Macromolecules

A Novel Bis-Lactam Acceptor with Outstanding Molar Extinction Coefficient and Structural Planarity for Donor-Acceptor Type **Conjugated Polymer**

Won Sik Yoon, Dong Won Kim, Jun-Mo Park, Illhun Cho, Oh Kyu Kwon, Dong Ryeol Whang, Jin Hong Kim, Jung-Hwa Park, and Soo Young Park*

Center for Supramolecular Optoelectronic Materials, Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul, 151-744, Korea

Supporting Information

ABSTRACT: A novel electron-accepting bis-lactam building block, 3,7-dithiophen-2-yl-1,5-dialkyl-1,5-naphthyridine-2,6dione (NTDT), and a conjugated polymer P(NTDT-BDT) comprising NTDT as an electron acceptor and benzo[1,2b:4,5-b' dithiophene (BDT) as an electron donor are designed and synthesized for producing efficient organic solar cells. The thermal, electronic, photophysical, electrochemical, and structural characteristics of NTDT and P(NTDT-BDT) are studied in detail and compared with those of the widely used bis-lactam acceptor 3,6-dithiophen-2-yl-2,5-dialkylpyrrolo[3,4-c]pyrrole-1,4-dione (DPPT) and its polymer P(DPPT-BDT). Compared to DPPT derivatives, NTDT and P(NTDT-BDT) exhibit remarkably higher absorption coefficients, deeper highest



occupied molecular orbital energy levels, and more planar conformations. A bulk heterojunction solar cells based on P(NTDT-BDT) exhibit power conversion efficiency of up to 8.16% with high short circuit current (I_{sc}) of 18.51 mA cm⁻², one of the highest Jsc values yet obtained for BDT-based polymer. Thus, it is successfully demonstrated that the novel bis-lactam unit NTDT is a promising building block for use in organic photovoltaic devices.

1. INTRODUCTION

Over the past few decades, π -conjugated polymer semiconductors have drawn great attention for use in solutionprocessed organic photovoltaic devices owing to their applicability in flexible, large-area devices.^{1–5} Recently, bulk heterojunction (BHJ) type polymer solar cells (PSCs) with a power conversion efficiency (PCE) greater than 10% have been reported.⁶⁻¹² Although a PCE of this level for PSCs is quite impressive, further improvements in the conversion efficiency are necessary for these devices to find practical use. To this end, great efforts are being devoted not only to optimizing the device architecture^{13,14} but also to developing high-performance materials.^{15–17}

Donor-acceptor (D-A) type conjugated polymers, involving intramolecular charge transfer via an alternative combination of D and A building blocks along the π -conjugated backbone, are being investigated intensively for use in PSCs, since these materials allow for the facile control of the electronic characteristics based on the rational choice of the D and A units.^{18–25} A large number of studies have revealed that the photovoltaic properties of D-A conjugated polymers are closely associated with the characteristics of both the D and the A moieties in the polymer backbone: 26,27 (a) the quasi-planar conjugated backbones of these polymers, which contain the D

and A units, enhance the charge-carrier mobility owing to the strong π -stacking interactions²⁸ and (b) the light absorptivity of these polymers scales with the oscillator strength of the conjugated backbone, which, in turn, is modulated by the transition dipole moments of the D and A units.²⁹ To this end, numerous studies have reported the synthesis as well as the optoelectrical properties of conjugated polymers comprising different D and A building blocks and also the characteristics of devices based on these polymers.^{30–37} However, while many D building blocks have been studied, only a few A building blocks have been reported so far. These include benzothiadiazole,³⁸⁻⁴⁰ quinoxaline, $^{41-43}$ thieno[3,4-*c*]pyrrole-4,6-dione, 44,45 and lac-tam moieties. $^{46-51}$ Therefore, it is imperative that more A building blocks should be developed through the proper design strategy for high-performance D-A type conjugated polymers.

In this context, planar bis-lactam-based materials, such as thiophenyl substituted diketopyrrolopyrrole (DPPT),52-54 isoindigo (IID),^{55,56} and isoDPPT^{57,58} (Figure 1) have attracted much attention lately as desirable electron-accepting building blocks because of their unique features, which include

Received: August 3, 2016 **Revised:** October 24, 2016



Figure 1. Molecular structures of widely used bis-lactam acceptors and NTDT.

(a) a high electron affinity because of the electron-withdrawing effect of the lactam units, (b) high degree of $\pi-\pi$ stacking, which is driven by their quasi-planar backbone structure, and (c) the possibility of controlling their solubility by incorporating suitable alkyl and aryl side chains in the lactam *N*-atom position.⁵⁹

Inspired by such beneficial effects of bis-lactam compounds, we attempted to develop a high-performance bis-lactam compound of 3,7-dithiophen-2-yl-1,5-dialkyl-1,5-naphthyridine-2,6-dione (NTDT) (Figure 1) in this work. NTDT is structurally based on 1,5-dihydro-1,5-naphthyridine-2,6-dione,

Scheme 1. Synthesis of P(NTDT-BDT) and P(DPPT-BDT)

which was first synthesized by Rapoport in 1971⁶⁰ and barely used as monomer of conjugated polymer.^{61,62} While both NTDT and DPPT are expected to be electron deficient, based on the bis-lactam unit, their electronic and photophysical properties are probably different, owing to the difference in the ring sizes of their lactam units. Interestingly, density functional theory (DFT) calculations and single-crystal analyses have revealed that the optimized geometry of NTDT corresponds to a coplanar conformation. It is worth noting that, through timedependent DFT (TD-DFT) calculations, we found that NTDT has a higher oscillator strength (f value) than that of DPPT, which is known to be a compound with a high molar absorption coefficient. In addition, NTDT allows for alkylation through the introduction of various solubilizing side groups at the lactam N-position. This could allow for the realization of simple solubility control without having to use any solubilizing comonomers.

Given these advantages of NTDT, we designed and synthesized a new D-A type conjugated copolymer P-(NTDT-BDT) with NTDT as a novel bis-lactam-based A



P(DPPT-BDT)

	$M_{\rm n}^{\ a}$ (kDa)	PDI ^a	$T_d^{\ b}$ (°C)	$\lambda_{ ext{max,sol}/ ext{film}}^{c} \binom{d}{(ext{nm})}$	$\varepsilon \text{ at } \lambda_{\max} \times 10^4 {}^e (\mathrm{M}^{-1} \mathrm{cm}^{-1})$	absorption coefficient at $\lambda_{\rm max} \times 10^{4f} ({\rm cm}^{-1})$	HOMO/LUMO ^g (eV)	HOMO/LUMO ^h (eV)	$E_{g}^{opt i}$ (eV)
NTDT	-	-	350	497/533	5.10	-	-5.15/-2.56	-5.42/-3.13	2.29
DPPT	-	-	316	549/601	3.14	-	-4.97/-2.52	-5.22/-3.26	1.96
P(NTDT-BDT)	60.7	3.15	358	651/667	-	31.7	-4.89/-2.86	-5.33/-3.67	1.66
P(DPPT-BDT)	59.3	2.84	343	748/754	-	15.7	-4.79/-2.93	-5.23/-3.91	1.32
					1				

^{*a*}Determined by GPC using polystyrene standards in CHCl₃. ^{*b*}5% weight-loss temperature measured by TGA under nitrogen flow. ^{*c*}Measured in CHCl₃ solution (5 × 10⁻⁵ M). ^{*d*}Thin film was spin-coated from CHCl₃ solution onto a quartz substrate. ^{*c*}Measured from solution absorption spectra at λ_{max} . ^{*f*}Measured from solution absorption spectra at λ_{max} . ^{*f*}Measured from DFT calculations. ^{*h*}HOMO: measured by cyclic voltammetry. LUMO: HOMO + E_g^{opt} . ^{*i*}Determined from the onset of UV–vis absorption spectra.

building block and the representative D unit of benzo[1,2-*b*:4,5*b'*]dithiophene (BDT) as the first example of an NTDTincorporating polymer semiconductor. P(DPPT-BDT)⁶³⁻⁶⁵ was also synthesized as a reference sample for P(NTDT-BDT), since the DPPT unit has extensively been used as the most efficient bis-lactam unit in the D–A type conjugated polymer. Furthermore, the electronic, thermal, photophysical, electrochemical, structural, and photovoltaic properties of P(NTDT-BDT) were studied in depth, in order to demonstrate the high potential of NTDT for use in organic optoelectronics.

2. RESULTS AND DISCUSSION

Synthesis and Characterization. The route for synthesizing the thienyl-substituted NTD monomer (NTDT) is depicted in Scheme 1. 6-methoxy-1,5-naphthyridin-2(1H)-one (2) was synthesized as reported.⁶⁶ The subsequent Odemethylation of 2 with hydrogen bromide yielded the 1,5dihydro-1,5-naphthyridine-2,6-dione compound 3, which was then N-alkylated with 1-bromooctane in the presence of cesium carbonate to obtain 1,5-dioctyl-1,5-naphthyridine-2,6-dione (4, NTD). This compound was brominated with bromine to obtain 3,7-dibromo-1,5-dioctyl-1,5-naphthyridine-2,6-dione (5), which was then reacted with tributyl(thiophen-2-yl)stannane under typical Stille coupling reaction conditions; this yielded the NTDT monomer 6. The copolymers containing the NTDT and DPPT building blocks, namely, P(NTDT-BDT) and P(DPPT-BDT), were prepared through Stille-coupling polymerization using BDT as an electron-rich counterpart. The number-average molecular weight $(M_{\rm p})$ and polydispersity index (PDI) values of P(NTDT-BDT) and P(DPPT-BDT) were determined by gel permeation chromatography (GPC). The results revealed that both polymers had a high molecular weight ($M_n = 60.7 \text{ kDa}$, PDI = 3.15 for P(NTDT-BDT) and $M_n = 59.3$ kDa, PDI = 2.84 for P(DPPT-BDT)). Thermal gravimetric analysis (TGA) measurements were performed to investigate the thermal stabilities of the monomers (NTDT and **DPPT**) and polymers (**P**(**NTDT-BDT**) and **P**(**DPPT-BDT**)). As shown in Figure S1 (Supporting Information), the NTDTbased materials (NTDT thermally stable up to 350 °C and P(NTDT-BDT)) up to 358 °C) exhibited higher thermal stabilities than the DPPT-based materials (DPPT thermally stable up to 316 °C and P(DPPT-BDT) up to 343 °C).

Theoretical Calculations. The molecular structures and optimized geometries of the electron-deficient building blocks (NTDT and DPPT (R = Me)) were analyzed through theoretical quantum chemical calculations, which were performed using Gaussian 09 at the B3LYP level with the basis set of 6-31G**, as shown in Figure S2, parts a and b (Supporting Information), respectively. As expected, both NTDT and DPPT exhibited a higher degree of planarity with

a small thiophene-core dihedral angle (<1°), which facilitated charge-carrier transport via strong $\pi - \pi$ stacking interactions.⁶⁷ The calculated highest occupied molecular orbital (HOMO)/ lowest unoccupied molecular orbital (LUMO) values for the two building blocks were found to be -5.15/-2.56 eV (for NTDT) and -4.97/-2.52 eV (for DPPT) (Table 1). Furthermore, to be able to predict the optimized geometries of P(NTDT-BDT) and P(DPPT-BDT), we performed calculations on double-repeat units ((NTDT-BDT)₂ and (DPPT-BDT)₂) of the two polymers with methyl-substituted alkyl chains (Figure S2, parts c and d, Supporting Information). The computational results confirmed that they also had highly planar geometries, with the NTDT-based molecules having deeper HOMO levels than those of the DPPT-based molecules.

Single Crystal Analysis. To gain a deeper insight into the conformations of these core units, single-crystal X-ray diffraction analyses were conducted. Single crystals of NTDT and DPPT were prepared by the solvent diffusion crystal growth method using a dichloromethane/methanol (7:3 v/v for NTDT and 8:2 v/v for DPPT) solution. As shown in Figure 2, the single-crystal XRD structures of both NTDT (Figure 2a)



Figure 2. Crystal structures and molecular stacking structures of (a) NTDT and (b) DPPT.



Figure 3. UV-vis absorption spectra of (a, b) NTDT and DPPT and (c, d) P(NTDT-BDT) and P(DPPT-BDT) in CHCl₃ solution and thin-film form on glass substrates. Energy level diagrams of (e) NTDT and DPPT and (f) P(NTDT-BDT) and P(DPPT-BDT). Light bars denote data obtained from DFT calculations while dark bars represent experimental data.

and DPPT (Figure 2b) belong to the monoclinic crystal system (see Tables S1 and S2 for the crystallographic data, Supporting Information). It can be seen clearly that, in DPPT, intramolecular hydrogen-bonded (O…H) interactions occur with the bond distance being 2.28 Å. In contrast, in NTDT, S…O interactions occur between the sulfur of the thiophene molecule and the oxygen of the carbonyl group, with the bond distance being 2.69 Å. These results indicated that the energetically preferable conformations of the two units are determined by different nonbonding interactions, which, in turn, are influenced by the steric factor, inter- and intramolecular interactions, and the degree of π -conjugation.⁶⁸ Interestingly, the single crystal of NTDT showed a quasi-planar structure, with the torsional angle (1.38°) between thiophene and the mean plane of the NTDT core being much smaller than that in the case of DPPT (10.93°). In addition, the intermolecular $\pi - \pi$ distance in the NTDT crystal (3.40 Å) is slightly smaller than that in **DPPT** (3.42 Å), indicating that the $\pi - \pi$ interaction in the NTDT is as strong as DPPT, owing to the rigid molecular structure.

Optical and Electrochemical Properties. The photophysical properties of the bis-lactam monomers (NTDT and DPPT) as well as the polymers (P(NTDT-BDT) and P(DPPT-BDT)) were examined by UV-vis absorption spectroscopy both in the solution state $(1.0 \times 10^{-5} \text{ M},$ CHCl₃) and in the film state (using spin-cast films formed on quartz substrates). NTDT exhibited the maximum absorption (λ_{\max}^{abs}) at 497 nm in solution (533 nm in film form) whereas that of DPPT was observed at 549 nm (601 nm in film form) (Figure 3a and Table 1), indicating that NTDT exhibits a relatively weaker intramolecular charge transfer (ICT) transition between the NTD unit and the flanked thiophene unit than that seen in DPPT. However, NTDT showed a markedly larger molar extinction coefficient (51 000 $M^{-1} cm^{-1}$) at the λ_{max}^{abs} level in solution form than that of **DPPT**, which was 31 400 M⁻¹ cm⁻¹ (Figure 3b). To elucidate the reason for these differences in the absorption characteristics, TD-DFT calculations were performed for NTDT and DPPT. As shown in Figure S3 (Supporting Information), the S_0-S_1 transition energy spectra of the two units matched well with the corresponding experimental results. Furthermore, the computed oscillator strength indicated that the f value of NTDT (=0.9064) was much larger than that of **DPPT** (=0.4773); this was consistent with the trend observed in the experimentally

determined molar extinction coefficients. Parts c and d of Figure 3 show the UV-vis absorption spectra of P(NTDT-BDT) and P(DPPT-BDT); As for the solid-state film, the absorption spectra of both polymers are broadly spanned and extended to the longer wavelength region compared to the solution-state absorption region. However, both polymers showed different degrees of bathochromically shifted maximum absorption ($\Delta \lambda_{\max}^{abs}$) in the solid states from those in solution (16 nm for P(NTDT-BDT) and 6 nm for P(DPPT-BDT) (Table 1)). Compared to P(DPPT-BDT), P(NTDT-BDT) showed a larger solution-to-thin film peak shift, indicating that the intermolecular $\pi - \pi$ stacking of P(NTDT-BDT) is more efficient than that of P(DPPT-BDT) in the solid state. Most significantly, P(NTDT-BDT) exhibits absorption maximum in the shorter-wavelength but with much higher absorption coefficient when compared with P(DPPT-BDT) (317 000 cm⁻¹ for P(NTDT-BDT) and 157 000 cm⁻¹ for P(DPPT-BDT)) in the film state). It should be noted that this value of the absorption coefficient is one of the highest reported for D-A type copolymers and would ensure that the material is suitable for harvesting photons and increasing the short-circuit current (J_{sc}) in photovoltaic devices.

To estimate the frontier MO energies of the core units and polymers, cyclic voltammetry (CV) analyses were performed on the solutions (CH₂Cl₂/0.1 M Bu₄NBF₄) and solid-state films (spin-coated on indium tin oxide (ITO) substrates) of the compounds (Figure S4, Supporting Information). From the CV analyses, the HOMO energy levels of NTDT, DPPT, P(NTDT-BDT), and P(DPPT-BDT) were determined to be -5.42, -5.22, -5.33, and -5.23 eV, respectively. In addition, the LUMO energy levels of these molecules were evaluated from their HOMO levels and optical band gaps (E_{σ}^{opt}) of NTDT, 2.29 eV; E_{g}^{opt} of DPPT, 1.96 eV; E_{g}^{opt} of P(NTDT-**BDT**), 1.66 eV; E_g^{opt} of **P(DPPT-BDT**), 1.32 eV), as depicted in Figure 3, parts e and f. The experimental HOMO/LUMO values of these molecules were in good agreement with the calculated ones. Specifically, the NTDT monomer and its polymer were found to exhibit relatively deeper HOMO levels than those of the corresponding **DPPT** derivatives. This should make the former suitable for increasing the open-circuit voltage $(V_{\rm oc})$ of PSCs.

Photovoltaic Properties. PSCs were fabricated using each of the two polymers as the electron donor and $PC_{71}BM$ as the electron acceptor. The structure of the devices was that of a



Figure 4. (a) Current density-voltage (J-V) curves and (b) IPCE spectra of optimized inverted photovoltaic devices based on P(NTDT-BDT):PC₇₁BM and P(DPPT-BDT):PC₇₁BM blends.

Table 2. Photovoltaic Parameters of Optim	ized P(NTDT-BDT	'):PC ₇₁ BM and P(DPPT-BDT):F	PC ₇₁ BM BHJ Device	es'
---	-----------------	-------------------------------	-------------	--------------------------------	-----

material ^b	$V_{\rm oc}^{\ \ c}$ (V)	$J_{\rm sc}^{c}$ (mA cm ⁻²)	FF ^c	PCE ^c (%)			
P(NTDT-BDT):PC ₇₁ BM	$0.70 \ (0.70 \ \pm \ 0.01)$	$18.51 (17.10 \pm 0.89)$	$0.63 \ (0.64 \pm 0.01)$	$8.16 (7.64 \pm 0.27)$			
P(DPPT-BDT):PC ₇₁ BM	$0.66 \ (0.65 \pm 0.01)$	$7.24 \ (6.74 \pm 0.35)$	$0.68 \ (0.67 \pm 0.01)$	$3.26~(2.95~\pm~0.18)$			
^{<i>a</i>} ITO/ZnO/PEI/polymer:PC ₇₁ BM/MoO ₃ /Ag. ^{<i>b</i>} Weight ratio of polymer:PC ₇₁ BM is 1:2. ^{<i>c</i>} Average values were obtained from 10 devices.							

conventional BHJ device: ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. In order to optimize the performances of the PSCs, we fabricated the devices under different conditions by varying the solvent conditions and polymer concentrations. To optimize the charge-transporting network of the photoactive layer, we also used various additives, such as 1,2-dichlorobenzene (DCB) and 1,8-diiodooctane (DIO) (Table S3, Supporting Information).^{69,70} The PSC devices without an additive were found to exhibit low PCEs; this was the case for both P(NTDT-BDT) and P(DPPT-BDT). The device formed using $P(NTDT-BDT)/PC_{71}BM = 1:2 (w/w)$ and in which DCB was added to $CHCl_3$ ($CHCl_3/DCB = 85:15$ v/v) showed the best performance, with the $V_{\rm oc}$ of 0.72 V, the $J_{\rm sc}$ of 16.99 mA cm⁻², the fill factor (FF) of 0.58, and the PCE of 7.11% (Table S3 and Figure S5a, Supporting Information). In the case of the P(DPPT-BDT)-based device, the addition of DIO to CHCl₃ (CHCl₃/DIO = 95:5 v/v) resulted in the optimization of its performance, with V_{oc} of 0.66 V, J_{sc} of 7.72 mA cm⁻², FF of 0.60, and PCE of 3.08% (Table S3 and Figure S5b, Supporting Information); these values are comparable to previously reported results.⁶³⁻⁶⁵ The higher V_{oc} value of the P(NTDT-BDT):PC71BM device was consistent with the fact that the HOMO level of P(NTDT-BDT) was lower than that of P(DPPT-BDT).

To further improve the performance of the P(NTDT-BDT) device, inverted devices were fabricated with the ITO/ZnO/ polyethylenimine/polymer:PC₇₁BM/MoO₃/Ag configuration. Figure 4a shows the current–voltage (J-V) characteristics of the optimized inverted PSC device; the other related data are listed in Table 2. The inverted device exhibited higher J_{sc} (18.51 mA cm⁻²) and FF (0.63) than those of the conventional cell. To the best of our knowledge, this J_{sc} value of P(NTDT-BDT) is the highest value yet reported for BDT-based polymer in PSCs.⁷¹ As a result, the inverted device exhibited the highest PCE, which was 8.16%. The corresponding incident photon-to-current efficiency (IPCE) of the polymer:PC₇₁BM devices under the optimized conditions are displayed in Figure 4b; it can be seen that the integrated current values from the IPCE

spectrum (18.06 mA cm⁻² for **P(NTDT-BDT)** device and 7.22 mA cm⁻² for **P(DPPT-BDT)** device) are well matched with the J_{sc} values obtained from their J-V curves.

Morphology Investigation. To investigate the ordered structures of solid-state films of these polymers, grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were carried out on pristine films of the polymer: $PC_{71}BM$ blended films and polymer: $PC_{71}BM$ blended films and polymer: $PC_{71}BM$ blended films with additives (Figure 5). The GIWAXS pattern of the pristine **P(NTDT-BDT)** film showed interlamellar stacking (h00) peaks in the in-plane direction and a $\pi - \pi$ stacking peak (010) in the out-of-plane direction at $q_z = 1.68$



Figure 5. Two-dimensional GIWAXS images of pristine films of (a) P(NTDT-BDT) and (b) P(DPPT-BDT), films of (c) $P(NTDT-BDT):PC_{71}BM$ and (d) $P(DPPT-BDT):PC_{71}BM$ blends and optimized films of (e) $P(NTDT-BDT):PC_{71}BM$ with 15 vol % DCB and (f) $P(DPPT-BDT):PC_{71}BM$ with 5 vol % DIO blends.



Figure 6. (a–d) AFM height images (5 μ m × 5 μ m) of (a) **P(NTDT-BDT)**:PC₇₁BM blend film, (b) **P(NTDT-BDT)**:PC₇₁BM:additive (DCB; 15 vol %) blend film, (c) **P(DPPT-BDT)**:PC₇₁BM blend film, and (d) **P(DPPT-BDT)**:PC₇₁BM:additive (DIO; 5 vol %) blend film; (e–h) TEM images of (e) **P(NTDT-BDT)**:PC₇₁BM blend film, (f) **P(NTDT-BDT)**:PC₇₁BM:additive (DCB; 15 vol %) blend film, (g) **P(DPPT-BDT)**:PC₇₁BM blend film, and (h) **P(DPPT-BDT)**:PC₇₁BM:additive (DIO; 5 vol %) blend film, (g) **P(DPPT-BDT)**:PC₇₁BM blend film, and (h) **P(DPPT-BDT)**:PC₇₁BM:additive (DIO; 5 vol %) blend film, (g) **P(DPPT-BDT)**:PC₇₁BM:additive (DIO; 5 vol %) blend film.

Å⁻¹, which corresponded to face-on $\pi - \pi$ stacking. The face-on orientation of P(NTDT-BDT) is suitable for increasing the vertical charge-carrier mobility and resulted in a high J_{sc} value in the corresponding PSCs.⁷²⁻⁷⁴ On the other hand, the GIWAXS pattern of the pristine P(DPPT-BDT) film displayed weak and broad interlamellar scattering (h00) and (010) peaks in both the in-plane and the out-of-plane directions, indicating that P(DPPT-BDT) exhibits a mix of face-on and edge-on orientations. Furthermore, the π -overlap distances (d_{π}) in the pristine polymer films were calculated to be 3.74 Å (q_z = 1.68 Å⁻¹) and 3.78 Å ($q_z = 1.66$ Å⁻¹) for P(NTDT-BDT) and P(DPPT-BDT), respectively. When P(NTDT-BDT) was blended with PC₇₁BM (Figure 5c) and PC₇₁BM/DCB additive (Figure 5e), the intensities of the $\pi - \pi$ stacking peak (010) in the out-of-plane direction somewhat decreased; however, the blended films exhibited diffraction patterns similar to those of the pristine polymer films; the only difference was that the diffraction pattern of PC71BM was present in the case of the blended films, indicating that the blend films maintain the faceon orientation due to the highly crystalline nature of P(NTDT-BDT). In case of P(DPPT-BDT), however, diffraction patterns of the blended films were quite different from those of the pristine film. As shown in Figure 5d, the $\pi-\pi$ stacking peak (010) in the q_z direction disappered, indicating that the molecular ordering of P(DPPT-BDT) could be easily affected by the presence of $PC_{71}BM$. After adding the DIO additive (Figure 5f), however, the molecular orientation largely changed to normal to the substrate plane again, which is beneficial for vertical charge transport.

Atomic force microscopy (AFM) and transmission electron microscopy (TEM) were used for investigating the nanoscale morphologies of the two polymers (Figure 6). The effect of the additive treatment could be visualized through the AFM and TEM images. When an additive was not used, both the $P(NTDT-BDT):PC_{71}BM$ and $P(DPPT-BDT):PC_{71}BM$ blend films exhibited macroscopic phase separation between the polymer and $PC_{71}BM$. After treatment with an additive, however, bicontinuous network with finer nanoscale features was observed in the $P(NTDT-BDT):PC_{71}BM$ blend film.

Although the additive treatment of P(DPPT-BDT):PC₇₁BM blend was also effective to form the nanoscale morphology, they showed poorer film homogeneity with high root-meansquare roughness (6.23 nm) than the P(NTDT-BDT):PC₇₁BM blend film (1.02 nm). Thus, the more extensive and homogeneous interface formed in the P(NTDT-BDT):PC₇₁BM blend film led to more efficient charge separation, resulting in the J_{sc} values of the PSC devices based on this blend film being higher than those of the devices based on the P(DPPT-BDT):PC₇₁BM blend film.

Charge Carrier Transport Properties. To further elucidate the charge-transport characteristics of the polymers, their charge-carrier mobilities were investigated by using the space-charge-limited current (SCLC) model as well as organic field-effect transistors (OFETs). The measured SCLC hole mobilities of P(NTDT-BDT) and P(DPPT-BDT) were found to be 3.4×10^{-3} cm² V⁻¹ s⁻¹ and 2.5×10^{-4} cm² V⁻¹ s⁻¹, respectively (Figure S6, Supporting Information). The fieldeffect mobilities of the two polymers were determined by using the polymers for the active layers in typical bottom-gate topcontact OFETs. As shown in Figure S7 (Supporiting Information), P(NTDT-BDT) and P(DPPT-BDT) exhibited p-type organic semiconductor characteristics (hole mobility of $5.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for P(NTDT-BDT) and $1.2 \times 10^{-2} \text{ cm}^2$ V^{-1} s⁻¹ for P(DPPT-BDT)). That is to say, P(NTDT-BDT) exhibited a much higher hole mobility than P(DPPT-BDT) in the vertical direction (SCLC method; the charge carriers flowed in the vertical direction), while P(DPPT-BDT) showed a higher hole mobility than P(NTDT-BDT) in the lateral direction (OFET; the charge carriers flowed in the lateral direction). From these results, it was concluded that the preferentially face-on oriented P(NTDT-BDT) film was more suitable for vertical charge transport than the mixed (face-on + edge-on) orientation P(DPPT-BDT) film. This leads to a higher J_{sc} values for P(NTDT-BDT).

3. CONCLUSION

We synthesized and characterized a novel bis-lactam-based A building block, NTDT, for D-A type conjugated polymers.

The NTDT unit exhibits a high coplanarity of the conjugated backbone owing to the intramolecular S…O interactions. The electron-deficient nature and quasi-planar structure with remarkably high molar extinction coefficient of the NTDT unit could allow for the realization of high efficient D-A copolymer. In fact, the NTDT incorporated conjugated polymer P(NTDT-BDT) exhibited a deeper HOMO level, higher absorption coefficient, and higher vertical charge-carrier mobility than those of the widely used copolymer P(DPPT-BDT). Furthermore, P(NTDT-BDT) also exhibited the appropriate nanoscale morphology and the proper ordered structure with a coplanar geometry. All these factors ensured that the PSCs based on P(NTDT-BDT) exhibited better performance. As a result, a BHJ PSC device based on P(NTDT-BDT) with $PC_{71}BM$ showed an high PCE of 8.16% with a high J_{sc} value of 18.51 mA cm⁻². This J_{sc} value is one of the highest values yet obtained for BDT-based polymer in PSCs. On the basis of these results, we strongly believe that the NTDT is a promising A building block for conjugated polymers and can potentially replace DPPT in organic solar cells.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.6b01680.

Experimental details, Figures S1–S7, and Tables S1–S3 (PDF)

Structure of NTDT (CIF) Structure of DPPT (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: parksy@snu.ac.kr (S.Y.P.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) through a grant funded by the Korean Government (MSIP; No. 2009-0081571[RIAM0417-20150013]).

REFERENCES

(1) Günes, S.; Neugebauer, H.; Sariciftci, N. S. Conjugated Polymer-Based Organic Solar Cells. *Chem. Rev.* 2007, 107, 1324–1338.

(2) Krebs, F. C. Fabrication and Processing of Polymer Solar Cells: A Review of Printing and Coating Techniques. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 394–412.

(3) Brabec, C. J. Organic Photovoltaics: Technology and Market. Sol. Energy Mater. Sol. Cells 2004, 83, 273–292.

(4) Darling, S. B.; You, F. The Case for Organic Photovoltaics. *RSC Adv.* **2013**, *3*, 17633–17648.

(5) Scharber, M. C.; Sariciftci, N. S. Efficiency of Bulk-Heterojunction Organic Solar Cells. *Prog. Polym. Sci.* 2013, 38, 1929–1940.

(6) You, J. B.; Dou, L. T.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C.-C.; Gao, J.; Li, G.; Yang, Y. A Polymer Tandem Solar Cell with 10.6% Power Conversion Efficiency. *Nat. Commun.* **2013**, *4*, 1446.

(7) Liu, Y. H.; Zhao, J. B.; Li, Z. K.; Mu, C.; Ma, W.; Hu, H.; Jiang, K.; Lin, H. R.; Ade, H.; Yan, H. Aggregation and Morphology Control

Enables Multiple Cases of High-Efficiency Polymer Solar Cells. Nat. Commun. 2014, 5, 5293.

(8) He, Z.; Xiao, B.; Liu, F.; Wu, H.; Yang, Y.; Xiao, S.; Wang, C.; Russell, T. P.; Cao, Y. Single-Junction Polymer Solar Cells with High Efficiency and Photovoltage. *Nat. Photonics* **2015**, *9*, 174–179.

(9) Liu, C.; Yi, C.; Wang, K.; Yang, Y.; Bhatta, R. S.; Tsige, M.; Xiao, S.; Gong, X. Single-Junction Polymer Solar Cells with Over 10% Efficiency by a Novel Two-Dimensional Donor–Acceptor Conjugated Copolymer. *ACS Appl. Mater. Interfaces* **2015**, *7*, 4928–4935.

(10) Zhou, H. Q.; Zhang, Y.; Mai, C. K.; Collins, S. D.; Bazan, G. C.; Nguyen, T.-Q.; Heeger, A. J. Polymer Homo-Tandem Solar Cells with Best Efficiency of 11.3%. *Adv. Mater.* **2015**, *27*, 1767–1773.

(11) Zhao, J.; Li, Y.; Yang, G.; Jiang, K.; Lin, H.; Ade, H.; Ma, W.; Yan, H. Efficient Organic Solar Cells Processed from Hydrocarbon Solvents. *Nat. Energy* **2016**, *1*, 15027.

(12) Zhao, W.; Qian, D.; Zhang, S.; Li, S.; Inganäs, O.; Gao, F.; Hou, J. Fullerene-Free Polymer Solar Cells with over 11% Efficiency and Excellent Thermal Stability. *Adv. Mater.* **2016**, *28*, 4734–4739.

(13) Hau, S. K.; Yip, H.-L.; Jen, A. K.-Y. A Review on the Development of the Inverted Polymer Solar Cell Architecture. *Polym. Rev.* **2010**, *50*, 474–510.

(14) Cao, W.; Xue, J. Recent Progress in Organic Photovoltaics: Device Architecture and Optical Design. *Energy Environ. Sci.* 2014, 7, 2123–2144.

(15) Facchetti, A. π -Conjugated Polymers for Organic Electronics and Photovoltaic Cell Applications. *Chem. Mater.* **2011**, 23, 733–758.

(16) Bian, L.; Zhu, E.; Tang, J.; Tang, W.; Zhang, F. Recent Progress in The Design of Narrow Bandgap Conjugated Polymers for High-Efficiency Organic Solar Cells. *Prog. Polym. Sci.* **2012**, *37*, 1292–1331.

(17) Benten, H.; Mori, D.; Ohkita, H.; Ito, S. Recent Research Progress of Polymer Donor/Polymer Acceptor Blend Solar Cells. *J. Mater. Chem. A* 2016, *4*, 5340–5365.

(18) Svensson, M.; Zhang, F.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inganäs, O.; Andersson, M. R. High-Performance Polymer Solar Cells of an Alternating Polyfluorene Copolymer and a Fullerene Derivative. *Adv. Mater.* **2003**, *15*, 988– 991.

(19) Thompson, B. C.; Fréchet, J. M. J. Polymer-Fullerene Composite Solar Cells. *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77.

(20) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. Synthesis of Conjugated Polymers for Organic Solar Cell Applications. *Chem. Rev.* 2009, 109, 5868–5923.

(21) Li, G.; Zhu, R.; Yang, Y. Polymer Solar Cells. *Nat. Photonics* **2012**, *6*, 153–161.

(22) Subramaniyan, S.; Xin, H.; Kim, F. S.; Murari, N. M.; Courtright, B. A. E.; Jenekhe, S. A. Thiazolothiazole Donor–Acceptor Conjugated Polymer Semiconductors for Photovoltaic Applications. *Macromolecules* **2014**, *47*, 4199–4209.

(23) Liu, C.; Wang, K.; Gong, X.; Heeger, A. J. Low Bandgap Semiconducting Polymers for Polymeric Photovoltaics. *Chem. Soc. Rev.* **2016**, *45*, 4825–4846.

(24) Li, Y.; Xue, L.; Li, H.; Li, Z.; Xu, B.; Wen, S.; Tian, W. Energy Level and Molecular Structure Engineering of Conjugated Donor– Acceptor Copolymers for Photovoltaic Applications. *Macromolecules* **2009**, *42*, 4491–4499.

(25) Li, Y.; Chen, Y.; Liu, X.; Wang, Z.; Yang, X.; Tu, Y.; Zhu, X. Controlling Blend Film Morphology by Varying Alkyl Side Chain in Highly Coplanar Donor–Acceptor Copolymers for Photovoltaic Application. *Macromolecules* **2011**, *44*, 6370–6381.

(26) Lu, L.; Zheng, T.; Wu, Q.; Schneider, A. M.; Zhao, D.; Yu, L. Recent Advances in Bulk Heterojunction Polymer Solar Cells. *Chem. Rev.* **2015**, *115*, 12666–12731.

(27) Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; de Boer, B. Small Bandgap Polymers for Organic Solar Cells (Polymer Material Development in the Last 5 Years). *Polym. Rev.* **2008**, *48*, 531–582.

(28) Kranthiraja, K.; Gunasekar, K.; Cho, W.; Song, M.; Park, Y. G.; Lee, J. Y.; Shin, Y.; Kang, I.-N.; Kim, A.; Kim, H.; Kim, B.; Jin, S.-H. Alkoxyphenylthiophene Linked Benzodithiophene Based Medium Band Gap Polymers for Organic Photovoltaics: Efficiency Improvement upon Methanol Treatment Depends on the Planarity of Backbone. *Macromolecules* **2014**, *47*, 7060–7069.

(29) Carsten, B.; Szarko, J. M.; Son, H. J.; Wang, W.; Lu, L.; He, F.; Rolczynski, B. S.; Lou, S. J.; Chen, L. X.; Yu, L. Examining the Effect of the Dipole Moment on Charge Separation in Donor-Acceptor Polymers for Organic Photovoltaic Applications. *J. Am. Chem. Soc.* **2011**, *133*, 20468–20475.

(30) Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.; Neagu-Plesu, R.; Belletête, M.; Durocher, G.; Tao, Y.; Leclerc, M. Toward a Rational Design of Poly(2,7-Carbazole) Derivatives for Solar Cells. J. Am. Chem. Soc. **2008**, 130, 732–742.

(31) Hou, J.; Chen, H.-Y.; Zhang, S.; Li, G.; Yang, Y. Synthesis, Characterization, and Photovoltaic Properties of a Low Band Gap Polymer Based on Silole-Containing Polythiophenes and 2,1,3-Benzothiadiazole. J. Am. Chem. Soc. 2008, 130, 16144–16145.

(32) Huang, Y.; Huo, L.; Zhang, S.; Guo, X.; Han, C. C.; Li, Y.; Hou, J. Sulfonyl: A New Application of Electron-Withdrawing Substituent in Highly Efficient Photovoltaic Polymer. *Chem. Commun.* **2011**, *47*, 8904–8906.

(33) Wu, Y.; Li, Z.; Ma, W.; Huang, Y.; Huo, L.; Guo, X.; Zhang, M.; Ade, H.; Hou, J. PDT-S-T: A New Polymer with Optimized Molecular Conformation for Controlled Aggregation and π - π Stacking and Its Application in Effi cient Photovoltaic Devices. *Adv. Mater.* **2013**, *25*, 3449–3455.

(34) Kim, J.-H.; Song, C. E.; Kim, B.; Kang, I.-N.; Shin, W. S.; Hwang, D.-H. Thieno[3,2-b]thiophene-Substituted Benzo[1,2-b:4,5b']dithiophene as a Promising Building Block for Low Bandgap Semiconducting Polymers for High-Performance Single and Tandem Organic Photovoltaic Cells. *Chem. Mater.* **2014**, *26*, 1234–1242.

(35) Kroon, R.; Diaz de Zerio Mendaza, A.; Himmel-berger, S.; Bergqvist, J.; Bäcke, O.; Faria, G. C.; Gao, F.; Obaid, A.; Zhuang, W.; Gedefaw, D.; Olsson, E.; Inganäs, O.; Salleo, A.; Müller, C.; Andersson, M. R. A New Tetracyclic Lactam Building Block for Thick, Broad-Bandgap Photovoltaics. *J. Am. Chem. Soc.* **2014**, *136*, 11578–11581.

(36) Wang, M.; Wang, H.; Yokoyama, T.; Liu, X.; Huang, Y.; Zhang, Y.; Nguyen, T.-Q.; Aramaki, S.; Bazan, G. C. High Open Circuit Voltage in Regioregular Narrow Band Gap Polymer Solar Cells. *J. Am. Chem. Soc.* **2014**, *136*, 12576–12579.

(37) Saito, M.; Osaka, I.; Suda, Y.; Yoshida, H.; Takimiya, K. Dithienylthienothiophenebisimide, a Versatile Electron-Deficient Unit for Semiconducting Polymers. *Adv. Mater.* **2016**, *28*, 6921–6925.

(38) Beaujuge, P. M.; Pisula, W.; Tsao, H. N.; Ellinger, S.; Müllen, K.; Reynolds, J. R. Tailoring Structure-Property Relationships in Dithienosilole-Benzothiadiazole Donor-Acceptor Copolymers. J. Am. Chem. Soc. 2009, 131, 7514–7515.

(39) Subbiah, J.; Purushothaman, B.; Chen, M.; Qin, T. S.; Gao, M.; Vak, D.; Scholes, F. H.; Chen, X. W.; Watkins, S. E.; Wilson, G. J.; Holmes, A. B.; Wong, W. W. H.; Jones, D. J. Organic Solar Cells Using a High-Molecular-Weight Benzodithiophene–Benzothiadiazole Copolymer with an Efficiency of 9.4%. *Adv. Mater.* **2015**, *27*, 702–705. (40) Sonar, P.; Williams, E. L.; Singh, S. P.; Dodabalapur, A. Thiophene–Benzothiadiazole–Thiophene (D–A–D) Based Polymers: Effect of Donor/Acceptor Moieties Adjacent to D–A–D Segment on Photophysical and Photovoltaic Properties. *J. Mater. Chem.* **2011**, *21*, 10532–10541.

(41) Wang, E. G.; Hou, L.; Wang, Z.; Hellström, S.; Zhang, F. L.; Inganäs, O.; Andersson, M. R. An Easily Synthesized Blue Polymer for High-Performance Polymer Solar Cells. *Adv. Mater.* **2010**, *22*, 5240– 5244.

(42) Zhou, E.; Cong, J.; Tajima, K.; Hashimoto, K. Synthesis and Photovoltaic Properties of Donor-Acceptor Copolymers Based on 5,8-Dithien-2-yl-2,3-diphenylquinoxaline. *Chem. Mater.* **2010**, *22*, 4890–4895.

(43) Zhang, Y.; Zou, J.; Yip, H.-L.; Chen, K.-S.; Zeigler, D. F.; Sun, Y.; Jen, A. K.-Y. Indacenodithiophene and Quinoxaline-Based Conjugated Polymers for Highly Efficient Polymer Solar Cells. *Chem. Mater.* **2011**, *23*, 2289–2291.

(44) Piliego, C.; Holcombe, T. W.; Douglas, J. D.; Woo, C. H.; Beaujuge, P. M.; Fréchet, J. M. J. Synthetic Control of Structural Order in N-Alkylthieno[3,4-c]pyrrole-4,6-dione-Based Polymers for Efficient Solar Cells. J. Am. Chem. Soc. **2010**, 132, 7595–7597.

(45) Zou, Y.; Najari, A.; Berrouard, P.; Beaupré, S.; Réda Aïch, B. R.; Tao, Y.; Leclerc, M. A Thieno[3,4-c]pyrrole-4,6-dione-Based Copolymer for Efficient Solar Cells. J. Am. Chem. Soc. **2010**, *132*, 5330–5331.

(46) Li, Y.; Sonar, P.; Murphy, L.; Hong, W. High Mobility Diketopyrrolopyrrole (DPP)-Based Organic Semiconductor Materials for Organic Thin Film Transistors and Photovoltaics. *Energy Environ. Sci.* **2013**, *6*, 1684–1710.

(47) Li, W.; Hendriks, K. H.; Wienk, M. M.; Janssen, R. A. J. Diketopyrrolopyrrole Polymers for Organic Solar Cells. *Acc. Chem. Res.* **2016**, *49*, 78–85.

(48) Cao, J.; Liao, Q.; Du, X.; Chen, J.; Xiao, Z.; Zuo, Q.; Ding, L. A Pentacyclic Aromatic Lactam Building Block for Efficient Polymer Solar Cells. *Energy Environ. Sci.* **2013**, *6*, 3224–3228.

(49) Cao, J.; Qian, L.; Lu, F.; Zhang, J.; Feng, Y.; Qiu, X.; Yip, H.-L.; Ding, L. A Lactam Building Block for Efficient Polymer Solar Cells. *Chem. Commun.* **2015**, *51*, 11830–11833.

(50) Cao, J.; Zuo, C.; Du, B.; Qiu, X.; Ding, L. Hexacyclic Lactam Building Blocks for Highly Efficient Polymer Solar Cells. *Chem. Commun.* 2015, *51*, 12122–12125.

(51) Qian, L.; Cao, J.; Ding, L. A Hexacyclic Ladder-Type Building Block for High-Performance D–A Copolymers. *J. Mater. Chem. A* **2015**, *3*, 24211–24214.

(52) Subramaniyan, S.; Kim, F. S.; Ren, G.; Li, H.; Jenekhe, S. A. High Mobility Thiazole-Diketopyrrolopyrrole Copolymer Semiconductors for High Performance Field-Effect Transistors and Photovoltaic Devices. *Macromolecules* **2012**, *45*, 9029–9037.

(53) Choi, H.; Ko, S. J.; Kim, T.; Morin, P. O.; Walker, B.; Lee, B. H.; Leclerc, M.; Kim, J. Y.; Heeger, A. J. Small-Bandgap Polymer Solar Cells with Unprecedented Short-Circuit Current Density and High Fill Factor. *Adv. Mater.* **2015**, *27*, 3318–3324.

(54) Ma, T.; Jiang, K.; Chen, S.; Hu, H.; Lin, H.; Li, Z.; Zhao, J.; Liu, Y.; Chang, Y.-M.; Hsiao, C.-C.; Yan, H. Efficient Low-Bandgap Polymer Solar Cells with High Open-Circuit Voltage and Good Stability. *Adv. Energy Mater.* **2015**, *5*, 1501282.

(55) Stalder, R.; Mei, J.; Graham, K. R.; Estrada, L. A.; Reynolds, J. R. Isoindigo, a Versatile Electron-Deficient Unit For High-Performance Organic Electronics. *Chem. Mater.* **2014**, *26*, 664–678.

(56) Deng, P.; Zhang, Q. Recent Developments on Isoindigo-Based Conjugated Polymers. *Polym. Chem.* **2014**, *5*, 3298–3305.

(57) Lu, S.; Drees, M.; Yao, Y.; Boudinet, D.; Yan, H.; Pan, H.; Wang, J.; Li, Y.; Usta, H.; Facchetti, A. 3,6-Dithiophen-2-yl-diketopyrrolo[3,2-b]pyrrole (isoDPPT) as an Acceptor Building Block for Organic Opto-Electronics. *Macromolecules* **2013**, *46*, 3895–3906.

(58) Guo, X.; Puniredd, S. R.; He, B.; Marszalek, T.; Baumgarten, M.; Pisula, W.; Müllen, K. Combination of Two Diketopyrrolopyrrole Isomers in One Polymer for Ambipolar Transport. *Chem. Mater.* **2014**, *26*, 3595–3598.

(59) Guo, X.; Facchetti, A.; Marks, T. J. Imide- and Amide-Functionalized Polymer Semiconductors. *Chem. Rev.* 2014, 114, 8943–9021.

(60) Frydman, B.; Los, M.; Rapoport, H. Synthesis of Substituted 1,5- and 1,7-Naphthyridines and Related Lactams. *J. Org. Chem.* **1971**, 36, 450–454.

(61) Mishra, A. K.; Vaidyanathan, S.; Noguchi, H.; Doetz, F.; Guan, Y. Semiconductor Materials Based on Diketopiperidinopiperidine Copolymers. PCT Int. Appl. WO 2012146574 A1, November 1, 2012. (62) Nanson, L.; Blouin, N.; Mitchell, W.; Tierney, S.; Cull, T. Organic Semiconductors Containing One or More Units Derived from 1,5-Disubstituted-1,5-dihydro-[1,5]naphthyridine-2,6-dione. PCT Int. Appl. WO 2013182262 A1, December 12, 2013.

(63) Huo, L. J.; Hou, J.; Chen, H.-Y.; Zhang, S. Q.; Jiang, Y.; Chen, T. L.; Yang, Y. Bandgap and Molecular Level Control of The Low-Bandgap Polymers Based on 3,6-Dithiophen-2-yl-2,5-dihydropyrrolo-[3,4-c]pyrrole-1,4-dione Toward Highly Efficient Polymer Solar Cells. *Macromolecules* **2009**, *42*, 6564–6571. (64) Peng, Q.; Huang, Q.; Hou, X.; Chang, P.; Xu, J.; Deng, S. Enhanced Solar Cell Performance by Replacing Benzodithiophene with Naphthodithiophene in Diketopyrrolopyrrole-based Copolymers. *Chem. Commun.* **2012**, *48*, 11452–11454.

(65) Woong Jung, J.; Woong Jo, J.; Liu, F.; Russell, T. P.; Ho Jo, W. A Low Band-gap Polymer Based on Unsubstituted Benzo[1,2-b:4,5-b']-dithiophene for High Performance Organic Photovoltaics. *Chem. Commun.* **2012**, *48*, 6933–6935.

(66) Hameed P, S; Patil, V.; Solapure, S.; Sharma, U.; Madhavapeddi, P.; Raichurkar, A.; Chinnapattu, M.; Manjrekar, P.; Shanbhag, G.; Puttur, J.; Shinde, V.; Menasinakai, S.; Rudrapatana, S.; Achar, V.; Awasthy, D.; Nandishaiah, R.; Humnabadkar, V.; Ghosh, A.; Narayan, C.; Ramya, V. K.; Kaur, P.; Sharma, S.; Werngren, J.; Hoffner, S.; Panduga, V.; Kumar, C. N. N.; Reddy, J.; Kumar KN, K.; Ganguly, S.; Bharath, S.; Bheemarao, U.; Mukherjee, K.; Arora, U.; Gaonkar, S.; Coulson, M.; Waterson, D.; Sambandamurthy, V. K.; de Sousa, S. M. Novel N-Linked Aminopiperidine-Based Gyrase Inhibitors with Improved hERG and in Vivo Efficacy against Mycobacterium Tuberculosis. J. Med. Chem. **2014**, *57*, 4889–4905.

(67) Hultell, M.; Stafström, S. Impact of Ring Torsion on The Intrachain Mobility in Conjugated Polymers. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75*, 104304.

(68) Jackson, N. E.; Savoie, B. M.; Kohlstedt, K. L.; Olvera de la Cruz, M.; Schatz, G. C.; Chen, L. X.; Ratner, M. A. Controlling Conformations of Conjugated Polymers and Small Molecules: The Role of Nonbonding Interactions. *J. Am. Chem. Soc.* **2013**, *135*, 10475–10483.

(69) Liao, H.-C.; Ho, C.-C.; Chang, C.-Y.; Jao, M.-H.; Darling, S. B.; Su, W.-F. Additive for Morphology Control in High-Efficiency Organic Solar Cells. *Mater. Today* **2013**, *16*, 326–336.

(70) Li, C.; Chen, Y.; Zhao, Y.; Wang, H.; Zhang, W.; Li, Y.; Yang, X.; Ma, C.; Chen, L.; Zhu, X.; Tu, Y. Acceptor–Donor–Acceptorbased Small Molecules with Varied Crystallinity: Processing Additive-Induced Nanofibril in Blend Film for Photovoltaic Applications. *Nanoscale* **2013**, *5*, 9536–9540.

(71) Yao, H.; Ye, L.; Zhang, H.; Li, S.; Zhang, S.; Hou, J. Molecular Design of Benzodithiophene-Based Organic Photovoltaic Materials. *Chem. Rev.* **2016**, *116*, 7397–7457.

(72) Murphy, L.; Sun, B.; Hong, W.; Aziz, H.; Li, Y. Study of Vertical and Lateral Charge Transport Properties of DPP-Based Polymer/ PC61BM Films Using Space Charge Limited Current (SCLC) and Field Effect Transistor Methods and their Effects on Photovoltaic Characteristics. *Aust. J. Chem.* **2015**, *68*, 1741–1749.

(73) Chen, M. S.; Niskala, J. R.; Unruh, D. A.; Chu, C. K.; Lee, O. P.; Fréchet, J. M. J. Control of Polymer-Packing Orientation in Thin Films through Synthetic Tailoring of Backbone Coplanarity. *Chem. Mater.* **2013**, *25*, 4088–4096.

(74) Vohra, V.; Kawashima, K.; Kakara, T.; Koganezawa, T.; Osaka, I.; Takimiya, K.; Murata, H. Efficient Inverted Polymer Solar Cells Employing Favourable Molecular Orientation. *Nat. Photonics* **2015**, *9*, 403–409.