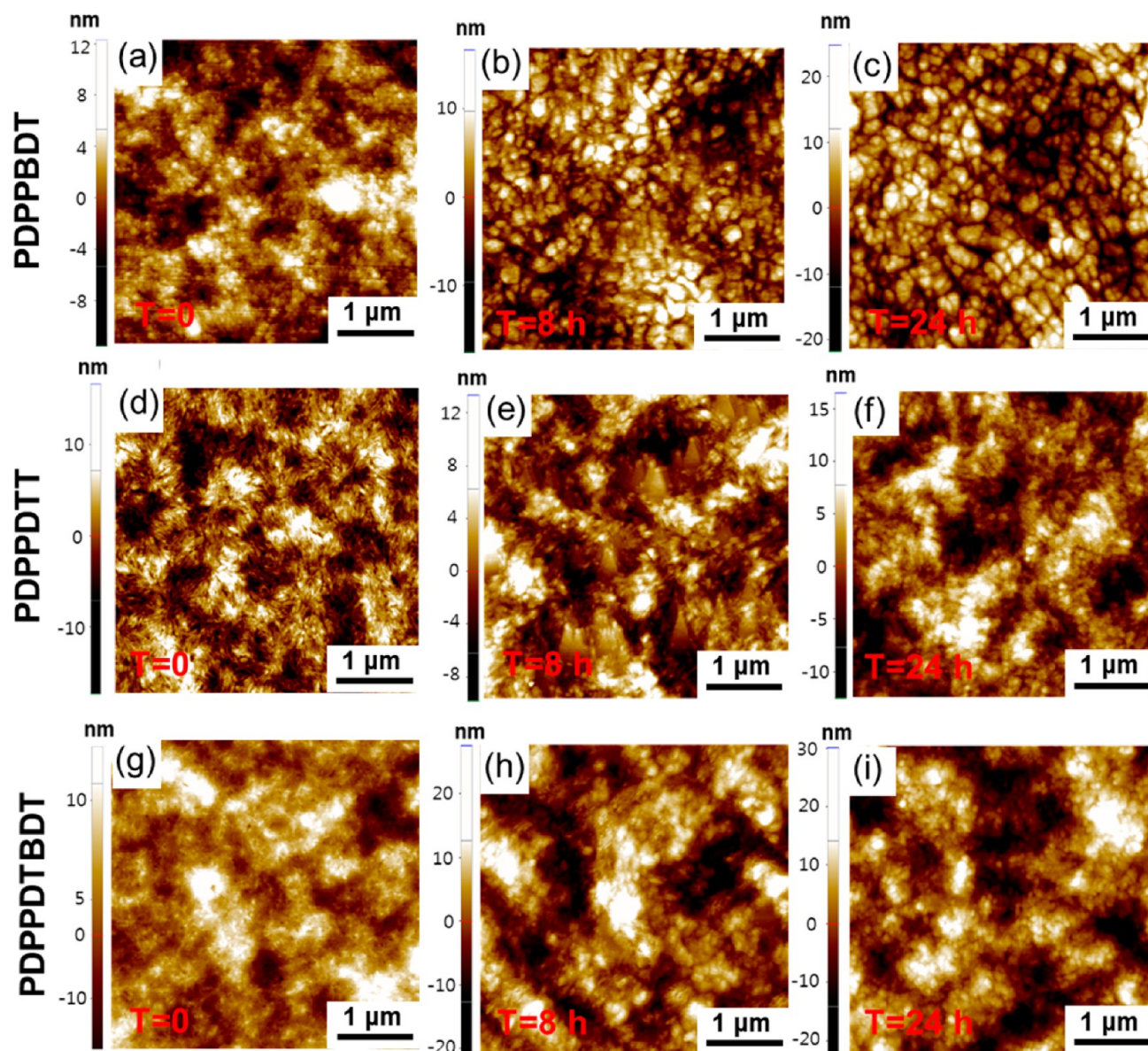
**Figure 6.** Photovoltaic parameter changes of polymer solar cells measured during illumination as a function of time: (a)  $V_{oc}$ , (b)  $J_{sc}$ , (c) FF, and (d) PCE.

advantageous physical properties that contributed to the high solar cell performance. First, the large effective conjugation length decreased the polymer's energy bandgap, which increased photon absorption in the near-IR range. Next, the relatively well-distributed frontier orbitals on PDPPD TT could enhance the intermolecular interactions among the polymer by improving orbital overlap across the smaller  $\pi$ - $\pi$  stacking distance between the polymer chains. These effects improved the charge carrier mobility.<sup>28a,31</sup> The small DTT unit is capable of docking easily into the DPP unit to facilitate effective intermolecular interactions between the polymer chains. The strong intermolecular interactions most likely decreased the solubility of the polymer and prevented overgrowth of the polymer chain during the polycondensation reaction. The proper molecular weight of PDPPD TT contributed to the miscibility with PC<sub>71</sub>BM.<sup>32</sup> By contrast, the high molecular weight of PDPPBDT induced polymer aggregation and the formation of large polymer fibrils and the unoptimized morphology in the polymer:PC<sub>71</sub>BM blend film.<sup>33</sup>

**Stability of Polymer Solar Cells.** Long-term stabilities of the polymer solar cells were studied by monitoring evolution of the photovoltaic parameters of the cell during UV-vis light

soaking as keeping a temperature below 35 °C, and the results are presented in Figure 6. After the light soaking, the PCEs of the solar cells gradually decreased as a function of time while the degrees of decrements are different among the polymers; the PDPPD TT solar cell device was most stable, and PDPPBDT showed the largest degradation during the light-soaking test. After 170 h exposure, PDPPD TT exhibited 80% of its initial PCE while PDPPBDT's performance was reduced to a half. The PCE decrease is mostly due to FF and  $J_{sc}$  reduction. Figure 7 shows atomic force microscopy (AFM) image of the polymer:PC<sub>71</sub>BM blend film prepared with the same condition as the solar cell device. Illumination of the blend films in air at <35 °C induced morphological changes, forming a larger scale phase separation with a higher surface roughness compared with the corresponding films before light soaking. Notably, PDPPBDT exhibiting the fastest device degradation showed a significant increase in the surface root-mean-square (RMS) roughness after illumination whereas the most stable PDPPD TT yielded a small change in a RMS roughness value; after 24 h illumination, values of RMS roughness increased from 3.57 and 3.55 nm to 6.13 and 3.93 nm for PDPPBDT and PDPPD TT, respectively. PDPPDTBDT also



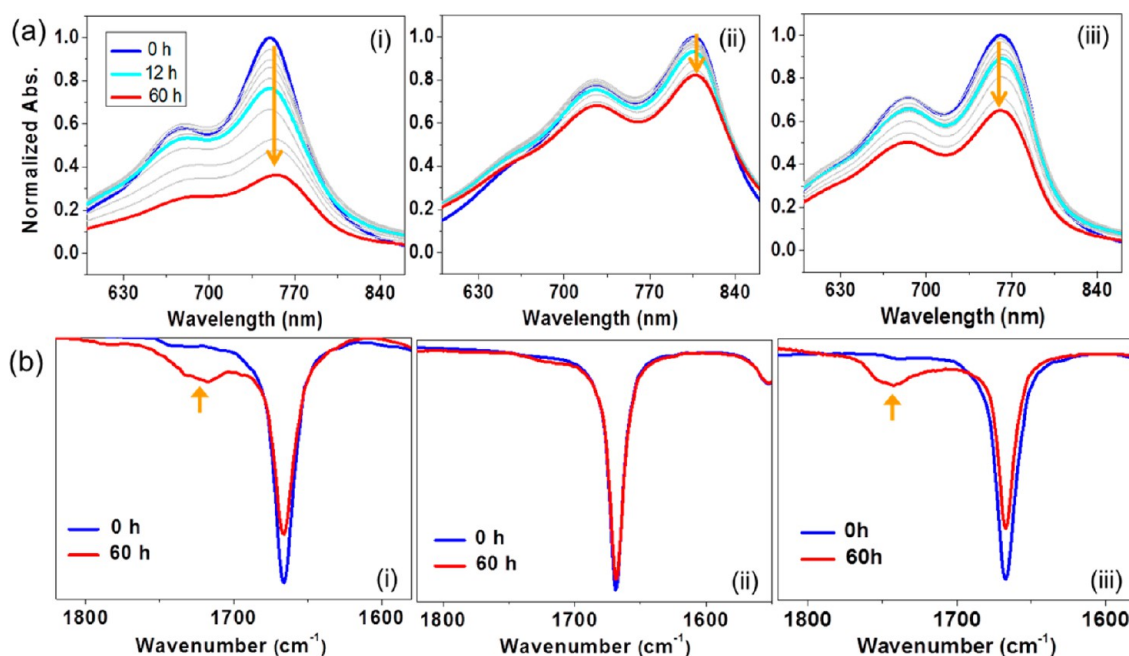


**Figure 7.** AFM topographies of polymer:PC<sub>71</sub>BM blend films at an illumination time of  $T = 0$  h for (a) PDPPBDT, (d) PDPPDTT and (g) PDPPDTBDT,  $T = 8$  h for (b) PDPPBDT, (e) PDPPDTT, and (h) PDPPDTBDT, and  $T = 24$  h for (c) PDPPBDT, (f) PDPPDTT, and (i) PDPPDTBDT.

experienced a roughness increase from 3.21 to 5.27 nm, a degree of which is higher than PDPPDTT but not than PDPPBDT. These results suggest that decreases of the solar cell performance after light soaking are correlated with the morphology alternation, particularly surface roughness increases, induced by device degradation. The unfavorable morphology change may yield poor contact between the active layer and the electrode as well as unfavorable conditions for charge separation and transport.

The device structures and processing conditions were identical for all of the polymers; therefore, the differences between the device stabilities most likely arose from the different stabilities of the polymer in the active layer. The absorption spectra of the spin-coated polymer films were measured after illumination in air and the polymer's relative photochemical stabilities were estimated by comparing the degrees to which the spectral optical densities (ODs) decreased. After 12 h, the ODs of the corresponding  $\lambda_{\max}$

values in the spectra were reduced to 77%, 96%, and 89% of their initial ODs for PDPPBDT, PDPPDTT, and PDPPDTBDT, respectively (Figure 8 and Figure S6). As a result, the photochemical stability was expected to follow the order PDPPDTT > PDPPDTBDT > PDPPBDT, which agreed with the PCE reduction trend observed in the solar cell stability tests. The long-term stability of the solar cell was strongly related to the photochemical stability of the polymer. The degraded polymer may negatively affect the polymer's physical properties such as its photon absorption efficiency and charge carrier mobility and increase charge recombination in the solar cell device, resulting in a decrease in the  $J_{sc}$  and FF. The differences in the polymer stabilities were related to the chemical structures of the donating units in the polymer (all polymers included the DPP unit and the electron-donating units differed). The substitution of alkyl or alkoxy side chains into the benzene moieties in the BDT and DTBDT units can promote a chain dissociation reaction through photooxidation



**Figure 8.** (a) UV-vis absorption spectrum changes after illumination of (i) PDPPBDT, (ii) PDPPDTT, and (iii) PDPPDTBDT films on glass. (b) FT-IR spectrum changes after illumination of (i) PDPPBDT, (ii) PDPPDTT, and (iii) PDPPDTBDT films on glass.

reactions.<sup>34</sup> Anthracene derivatives have been shown to react with singlet oxygen to form 9,10-endoperoxide derivatives.<sup>35</sup> We believe that the BDT or DTBDT units were similarly attacked by singlet oxygen during the photooxidation process. These photooxidation reactions would be expected to break the polymer backbone conjugation. The FT-IR spectra of the degraded polymer films (Figure 8) revealed the presence of new vibration peaks that corresponded to carbonyl groups on both of the oxidized PDPPBDT and PDPPDTBDT polymers. By contrast, PDPPDTT did not show any significant spectral changes over the range 1600–1800 cm<sup>-1</sup>, thereby providing support that the photooxidation mechanism contributed significantly to polymer degradation. Photooxidation reactions are generally favored at electron-rich sites in organic molecules. The high electron density in the dialkoxy-substituted BDT unit was thought to further accelerate the polymer degradation process. We argue that the incorporation of electron-donating solubilizing groups into the low bandgap polymers should be performed carefully so as to maintain a separation distance from the electron-rich photoreactive sites. Such polymer design strategy is expected to enhance the photochemical stability of the polymer.

## CONCLUSION

A series of push-pull-type copolymers PDPPBDT, PDPPDTT, and PDPPDTBDT were synthesized by systematically modifying the chemical structure of the BDT unit in the benzodithiophene and diketopyrrolopyrrole copolymer. Among the polymers, PDPPDTT showed the highest PCE of 6.11% due to the significantly improved  $J_{sc}$ . PDPPDTBDT displayed a high PCE of 4.75% compared to 3.31% for PDPPBDT although its PCE was lower than that of PDPPDTT. The DTT units incorporated into the polymer backbone effectively decreased the polymer's energy bandgap and induced the formation of an appropriate morphology in the polymer:PC<sub>71</sub>BM blend film along with good crystalline properties, thereby improving charge carrier transport. By contrast,

PDPPDTBDT unexpectedly showed a less crystalline film structure despite having a high molecular planarity. Although the performance of PDPPDTBDT was enhanced relative to PDPPBDT due to the improved morphology of the blend film with PC<sub>71</sub>BM, the low charge carrier mobility in PDPPDTBDT reduced the photocurrent density in the solar cell compared with PDPPDTT. These results originated from the differences between the chemical structures of the electron-donating units in the polymer backbone. The frontier orbitals on the PDPPDTBDT polymer backbone were more localized, whereas the effectively delocalized  $\pi$ -orbitals in PDPPDTT provided a long effective conjugation length and enhanced intermolecular  $\pi$ -orbital overlap. The relatively small DTT favored donor-acceptor interactions between neighboring polymer chains, thereby improving  $\pi$ - $\pi$  stacking. Importantly, PDPPDTT exhibited much higher device stability under light-soaking conditions compared with the other polymers. This stability arose mainly from the enhanced photochemical stability of the polymer backbone. In conclusion, several points should be considered in the development of novel push-pull-type conjugated polymers for use in high-performance stable solar cells. First, it is beneficial to incorporate small electron-donating units which induce effective  $\pi$ -orbital delocalization along the polymer backbone. Second, the introduction of electron-donating functional groups such as alkoxy or alkyl groups into a polymer must be performed such that these groups are positioned far from electron-rich sites, particularly photochemically weak sites in the polymer backbone. The PDPPDTT polymer characterized here provides a good example polymer that simultaneously satisfies these guidelines. Ongoing work will continue to explore PDPPDTT derivatives for use in high-efficiency polymer solar cells with a high stability.

## ASSOCIATED CONTENT

### Supporting Information

Experimental details for polymer synthesis and characterization, solar cell device fabrication and measurements, long-term



stability test of solar cells, and GIWAXS, TEM, and AFM measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Authors

\*N.G.P.: Tel +82-31-290-7241; e-mail [npark@skku.edu](mailto:npark@skku.edu).

\*B.S.K.: Tel +82-2-958-5516; e-mail [bongsoo@kist.re.kr](mailto:bongsoo@kist.re.kr).

\*H.J.S.: Tel +82-2-958-5320; e-mail [hjson@kist.re.kr](mailto:hjson@kist.re.kr).

### Author Contributions

T.I.R. and Y.Y. equally contributed to this work.

### Notes

The authors declare no competing financial interest.

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