# Macromolecules

# Effect of Incorporated Nitrogens on the Planarity and Photovoltaic Performance of Donor–Acceptor Copolymers

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**Supporting Information** 

**ABSTRACT:** Systematic control of the chemical structure of conjugated polymers is critically important to elucidate the relationship between the conjugated polymer structures and properties and to optimize their performance in bulk heterojunction (BHJ) polymer solar cell (PSC) devices. Herein, we synthesized three new copolymers, i.e., **P0**, **P1**, and **P2**; these copolymers contain the same benzodithiophene donor unit but have different acceptor units with different numbers of nitrogen atoms in the range of 0–2. The effects of the introduced nitrogen atoms on the structural, optical,



electrical, and photovoltaic properties of the conjugated polymers were investigated; the structural properties of the polymers, in particular, were studied using both experimental (grazing-incidence X-ray scattering (GIXS) measurements) and computational methods (molecular simulation). As the number of introduced nitrogen atoms increased, the planarity of the main chain conformation increased in the order of P0 < P1 < P2. Additionally, the P0, P1, and P2 polymers showed increased interlayer domain spacings of 1.61, 1.72, and 1.78 nm, respectively, with increased intermolecular ordering. These results were in excellent agreement with the simulation results. In addition, the enhanced planarity resulted in a red-shifting at the onset of absorption in the polymer film from 544 to 585 nm, a downshift in the lowest unoccupied molecular orbital (LUMO) energy level from -3.02 to -3.26 eV, and an increase in the hole mobility from  $2.33 \times 10^{-6}$  to  $3.78 \times 10^{-5}$  cm<sup>2</sup>/(V s). As a result, we observed dramatically enhanced performance of the PSCs in the order of P0 < P1 < P2. For example, the  $P2:PC_{61}BM$  device exhibited a 3.5-fold improvement in power conversion efficiency (PCE) compared to that of  $P0:PC_{61}BM$ . The further optimization of P2 with PC<sub>71</sub>BM showed the PCE of 3.22%.

# INTRODUCTION

Polymer solar cells (PSCs) have attracted significant attention as a promising candidate for renewable energy sources because of their flexibility, solution processability, and potential for lowcost fabrication.<sup>1-4</sup> Over the past decade, research efforts have been focused on the development of new conducting polymers and fullerene acceptors to achieve high power conversion efficiency (PCE).<sup>5-13</sup> A facile route for achieving a lowbandgap polymer is the combination of electron-rich donor units with electron-deficient acceptor units, resulting in the formation of donor–acceptor alternating structures. However, challenges still remain in further improving the PCE of PSCs with enhanced stability.

The ability to control the chemical structure of conjugated polymers is critically important to determine their properties and optimize the performance of PSCs. Even small modifications can induce dramatic effects on the physical and chemical properties of conjugated polymers, including their solubility, crystallinity, interchain packing, light absorption, and electrochemical properties.<sup>14–20</sup> In this regard, the effects of the structural modifications in the alkyl solubilizing groups and the polymer backbone on the properties of conjugated polymers have been widely investigated.<sup>21–33</sup> In particular, the

introduction of an additional atom into the polymer backbone provides a promising pathway to fine-tune the electrochemical and physical properties of conjugated polymers, and this approach generally causes dramatic changes in the photovoltaic performance of the polymers.<sup>34,35</sup> For example, Yu and coworkers have reported that the introduction of fluorine atoms into a polymer backbone lowered both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels, which induced changes in the polymer's electrochemical properties and significantly increased the PCE of PSCs from 2.3% to 7.2%.<sup>29</sup> In addition to fluorination, other research groups have reported the effects of introduced oxygen atoms on the properties and the photovoltaic performance of polymers.<sup>36–39</sup>

The introduction of electronegative nitrogen atoms into the conjugated polymers has advantages in that they can be incorporated into the polymer backbone without interfering the conjugation of the polymers due to their multiple binding sites. Thus, it is important to examine the effects of structural

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Figure 1. Synthetic routes and chemical structures of three different polymers, P0, P1, and P2.

changes in the polymer backbone on the properties of conjugated polymers through the introduction of nitrogen atoms. Recently, both the You and Leclerc groups studied the effects of the introduction of nitrogen atoms in conjugated polymers by replacing the benzene in the benzothiadiazole group with a pyridine moiety.<sup>38,40</sup> Interestingly, they observed change in the LUMO levels and in the photovoltaic properties of the polymers. However, the variation of the structural changes by the substitution of benzene with pyridine moiety is limited to the addition of one nitrogen atoms. In addition, the effect of the incorporated nitrogen atoms on the structural properties of the polymer and its correlation with changes in the device performance has not been investigated.

Herein, we systematically investigated the effect of nitrogen atoms introduced into the backbone of conjugated polymers with respect to the polymers' structural properties and focused on their correlation with the polymers' photovoltaic performance. A series of three different polymers, **P0**, **P1**, and **P2**, with 0–2 nitrogen atoms were carefully designed and synthesized (Figure 1). To control the number of nitrogen atoms in the polymer backbone, 1,4-bis(4-hexylthiophen-2-yl)benzene (HTB), 2,5-bis(4-hexylthiophen-2-yl)pyridine (HTP), and 3,6-bis(4-hexylthiophen-2-yl)pyridazine (HTPz) were used as the acceptor unit in the donor–acceptor (D–A) alternating conjugated polymer. Benzo[1,2-b:4,5-b']dithiophene (BDT) was used as the donor unit in the D–A conjugated polymers because it has a planar conjugated structure that can enhance electron delocalization and easily form  $\pi$ – $\pi$  stacking.<sup>10,25,41,42</sup> The effects of the introduced nitrogen atoms on the structural properties of the polymers were investigated using X-ray analysis, and the results were compared with those obtained from molecular simulations. The introduction of nitrogen atoms into the main backbone of the polymers caused an increase in the interlayer domain spacing, a decrease in the  $\pi$ - $\pi$  stacking distance, and significant improvement in the planarity of the polymer. In addition, the increased planarity resulted in a red-shifted absorption onset of the polymer film, a downshifted LUMO level, and an increase in hole mobility by more than an order of magnitude. As a result, dramatic enhancement in the performance of the PSCs was observed in the order of **P0** < **P1** < **P2**.

# RESULTS AND DISCUSSION

**Synthesis of Monomers and Polymers.** To investigate the effect of introduced nitrogen atoms on the properties of the D–A conjugated polymers, three polymers were designed with different numbers of nitrogen atoms. The new copolymers, **P0**, **P1**, and **P2**, were composed of the same BDT donor unit but contained different acceptor units, i.e., HTB, HTP, and HTPz, respectively. These acceptor units contain benzene, pyridine, and pyridazine groups with the number of nitrogen atoms ranging from 0 to 2, respectively. We replaced the benzene in the HTB unit with pyridine and pyridazine, which led to the new acceptor units of HTP and HTPz. The chemical structures and synthetic routes for the new series of three different monomers are outlined in Figure 1. The monomer 2-(tri-*n*-



**Figure 2.** (a) 2D-GIXS images of films of **P0**, **P1**, and **P2**; (b) out-of-plane line cuts of GIXS. Inset: schematic illustration of the edge-on orientation of the polymers with the backbone perpendicular to the substrate. The interchain lamellar spacing and the  $\pi$ - $\pi$  stacking distance are labeled as  $d_1$  and  $d_{2j}$  respectively.

butylstannyl)-4-hexylthiophene (1) was synthesized via the method described in the literature,<sup>43</sup> and the key acceptor units, HTB, HTP, and HTPz, were obtained via the Pd-catalyzed Stille coupling reaction of 1 with the corresponding monomers, 2, 3, and 4, under the same conditions. The bromination of each monomer was then performed with *N*-bromosuccinimide (NBS) to produce compounds 8, 9, and 10, which were prepared successfully and identified by <sup>1</sup>H NMR spectroscopy. The BDT donor unit 11 was synthesized according to the method described in the literature.<sup>10</sup> Then, P0, P1, and P2 were synthesized via the Stille coupling reaction between compounds 8–10 and 11, respectively.

The number-average molecular weight  $(M_n)$  and the polydispersity index (PDI) were measured using high-temperature gel-permeation chromatography (GPC) with *o*-dichlorobenzene (DCB) as the eluent; the instrument was calibrated with polystyrene standards using UV and RI detectors. The polymerization conditions, including the reaction time, were carefully controlled to produce similar  $M_n$  and PDI values for **P0**, **P1**, and **P2**. The  $M_n$  of all the polymers ranged from 10 to 15 kg/mol, with similar PDI values of 1.5–1.7. The thermal properties of the three different polymers were measured by thermal gravimetric analysis (TGA). The onset points of weight loss of **P0**, **P1**, and **P2** occurred at temperatures greater than 300 °C, which demonstrated the high thermal stability of the polymers (Figure S5).

**Structural Properties: X-ray Analysis.** The effect of the incorporated nitrogen atoms on the structural properties of the polymers was investigated by examination of **P0**, **P1**, and **P2** via GIXS measurements. A thin layer (40–50 nm) of PEDOT:PSS was spin-coated onto silicon substrates, and the polymer thin films were subsequently spin-coated on top of the PEDOT:PSS layer. The samples were annealed for 1 h at 180 °C and then slowly cooled. Figure 2 shows the GIXS images of **P0**, **P1**, and

P2, in which each of the 2D GIXS pattern images is divided into a component in the plane of the substrate  $(q_{xy})$  and a component perpendicular to the substrate  $(q_z)$ . For all samples, the diffraction peaks were strongest in the out-of-plane direction, which indicates that the polymer films had a wellorganized structure with lamellar conjugated polymer stacks oriented along the perpendicular axis of the substrate. The domain spacings of the polymers were extracted from the scattering pattern in the in-plane direction. The (100) peak for the **P0** film in Figure 2 was observed at  $q_{xy} = 0.39$  Å<sup>-1</sup>, indicating the corresponding interlayer domain spacing  $(d_1)$ (inset, Figure 2b) was 1.61 nm. Similarly, the  $d_1$  values of P1 and P2 were found to be 1.72 and 1.78 nm, respectively. Therefore, as more nitrogen atoms were introduced into the polymer backbone, the  $d_1$  values of P0, P1, and P2 increased from 1.61 to 1.72 to 1.78 nm, respectively. In addition, as shown in Figure 2b, the P0 film exhibited the only strong firstorder diffraction of a (100) peak in the out-of-plane direction, whereas both P1 and P2 films showed strong (100), (200), and (300) peaks with more pronounced reflections; this result indicates that the polymer stacks in the P1 and P2 films exhibited a higher structural organization. The introduced nitrogen atoms also affected the  $\pi - \pi$  stacking distance between the conjugated polymers. The (010) peaks that correspond to the  $\pi - \pi$  stacking distance  $(d_2)$  (inset, Figure 2b) were the strongest in the in-plane direction for all three polymers. However, the (010) peaks of the P0, P1, and P2 films were observed at different  $q_{xy}$  values of 1.51, 1.72, and 1.75 Å<sup>-1</sup> respectively, which indicates that the  $d_2$  values of the P0, P1, and P2 were 0.42, 0.37, and 0.36 nm, respectively. Furthermore, as shown in Figure 2a, the intensity of the (010) peak of P0 was significantly weaker than those of P1 and **P2**. Because  $\pi - \pi$  stacking is critical for both charge transport and light absorption in the conjugated polymers,44-46 the change in the number of nitrogen atoms can induce different intermolecular interactions that lead to different optical and electrical properties. Therefore, the GIXS results indicated that the planarity of the main chains and their intermolecular ordering increased in the order of P0 < P1 < P2.

Structural Properties: Theoretical Calculation. To gain insight into the effect of the incorporated nitrogen atoms on the planarity of the polymer main chain, molecular simulations were performed using density functional theory (DFT) at the B3LYP/6-31G(d,p) level. The characteristic change in the packing structure of the polymers can be explained by the calculated results of the oligomers' optimized conformation that corresponds to the three different polymers. The dihedral angles between adjacent rings in the repeating unit are denoted as  $D_1$ ,  $D_2$ , and  $D_3$ , as shown in Table 1. The values of the dihedral angles,  $D_1$ ,  $D_2$ , and  $D_3$ , can be controlled by tuning the number of nitrogen atoms in the acceptor unit of the polymer main chain. The dihedral angles  $D_1$ ,  $D_2$ , and  $D_3$  of P0 were estimated to be 27.3°, 23.5°, and 24.7°, respectively. Similarly, those for P1 were 18.6°, 4.5°, and 24.7°, respectively, and those for P2 were 21.0°, 1.9°, and 1.6°, respectively. No significant change was found for the dihedral angles between the BDT unit and thiophene  $(D_1)$ . In contrast, the dihedral angle  $D_2$  of PO (23.5°) was significantly larger than that of P1 ( $D_2 = 4.5^\circ$ ) or **P2**  $(D_2 = 1.9^\circ)$ . Additionally, **P2** exhibited a dramatically lower  $D_3$  value (1.6°) relative to that of P0 ( $D_3 = 24.7^\circ$ ) or P1 ( $D_3 =$ 24.7°). The reduced dihedral angle was likely due to the interaction between the thiophene and the nitrogen atom in the pyridine or pyridazine, which stabilizes the conformation of the

Table 1. Key Dihedral Angles (deg) of the Three Different Polymers



polymers with less-twisted structures.<sup>47,48</sup> As a result, in the case of **P1**, the nitrogen atom oriented toward the thiophene on the left-hand side induced the decrease in the dihedral angle  $D_2$ . Furthermore, in the case of **P2**,  $D_2$  and  $D_3$  decreased simultaneously because the nitrogen atoms were located on both sides of the pyridazine group, which promoted the interaction of the pyridazine group with the adjacent thiophenes. Therefore, the planarity was increased significantly in the order of **P0** < **P1** < **P2** when the nitrogen atoms were added, and the most planar conformation of the main backbone of **P2** led to the strongest interchain interaction, which is consistent with the GIXS results.

Deeper insight into the effect of the nitrogen atoms on the structural properties of the polymers can be obtained from calculations of the interlayer domain spacings  $(d_1)$  of the polymers P0, P1, and P2. The  $d_1$  values of the polymers can be estimated by taking the previously calculated dihedral angles of  $D_2$  and  $D_3$  into account. Since all three polymers have the same electron-rich moiety of BDT even though they showed different  $d_1$  values, the  $d_1$  spacing between the polymer backbones is assumed to be dependent predominantly on the acceptor unit of each polymer. The center-to-end distance of 3hexylthiophene in the electron-deficient unit (0.87 nm) was used in the calculation. As shown in Figure 3 and Table 2, the calculated d<sub>1</sub> spacings of P0, P1, and P2 were 1.59, 1.69, and 1.75 nm, respectively; these values show excellent agreement with the  $d_1$  spacings of P0 (1.61 nm), P1 (1.72 nm), and P2 (1.78 nm) determined from the GIXS patterns. The agreement is remarkable and shows that the measured values of the



**Figure 3.** Calculated  $d_1$  values for **P0**, **P1**, and **P2** based on the dihedral angles  $D_2$  and  $D_3$ .

Table 2. Comparison of the Measured  $d_1$  Spacings (GIXS) with the Spacings Calculated from the Simulations

	domain spacing <sup>a</sup> (nm) $d_1$	calcd domain spacing $(nm) d_1$	$\pi - \pi$ stacking distance (nm) $d_2$						
PO	1.61	1.59	0.42						
P1	1.72	1.69	0.37						
P2	1.78	1.75	0.36						
<sup>a</sup> Obtained from GIXS measurements.									

differences between the  $d_1$  spacings of **P0** and **P1** (0.11 nm) and between the  $d_1$  spacings of **P1** and **P2** (0.06 nm) are identical to the calculated values of the differences. Therefore, the nitrogen atoms resulted in reduced dihedral angles and, thus, the increased planarity. In addition, the trend of the change in the planarity clearly explains the decreasing trend in the  $\pi-\pi$  stacking distance via the incorporation of nitrogen atoms (Table 2). Similar trends have been observed in previous studies:<sup>49-52</sup> poly(3,3'-dioctyl-2,2'-bithiophene) showed a reduced interlayer domain spacing relative to that of poly(3octylthiophene) because of the 40° twisted structure that was induced by head-to-head and tail-to-tail coupling.

**Optical and Electrochemical Properties.** The absorption spectra of the polymers were strongly dependent on their planarity and packing structure. The UV–vis absorption spectra of the three polymers as thin films were measured (Figure 4).



Figure 4. UV-vis absorption spectra of the polymer films.

Table 3. Optical and Electrochemical Properties of thePolymers Used in This Study

polymer	$\lambda_{\max}$ (nm)	$\lambda_{\mathrm{onset}}$ (nm)	$E_{\rm g}~({\rm eV})$	HOMO (eV)	LUMO (eV)
P0	470	544	2.28	-5.30	-3.02
P1	487	573	2.16	-5.35	-3.19
P2	507	585	2.12	-5.38	-3.26

The results are summarized in Table 3. The absorption spectra of **P0**, **P1**, and **P2** exhibited two maxima in the range from 450 to 600 nm; however, significant differences were observed in the locations of the peaks. The spectrum of **P0** showed an absorption maximum ( $\lambda_{max}$ ) at 470 nm with an absorption onset ( $\lambda_{onset}$ ) at 544 nm. The  $\lambda_{max}$  and  $\lambda_{onset}$  values of **P1** were 487 and 573 nm, respectively; these values were considerably red-shifted compared to those of **P0**. In addition, **P2** showed

the strongest red-shifted  $\lambda_{max}$  of 507 nm and  $\lambda_{onset}$  of 585 nm. The optical bandgaps of **P0**, **P1**, and **P2** were estimated to be 2.28, 2.16, and 2.12 eV, respectively, based on the onset of the light-absorption spectra. Therefore, the polymers displayed stronger red-shifts in the absorption onsets and maxima and, thus, lower bandgaps as the number of incorporated nitrogen atoms in the polymer backbone was increased. This phenomenon can be accurately predicted from the changes in the structural properties of the polymers. The GIXS results clearly revealed that the planarity of the main chains and their intermolecular ordering increased in the order of **P0** < **P1** < **P2**, which resulted in the red-shift absorption feature and, thus, better light-absorption ability.<sup>35</sup>

The incorporated nitrogen atoms in the polymer backbone and the resulting change in the planarity of the polymers could affect the electron distribution and consequently alter their HOMO and LUMO levels.53 The electrochemical properties of P0, P1, and P2 were measured using cyclic voltammetry (CV) (Figure S6). The CV curves were recorded with an Ag quasireference electrode, which was calibrated with the absolute energy level of Fc/Fc<sup>+</sup> (4.8 eV under vacuum) as an external standard. The electrochemical properties of these materials are summarized in Table 3. On the basis of the onset oxidation potentials, the HOMO energy levels of P0, P1, and P2 were determined to be -5.30, -5.35, and -5.38 eV, respectively; the LUMO levels of P0, P1, and P2 were estimated to be -3.02, -3.19, and -3.26 eV, respectively, based on the difference between the HOMO level and the optical bandgap of each polymer. The results showed that the incorporation of the nitrogen atoms into the polymer backbone reduced both the HOMO and the LUMO energy levels; however, the trend in the change of LUMO energy levels was significantly more pronounced than that for the HOMO energy levels. This result was probably due to the change in the strength of the electrondeficient acceptor unit in the polymers. The nitrogen atoms acted as electron-withdrawing substituents because of their high electronegativity;54,55 the strength of the acceptor unit consequently increased, which resulted in the decrease in the LUMO levels and the bandgap of the polymers.<sup>56</sup> In addition, because the  $\pi$  electrons tend to delocalize in the planar structure and to localize in the twisted structure, the bandgaps of the polymers decreased in the order of P0 > P1 > P2.

Photovoltaic Properties. To elucidate the relationship between the molecular structure of the conjugated polymers and the performance of the solar cell devices, BHJ-type PSCs (ITO/PEDOT:PSS/active layer/LiF/Al) were fabricated based on blends of P0, P1, and P2 with PC<sub>61</sub>BM, and their performance was measured. Figure 5 shows the current density versus voltage (I-V) curves for the devices under AM 1.5 illumination at 100 mW/cm<sup>2</sup>. The representative characteristics of the PSC devices are summarized in Table 4. Each of the devices was prepared under optimized conditions. The active layers were spin-coated with DCB solution of the polymers and PC<sub>61</sub>BM. The thicknesses of the films of P0, P1, and P2 with  $PC_{61}BM$  showed similar values of ~100 nm, as measured using an alpha-step profiler. The PCEs of the devices increased in order of P0 < P1 < P2, which indicates a linear dependence of the device performance on the number of the nitrogen atoms in the polymer backbone. Among the P0-, P1-, and P2-based BHJ PSCs, the device that consisted of P2:PC<sub>61</sub>BM (1:0.7, w/w) exhibited the highest PCE of 2.78% with  $V_{oc} = 0.73$  V,  $J_{sc} = 6.78$  $mA/cm^2$ , and FF = 0.56, which represents a 3.5-fold increase compared with the PCE of  $P0:PC_{61}BM$  (1:0.6, w/w) (PCE =

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**Figure 5.** (a) Current density–voltage (J-V) characteristics of the PSCs: (i) **P0**:PC<sub>61</sub>BM (1:0.6), (ii) **P1**:PC<sub>61</sub>BM (1:0.7), (iii) **P2**:PC<sub>61</sub>BM (1:0.7), and (iv) **P2**:PC<sub>71</sub>BM (1:0.7)-based BHJ devices under AM 1.5 illumination at 100 mW/cm<sup>2</sup>. (b) Measured space-charge-limited J-V characteristics of the films of **P0**, **P1**, and **P2** under dark conditions.

Table 4. Characteristics of the PSC Devices Composed of Three Different Polymers as the Electron Donor and Fullerene as the Electron Acceptor under AM 1.5G-Simulated Solar Illumination  $(100 \text{ mW/cm}^2)$ 

active layer (w/w)	$\begin{pmatrix} V_{ m oc} \\ (V) \end{pmatrix}$	$J_{\rm sc}$ (mA/cm <sup>2</sup> )	FF	PCE (%)	$({ m cm}^2/({ m V~s}))^a$			
P0:PC <sub>61</sub> BM (1:0.6)	0.52	4.19	0.37	0.81	$2.33 \times 10^{-6}$			
P1:PC <sub>61</sub> BM (1:0.7)	0.59	4.89	0.39	1.13	$8.63 \times 10^{-6}$			
<b>P2</b> :PC <sub>61</sub> BM (1:0.7)	0.73	6.78	0.56	2.78	$3.78 \times 10^{-5}$			
<b>P2</b> :PC <sub>71</sub> BM (1:0.7)	0.72	7.97	0.56	3.22				
<sup><i>a</i></sup> Hole mobility of the pristine polymer films of <b>P0</b> , <b>P1</b> , and <b>P2</b>								

0.81% with  $V_{\rm oc} = 0.52$  V,  $J_{\rm sc} = 4.19$  mA/cm<sup>2</sup>, and FF = 0.37). To gain insight into the performance of the PSCs, the spacecharge-limited current (SCLC) for the polymers was measured (Figure 5). The SCLC mobilities of the polymers are summarized in Table 4. Hole-only devices were constructed with the structure of ITO/PEDOT:PSS/polymer/Au, and hole mobilities were calculated using the Mott-Gurney equation. For films of pristine P0, P1, and P2 polymers, the SCLC mobilities were  $2.33 \times 10^{-6}$ ,  $8.63 \times 10^{-6}$ , and  $3.78 \times 10^{-5}$  cm<sup>2</sup>/ (V s), respectively. The SCLC results can be explained by the structural changes in the polymers in that the nitrogen atoms induced better planarity in the conjugated polymer chain, a decrease in the  $\pi - \pi$  stacking distance, and a highly ordered polymer packing, which are critical factors that determine the charge mobility. Thus, P2, having a shorter  $\pi - \pi$  stacking distance relative to those of P0 and P1, showed the highest hole mobility. Therefore, the trend observed for SCLC mobility clearly explained the increase in the  $J_{sc}$  and FF of the PSCs in the order of P0 < P1 < P2. Further optimization to enhance the PCE was performed with P2:PC71BM. When PC71BM was used as an electron acceptor, the resulting solar cell could exhibit an increased  $J_{sc}$  due to the absorption of PC<sub>71</sub>BM itself, whereas other parameters, including  $V_{oc}$  and FF, remained almost unchanged compared to those in the P2:PC61BM device. Finally, an even higher PCE (3.22%) was achieved with  $V_{\rm oc} = 0.72$  V,  $J_{\rm sc} = 7.97$  mA/cm<sup>2</sup>, and FF = 0.56. Therefore, the small modification in the structure of the conjugated polymer induced by the introduction of nitrogen atoms led to

pronounced improvements in the structural and electronic properties and in the PSC performance.

# CONCLUSIONS

In summary, we successfully synthesized the conjugated polymers P0, P1, and P2, which contain 0-2 nitrogen atoms in their repeating unit, and investigated the effects of the introduced nitrogen atoms on the structural and photovoltaic properties of the polymers. As the number of the introduced nitrogen was increased, the planarity of the polymer was dramatically enhanced, with increased  $d_1$  spacings, decreased  $d_2$ spacings, and better interchain packing between the polymers, as demonstrated by GIXS measurements. The changes in the polymer structure can be explained quantitatively using molecular simulations, which clearly revealed the reduction in the dihedral angles of the polymer chain as a result of the introduction of the nitrogen atoms. In addition, the red-shifted absorption onset and the increased hole mobility of the polymers were achieved due to the increase in planarity and resulted in an increase in the  $J_{sc}$  and FF in the PSCs. Thus, an increased PCE of 3.22% was finally obtained from the P2:PC<sub>71</sub>BM-based PSC, which is  $\sim$ 4-fold increase in the PCE compared to that of P0:PC<sub>61</sub>BM. Therefore, our study provides a model system to investigate the effect of the addition of electronegative nitrogen atoms on the properties of conjugated polymers.

### EXPERIMENTAL SECTION

Synthesis of Monomers and Polymers. All commercially available reagents were used without further purification. The organic solvents were used as anhydrous solvents. Analytical thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates (0.25 mm) with a fluorescent indicator and visualized with UV light S2 (254 and 365 nm). Silica gel chromatography was performed on Merck silica gel 60 (230–400 mesh).

**2-(Tri-***n***-butylstannyl)-4-hexylthiophene (1).** Under an argon atmosphere, 3-hexylthiophene (18.24 g, 108 mmol) and 500 mL of freshly distilled dry THF were placed in a 1000 mL one-necked flask. *n*-Butyllithium (47.69 mL, 2.5 M in hexane, 119 mmol) was added dropwise at -78 °C, and the solution was stirred at -78 °C for 1 h. Then, tributyltin chloride (38.74 g, 119 mmol) was added, and the mixture was allowed to reach room temperature slowly; the mixture was poured into 200 mL of cooled water and extracted with hexane. The organic layer was dried over anhydrous MgSO<sub>4</sub>. Removal of the

solvent by rotary evaporation yielded a brown liquid (48.00 g, 97%). The crude product was used in the next step without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.19 (s, 1H), 6.98 (s, 1H), 2.69 (t, 2H), 1.50-1.67 (m, 14H), 1.30-1.50 (m, 12H), and 0.92 (t, 12H).

**1,4-Bis(4-hexylthiophen-2-yl)benzene (5).** A mixture of 2-(tri*n*butylstannyl)-4-methylthiophene (4.57 g, 10.0 mmol), 1,4-diiodobenzene (1.5 g, 4.5 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.053 g, 0.05 mmol) in toluene (100 mL) was degassed twice with N<sub>2</sub>. The reaction mixture was then heated at 80 °C for 6 h; after cooling, the mixture was poured into water (100 mL) and extracted with diethyl ether. The organic layer was dried over anhydrous MgSO<sub>4</sub>. The crude compound was purified by silica gel chromatography, and white crystals were obtained (0.95 g, 51%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.62 (d, 4H), 7.19 (s, 2H), 6.90 (s, 2H), 2.66 (t, 4H), 1.55–1.65 (m, 4H) 1.20–1.40 (m, 12H), and 0.88 (t, 6H).

**2,5-Bis(4-hexylthiophen-2-yl)pyridine (6).** The synthetic procedure for 6 was similar to that for 5, except that 2,5-dibromopyridine (1 g, 4.2 mmol) was used as the reactant instead of 1,4-diiodobenzene. The crude product of yellow oil (1.05 g, 60%) was obtained and used in the next step without further purification.

**3,6-Bis(4-hexylthiophen-2-yl)pyridazine (7).** The synthetic procedure for 7 was similar to that for **5**, except that 3,6-diiodopyridazine (2 g, 6 mmol) was used as the reactant instead of 1,4-diiodobenzene. After silica gel chromatography, the product of yellow oil (1.64 g, 66%) was obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.73 (d, 2H), 7.54 (s, 2H), 7.10 (s, 2H), 2.73 (t, 4H), 1.55–1.73 (m, 4H), 1.27–1.42 (m, 12H), and 0.77 (t, 6H).

**1,4-Bis(5-bromo-4-hexylthiophen-2-yl)benzene (8).** To a solution of compound **5** (0.95 g, 2.3 mmol) in chloroform (20 mL) and acetic acid (30 mL), NBS (0.91 g, 5.1 mmol) was added at room temperature. The mixture was stirred at room temperature under darkness for 6 h. The solution was then poured into distilled water (200 mL) and extracted with chloroform (200 mL). The organic layer was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed using a rotary evaporator, and the residue was purified by silica gel chromatography to yield the product (0.48 g, 37%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.52 (d, 4H), 7.06 (s, 2H), 2.61 (t, 4H), 1.55–1.66 (m, 4H) 1.20–1.41 (m, 12H), and 0.97 (t, 6H).

**2,5-Bis(5-bromo-4-hexylthiophen-2-yl)pyridine (9).** The synthetic procedure for **9** was similar to that for **8**, except that compound **6** (1.05 g, 2.55 mmol) was used as the reactant instead of compound **5**. The product was purified by silica gel chromatography and then recrystallized in hexane to yield a yellowish-white solid (0.32 g, 22%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 8.74 (s, 1H), 7.80 (d, 1H), 7.59 (d, 1H), 7.36 (s, 1H), 7.09 (s, 1H), 2.65 (t, 4H), 1.45–1.68 (m, 4H), 1.25–1.41 (m, 12H), and 0.89 (t, 6H).

**3,6-Bis(5-bromo-4-hexylthiophen-2-yl)pyridazine (10).** The synthetic procedure for **10** was similar to that for **8**, except that compound 7 (1.64 g, 3.97 mmol) was used as the reactant instead of compound **5**. The product was purified by silica gel chromatography and then recrystallized in hexane to yield a yellow solid (0.32 g, 15%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.65 (d, 2H), 7.34 (s, 2H), 2.61 (t, 4H), 1.59–1.70 (m, 4H), 1.25–1.41 (m, 12H), and 0.85 (t, 6H).

**2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2b:4,5-b']dithiophene.** This compound was synthesized according to the reported procedure.<sup>10</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.50 (*s*, 2H), 4.18 (d, 4H), 1.54–1.83 (m, 8H), 1.32–1.50 (m, 10H), 1.01 (t, 6H), 0.93 (t, 6H), and 0.42 (*s*, 18H).

General Procedure for Polymerization of P0, P1, and P2. 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene, electron-deficient monomers (8, 9, and 10), Pd<sub>2</sub>(dba)<sub>3</sub> (4 mol %), and P(o-tol)<sub>3</sub> (16 mol %) were added into 100 mL flask, and the flask was purged three times with successive vacuum and argon filling cycles. Then, 8 mL of dry chlorobenzene was added subsequently. The mixture was stirred for 36 h at 110 °C. The mixture was cooled to room temperature and poured slowly in methanol (400 mL). The precipitate was filtered through a Soxhlet thimble, purified via Soxhlet extraction for 12 h with methanol, 24 h with hexanes, 12 h with dichloromethane, and 24 h with chloroform, and finally collected with chlorobenzene. The chloroform solution was then concentrated by evaporation and precipitated into methanol (200 mL).

Poly[4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-*alt*-1,4-bis(4-hexylthiophen-2-yl)benzene] (PBDTHTB, PO). 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo-[1,2-b:4,5-b'] dithiophene (0.380 g, 0.492 mmol) and compound 8 (0.28 g, 0.492 mmol) were used. The reddish-brown solid was obtained (183 mg).  $M_n$  = 12.5 kg/mol;  $M_w$  = 21.3 kg/mol; PDI = 1.7.

Poly[4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-*alt*-2,5-bis(4-hexylthiophen-2-yl)pyridine] (PBDTHTP, P1). 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo-[1,2-b:4,5-b'] dithiophene (0.271 g 0.351 mmol) and compound 9 (0.200 g, 0.351 mmol) were used. The reddish-brown solid was obtained (80 mg).  $M_n$  = 10.1 kg/mol;  $M_w$  = 15.2 kg/mol; PDI = 1.5.

Poly[4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-alt-3,6-bis(4-hexylthiophen-2-yl)pyridazine] (PBDTHTPz, P2). 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b'] dithiophene (0.271 g 0.351 mmol) and compound 10 (0.200 g, 0.351 mmol) were used. The brown solid was obtained (83 mg).  $M_n$  = 15.2 kg/mol;  $M_w$  = 22.8 kg/mol; PDI = 1.5.

Characterization Methods. All <sup>1</sup>H NMR spectra were recorded at 400 MHz using CDCl<sub>3</sub> as the solvent, unless otherwise stated. The chemical shifts of all <sup>1</sup>H NMR spectra were referenced to the residual signal of CDCl<sub>3</sub> ( $\delta$  7.26 ppm) on a Bruker 400-MHz NMR instrument. UV-vis absorption spectra were obtained with a JASCO V-570 spectrophotometer. CV curves were measured using a CHI 600C electrochemical analyzer at room temperature with a conventional three-electrode system (Pt-disk working electrode, Pt-wire counter-electrode and Ag-wire quasi-reference electrode). The oxidation potentials of the polymer solutions against the Ag quasireference electrode were measured and calibrated against a ferrocene/ ferrocenium  $(Fc/Fc^+)$  redox couple, where the absolute energy level of Fc/Fc<sup>+</sup> was assumed to be -4.80 eV. GIXS measurements were performed on beamline 9A at the Pohang Accelerator Laboratory (South Korea). X-rays with a wavelength of 1.1010 Å were used. The incidence angle ( $\sim 0.15^{\circ}$ ) was chosen to allow for complete penetration of the X-rays into the polymer film.

Device Fabrication and Measurement. BHJ PSC cells were fabricated using an ITO/PEDOT:PSS/active layer/LiF/Al structure. P0, P1, and P2 were used as electron donors, and either PC<sub>61</sub>BM or PC71BM was used as the electron acceptor. ITO-coated glass substrates were ultrasonicated in acetone and 2% Helmanex soap in water; the substrates were then extensively rinsed with deionized water and then ultrasonicated in deionized water and isopropyl alcohol. The substrates were dried for 1 h in an oven at 80 °C. The ITO substrates were treated with UV-ozone prior to PEDOT:PSS deposition. A filtered dispersion of PEDOT:PSS in water (PH 500) was applied by spin-coating at 3000 rpm for 40 s and baking for 30 min at 140 °C in air. After application of the PEDOT:PSS layer, all subsequent procedures were performed in a glovebox under a N<sub>2</sub> atmosphere. Separate solutions of P0, P1, P2, PC<sub>61</sub>BM, and PC<sub>71</sub>BM in DCB (30 mg/mL) were prepared and stirred at 120 °C for at least 24 h before being filtered through a 0.45  $\mu$ m PTFE syringe filter. Blend solutions composed of P0, P1, and P2 mixed with PC<sub>61</sub>BM or PC<sub>71</sub>BM were prepared to a final polymer concentration of 14 mg/mL. Each solution was spin-cast onto an ITO/PEDOT:PSS substrate at 1200 rpm for 90 s. The substrates were then placed in an evaporation chamber and held under high vacuum (less than  $10^{-6}$  Torr) for at least 1 h before deposition of ~0.7 nm of LiF and 100 nm of Al with a shadow mask that produced four independent devices on each substrate. The photovoltaic performances of the devices were characterized with an AM 1.5G filter. The intensity of the solar simulator was carefully calibrated using an AIST-certified silicon photodiode. Current-voltage behavior was measured using a Keithley 2400 SMU. The active area of the fabricated devices was 0.102 cm<sup>2</sup>. The hole mobilities of the synthesized polymer were measured via the SCLC method using an ITO/PEDOT:PSS/polymer/Au device structure. The SCLC is described by

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$$J_{\rm SCLC} = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{L^3}$$

where  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon$  is the dielectric constant of the polymer,  $\mu$  is the charge-carrier mobility, V is the potential across the device ( $V = V_{applied} - V_{bi} - V_r$ ), and L is the thickness of the polymer layer. The series and contact resistances of the device (~25  $\Omega$ ) were measured using a blank device (ITO/PEDOT:PSS/Au), and the voltage drop caused by this resistance ( $V_r$ ) was subtracted from the applied voltage.

**Theoretical Calculations.** The simulations were performed using density functional theory (DFT) at the B3LYP/6-31G(d,p) level with the Spartan 08 software package. The oligomers with a chain length of n = 3 were chosen as simplified models, and all of the alkyl chains were replaced with methyl chains to make computation possible. In addition, we selected one isomer between two regiochemical isomers of P1 resulting from the asymmetric structure of 1,4-diiodopyridazine.

# ASSOCIATED CONTENT

# **Supporting Information**

TGA data, CV curves, and <sup>1</sup>H NMR spectra of materials. 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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