Naphthodithiophenediimide–Bithiopheneimide Copolymers for High-Performance n-Type Organic Thermoelectrics: Significant Impact of Backbone Orientation on Conductivity and Thermoelectric Performance

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The development of n-type conjugated polymers with high electrical conductivity ($\sigma$) has continued to pose a massive challenge in organic thermoelectrics (OTEs). New structural insights into the charge-carrier transport are necessitated for the realization of high-performance OTEs. In this study, three new n-type copolymers, named pNB, pNB-Tz, and pNB-TzDP, consisting of naphthodithiophenediimide (NDTI) and bithiopheneimide (BTI) units, are synthesized by direct arylation polymerization. The backbone orientation is altered by incorporating thiazole units into the backbone and tuning the branching point of the side chain. The alteration of the backbone orientation from face-on to bimodal orientation with both face-on and edge-on fractions significantly impacts the $\sigma$ and the power factors (PFs) of the polymers. As a result, pNB-TzDP, with the bimodal orientation, demonstrates a high $\sigma$ of up to 11.6 S cm$^{-1}$ and PF of up to 53.4 $\mu$W m$^{-1}$ K$^{-2}$, which are among the highest in solution-processed n-doped conjugated polymers reported so far. Further studies reveal that the bimodal orientation of pNB-TzDP introduces 3D conduction channels and leads to better accommodation of dopants, which should be the key factors for the excellent thermoelectric performance.

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Conjugated polymers are a class of promising semiconductors for mechanically flexible and solution-processable electronic, energy conversion, and storage devices.[1–3] Since 2010, conjugated-polymer-based organic thermoelectrics (OTEs) have attracted increasing interest due to their unique advantages over inorganic alloys, including intrinsically low thermal conductivity, solution processability, and chemical tunability.[4] The promising thermoelectric performance near room temperature and the above-mentioned attractive properties of conjugated polymers make them particularly suitable as a flexible power source for state-of-the-art wearable and portable electronics.[5,6]

To achieve high-performance thermoelectrics, both p- and n-doped conducting materials with comparable performance are required. Such p-doped conducting polymers as poly(3,4-ethylenedioxythiophene) (PEDOT) have demonstrated impressive electrical conductivity ($\sigma$ >1000 S cm$^{-1}$).[7] On the other hand, n-doped conjugated polymers have shown far more inferior OTE performance than their p-doped counterparts.[8–11] Only a handful of n-doped conjugated polymers exhibit $\sigma$ values >5 S cm$^{-1}$ (Table S1, Supporting Information). Therefore, the development of high-performance n-doped conjugated polymers is highly awaited.

The last two decades have witnessed significant improvements in the performance of organic electronics. For instance, organic thin-film transistors (OTFTs) have achieved excellent mobilities of approximately 10 cm$^2$ V$^{-1}$ s$^{-1}$ and organic photovoltaics (OPVs) have demonstrated quite high power conversion efficiency (PCE) exceeding 16%.[12–15] An in-depth understanding of the relationship between the backbone configuration (or side-chain composition) and the solid-state packing (e.g., degree of order, backbone orientation) and their interplay with device performance is considered one of the driving forces for the progress in OTFTs and OPVs.[16–20] For instance, it is now widely understood that polymers with (pseudo)straight-line backbones can pack into a highly ordered microstructure with the edge-on orientation and show high mobilities in OTFTs.[17,19] As another example, it is well demonstrated that the backbone orientation can be changed from edge-on to
face-on by the introduction of an additional side chain, which is beneficial for carrier transport in solar cells and the enhancement of PCEs of OPVs.[18,21,22]

However, different from OTFTs and OPVs, the influence of the backbone orientation on OTE performance has not been fully elucidated. Either amorphous polymers without packing information or semicrystalline polymers with the edge-on orientation were reported recently in the literature.[23–25] In some cases, doping-induced aggregates in solution resulted in a poorly connected solid-state nanostructure, making the analysis of packing structures after doping quite challenging.[26] Currently, it is not well understood which backbone orientation is the most suitable for maximizing $\sigma$ and PF, especially for n-doped conjugated polymers. This is indeed a simple yet important question for the further development of high-performance n-type OTEs.

In this work, we design and synthesize a new all-acceptor polymer pNB (Figure 1a) by the alternating polymerization of two promising acceptors, naphthodithiophenediimide (NDTI)[27–29] and bithiopheneimide (BTI).[30,31] It has been reported that one NDTI-based polymer (PNDTI-BBT-DP) has a decent $\sigma$ value of 5 S cm$^{-1}$ and a BTI-derivative-based polymer (PDTzTI) demonstrates a promising PF of 7.6 $\mu$W m$^{-1}$ K$^{-2}$ and ZT of 0.01 at room temperature (Table S1, Supporting Information).[23,31]

Through density functional theory (DFT) calculations, we find that pNB has a wave-line backbone (Figure 1b, left) that gives rise to poor packing ordering. We then propose two modifications to improve the packing ordering: The first one involved the incorporation of a thiazole (Tz) unit into the polymer backbone to form polymer pNB-Tz (Figure 1a). Besides the favorable electron-deficient properties of Tz, the introduction of Tz makes polymer pNB-Tz form a (pseudo)straight-line backbone according to DFT calculations, which might help improve intermolecular packing ordering and electron transport (Figure 1b, right).[8] The second modification involves changing the side chain from 2-decyltetradecyl (DT) to 3-decylpentadecyl (DP), forming polymer pNB-TzDP (Figure 1a). This modification is inspired by our previous work showing that enhanced packing ordering and thermoelectric performance could be achieved by moving the branching point of the side chain away from the backbone.[23] Due to the synergistic effect of the above two modifications, pNB-TzDP shows dramatically improved packing ordering. Furthermore, these polymers demonstrate three different backbone orientations that significantly impacted their thermoelectric properties. Hence, pNB-TzDP characterized by the bimodal orientation with the face-on and edge-on fractions shows an impressive $\sigma$ value of up to 11.6 S cm$^{-1}$ and PF of up to 53.4 $\mu$W m$^{-1}$ K$^{-2}$ near room temperature, which are among

Figure 1. a) Chemical structures of polymers pNB, pNB-Tz, and pNB-TzDP and n-dopant N-DMBI. b) DFT calculation results of backbone geometry. c) Syntheses of monomers and polymers.
the highest in solution-processed n-doped conjugated polymers so far reported (Table S1, Supporting Information).

We initially carried out the theoretical calculations of trimers as models for pNB and pNB-Tz (or pNB-TzDP with the same backbone) by using DFT calculations at the B3LYP/6-31G(d) level (Figure 1b), which can afford the plausible local backbone geometry.[17,19] It turned out that the backbone geometries of the two polymers were significantly different (Figure 1b). Polymer pNB shows a wave-line backbone (Figure 1b, left), whereas pNB-Tz has a (pseudo)straight-line backbone (Figure 1b, right). The wave-line backbone might result in relatively poor packing ordering whereas the (pseudo)straight-line backbone might lead to high molecular packing ordering.[17,19,32]

The monomers of NDTI with two kinds of side chains (i.e., DT and DP), BTI and its dibromo compound (BTI-Br), were synthesized according to literature.[23,27,33] New monomer BTI-Tz was synthesized from BTI-Br and 2-(tributylstannyl)thiazole (Tz-tin) through the Stille coupling reaction in a high yield of 78% (Figure 1c). Then, the three new copolymers were synthesized by using the direct arylation polymerization (Figure 1c and Scheme S1 in the Supporting Information; synthetic details in the Supporting Information). All the three polymers show acceptable number average molecular weights (Mn) of 11.5 to 15.4 kg mol⁻¹ with polydispersity indices (PDIs) of around 2 as evaluated by high-temperature gel permeation chromatography (GPC) at 140 °C (Table 1 and Figure S1, Supporting Information). In addition, the three polymers demonstrate excellent thermal stability, their decomposition temperature (Td) values exceeding 430 °C (Figure S2, Supporting Information). From the differential scanning calorimetry (DSC) thermograms, all three polymers showed one endothermic peak in the heating process and one exothermic peak in the cooling process around 60–70 °C (Figure S3, Supporting Information), which are related to the melting of the side chains.[34,35] No further phase transition in the range of 70 to 300 °C is observable (Figure S3, Supporting Information).

Then, the cyclic voltammograms (CVs) of the polymer thin films were measured to estimate their energy levels. From the reduction (Ered) onsets in the CVs, EFLUMO, are ≈−4.2 eV for all the three polymers (Table 1 and Figure S4, Supporting Information). In contrast, the oxidation peaks are irreversible and have smaller current response than the reduction peaks (Figure S4, Supporting Information), indicative of the fairly electron-deficient nature of these polymers. The very deep EFLUMO, together with the deep EHOMO of ≈−6.0 V indicate the unipolar n-type charge transport properties of these polymers.

Next, OTFTs with the top-contact/bottom-gate (TC/BG) device structure were fabricated by spin-coating the polymer solutions (chlorobenzene, 3 mg L⁻¹) on octadecyltrichlorosilane (ODTS)-treated Si/SiO2 substrates (detailed procedure in Supporting Information). The OTFT devices were evaluated in ambient conditions and the field-effect mobilities were extracted from the saturation regime. As expected from the energy levels, all polymers demonstrate unipolar n-type charge transport properties. Specifically, polymer pNB shows a relatively low electron mobility (µe) of 5.6 × 10⁻¹⁵ cm² V⁻¹ s⁻¹, whereas pNB-Tz with additional thiazole units displays an improved µe value of 0.12 cm² V⁻¹ s⁻¹ (Table 1, Figure 2 and Figure S5, Supporting Information). After further modification of the side chain, pNB-TzDP demonstrates the highest µe value of 0.55 cm² V⁻¹ s⁻¹ (Figure 2c and Figure S5c, Supporting Information), which is approximately two orders of magnitude higher than that of pNB and fivefold higher than that of pNB-Tz. To the best of our knowledge, this is the highest µe among those reported for NDTI-based polymers.[23,27–29] In addition, we evaluated the reliability of mobility values according to Choi et al., who proposed the measurement reliability factor γ (Figure S6, Supporting Information).[36] The γ values for our OTFT devices are in the range of 70% to 85%, indicating the high reliability of the extracted mobility herein.[36]

As the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of all the polymers are very similar, we considered that solid-state packing would be the key contributor to their huge difference in mobility. Therefore, grazing-incidence wide-angle X-ray scattering (GIWAXS) was performed on polymer films that were formed by casting the polymer solution on ODTDs-treated Si/SiO2 substrates. For polymer pNB, we observe only a (010) peak in the out-of-plane direction (corresponding to the π–π stacking, Figure 2d). On the other hand, (100) lamellar diffraction is found in the in-plane direction (Figure 2e). As a consequence, pNB adopts the face-on orientation (Figure 2f) that results in its low OTFT mobility according to the classic charge carrier hopping mechanism.[17,18] Intriguingly, polymer pNB-Tz demonstrates a different packing texture with much higher packing ordering and out-of-plane (h00) reflection up to the third order (Figure 2g). The lamellar packing distance is 21.2 Å, which is much shorter than that of pNB (24.9 Å). Furthermore, we observe a strong in-plane (010) π–π stacking peak (Figure 2h). As a result, pNB-Tz adopts the edge-on orientation with high crystallinity, thereby resulting in the improved mobility (Figure 2i).[17,30] Similar to pNB-Tz, polymer pNB-TzDP also shows a crystalline microstructure with high ordering (Figure 2j,k). Unexpectedly, additional out-of-plane (010) and in-plane (100) peaks appear (Figure 2j,k), indicating that pNB-TzDP adopts the bimodal orientation with both face-on and edge-on fractions (Figure 2l). The bimodal orientation

### Table 1. Summary of molecular weights, thermal decomposition temperatures, energy levels, and electron mobilities of pristine polymers and electrical conductivities and power factors of N-ODTBSiO2-doped polymers.

| Polymer    | Mn [kg mol⁻¹] | PDI | Td [°C] | E_FLUMO [eV] | E_HOMO [eV] | E_EFF [eV] | µ_e [cm² V⁻¹ s⁻¹] | σ║ [S cm⁻¹] | PF∥ [μW m⁻¹ K⁻¹] |
|------------|---------------|-----|---------|--------------|-------------|------------|-----------------|-------------|-----------------|
| pNB        | 11.5          | 1.6 | 449     | −4.20        | −6.00       | 1.80       | 0.0056 (0.0031 ± 0.0013) | 0.011 (0.010 ± 0.001) | 0.3 (0.2 ± 0.1) |
| pNB-Tz     | 11.6          | 1.9 | 438     | −4.22        | −6.05       | 1.83       | 0.12 (0.086 ± 0.039) | 0.87 (0.55 ± 0.33) | 9.9 (6.5 ± 3.3) |
| pNB-TzDP   | 15.4          | 2.3 | 431     | −4.22        | −6.05       | 1.83       | 0.55 (0.35 ± 0.17)  | 11.6 (9.39 ± 1.99) | 53.4 (42.8 ± 9.2) |

| a | Temperature at 5% weight loss; b | Estimated from cyclic voltammetry measurements; c | Maximum mobilities measured using field-effect transistors; d | Maximum electrical conductivities under optimized conditions; e | Maximum power factors under optimized conditions. (Average values and standard deviations are shown in parentheses.)
should also be promising for OTFTs because there are grain boundaries (or traps and defects) in the polymer microstructures and for the charge carriers to move around the grain boundaries, the presence of multiple parallel and perpendicular orientations of the π-stacking planes (so-called “3D conduction channels”) should be advantageous. A detailed investigation of the bimodal orientation leading to the enhanced charge transport in other conjugated polymers has been reported.\(^\text{[39–41]}\) From GIWAXS and DFT calculation results,\(^\text{[17,19,32]}\) we assume that the interpolymer docking models depicted in Figure 2m would be suitable for describing the packing of pNB and pNB-Tz (or pNB-TzDP with the same backbone). A backbone with a large curvature would more likely adopt the face-on orientation with a longer lamellar packing distance, whereas the

Figure 2. a–c) Transistor performances of transfer characteristics for: a) pNB, b) pNB-Tz, and c) pNB-TzDP. d–l) GIWAXS patterns of thin films after annealing and corresponding cartoon representations of backbone orientations: d–f) for pNB, g–i) for pNB-Tz, and j–l) for pNB-TzDP. m) Cartoon representations of interpolymer docking models: pNB (left) and pNB-Tz (right).
linear-like backbone would lead to the edge-on orientation with shorter stacking distances due to the interdigital alignment of the side chain.\[19,32\] Moreover, based on the interpolymer docking models (Figure 2m), larger free spaces in the side-chain layer could be postulated for pNB-Tz than pNB, implying good accommodation of dopants or dopant cations after doping in the case of pNB-Tz (or pNB-TzDP with the same backbone). Therefore, better host/dopant miscibility and higher n-doping efficiency can be expected, which would contribute to higher conductivity and thermoelectric performance.

In order to investigate the thermoelectric properties of the polymers, we doped the polymers with N,N-dimethyl-2-phenyl-2,3-dihydro-1H-benzoimidazole (N-DMBI, Figure 1a, right), a commercially available dopant with strong n-doping ability and good solution processability.\[42,43\] Then, we measured the \(\sigma\) (for details, see the Experimental Section). The results are summarized in Figure 3a and Table 1. All pristine polymers have very low intrinsic \(\sigma\) that could not be accurately measured because they are closed-shell molecules.\[23,25\] After n-doping, the \(\sigma\) of all the polymers increase due to the generation of mobile carrier species. Furthermore, we find that \(\sigma\) dependence on the dopant ratio differs between pNB and pNB-Tz. For pNB, \(\sigma\) reaches the near-saturation value of 0.009 S cm\(^{-1}\) at the nominal dopant ratio of 20 mol% and the maximum value of 0.011 S cm\(^{-1}\) at the dopant ratio of 30 mol% (Figure 3a, black trace). In the case of pNB-Tz, \(\sigma\) increases continuously to 0.87 S cm\(^{-1}\) for dopant ratios ranging from 0 to 30 mol% and decreases thereafter (Figure 3a, red trace). The trend of pNB-TzDP is similar to that of pNB-Tz (Figure 3a, blue trace). The maximum \(\sigma\) of pNB-TzDP doped with 30 mol% N-DMBI reaches 11.6 S cm\(^{-1}\) (average: 9.38 \(\pm\) 1.99 S cm\(^{-1}\)), which is more than 1000- and 10-fold higher than those of pNB and pNB-Tz, respectively. A higher dopant ratio (i.e., more than 30 mol%) results in a decrease in \(\sigma\), probably because of overdoping, which could lead to the formation of a large amount of bipolarons with low mobilities.\[23–25,44\]

Subsequently, we investigated the Seebeck coefficient (\(S\)) and the power factor (PF) of the doped films by imposing a temperature difference across the samples (for details, see the Experimental Section and Figure S7, Supporting Information). As Figure 3b shows, all the \(S\) values of the doped polymer films...
are negative values, confirming that the electron transport is
dominant. The $S$ values decrease as the dopant ratio increases,
consistent with previous results.$^{23-25}$ By combining $\sigma$ and $S$,
PF is estimated using Equation (1)

$$PF = S^2/\sigma$$

The best PF for pNB-TzDP around room temperature is
53.4 $\mu$W m$^{-1}$ K$^{-2}$ (Figure 3c), which is significantly higher than
those of pNB (0.3 $\mu$W m$^{-1}$ K$^{-2}$) and pNB-Tz (0.9 $\mu$W m$^{-1}$ K$^{-2}$).
To the best of our knowledge, this PF value is among the
highest for solution-processed n-doped conjugated polymers so
far reported (Table S1, Supporting Information).

In order to clarify the reasons for the high $\sigma$ of pNB-Tz and
pNB-TzDP, UV/vis-NIR spectroscopy was employed to char-
acterize the n-doping properties of the polymers. The pristine
polymers in dilute chlorobenzene solution and as thin-film
state demonstrate intense absorption from UV to the near-infrared region without obvious absorption at wavelengths
higher than 800 nm (Figure S8 in the Supporting Information). This phenomenon is also observed in their film state (Figure 3e,f, black trace). It is because the steric effect originated
from the branched side chains can influence the efficiency of $\pi$-conjugation along the polymer backbone. pNB-Tz with
the DT side chain shows relatively large steric hindrance while pNB-TzDP with the branched point of side chain far
away from the backbone should have relatively small steric hin-
drance. Therefore, pNB-TzDP should have the higher efficiency of the $\pi$-conjugation along the polymer backbone than that of
pNB-Tz, which is consistent with our previous result.$^{23}$ After
doping with 10 mol% N-DMBI, a new absorption band (P1) for
pNB and two new absorption bands (P1 and P2) for pNB-Tz or
pNB-TzDP emerge in the near-infrared region (Figure 3d–f, red trace). P1 (800–1200 nm) might have originated from polaron.$^{23,25,44}$ For pNB-Tz and pNB-TzDP, P1 (800 to 1100 nm)
could be ascribed to polaron absorption whereas P2 (1200 to
1600 nm), to bipolaron absorption.$^{23,25,44}$ This is because bipolarons are reported to show more redshifted absorption than polarons.$^{44}$ In addition, we find that further increasing the doping concentration from 10 to 50 mol% results in different
trends of the spectra. For pNB, the intensity of P1 shows no
change after 10 mol% doping due to dopant segregation in the
polymer matrix, which is supported by atomic force micro-
scopy (AFM) images (vide infra)$^{23,25,44}$ In sharp contrast, we
observe continuously growing P1 and P2 intensities for pNB-Tz
or pNB-TzDP (Figure 3e,f, blue and green traces), indicating higher doping efficiency (effectiveness) than pNB.$^{23,44}$ Fur-
thermore, the intensities of P1 and P2 are different between
pNB-Tz and pNB-TzDP. At each nominal doping ratio of 10 to
50 mol%, the intensity of P1 for pNB-TzDP is estimated to be
larger than that of P1 for pNB-Tz, indicating that the polaron concentration of pNB-TzDP is higher than that of pNB-Tz.
Because the mobility of polaron is much higher than that of
bipolaron, the high polaron concentration of pNB-TzDP can make a great contribution to the polymer conductivity.$^{44}$

Then, we estimated the doping efficiencies of the three
polymers by comparing the charge carrier concentration ($n$) and the total number of N-DMBI molecules ($n_{DMBI}$), i.e., the $n/n_{DMBI}$ ratio. A dopant concentration of 30 mol% can translate into $\approx 2.2 \times 10^{20}$ cm$^{-3}$ N-DMBI molecules for all the three poly-
mers, assuming that the host and the dopant are well mixed. The volumes of the polymers (repeat units) are described with
orthogonal unit cells with the parameters from the GIWAXS
results (detailed calculations are shown in Figure S9, Sup-
porting Information). Next, we calculate $n$ via Equation (2) by
assuming $\mu_{OFET}$ as an estimate of the electron mobility in the doped films

$$\sigma = nq\mu_{OFET}$$

where $q$ is the elementary charge ($1.6 \times 10^{-19}$ C). Notably, the
mobility of a doped organic semiconductor can be different
from the OTFT mobility in the un-doped state, which is mainly caused by the coulomb interaction.$^{31}$ If polymers have good
backbone planarity, which can help to overcome the coulomb interaction, a bulk mobility will be close to the OTFT mobility.$^{31}$ From the polymers’ geometry optimized by the DFT calculation (Figure S10, Supporting Information), we observe that all three polymers in both neutral and radical anion states show very planar backbone, thus justifying the method we used herein.

As a result, the $n$ value is calculated to be $1.2 \times 10^{20}$ cm$^{-3}$ for
pNB, $4.5 \times 10^{20}$ cm$^{-3}$ for pNB-Tz, and $1.3 \times 10^{20}$ cm$^{-3}$ for pNB-
TzDP (detailed calculations in Figure S9, Supporting Information).
Hence, the calculated approximate doping efficiency is
5% for pNB, 20% for pNB-Tz, and 60% for pNB-TzDP. Overall,
the above estimation is consistent with UV/vis–NIR results. In
comparison, Chabinyc and co-workers reported a doping effi-
ciency of 1% for a benchmark naphthalene diimide (NDI)-based
polymer (N2200)$^{45}$ and Müller and co-workers reported an
improved doping efficiency of 13% for an oligoethyleneglycol modified NDI-based polymer doped with N-DMBI.$^{46}$ Gener-
ally, the low doping efficiency of pNB leads to low conductivity. In
addition, the above results are consistent with the trend of the measured $S$ values; a higher charge carrier concentration
would result in a lower $S$ value.$^{23}$ For the same reason, the $S$
values are decreased when the dopant ratio is increased due to the
generation of more free carriers.

To further obtain insights into the charge transport behavior
in the doped polymers, the temperature-dependent $\sigma$, $S$, and
PF were measured (Figure 3g–i). The $\sigma$ show a positive cor-
relation with temperature (Figure 3g and Figure S11, Sup-
porting Information). In contrast, the $S$ values demonstrate a
less evident temperature dependence in general (Figure 3h).
According to the charge transport dependence on the extent of
doping (Figure 3a) and the temperature-dependent $\sigma$
(Figure 3g), the Mott polaron model is probably suitable for
describing the charge transport property.$^{67}$ In the Mott polaron
model, $\sigma$ is expressed as a function of temperature, as shown in Equation (3)

$$\sigma = \sigma_0 \exp \left(-\left(E + W_{hi}\right)/k_BT\right)$$

where $\sigma_0$ is the pre-exponential conductivity that represents
the maximum electrical conductivity achievable herein,$^{25,67,44}$ $k_B$ is
the Boltzmann constant, \(E\) is the (average) ionization energy, and \(W_H\) is the energetic spread of states. Collectively, \((E + W_H)\) represents the Arrhenius activation energy \((E_a)\), which is related to the energy barrier for charge transport.\(^4\)

To avoid thermally induced dedoping of films, temperatures below 380 K were selected to calculate \(E_a\) (ln\(\sigma\) vs 1/\(T\)). As shown in Figure 3g, the calculated \(E_a\) of pNB-TzDP is 57 meV, which is much lower than that of pNB-Tz (213 meV) and pNB (291 meV). The above \(E_a\) values indicate that the trend of the hopping barrier in the doped films should be as follows: pNB-TzDP < pNB-Tz < pNB. Notably, the \(E_a\) of pNB-TzDP is quite low among the high-performance n-doped conjugated polymers (Table S1, Supporting Information). Interestingly, the PFs of the three polymers are positively correlated with the temperature and a maximum value of 67 \(\mu\)W m\(^{-1}\)K\(^{-2}\) is achieved for pNB-TzDP at 85 °C (Figure 3i).

Macroscopically, the high \(\sigma\) of pNB-TzDP can be attributed to the fact that pNB-TzDP has a higher doping efficiency and a lower \(E_a\) than pNB and pNB-Tz. However, a fundamental understanding of their structure–property relationships at the molecular level has remained elusive. Therefore, new structural insights should be obtained by unraveling the relationship between the packing structures of doped polymers and their thermoelectric properties. To this end, GIWAXS of the polymer films on the glass substrates before and after doping was performed (Figure 4). The backbone orientations after doping are almost the same as those of pristine samples in Figure 2. At the low dopant ratio of 10 mol%, pNB with the face-on orientation shows a broadened lamellar packing distance of 24.9 to 27.2 Å (Figure 4c), indicating the less ordered packing and the disrupted crystalline domain of the polymer.\(^{[23]}\)

On the other hand, pNB-Tz with the edge-on orientation shows less varied lamellar packing distance even at the high dopant ratio of 50 mol% (only from 21.2 to 22.1 Å). Meanwhile, its \(\pi-\pi\) stacking distance only slightly expands from 3.45 to 3.48 Å (Figure 4f). The above results imply that pNB-Tz can better accommodate dopants and has a less damaged crystalline domain after doping, consistent with the interpolymer docking model based on DFT calculations (Figure 2m). For pNB-TzDP with the bimodal orientation, the samples show almost unchanged packing ordering after doping. The lamellar packing distance of the polymer film with 10 mol% dopant ratio is the same as that of the pristine one. At the high dopant ratio of 50 mol%, the lamellar packing distance only slightly increases from 22.1 to 22.6 Å. Besides, the \(\pi-\pi\) stacking distance remains the same before and after doping with various ratios (3.45 Å, Figure 4i). Therefore, we infer that the dopants or dopant cations preferentially exist in the amorphous regions, including the space in the side-chain layer of pNB-Tz and pNB-TzDP.\(^{[48]}\)

In conclusion, we have designed and synthesized a series of new n-type copolymers composed of NDTI and BTI units through direct arylation polymerization. Such molecular
modifications as incorporating thiazole units into the backbone and tuning the branching point of the side chain enable us to control the packing ordering and orientation. Most importantly, we establish that the backbone orientation plays an important role in dictating the electrical conductivity and the thermolectric performance. As a result, pNB-TzDP characterized by the bimodal orientation with face-on and edge-on fractions exhibits excellent electrical conductivity of up to 11.6 S cm\(^{-1}\) and power factor of up to 53.4 \(\mu\text{W m}^{-1}\text{K}^{-2}\), which are among the highest in solution-processed n-doped conjugated polymers. GIWAXS and AFM measurements before and after doping reveal that the observed increase in electrical conductivity as a result of the bimodal orientation can be attributed to the formation of 3D conduction channels and the better accommodation of dopants. Together, the results demonstrate that tuning the solid-state packing by molecular design and synthesis should be a promising strategy. We believe that these findings can serve as important guidelines for molecular engineering toward practically useful high-performance n-type organic thermolectrics.

**Experimental Section**

**Doping of Polymers and Evaluation of Conductivity and Thermolectric Properties:** Chlorobenzene solutions of polymers (4 g L\(^{-1}\)) and N-DMBI (2 g L\(^{-1}\)) were prepared separately. Aliquots of N-DMBI and polymer solutions were mixed at room temperature, and then the thin films were fabricated by spin-coating on glass substrates and annealed at 120 °C for 8 h. Four-probe conductivity measurements were carried out under nitrogen atmosphere with a Thermolectric Property Measurement System (Model RZ2001i-HS, Ozawa Science Co., Ltd.). After the electrical conductivity measurements, the Seebeck coefficients were measured using the same equipment under the same conditions. By imposing a temperature difference across the sample (\(|\Delta T| = 2 \text{ K}\)) and measuring the thermovoltages, the Seebeck coefficients were calculated with \(S = \Delta V/\Delta T\), where \(\Delta V\) is the thermal voltage obtained from the two ends of the device exposed to temperature gradient \(\Delta T\). The accuracies of the electrical conductivities (current–voltage) and the Seebeck coefficients (\(\Delta T\)-\(\Delta V\)) were evaluated on the basis of the correlation coefficients obtained by the least squares method (\(|r|\)). All |\(r|\) values were higher than 0.98 in this study.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

backbone orientation, conducting polymers, electrical conductivity, n-doping efficiency, n-type organic thermolectrics

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