

Novel Dithienopyrrole-Based Conjugated Copolymers: Importance of Backbone Planarity in Achieving High Electrical Conductivity and Thermoelectric Performance

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The development of conjugated polymers with structures that are suitable for efficient molecular doping and charge transport is a key challenge in the construction of high-performance conjugated polymer-based thermoelectric devices. In this study, three novel conjugated polymers based on dithienopyrrole (DTP) are synthesized and their thermoelectric properties are compared. When doped with p-dopant, a donor–acceptor type copolymer, DPP-MeDTP, exhibits higher electrical conductivity and thermoelectric power factor compared to the other donor–donor type copolymers. The high electrical conductivity of DPP-MeDTP compared to the other polymers originates from the high degree of backbone planarity and molecular order, which contributes to its high charge carrier mobility. In addition, the highly crystalline structure of DPP-MeDTP is well maintained upon doping, while the crystalline order of the other polymers decreases significantly upon doping. The findings of this work not only provide insights into the design of DTP-based conjugated polymers for thermoelectric use but also demonstrate the significance of a high degree of molecular order and structural robustness upon doping to achieve high thermoelectric performance.

materials are the most intensively used thermoelectric materials; however, their toxicity, heavy weight, brittleness, and requirements for energy-demanding processes remain the critical limitations of inorganic thermoelectric materials. Organic thermoelectric materials, on the contrary, are lightweight, have high mechanical flexibility, and can be produced using cost-effective low-temperature solution processes. These unique advantages of organic thermoelectric materials make them promising next-generation thermoelectric materials, especially for applications in flexible or wearable electronic devices.^[4,5]

Organic materials have advantages in achieving good thermoelectric performance, which is usually expressed as $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is electrical conductivity, T is temperature, and κ is thermal conductivity, because of their intrinsically low thermal conductivity.^[5,6] Unfortunately, the thermoelectric performance of most organic

thermoelectric materials is still poor. The major difficulty comes from the relatively low electrical conductivity of organic thermoelectric materials, and therefore, many efforts have been made to increase their electrical conductivity.^[5,7,8] For conjugated polymers, one of the most effective strategies to dramatically increase their electrical conductivity is doping.^[7,9–14] For a p-type conjugated polymer, electrons are transferred from the polymer to the acceptor dopant, increasing the hole concentration in the

1. Introduction

Thermoelectric energy conversion, which involves the conversion of heat into electrical energy through the Seebeck effect has been of great interest in energy harvesting research.^[1–3] Thermoelectric devices have a wide range of possible applications, such as the collection of waste heat in industrial facilities and small-scale power generation using body temperature. Inorganic

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polymer. However, the efficiency of doping depends not only on the energy offset between the highest occupied molecular orbital (HOMO) of the conjugated polymer and the acceptor level (or the lowest unoccupied molecular orbital (LUMO) energy level) of the dopant,^[10] but also on the microstructure formed by the polymer and dopant complex.^[8,15,16] Therefore, to realize a high-performance conjugated polymer-based thermoelectric material, it is important to design a conjugated polymer possessing efficient intrinsic charge transport and high doping efficiency when combined with dopants.

Among the various building blocks for conjugated polymers, dithieno[3,2-b:2',3'-d]pyrrole (DTP) is an attractive building block for the development of high-performance conjugated polymers for organic electronic devices because of its good planarity and strong electron-donating ability.^[17–19] The fused-ring structure of the DTP unit prevents chain distortion, thus planarizing the polymer chain and improving π - π stacking. As a result, DTP-based polymers often exhibit good charge carrier mobilities.^[18] In addition, owing to the low oxidation potential of the dithiophene unit, polymers containing DTP units tend to show elevated HOMO energy levels,^[20] which would be favorable for providing sufficient energetic driving force for charge transfer to the dopants. These characteristics, the possibility of achieving high charge carrier mobility and elevated HOMO energy level, make the DTP unit promising for the preparation of conjugated polymers with high thermoelectric performance.

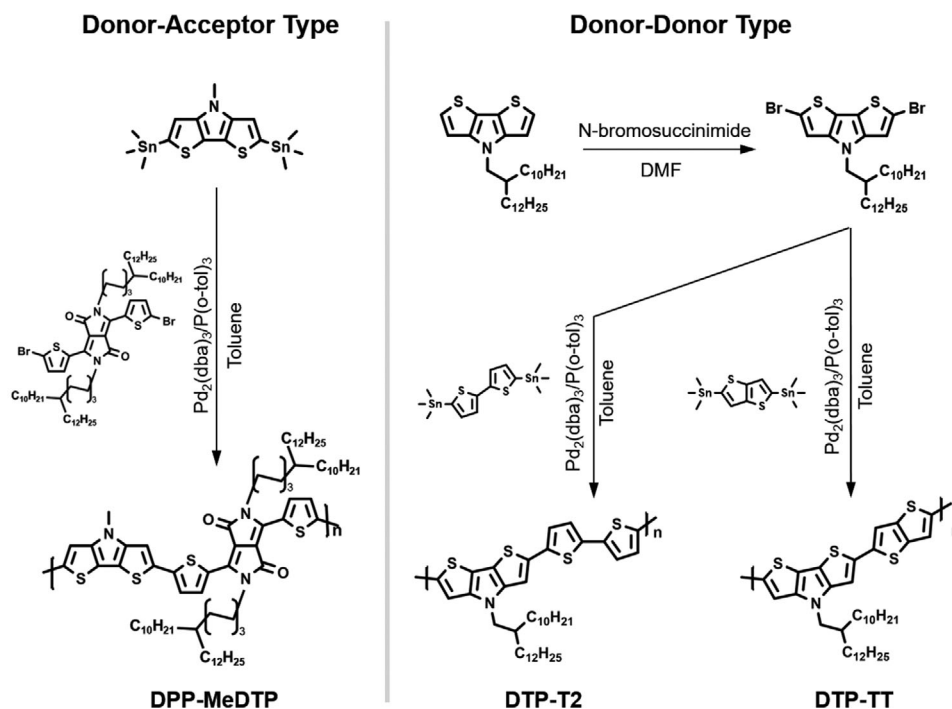
In this study, we aim to investigate how the combination of DTP unit with other different chemical moieties affect the structure and thermoelectrical properties of the resulting DTP-containing conjugated polymers and gain insights on the design strategy of high-performance DTP-based conjugated polymers for thermoelectric applications. As an attempt to achieve this, we synthesized and compared three conjugated copolymers that incorporated a DTP unit as a building block: one of them is a donor-acceptor (D-A) type copolymer containing a diketopyrrolopyrrole (DPP) unit with two flanking thiophenes as the acceptor building block, while the others are donor-donor (D-D) type copolymers that contain a bithiophene (T2) or thienothiophene (TT) unit as the other donor unit. The DPP unit was selected because it is a representative strong electron-acceptor unit widely used in the construction of D-A copolymers; DPP-containing conjugated polymers usually exhibit high charge carrier mobility because of their good planarity and strong aggregation tendency in films;^[21] therefore, copolymerization of DTP and DPP units was expected to result in a polymer with high electrical conductivity required for high thermoelectric performance. At the same time, copolymerization of DTP with TT or T2 was expected to extend the effective conjugation length of the polymer and improve π - π interactions between polymer chains,^[22] possibly leading to improved charge carrier mobility and thermoelectric performance. The microstructural, electrical, and thermoelectric properties of the three DTP-based conjugated polymers were investigated by doping the polymers with 2,3,4,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) or FeCl₃ dopants. Among the tested polymers, the DPP-containing polymer, DPP-MeDTP, exhibited the highest electrical conductivity when doped, which was attributed to its high charge carrier mobility originating from its high backbone planarity and crystallinity. The high conductivity of DPP-MeDTP

led to a maximum power factor of 85.2 $\mu\text{W m}^{-1} \text{K}^{-2}$, which is several to tens of times higher than that of the other polymers. Structural and electrical analyses suggest that a high degree of backbone planarity and structural order is essential for achieving high electrical conductivity and thermoelectric performance, although such a highly crystalline structure may partly limit the effective incorporation of dopant molecules into the polymer film and thus lower the doping efficiency to a certain extent.

2. Results and Discussion

The DTP-containing copolymers, poly[2,6-{N-methyl(dithieno[3,2-b:2'3'-d]pyrrol)-alt-3,6-{bis(5-thiophenyl)-2,5-bis(7-decylnonadecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione}}] (DPP-MeDTP), poly[2,6-{N-2-decylteradecyl(dithieno[3,2-b:2'3'-d]pyrrol)-alt-[2,2'-(5,5'-bithiophene)}] (DTP-T2), and poly[2,6-{N-decyltetradecyl(dithieno[3,2-b:2'3'-d]pyrrol)-alt-2,5(thenothiophene)}] (DTP-TT) were synthesized as shown schematically in **Scheme 1**. The polymers were synthesized by the Stille coupling reaction; details of the synthetic procedures are described in the Supporting Information (see the Synthesis section and Scheme S1, Supporting Information). The obtained polymers were purified by successive Soxhlet extractions with methanol, acetone, dichloromethane, and chloroform. Then the chloroform fraction was concentrated and precipitated into methanol. The structure of the monomer was confirmed by ¹H NMR, ¹³C NMR, and high-resolution mass spectroscopy (Figures S1–S3, Supporting Information), and the polymers were characterized by ¹H NMR (Figures S4–S6, Supporting Information). All the synthesized polymers exhibited good solubility in common organic solvents and good thermal stability with high degradation temperature ($T_d = 404, 390, \text{ and } 389^\circ\text{C}$ for DPP-MeDTP, DTP-T2, and DTP-TT, respectively) in thermogravimetric analysis (TGA) measurements and without thermal transition up to 250 $^\circ\text{C}$ in differential scanning calorimetry (DSC) measurements (Figures S7–S9, Supporting Information). The molecular weights (and polydispersity indices) of the polymers measured by gel permeation chromatography were 27.0 (1.5), 17.9 (1.2), and 76.7 (1.5) kDa for DTP-T2, DTP-TT, and DPP-MeDTP, respectively (Figure S10, Supporting Information).

Density functional theory (DFT) calculations were performed to understand the energy-minimized structural geometry and electronic properties of these polymers (**Figure 1a**). Note that the calculations were performed on dimers of the polymer repeating units (di-DTP-T2, di-DTP-TT, and di-DPP-MeDTP) bearing methyl-trimmed alkyl chains for the simplicity of the calculations. For all dimers, the HOMO wave functions are well delocalized along the conjugated backbone, indicating that the copolymerization of DTP units with T2, TT, or DPP units is effective for developing conjugated copolymers with a high degree of electron delocalization. The LUMO wave function of di-DPP-MeDTP is more localized on the DPP unit, whereas the LUMO wave functions of di-DTP-T2 and di-DTP-TT are well-delocalized over the backbone. This implies that the HOMO–LUMO transition of DPP-MeDTP includes intramolecular charge transfer between DTP and DPP units, which results in a decrease in the bandgap and thus improves light absorption of the polymer at long wavelengths,^[23] as shown later.



Scheme 1. Synthetic routes of the polymers, DPP-MeDTP, DTP-T2, and DTP-TT.

The dihedral angles of the three dimers were measured to compare conformational distortions. The dihedral angles between the DTP unit and the neighboring unit were much smaller in di-DPP-MeDTP ($\theta_1 = 2.3^\circ$ and $\theta_2 = 0.6^\circ$) than in the other units ($\theta_1 = 14.2^\circ$ and $\theta_2 = 10.4^\circ$ for di-DTP-T2; $\theta_1 = 17.2^\circ$ and $\theta_2 = 15.7^\circ$ for di-DTP-TT), indicating much higher planarity of the conjugated backbone of DPP-MeDTP compared to the other polymers. The high planarity of DPP-MeDTP is further supported by the potential energy surface scan of the dimers as a function of the torsion of the backbone (Figure S11, Supporting Information). The energy of the dimers was calculated with varying the torsional angle between the repeating units. The result clearly showed that the di-DPP-MeDTP has higher torsional barrier than the other dimers, indicating again the more planar backbone structure of DPP-MeDTP than the other polymers. The highly planar structure of the DPP-MeDTP backbone compared to the other polymers is attributed to the small steric hindrance of the DPP building block with the DPP core sandwiched between two thiophene units.^[24] The planar backbone of DPP-MeDTP is beneficial for the extended delocalization of charge carriers along the backbone and for the facilitated formation of dense π - π stacking within the polymer film.

The HOMO and LUMO energy levels of the polymers were determined experimentally using cyclic voltammetry measurements and optical band gaps ($E_{g, \text{opt}}$) measured from the UV-vis-near-infrared (NIR) absorption spectra of the polymer films (Figure 1b,c; Figure S12, Supporting Information). The optical, electrochemical, and thermal data of the polymers are summarized in **Table 1**. DTP-T2 and DTP-TT had similar energy levels, whereas DPP-MeDTP had much deeper energy levels and a much smaller band gap compared to DTP-T2 and DTP-TT. The low-lying energy levels and small band gap of DPP-MeDTP are

considered to originate from the strong electron-accepting ability of its DPP unit and intramolecular charge transfer between DTP and DPP units.^[19] In addition, significantly higher planarity of the conjugated backbone of DPP-MeDTP compared to DTP-T2 and DTP-TT would result in a longer conjugation length of DPP-MeDTP, thereby contributing to the small band gap of DPP-MeDTP.^[19] In the comparison between DTP-T2 and DTP-TT, the fused-ring structure of TT is generally expected to result in slightly higher HOMO and LUMO energy levels of the resulting conjugated polymer compared to the case of non-fused T2 because of its stronger electron-donating ability.^[22] Indeed, the measured HOMO and LUMO energy levels were slightly higher in DTP-TT than in DTP-T2. The slightly larger $E_{g, \text{opt}}$ of DTP-TT than that of DTP-T2 despite the fused-ring structure of DTP-TT can possibly be attributed to the larger twist angle between the TT and the neighboring DTP unit in DTP-TT compared to the twist angle between the thiophene unit and the neighboring DTP unit in DTP-T2; the larger twist angle in DTP-TT would result in less efficient electron delocalization along the polymer backbone.^[22]

Doping of the polymer films (the doping process is schematically illustrated in Figure 1d) with either FeCl_3 or F_4TCNQ resulted in the bleaching of the original absorption features of the pristine polymer films in their absorption spectra (Figure 1c). Instead, broad polaronic absorption bands appeared in the NIR region of the spectra; two absorption bands, one centered at ≈ 1250 nm and the other located at a longer wavelength (over 2000 nm), were observed for DPP-MeDTP, whereas an absorption band centered at ≈ 800 nm and the other at over 2000 nm were observed for DTP-T2 and DTP-TT. The low-energy absorption (over 2000 nm) and the intermediate-energy absorption (at ≈ 1250 nm for DPP-MeDTP and at ≈ 800 nm for DTP-T2 and DTP-TT) can be referred to bipolaronic and polaronic absorp-

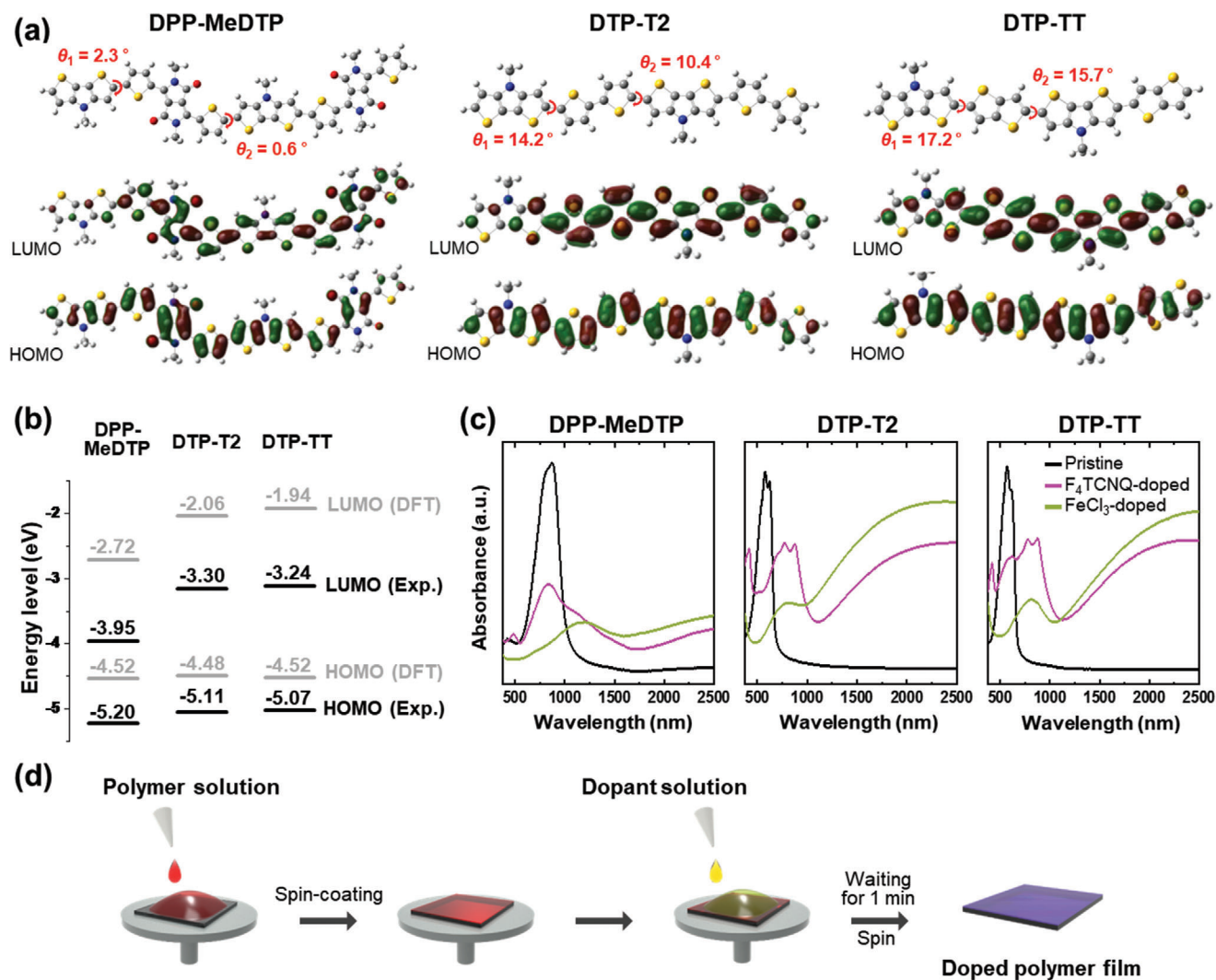


Figure 1. a) DFT-calculated energy-minimized structure and molecular orbitals for the model dimers for DPP-MeDTP, DTP-T2, and DTP-TT. b) HOMO and LUMO energy levels of each polymer determined from DFT calculation and CV measurement. c) UV-vis-NIR spectra of the polymers before and after the solution sequential doping (pristine, F₄TCNQ-doped, and FeCl₃-doped). d) Schematic illustration of the doping process.

Table 1. Physical properties of the DTP-based polymers.

	M_n [kDa]/PDI	$E_{g,opt}^a$ [eV]	E_{HOMO}^b [eV]	E_{LUMO}^c [eV]	T_d [°C]
DPP-MeDTP	76.7/1.45	1.25	-5.20	-3.95	404
DTP-T2	27.0/1.51	1.81	-5.11	-3.30	390
DTP-TT	17.9/1.22	1.83	-5.07	-3.24	389

^a) Estimated from the onset of the UV-vis-NIR spectra; ^b) Estimated from the onset potentials versus Fc/Fc⁺ as external reference; ^c) $E_{LUMO} = E_{HOMO} + E_{g,opt}$.

tion peaks, respectively, and the appearance of these peaks indicates efficient charge carrier generation by doping.^[25,26] For the absorption spectra of F₄TCNQ-doped DTP-T2 and DTP-TT, the peaks at 775 nm and 875 nm appear due to the absorption from F₄TCNQ anions, as reported in a previous literature.^[27] For all the polymers, doping with FeCl₃ resulted in more intense polaronic absorption bands than doping with F₄TCNQ, indicating that FeCl₃ had a higher doping efficiency than F₄TCNQ for these

polymer films. In general, the doping efficiency of a given p-type polymer-dopant system is known to be determined by two primary variables, the difference between the polymer's HOMO level and dopant's LUMO level, and the dopant miscibility with the polymer.^[28] Considering that FeCl₃ has higher LUMO level than F₄TCNQ, higher doping efficiency of FeCl₃ than F₄TCNQ for the three DTP-based polymers is expected to result from the higher miscibility of FeCl₃ with the polymers, as will be shown later. Other factors such as the dopant size and charge-transfer mechanism (e.g., integer charge transfer or the formation of charge-transfer complex) may affect the different doping efficiencies of FeCl₃ and F₄TCNQ,^[28] however, detailed investigations on these effects seem to be beyond the scope of the present study.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) analyses were performed to investigate and compare the microstructures of the polymer films before and after doping (Figure 2 and Table 2). The GIWAXS patterns of the pristine polymer films show that DPP-MeDTP has a preferential edge-on

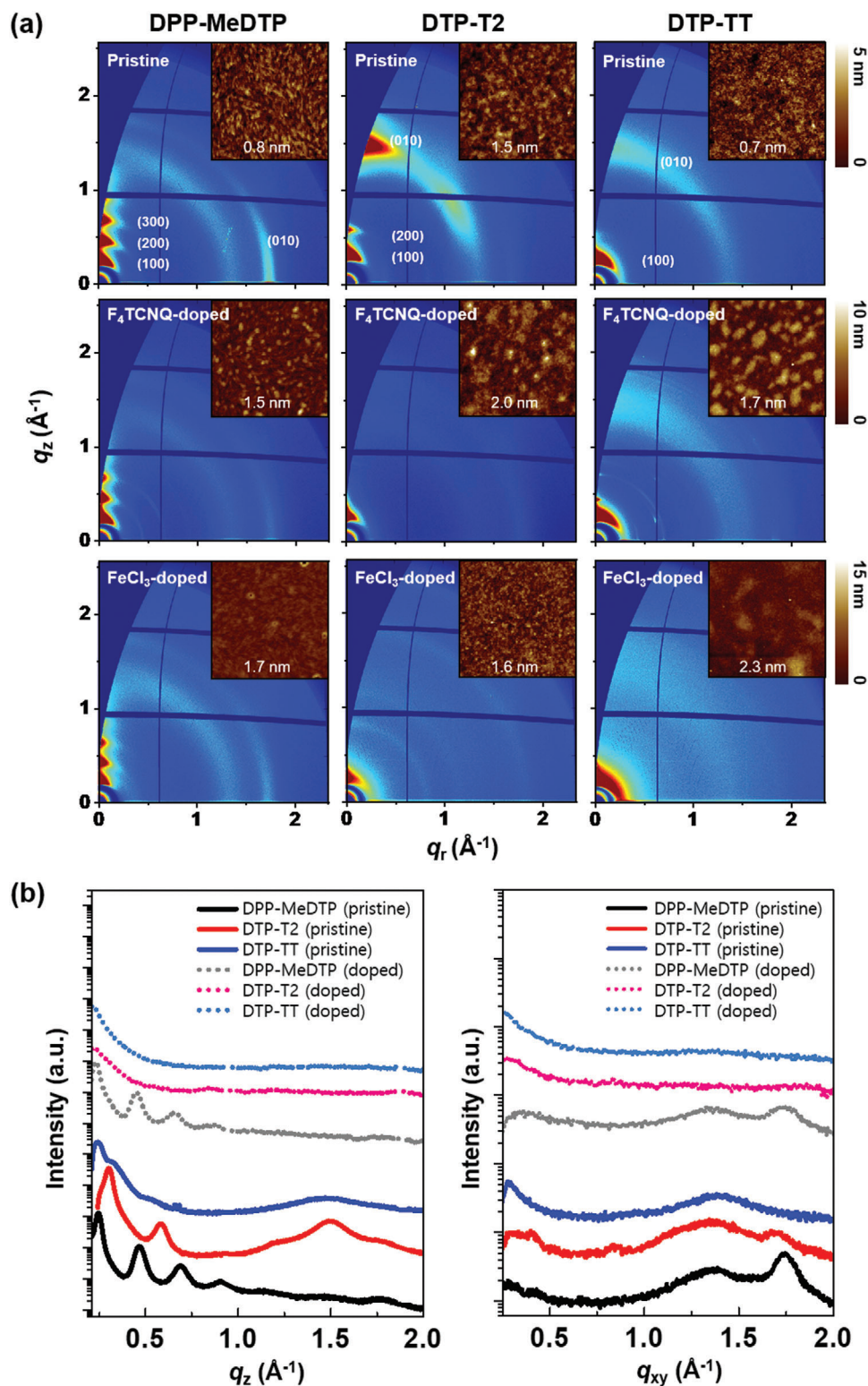


Figure 2. Structural analysis of the polymer films before and after the doping. a) 2D GIWAXS images of the pristine and doped polymer films. Inset: AFM height images (2 $\mu\text{m} \times 2 \mu\text{m}$) of the corresponding films. The numbers in the insets indicate root-mean-square roughness values calculated from the images. b) Corresponding line cut profiles of the pristine and FeCl₃-doped polymer films along the out-of-plane (left) and in-plane (right) directions.

Table 2. Crystallographic information of the polymer thin films before and after doping, corresponding to the GIWAXS images shown in Figure 2. The correlation length is determined from the full-width at half-maximum (FWHM) of diffraction peaks using Scherrer equation. The paracrystalline disorder parameter, g , is calculated from the slope of the $\delta b-h^2$ plot, where δb is the integral width of diffraction peak and h is the order of the diffraction peak.

Crystallographic parameters		DPP-MeDTP			DTP-T2			DTP-TT		
		Pristine	F ₄ TCNQ	FeCl ₃	Pristine	F ₄ TCNQ	FeCl ₃	Pristine	F ₄ TCNQ	FeCl ₃
Lamella stacking (100)	q [Å ⁻¹]	0.246	0.226	0.233	0.301	0.248	0.238	0.227	0.243	0.220
	d -spacing [Å]	25.58	27.80	27.02	20.85	25.35	26.37	27.62	25.83	28.57
	FWHM [Å ⁻¹]	0.029	0.044	0.035	0.038	0.068	0.075	0.023	0.069	0.063
	Correlation length [Å]	387.0	255.0	321.0	297.8	165.5	150.1	501.0	164.6	180.9
	g [%]	5.39	4.97	5.55	14.16	20.95	22.44	19.37	21.77	18.86
π - π stacking (010)	q [Å ⁻¹]	1.746	1.753	1.735	1.712	1.783	1.744	1.460	1.482	1.475
	d -spacing [Å]	3.60	3.58	3.62	3.67	3.52	3.60	4.30	4.24	4.26
	FWHM [Å ⁻¹]	0.130	0.178	0.148	0.160	0.170	0.375	0.344	0.441	0.329
	Correlation length [Å]	88.5	64.7	77.7	71.9	67.7	30.6	33.2	25.9	34.7

orientation, showing (h00) peaks along the out-of-plane direction and a (010) peak in the in-plane direction, whereas DTP-T2 and DTP-TT has a bimodal orientational distribution, showing both (h00) and (010) peaks along the out-of-plane direction. DPP-MeDTP has a much more pronounced molecular order than the other, and DTP-T2 showed stronger diffraction intensity than DTP-TT. This trend could be understood as a result of the difference in backbone planarity of the polymers, as discussed earlier. The paracrystalline disorder parameter g (Table 2), determined from the (100) peak of the GIWAXS data,^[29] is much smaller for DPP-MeDTP ($g \approx 5.4\%$) than for DTP-T2 ($g \approx 14\%$) or DTP-TT ($g \approx 19\%$), confirming the higher crystalline perfectness of DPP-MeDTP compared to other polymers.

Upon doping, the preferential orientational distribution of all the polymers remained unchanged, but the overall diffraction peak intensities decreased. Simultaneously, an increase in the lamellar stacking distance was also observed. These changes indicate that the incorporation of dopant molecules interrupted the packing of the polymer chains and that the dopant molecules tended to be located in the lamellar spacing of the polymer chains.^[30,31] Interestingly, the decrease in molecular order was more severe for DTP-T2 and DTP-TT than for DPP-MeDTP. While the paracrystalline disorder parameter showed little change upon doping with the DPP-MeDTP film, it increased considerably for the DTP-T2 film upon doping. The incorporation of dopant molecules into conjugated polymer films during solution sequential doping occurs via the swelling of the polymer by the solvent containing dopant molecules followed by the infiltration of the dopant molecules between polymer chains, which usually induces an increased structural disorder in molecular packing.^[32] Considering this, DPP-MeDTP was expected to be less favorable for doping than the other polymers in terms of the incorporation of dopant molecules because of relatively high crystallinity and robust crystalline structure. However, in terms of the generation of free charge carriers, the higher crystallinity of DPP-MeDTP, compared to the other polymers, was expected to be more beneficial for efficient doping, as a higher degree of molecular order would promote charge delocalization, which is required for charge carriers to escape the Coulombic interaction with ionized dopants.^[33]

The thin-film surface morphologies of the polymers were further investigated using atomic force microscopy (AFM) (Figure 2a, insets). Upon doping, the root-mean-square roughness of the film surface increased, reflecting the structural changes of the polymer films by the incorporation of dopant molecules into the film. After doping, spherical aggregates were found on the doped polymer surface; these features were attributed to the aggregation of excessive dopant molecules on polymer surface, which resulted from the poor solubility of polar dopants in the polymer matrix.^[34] The aggregation was more pronounced for the F₄TTCNQ-doped films than the FeCl₃-doped films, implying more efficient permeation of FeCl₃ compared to the F₄TTCNQ. The higher doping efficiency of FeCl₃-doped polymer films than that of F₄TTCNQ-doped films, characterized earlier by the UV-vis-NIR absorption spectra of the films (Figure 1c), agreed well with this observation.

To study the thermoelectric performance, the electrical conductivity and Seebeck coefficient of the doped polymer films (either with F₄TTCNQ or FeCl₃) were evaluated (Figure 3a, Table 3; Figure S13a, Supporting Information). Note that the pristine polymer films had poor electrical conductivity and Seebeck coefficients that were not measurable in our experimental setup. For the doped polymer films, the electrical conductivity was higher in the polymers doped with FeCl₃ than in the ones doped with F₄TTCNQ. This implied that the doping efficiency was higher for FeCl₃ than for F₄TTCNQ, as already inferred from the relative strength of the polaron absorption peaks of the UV-vis-NIR spectra of the doped polymer films (Figure 1c). The electrical conductivity was highest in the doped DPP-MeDTP film and the lowest in the doped DTP-TT film. The difference in the electrical conductivity of the polymers was mainly attributed to the large difference in the charge carrier mobility of the polymers. The charge carrier mobilities of the pristine polymers were measured and compared by fabricating the OFET devices (Figure 3b and Table 4). The detailed FET parameters are shown in Table S1, Supporting Information. For optimized device, the field-effect hole mobility was the highest for DPP-MeDTP and the lowest for DTP-TT, and this trend was consistent with the trend observed in electrical conductivity. The high charge carrier mobility of DPP-MeDTP was ascribed to its high backbone planarity and

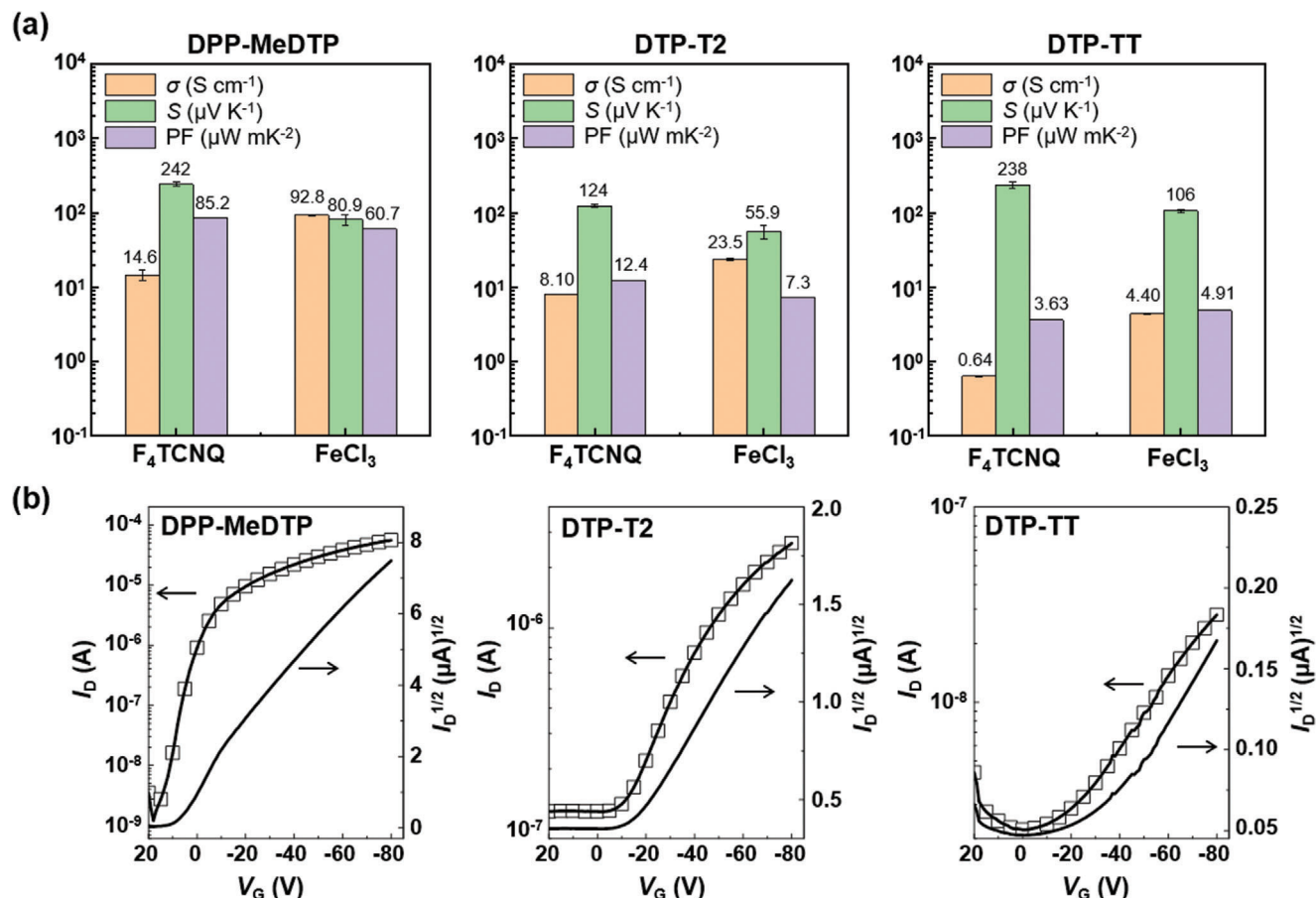


Figure 3. a) Thermoelectric properties of the polymers doped with either F₄TCNQ or FeCl₃. b) Transfer curves of FETs based on the pristine polymer films. The devices were thermally annealed at 200 °C. The field-effect mobilities were extracted at $V_G \approx -80$ V.

Table 3. Thermoelectric properties of the doped DTP-based conjugated polymers.

Polymer	Dopant	Electrical conductivity [S cm ⁻¹]	Seebeck coefficient [μV K ⁻¹]	Power factor [μW m ⁻¹ K ⁻²]
DPP-MeDTP	F ₄ TCNQ	14.6 (±2.38)	241.5 (±15.4)	85.2
	FeCl ₃	92.8 (±0.48)	80.9 (±12.8)	60.7
DTP-T2	F ₄ TCNQ	8.1 (±0.06)	123.8 (±6.42)	12.4
	FeCl ₃	23.5 (±0.91)	55.9 (±11.9)	7.3
DTP-TT	F ₄ TCNQ	0.64 (±0.01)	238.2 (±25.1)	3.63
	FeCl ₃	4.4 (±0.04)	105.6 (±4.51)	4.9

crystallinity as well as good intermolecular interaction between the donor and acceptor units (Figure 1a). The difference in charge carrier mobility of the polymers was expected to increase with doping, considering that DPP-MeDTP maintained its crystalline structure upon doping, while the other polymers lost a significant part of their molecular order upon doping, as indicated by the GIWAXS results (Figure 2). However, it should be noted that the differences in electrical conductivity between the polymers are not as large as the differences in their charge carrier mobilities, indicating a lower charge carrier density in the doped DPP-MeDTP compared to the other doped polymers. The charge carrier density in the doped polymer films was estimated from

the relation $\sigma = e\mu n$, where e is the elementary charge, and n is the charge carrier density, assuming that the charge carrier mobility is constant before and after doping (Table 4). This estimation would not provide the exact value of the charge carrier density but would be sufficient to roughly compare the relative density of charge carriers between the doped polymer films. The charge carrier density in F₄TCNQ-doped DPP-MeDTP was orders of magnitude lower than those in doped DTP-T2 and DTP-TT, indicating a lower doping efficiency of DPP-MeDTP compared to the other polymers. This result agrees well with the trend observed in the UV-vis-NIR spectra of the doped polymer films (Figure 1c), where the intensity of the polaronic absorption caused by doping

Table 4. Field-effect mobility of pristine DTP-based polymers and estimated charge carrier density within the doped polymer films.

Polymer	Undoped FET mobility ^{a)} [cm ² V ⁻¹ s ⁻¹]	Charge carrier density ^{b)} [10 ²² cm ⁻³]
DPP-MeDTP	0.075	0.77
DTP-T2	5.1 × 10 ⁻³	2.86
DTP-TT	1.2 × 10 ⁻⁴	21.7

^{a)} Devices were thermally annealed at 200 °C; ^{b)} Charge carrier density after doping (F₄TCNQ-doped DPP-MeDTP and DTP-T2; FeCl₃-doped DTP-TT).

is much smaller for DPP-MeDTP compared to DTP-T2 and DTP-TT. The weaker polaronic absorption of doped DPP-MeDTP than the others also indicates that doping efficiency and charge carrier density were lower in doped DPP-MeDTP than in doped DTP-T2 and DTP-TT. A possible reason is the less efficient dopant infiltration into the DPP-MeDTP film compared to the other polymers because of its higher crystallinity, which reduces the density of dopant molecules within the polymer film and thus reduces the free carrier density generated by doping. The high conductivity of DPP-MeDTP, despite such limitations, suggests that the high backbone planarity and crystallinity of the conjugated polymer are essential for achieving high electrical conductivity, although they may have negative effects to some extent in incorporating dopant molecules and generating free charge carriers by doping.

The Seebeck coefficients of the polymers did not show a clear tendency. Instead, for all the polymers, doping with FeCl₃ resulted in lower Seebeck coefficients than doping with F₄TNCQ. This is consistent with the electrical conductivities of the FeCl₃-doped polymer films being higher than those of the F₄TNCQ-doped films because the Seebeck coefficient and electrical conductivity have opposite relationship directions with the charge carrier density.^[35] That is, as the FeCl₃-doped films had higher doping levels than the F₄TNCQ-doped films, their electrical conductivities were higher and the Seebeck coefficients were lower than those of the F₄TNCQ-doped films. Comparison of the Seebeck coefficients between polymers is not easy, because of the absence of a well-established understanding of the effect of the microstructure on the Seebeck coefficient of organic thermoelectric materials.^[36] For hopping-transport dominant conjugated polymers, the Seebeck coefficient can be expressed as $S = (E_F - E_{tr})/eT$, where E_F is the Fermi level, and E_{tr} is the transport level.^[34] Therefore, the Seebeck coefficient of a doped polymer is determined by the density of states distribution and charge carrier density, which varies greatly from material to material.^[37] In addition, different doping efficiencies and morphological changes of different material systems upon doping further complicates the comparison of the Seebeck coefficients between material systems.^[38,39] Despite the complexity, we tried to interpret the relationship between the Seebeck coefficient and electrical conductivity for the doped polymers, using the charge transport model for conducting polymers (Figure S13b, Supporting Information). In this model, the electrical conductivity is expressed by the following equations^[37]

$$\sigma = \int \sigma_E (-\partial f / \partial E) dE \quad (1)$$

$$\sigma_E = \sigma_{E0} \left(\frac{E - E_t}{k_B T} \right)^s \quad (E > E_t) \quad (2)$$

where σ_{E0} is the transport coefficient, s is the transport parameter, E_t is the transport edge, and f is the Fermi-Dirac distribution function. Therefore, by plotting the Seebeck coefficient as a function of electrical conductivity, one can extract σ_{E0} and s for a conducting polymer film. More details on the model can be found elsewhere.^[37] For the doped DTP-based polymers in this study, fitting with the charge transport model gives $\sigma_{E0} = 0.255$, 0.017 , and 0.013 S cm⁻¹ for DPP-MeDTP, DTP-T2, and DTP-TT, respectively. The high σ_{E0} of DPP-MeDTP represents the superior electrical conducting ability of this polymer than the others. It has been suggested in previous studies that the magnitude of σ_{E0} depends on the microstructure of the conjugated polymer thin films; the more the conducting (ordered) domains are percolated, the higher the σ_{E0} value.^[37] On the basis of this interpretation, we could attribute the high S of DPP-MeDTP to its highly crystalline structure, which would provide efficient charge transport pathways that are well percolated throughout the polymer film. The high σ_{E0} of DPP-MeDTP also demonstrates further the excellence of the DTP unit as a building block for conjugated polymer-based thermoelectrics, especially when it is combined with a proper electron-accepting chemical moiety (e.g., DPP unit) to result in a donor-acceptor type conjugated copolymer.

The power factor, $PF = S^2 \sigma$, was the highest for DPP-MeDTP doped with F₄TNCQ, reaching a value of $85.2 \mu\text{W m}^{-1} \text{K}^{-2}$. For DTP-T2 and DTP-TT, the optimal PF values were 12.4 (doped with F₄TNCQ) and $4.9 \mu\text{W m}^{-1} \text{K}^{-2}$ (doped with FeCl₃), respectively. The superior PF of DPP-MeDTP compared to the other polymers originated from its high electrical conductivity and Seebeck coefficient. Collectively, our results indicate the importance of a high degree of molecular order and structural robustness of conjugated polymer thin films upon doping to achieve high electrical conductivity and thermoelectric performance of doped conjugated polymers. This study also demonstrates that constructing a copolymer possessing high backbone planarity and crystallinity by combining the DTP unit, which is a promising building block for conjugated polymers with high thermoelectric performance, with planar and strongly electron-accepting units, such as DPP can be an effective strategy to achieve superior thermoelectric properties.

3. Conclusion

In summary, we designed novel DTP-based conjugated copolymers and investigated their thermoelectric properties after doping with polymers using a sequential doping method. The DTP unit was combined with other conjugated moieties to produce three different copolymers: DPP-MeDTP, DTP-T2, and DTP-TT. Among these polymers, the donor-acceptor type copolymer DPP-MeDTP doped with F₄TNCQ exhibited the best thermoelectric performance, achieving a maximum PF of $85.2 \mu\text{W m}^{-1} \text{K}^{-2}$. Structural and electrical analyses of the polymer films revealed that the high thermoelectric performance of DPP-MeDTP is mainly attributed to its high electrical conductivity, which originates from its high conjugated backbone planarity and consequent efficient molecular packing, compared to the

other polymers. Our findings demonstrate the significance of a high degree of molecular order for achieving high conductivity in doped conjugated polymer films and provides insight into the design of DTP-containing conjugated polymers with excellent thermoelectric performance.

4. Experimental Section

Materials: DPP-MeDTP, DTP-T2, and DTP-TT were synthesized as described in the Supporting Information. F_4 TCNQ and $FeCl_3$, and all processing solvents were purchased from Sigma-Aldrich and were used without further purification.

Preparation of Pristine and Doped Polymer Films: The DTP-based polymers were dissolved in chlorobenzene (6 mg mL^{-1}) under N_2 atmosphere. F_4 TCNQ and $FeCl_3$ were dissolved in acetonitrile at various weight ratios under N_2 atmosphere. All solutions were stirred overnight at 60°C . The polymer solutions were spin-coated onto substrates at a speed of 2000 rpm under N_2 atmosphere. The thickness of the polymer films was $\approx 50 \text{ nm}$. For solution sequential doping of the polymer films, the F_4 TCNQ or $FeCl_3$ dopant solution was dripped onto the polymer films and left for some time to provide sufficient time for dopant molecules to penetrate the polymer thin film. The optimal doping condition was found by varying the concentration ($1\text{--}5 \text{ mg mL}^{-1}$) of the dopant solution and the time duration the dopant solution was remained on the polymer films. The highest power factor was obtained when the F_4 TCNQ solutions with the concentration of 2 mg mL^{-1} and the $FeCl_3$ solution with the concentration of 3 mg mL^{-1} were used and were left for $\approx 1 \text{ min}$ on the surface of the polymer films. Then, the remaining dopant solution on top of the polymer film was removed by spin-coating at a speed of 5000 rpm.

Fabrication of Field-Effect Transistors: Organic field-effect transistor (OFET) devices were fabricated on SiO_2/Si substrates. A highly doped p-Si wafer and 300 nm-thick thermally grown SiO_2 served as the gate electrode and gate dielectric, respectively. The substrate surface was cleaned using Piranha solution (7:3 ratio of sulfuric acid and hydrogen peroxide) and passivated with an octadecyltrimethoxysilane self-assembled monolayer.^[40] The polymer films were spin-coated onto the substrates, as described above. After drying at room temperature, the polymer films were thermally annealed at 100°C or at 200°C for 10 min under N_2 atmosphere, and then slowly cooled. The source/drain electrodes (Ti/Au) were thermally evaporated at a rate of $1 \text{ \AA s}^{-1}$. The channel length (L) and width (W) were 1500 and $150 \mu\text{m}$, respectively.

Characterizations of Electrical Properties and Seebeck Coefficient: Electrical conductivity was obtained from the sheet resistance and film thickness measurements. The sheet resistance was measured using the van der Pauw method (Keithley 4200-SCS). The electrical properties of the OFET devices were characterized (Keithley 4200) at room temperature under high vacuum ($\approx 10^{-6}$ Torr). The field-effect mobility (μ) was evaluated in the saturation regime using the following equation: $I_{D,sat} = (WC_i/2L)\mu(V_G - V_{th})^2$, where I_D is the drain current, V_G is the gate voltage, V_{th} is the threshold voltage, and C_i is the capacitance of the gate insulator (10.8 nF cm^{-2}).^[41] The Seebeck coefficient was measured using a homemade measurement setup, which included two Peltier modules (TEC1) that generated temperature differences and two K-type thermocouples that measured temperature and thermo-voltage simultaneously (Keithley 2460).

Other Characterizations: Absorption spectra were measured using a PerkinElmer Lambda 900 spectrophotometer (PerkinElmer) and a V-770 spectrometer (Jasco). TGA was performed under N_2 using a TA instrument TGA Q50. DSC was conducted under N_2 using a TA instrument DSC Q20, and both samples were heated at a rate of $10^\circ\text{C min}^{-1}$. The nanoscale morphology of the polymer films was observed using AFM in non-contact mode (XE-100, Park Systems). 2D GIWAXS measurements were performed at the 3C and 9A beamline of the Pohang Accelerator Laboratory, Korea. DFT calculations were performed using the Gaussian 09 package with the nonlocal hybrid Becke three-parameter Lee–Yang–Parr function and the 6–31G* basis set after optimizing the geometry of the dimers.

Supporting Information

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

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After initial online publication, S.L. was removed as a corresponding author on June 10, 2022, as their initial designation as corresponding author was made in error.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

conjugated polymers, dithienopyrroles, electrical conductivity, molecular doping, organic thermoelectrics

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