

RESEARCH ARTICLE OPEN ACCESS

High-Performance n-Type Organic Thermoelectrics Enabled by Control Over Microstructure, Orientation and Contact Plane in Naphthalenediimide-Bithiazole-Copolymer Films

Suhao Wang¹  | Said Oummouch² | Huan Wei³ | Karl Thorley⁴ | Adam Marks⁵  | Arianna Magni⁵ | Xiuming Sun⁶ | Alessandra Pistillo⁷ | Bruno Schmaltz⁸ | Olivier Bardagot⁷  | Sabine Ludwigs⁶ | Alberto Salleo⁵ | Yuanyuan Hu³  | Martin Brinkmann²

¹Unité de Dynamique et Structure des Matériaux Moléculaires, Université Du Littoral Côte d'Opale, Dunkerque, France | ²Institute Charles Sadron, UPR022 CNRS – University of Strasbourg, Strasbourg, France | ³Changsha Semiconductor Technology and Application Innovation Research Institute & International Science and Technology Innovation Cooperation Base for Advanced Display Technologies of Hunan Province, College of Semiconductors (College of Integrated Circuits), Hunan University, Changsha, China | ⁴Centre For Applied Energy Research, University of Kentucky, Lexington, Kentucky, USA | ⁵Department of Materials Science and Engineering, Stanford University, Stanford, California, USA | ⁶IPOC-Functional Polymers, Institute of Polymer Chemistry and Center for Integrated Quantum, Science and Technology (IQST), University of Stuttgart, Germany | ⁷Institute of Chemistry and Processes for Energy Environment and Health (ICPEES), CNRS, University of Strasbourg, Strasbourg, France | ⁸PCM2E EA 6299, Université de Tours, Tours, France

Correspondence: Suhao Wang (suhao.wang@univ-littoral.fr) | Yuanyuan Hu (yhu@hnu.edu.cn) | Martin Brinkmann (martin.brinkmann@ics-cnrs.unistra.fr)

Received: 22 December 2025 | **Revised:** 1 June 2026 | **Accepted:** 11 July 2026

Keywords: chain alignment | n-doping, charge transport | n-type conjugated polymers | organic thermoelectrics | polaron delocalization | seebeck coefficient

ABSTRACT

Conjugated polymers are promising thermoelectric materials offering solution processability, flexibility, and versatile synthesis. However, n-type polymers lag behind their p-type counterparts. Herein, we demonstrate that the combination of precise doping with control over crystalline contact plane, orientation, and microstructure helps design efficient n-type films of a naphthalenediimide-bithiazole-based copolymer (PNDIOE7-Tz2). Favorable fibrillar morphology and enhanced planarity lead to tight packing in films doped with N-DMBI, resulting in a high electrical conductivity $\sigma \approx 10 \text{ S cm}^{-1}$. GIWAXS indicates a predominantly face-on orientation in pristine films with a short π - π stacking distance of 3.47 Å. Incremental concentration doping enhances the σ to 45 S cm⁻¹ with a power factor (PF) $\approx 17.5 \mu\text{W m}^{-1} \text{ K}^{-2}$. Rubbing alignment causes a detrimental shift from face-on to edge-on, reducing σ below 5 S cm⁻¹ and PF below 4 $\mu\text{W m}^{-1} \text{ K}^{-2}$. Subsequent solvent vapor annealing converts aligned crystallites to mixed face-on/edge-on, promoting a strong enhancement of TE performance with a high PF up to 41 $\mu\text{W m}^{-1} \text{ K}^{-2}$, among the highest reported for n-type polymers. This work underscores that controlling the contact plane effectively decouples σ and S for high-performance n-type polymer thermoelectrics.

1 | Introduction

Polymer-based organic thermoelectric generators (OTEGs) [1, 2], capable of converting low-grade waste heat into distributed electricity, have been the focus of intense research interest over the preceding decade. This interest is underpinned by their

distinct advantages, most notably their naturally suppressed thermal conductivity (κ) [3], amenability to solution-based processing [4, 5], and intrinsic mechanical flexibility [6, 7], which collectively promise great scalability and low manufacturing cost [8, 9]. The realization of functional thermoelectric modules fundamentally necessitates the balanced integration of both

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p-type and n-type semiconducting polymers. To date, the development of p-type analogues has reached a visible maturity [10–12]. For instance, in terms of performance, many polymers exhibit electrical conductivities exceeding 1000 S cm^{-1} , exemplified by PEDOT-based polymers [13], polythiophenes (e.g., P3HT [14], PBTBT [11, 15–17] and its derivatives [18, 19]), and diverse other p-type architectures [20]. In stark contrast, the evolution of n-type candidates remains a formidable challenge [21, 22], with a majority of n-type polymers exhibiting electrical conductivities $< 100 \text{ S cm}^{-1}$ (and frequently $< 10 \text{ S cm}^{-1}$) [8, 9], notwithstanding the recently developed poly(benzodifurandione) (PBFDO) [23–25], and a few other conjugated polymers demonstrating significantly superior electrical performance [9, 26–28]. The disparity in performance constitutes a major bottleneck impeding the development of efficient, all-polymer thermoelectric devices.

Beyond molecular engineering, one of the major challenges in the design of thermoelectric polymers is the dopant-induced disorder, which leads to morphological degradation and thus the disruption of charge transport in the highly doped state [29]. For p-type conjugated polymers, several strategies have been developed to mitigate this point. For instance, modulation doping has been utilized to induce spontaneous doping, ensuring that dopants perfectly reside in the amorphous domains of the doped films such that actual charge transport primarily takes place in the crystalline domains without disrupting the film microstructure [30]. Moreover, side-chain cleavage has been employed to eliminate the bulky, insulating pendants, leading to tighter intermolecular packing and higher electrical performance [31–33]. Nevertheless, less progress has been made in enhancing the performance of n-doped conjugated polymers. To date, the development of n-type thermoelectric polymers has involved the use of several classic building blocks, notably naphthalenediimide (NDI)-based polymers [34–36], diketopyrrolopyrrole (DPP)-based polymers [37, 38], poly(p-phenylenevinylene) (PPV)-based polymers [39, 40], bithiopheneimide (BTI)-based polymers [28, 41], among others [9]. In particular, the pioneering investigations on the benchmark polymer P(NDI2OD-T2) (also referred to as N2200) revealed two fundamental limitations at the molecular level: (i) its poor miscibility with dopants [42], and (ii) its localization of polarons caused by the donor-acceptor (D-A) feature [43, 44]. Correspondingly, two strategies have been used to address these challenges: (i) by incorporating oligo(ethylene glycol) side chains into the polymer backbone, better miscibility between the polymer and the dopant is achieved [35, 45]; (ii) by replacing the bithiophene(T2) unit with the more electron-efficient bithiazole (Tz2) unit, a lower lowest unoccupied molecular orbital (LUMO) and a high planar backbone conformation are realized [34]. Remarkably, the simultaneous application of the two aforementioned strategies demonstrated a synergistic effect, resulting in both enhanced polymer-dopant miscibility and optimized electronic structure [46]. In addition, recent studies revealed the roles of side-chain nature (i.e., polar vs. amphiphilic, linear vs. branched) and side-chain length on the thermoelectric properties of NDI-based polymers [47–49]. Despite being the initial and most extensively investigated class of n-type polymers, NDI-based polymers have yet to exceed an electrical conductivity (σ) of 10 S cm^{-1} in the published literature. (Figure 1A and Figure S1) Note that σ is a critical metric for achieving a high thermoelectric power factor ($\text{PF} = \sigma S^2$), where S represents the

Seebeck coefficient. Thus far, much effort has been devoted to the molecular engineering of the polymer structures in NDI-based systems; Little is known, however, about the molecular packing and orientation on the thermoelectric performance of NDI-based polymers. In particular, a significant remaining hurdle in achieving higher performance is the decoupling of σ and S , which is essential for maximizing the power factor.

Herein, we report the modulated n-doping of P(NDI2OE7-Tz2) using benchmark n-dopant precursor N-DMBI (Figure 1B). A central objective of this work is to achieve control over molecular packing and chain alignment that facilitates the effective decoupling of σ and S . P(NDI2OE7-Tz2) was synthesized via a Stille coupling polymerization and has a number-averaged molar mass (M_n) of 33.7 kDa (See SI). According to cyclic voltammograms (CV) characterization and the standard reported by Bazan et al. [50], the LUMO energy level of P(NDI2OE7-Tz2) is determined to be $-4.4 \pm 0.1 \text{ eV}$. (Figure S2) Such a low-lying LUMO is critical, allowing for energetically favorable, efficient n-doping of P(NDI2OE7-Tz2) by N-DMBI. Mixed-solution doping (MsD, Figure 1C), where the solutions of P(NDI2OE7-Tz2) and N-DMBI are mixed prior to film deposition in a common solvent, resulting in a high σ of exceeding 10 S cm^{-1} . To date, this conductivity value represents the best ever reported for an NDI-based polymer. Structural analysis of the doped film indicates a predominantly face-on orientation of the pristine films with a short π - π stacking distance of 3.47 Å. Notably, the invariant packing distances along the π - π and lamellar packing directions suggest that the dopants are located in the amorphous polymer region, thus causing minimal hindrance to the charge transport in the doped films. Incremental concentration doping (ICD, Figure 1D), an advanced technique for sequential doping, led to a substantial enhancement in σ , reaching values up to 45 S cm^{-1} and a greater PF of $17.5 \mu\text{W m}^{-1} \text{ K}^{-2}$. Surprisingly, rubbing alignment of the as-cast films did not induce an enhancement in σ and PF. Instead, it deteriorated the thermoelectric performance, yielding films with σ ($< 5 \text{ S cm}^{-1}$) even inferior to the films processed by MsD, translating to a low PF of $< 4 \mu\text{W m}^{-1} \text{ K}^{-2}$. Such a degradation is attributed to the undesirable edge-on orientation of the films induced by rub-alignment. Remarkably, subsequent treatment of the rubbing-aligned films with solvent vapor annealing (SVA, Figure 1E) resulted in a significant enhancement in both σ and S , ultimately yielding films with the highest thermoelectric performance. Notably, a power factor up to $41 \mu\text{W m}^{-1} \text{ K}^{-2}$ is achieved, a record value for NDI-based thermoelectric polymers to date. This synergistic improvement is ascribed to SVA-modulated film orientation from edge-on to a mixed face-on/edge-on orientation while preserving the anisotropic ratio induced by the initial rubbing. This work underscores the importance of simultaneous tuning of polymer chain alignment and molecular orientation for the future pursuit of efficient n-type thermoelectrics.

2 | Results and Discussion

To verify the n-doping process and the resulting charge carrier generation within the P(NDI2OE7-Tz2) thin films, we performed Electron Spin Resonance (ESR) spectroscopy measurements on both the pristine and chemically doped samples from 3 to 20 mol% (Figure 2A). The pristine P(NDI2OE7-Tz2) thin film exhibited no discernible ESR signal, whereas N-DMBI-doped P(NDI2OE7-

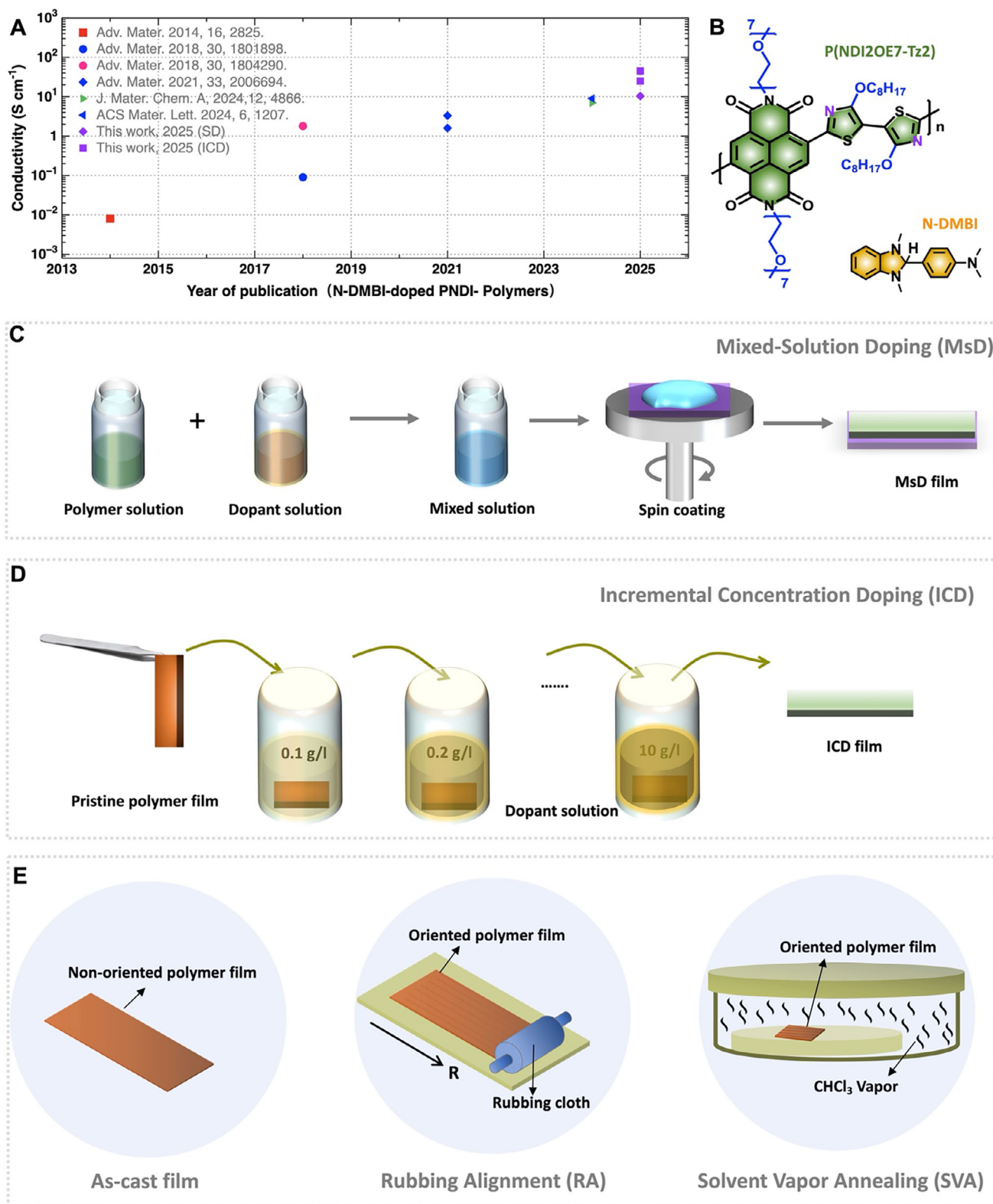


FIGURE 1 | (A) Electrical conductivities of n-doped PNDI-based polymers collected from the published literature. (B) Chemical structures of P(NDI2OE7-Tz2) and n-dopant precursor N-DMBI. (C) Schematic illustration of mixed-solution doping (MsD). (D) Schematic illustration of incremental concentration doping (ICD). (E) Schematic illustration of as-cast film, rubbing alignment (RA), and solvent vapor annealing (SVA).

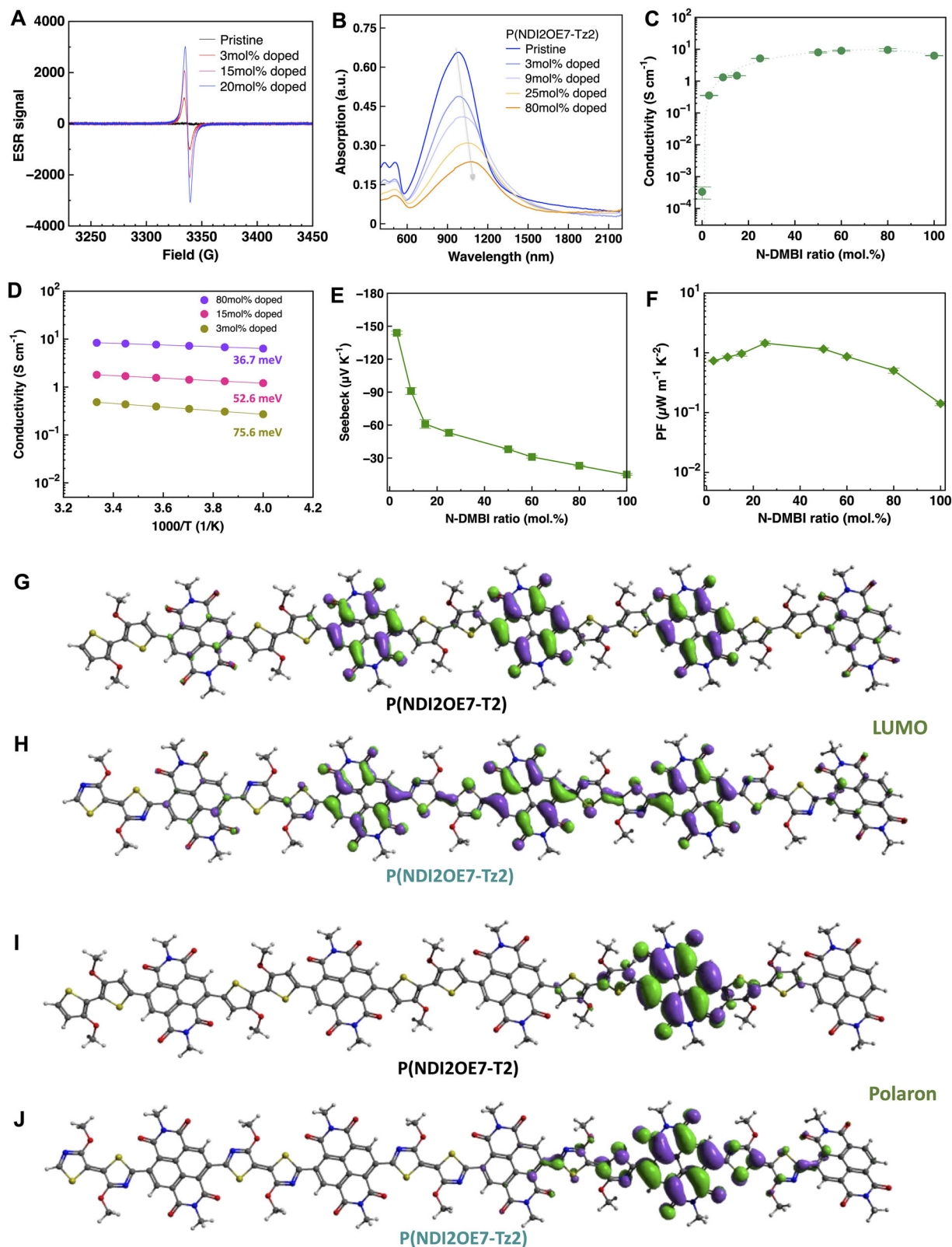


FIGURE 2 | (A) ESR spectroscopy of P(NDI2OE7-Tz2) films vs. N-DMBI content, (B) UV-vis-NIR absorbance spectra of P(NDI2OE7-Tz2) films vs. dopant concentration, (C) Evolution of the electrical conductivity vs. N-DMBI concentration, (D) Temperature dependence of the electrical conductivity for thin films with different doping concentrations, (E) Evolution of Seebeck coefficient, and (F) Power factor of the pristine and N-DMBI-doped P(NDI2OE7-Tz2) thin films for different doping concentrations.

Tz2) thin films displayed intense and characteristic ESR signals at 3340 G with symmetric line shapes (mostly Lorentzian), characteristic of free radicals and confirming efficient n-doping [34, 36]. Furthermore, the signal intensity progressively increases with increasing concentration of the N-DMBI dopant. No noticeable change in the linewidth is observed, confirming proper removal of dissolved oxygen and ensuring maximal efficiency of each N-DMBI molecule incorporated [51].

To further shed light on the electronic structure and detect the polaron formation upon doping, UV-vis-NIR absorbance spectroscopy was conducted on P(NDI2OE7-Tz2) thin films in both pristine and chemically doped states. As shown in Figure 2B, a high-energy band centered at approximately 500 nm from the pristine film is characteristic of the π - π^* transition band, whereas a low-energy band extending into the NIR region situated around 1000 nm is assigned to delocalized intramolecular charge-transfer (ICT) transition. Doping the polymer with N-DMBI results in a dramatic quenching of the low-energy CT band. Concurrently, the spectrum shows the emergence of new absorbance bands, indicating efficient charge transfer and polaron formation. The bleaching and redshift of the CT band and the appearance of the polaron bands are fully consistent with the ESR results. The σ of the P(NDI2OE7-Tz2) thin films was recorded as a function of the N-DMBI molar ratio (Figure 2C). The pristine P(NDI2OE7-Tz2) thin film exhibited an inherently low initial σ of $3.4 \times 10^{-4} \text{ S cm}^{-1}$. Upon doping with N-DMBI, the σ demonstrated a substantial enhancement by 3 orders of magnitude, reaching 0.35 S cm^{-1} at a modest dopant concentration of only 3 mol%. Notably, the σ continued to gradually increase as the molar ratio of N-DMBI increases to a high dopant concentration of 80 mol%, resulting in a σ of $9.6 \pm 0.9 \text{ S cm}^{-1}$ with a highest value of 10.4 S cm^{-1} . Note that this is the first report that NDI-based polymers exhibit higher than 10 S cm^{-1} , approximately 4 orders of magnitude higher than the reference N-DMBI-doped P(NDI2OD-T2) [45, 52]. Such a high σ value of N-DMBI-doped P(NDI2OE7-Tz2) may be attributed to the combination of a higher molecular weight, which facilitates the intrachain charge transport, as well as the use of long ethylene glycol (OE7) side chains, which significantly enhances the dopant miscibility with the polymer. Temperature-dependent electrical conductivity measurements were conducted across a series of P(NDI2OE7-Tz2) thin films doped with N-DMBI at dopant concentrations of 3, 15, and 80 mol% (Figure 2D), and very low activation energies (E_A) were measured following the sequence 0.076, 0.052, and 0.037 eV, respectively. This diminishing trend in E_A is a strong indication of highly efficient polaron delocalization and signifies a highly ordered molecular packing within the host matrix upon doping (See GIWAXS analysis). Notably, these E_A values represent a significant reduction compared to the one determined in the n-doped alkylated analogue, P(NDI-Tz2) (0.11 eV) [34], thereby pointing toward a substantially lower degree of energetic disorder within the n-doped P(NDI2OE7-Tz2) [53–55]. Evaluation of the thermoelectric performance of the N-DMBI-doped films was performed. As N-DMBI concentration was incrementally increased from 3 to 80 mol%, the Seebeck coefficient exhibited a marked drop, decreasing from -144 to $-23 \text{ } \mu\text{V K}^{-1}$ (Figure 2E), which is characteristic of n-type conduction and directly correlates with the doping-induced modulation of the charge carrier concentration within the polymer matrix. Consequently, an average PF of $1.5 \pm 0.1 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$ and a maximum value of $1.6 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$ were recorded at the intermediate

dopant concentration of 25 mol% (Figure 2F). DFT calculations were performed to elucidate the fundamental geometric and electronic properties of the P(NDI2OE7-Tz2) polymer in both its neutral and negatively charged (polaron) states. For comparative analysis, the structurally analogous polymer, P(NDI2OE7-T2), featuring a bithiophene (T2) substituent, was used as a reference system. As expected from prior findings on the alkylated P(NDI2OD-T2) analogue [43, 44], the LUMO of the structurally twisted P(NDI2OE7-T2) is highly localized predominantly over the NDI unit (Figure 2G). In sharp contrast, the remarkable planarity between NDI and Tz2 co-monomers in P(NDI2OE7-Tz2) favors a significantly enhanced delocalization of the LUMO extending proficiently from the NDI core onto the Tz2 co-monomer unit (Figure 2H). This extended spatial distribution is consistent with the more electron-deficient nature of the Tz2 moiety compared to the T2, which acts to effectively lower and delocalize the frontier orbitals. Upon n-doping, the resulting negative polaron in the reference P(NDI2OE7-T2) backbone is found to be highly confined primarily within the NDI unit of a single monomer repeat unit (Figure 2I). Conversely, the negative polaron within the P(NDI2OE7-Tz2) system demonstrates substantial spatial delocalization, distributing charge density across both the NDI and Tz2 units, and even extending slightly beyond the boundary of a single repeating unit (Figure 2J). This increased charge delocalization in the polaron state of P(NDI2OE7-Tz2) can be correlated with the aforementioned low activation energy for charge transport, as depicted in Figure 2D.

To gain critical insight into the impact of N-DMBI doping on the microstructure and molecular packing of P(NDI2OE7-Tz2), two-dimensional grazing-incidence wide-angle x-ray scattering (2D GIWAXS) measurements were conducted on the pristine, 25 mol%, and 80 mol% N-DMBI-doped thin films. As shown in Figure 3A, the GIWAXS pattern for the pristine P(NDI2OE7-Tz2) film reveals long-range ordering characterized by a mixed chain orientation, though face-on orientation is notably predominant. This microstructure is consistent with observations typically reported for NDI-based copolymer systems [56]. The films exhibit an out-of-plane π - π stacking peak ($q = 1.80 \text{ } \text{\AA}^{-1}$) and in-plane lamellar stacking peaks ($q_{100} = 0.19 \text{ } \text{\AA}^{-1}$), with three detectable higher-order reflections. Critically, the π - π stacking scattering peak observed along the out-of-plane (q_z) axis corresponds to an exceptionally short interchain distance (d -spacing) of $3.47 \text{ } \text{\AA}$. This value is substantially smaller than those reported for the analogous polymers P(NDI2OD-T2) ($3.93 \text{ } \text{\AA}$) [56] and also smaller than its alkylated derivative P(NDI2OD-Tz2) ($3.63 \text{ } \text{\AA}$) [34]. This observation provides experimental validation for the DFT-computed Tz2-induced planarization of the polymer backbone. Specifically, the utilization of linear OE side chains diminishes the steric hindrance typically associated with branched alkylated OD groups, consequently promoting tighter intermolecular π - π stacking. Upon doping P(NDI2OE7-Tz2) with the N-DMBI dopant at concentrations of 25 and 80 mol%, only negligible alterations were observed in the molecular packing and chain orientation (Figure 3B,C). A meticulous examination of the integrated linecuts for both the out-of-plane (π - π stacking) and in-plane (lamellar packing) reflections (Figure 3D,E) confirms the absence of structural change following the doping process. This invariance clearly suggests that either the dopant molecules primarily reside within the amorphous regions of the polymer matrix, or the substantial initial lamellar periodicity

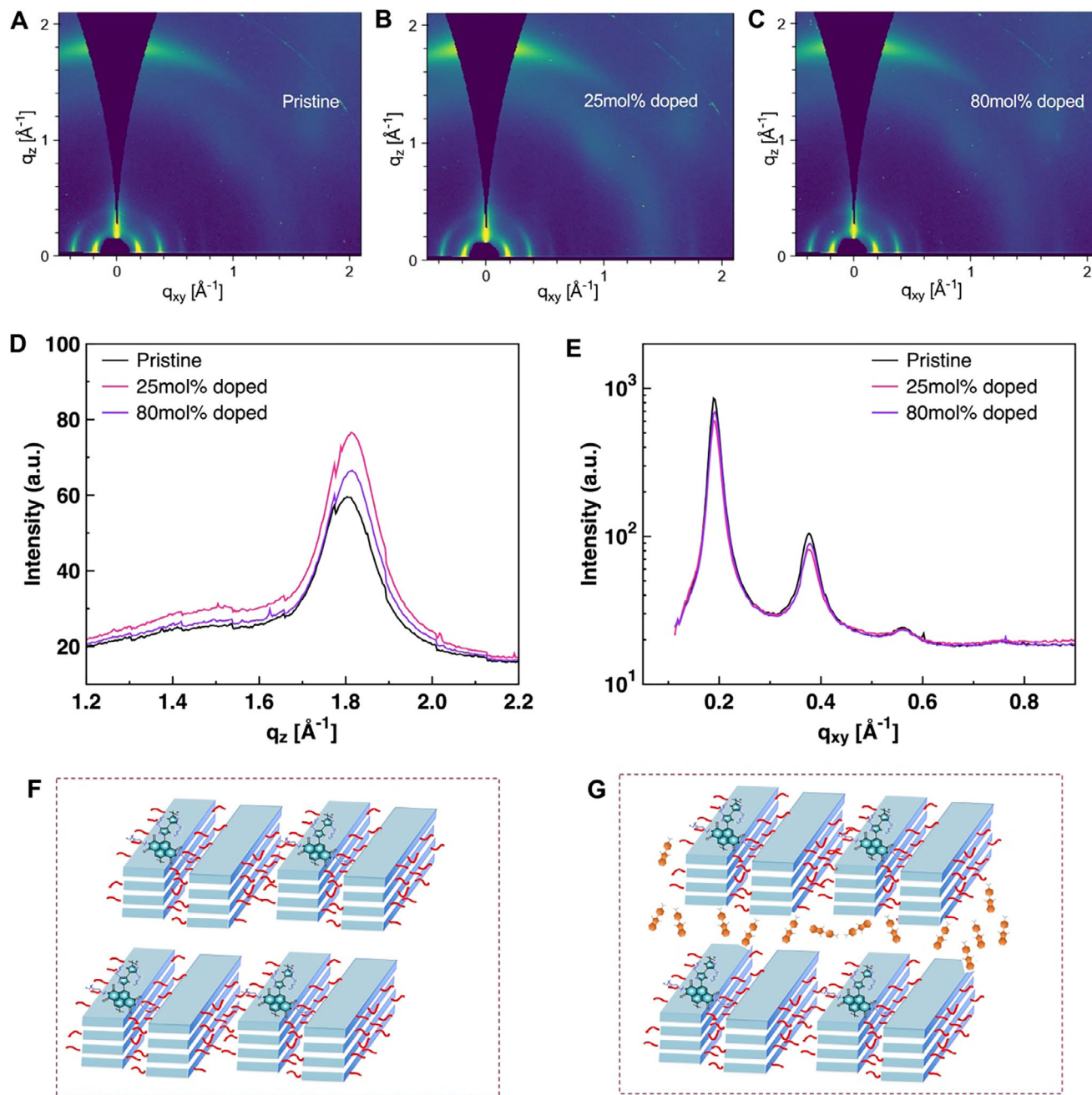


FIGURE 3 | 2D GIWAXS patterns collected for thin films of the pristine (A), 25 mol% N-DMBI-doped (B), and the 80 mol% (C) doped P(NDI2OE7-Tz2), and their corresponding linecut along q_z (D) and q_{xy} (E). Schematic illustrations on the pristine (F) and doped films (G) showing the possible accommodation sites for the dopants.

of P(NDI2OE7-Tz2) potentially provides sufficient molecular free volume within the ethylene glycol side-chain layers to accommodate the N-DMBI dopant molecules (Figure 3F,G). The GIWAXS analysis together with the high-resiliency of the films to the doping suggests that modulation doping may be involved [30, 57], with a spatial separation between the amorphous zones concentrating the dopant counter-ions and the crystalline domains with high order essential for efficient charge transport. This is the first report of a possible modulation doping mechanism for an n-type conjugated polymer, indicating the potential for further enhancement of the TE properties via a dedicated solution doping approach and chain alignment technique.

Sequential doping has been reported to enable introducing dopants into thin films of conjugated semiconducting polymers after crystallization of the polymer, thus minimizing the formation of defects and disruptive phase segregation between polymer and dopant that is detrimental for charge transport [58, 59]. As a result, this method generally results in superior electrical conductivity in doped films, compared to the conventional MsD approach [60, 61]. In particular, Incremental Concentration Doping (ICD) is a refinement of sequential doping [62] which allows for the progressive and controlled incorporation of dopants into the bulk of the polymer matrix. (Figure 1D) This doping approach helps preserve the molecular packing of the polymer.

Thus, we employed ICD to dope P(NDI2OE7-Tz2) to achieve enhanced performances. The as-cast P(NDI2OE7-Tz2) film was prepared by doctor blading. Note that the films revealed a fibrillar morphology, with fibers extending beyond 1 μm and with nearby fibers forming bunches with a common in-plane orientation. (Figure S3) To ensure a consistent comparison, we verified that the crystalline structure and morphology of spin-coated and doctor-bladed films of P(NDI2OE7-Tz2) are essentially identical. (see Figure S4) These results demonstrate that the specific film processing methods do not fundamentally alter the resulting microstructures. The electron diffraction (ED) pattern of the films (Figure 4A) shows a set of two Scherrer rings indexed as (1 0 0) and (2 0 0) of a lamellar structure with a periodicity $d_{100} = 3.2$ nm, indicating a dominant face-on orientation relative to the substrate surface. An additional Scherrer ring at 3.5 $\text{\AA}$ is assigned to the (0 0 4) reflections along the chain direction. These (0 0 4) reflections are also observed in the GIWAXS patterns of non-oriented films (see arrows in Figure S5). This confirms that the molecular packing and crystalline orientations are consistent across both characterization techniques and deposition methods. Selected area electron diffraction (SAED) measurements demonstrate that the fiber axis corresponds to the chain direction, consistent with observations previously reported for P(NDI2OD-T2) [63, 64]. This orientation is also seen in the High-Resolution TEM image revealing the semi-crystalline structure of P(NDI2OE7-Tz2) films by the alternation of fringed patterns with a 3.1 ± 0.1 nm periodicity corresponding to face-on domains and zones without such contrast associated with amorphous zones (Figure S3B). Despite local correlations in the orientations of adjacent P(NDI2OE7-Tz2) fibers, the overall in-plane orientation distribution of P(NDI2OE7-Tz2) domains is isotropic. P(NDI2OE7-Tz2) was doped with N-DMBI using ICD, and its thermoelectric properties were systematically investigated. As shown in Figure 4D,G,J, under a fixed doping time of 10s, the optimal performance was achieved at a dopant concentration of 2 g/L, yielding a peak σ of 45 ± 24 S cm^{-1} , and a corresponding S of -63 ± 1 $\mu\text{V/K}$, which translates to a power factor of $\text{PF} = 17.5 \pm 9$ $\mu\text{W m}^{-1} \text{K}^{-2}$. An increase in the N-DMBI concentration beyond 2 g/L, however, led to a reduction in electrical conductivity, a leveling of the Seebeck coefficient, and thus a drop in power factor (Figure 4D,G,J), suggesting the onset of over-doping. Having established this optimized doping protocol, we then applied it to probe the thermoelectric performance of highly oriented (rubbed) P(NDI2OE7-Tz2) films to investigate the influence of molecular anisotropy on charge transport efficiency.

Prior to the doping procedure, a critical prerequisite was the optimization of the alignment conditions for P(NDI2OE7-Tz2) films. To achieve this, the P(NDI2OE7-Tz2) films were subjected to mechanical rubbing at different rubbing temperatures (T_R) in the range 120°C–220°C, and rub-alignment was performed in a glovebox under inert atmosphere. Note that the thermal degradation transition temperature for P(NDI2OE7-Tz2) exceeds 300°C. (Figure S6) The level of orientation was quantified using polarized UV–vis–NIR spectroscopy and polarized optical microscopy. Notably, the rubbed films show a highly anisotropic absorbance and strong birefringence. The best alignment was estimated from the dichroic ratio (DR) in absorbance and was observed for $T_R = 180^\circ\text{C}$ with $\text{DR} = 8.4$ (see Figure S7 showing the evolution of the DR vs. T_R (measured at 965 nm)). The internal structure of the rub-aligned films was subsequently analyzed

across the temperature range of $T_R = 180^\circ\text{C}$ – 220°C . Interestingly, as indicated by the electron diffraction (ED) pattern (Figure 4B), rubbing completely transformed the structure of the films from face-on to fully edge-on at $T_R = 180^\circ\text{C}$. The ED pattern shows an intense and broad equatorial 0 1 0 reflection at $d_{010} = 3.45$ $\text{\AA}$ and a sharp meridional reflection that can be indexed as 0 0 4 at 3.5 $\text{\AA}$. The films are made exclusively of edge-on crystallites, without any trace of the original face-on texture observed prior to alignment. Subsequently, ICD was applied to the rub-aligned films to evaluate their resulting TE properties. Surprisingly, the molecular alignment induced by the rubbing process led to a significant deterioration in the TE properties of the P(NDI2OE7-Tz2) films. Specifically, it induced a reduction in σ to less than 5 S cm^{-1} in the chain direction (Figure 4E), causing the PF to drop to below 4 $\mu\text{W/m}^2\text{K}^2$. (Figure 4K) This is in strong contrast to previous findings on both p-type and n-type oriented conjugated polymers consistently showing enhanced TE performance in the polymer chain direction [61, 65]. As shown in Figure S8, upon doping the rub-aligned films, a marginal change in π -stacking periodicity is observed, while the in-plane orientation is preserved. Clearly, it can be verified that this deterioration in TE performance is not attributed to a loss of alignment. Furthermore, UV–vis–NIR spectroscopy demonstrates similar bleaching of the P(NDI2OE7-Tz2) absorbance in as-cast and rubbed films, hence indicating similar doping levels (Figure 5A,B). Unexpectedly, the TE properties of the rub-aligned films show two peculiarities. First, a crossover between $\sigma_{\parallel}$ and $\sigma_{\perp}$ is observed vs. increasing N-DMBI concentration. ($\parallel$ represents measurements taken along the rubbing direction, whereas $\perp$ represents measurements taken in the in-plane direction at 90° to the rubbing direction). Second, the anisotropy of the Seebeck coefficient shows unusually that $|S_{\parallel}| < |S_{\perp}|$. In all investigated p-type aligned polymers, the opposite relation ($|S_{\parallel}| > |S_{\perp}|$) is typically observed, and this can be well explained by the heterogeneous material model, i.e., $S_{\parallel}$ is dominated by the contribution from aligned and ordered domains of the polymer, whereas $S_{\perp}$ is dominated by the contribution from amorphous polymeric domains [66]. Note that this is the first time that alignment by rubbing reduces TE performance as compared to non-aligned films [65, 67–69]. We verified further that this situation is not restricted to the used rubbing temperature, as we observed a similar trend for the TE performance in P(NDI2OE7-Tz2) films rubbed at 75°C (See Figure S9). The unique anisotropic TE properties of P(NDI2OE7-Tz2) are likely linked to the specific microstructure of P(NDI2OE7-Tz2) films, which are made of exclusively edge-on oriented domains (Figure 5E) [65]. Indeed, rub-aligned P(NDI2OE7-Tz2) films are formed exclusively of edge-on crystals such that the direction perpendicular to rubbing is the π -stacking direction, whereas in most rub-aligned p-type films investigated so far, a majority of face-on crystals, sometimes co-existing with edge-on crystals, have been observed [65]. Accordingly, given the efficient transport path along the π -stacking direction in P(NDI2OE7-Tz2), it is consistent with theoretical frameworks that both $\sigma_{\perp}$ and $S_{\perp}$ can exceed $\sigma_{\parallel}$ and $S_{\parallel}$. This is also consistent with recent work on doped organic semiconductors showing that the dominant contact plane in the films impacts the observed TE properties after sequential doping for both n-type and p-type polymers [70, 71]. Hereby, to clarify the structural discussion, we define the ‘contact plane’ as the specific crystallographic plane of the polymer crystal that lies parallel to the substrate interface. In oriented conjugated polymers, the nature of this contact plane dictates the

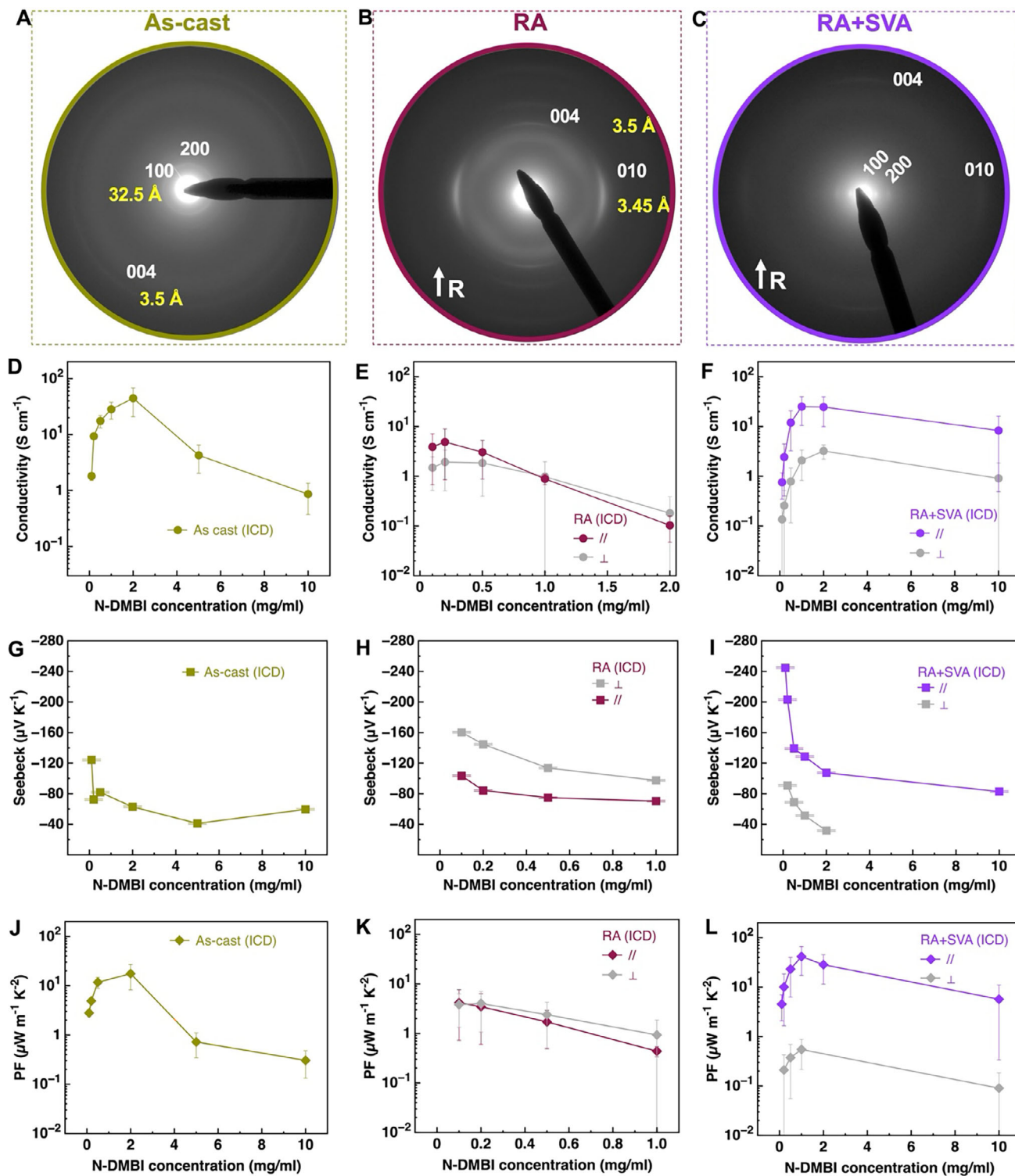


FIGURE 4 | (A–C) Representative electron diffraction patterns of P(NDI2OE7-TZ2) films in pristine form (As-cast), rub-aligned (RA), and rub-aligned after exposure to CHCl₃ vapors for 15 min (RA+SVA). (D–L) electrical conductivity, Seebeck coefficient, and power factor of P(NDI2OE7-TZ2) films upon ICD doping. For the aligned films S and σ are probed both parallel (//) and perpendicular ($\perp$) to the rubbing direction.

dominant thin-film texture: a (1 0 0) contact plane corresponds to an edge-on orientation (lamellar stacking perpendicular to the substrate), whereas a (0 1 0) contact plane results in a face-on orientation (π -stacking perpendicular to the substrate) [70, 71]. This crystallographic orientation is distinct from, and should not be confused with, the physical contacts at the electrode

interfaces or the molecular-level interactions with dopants. In particular, it was observed that a mixture of edge-on and face-on domains shows superior TE properties than films made of purely edge-on or purely face-on domains. Although the explanations are inconclusive, according to Diao et al., DPP polymer films possessing a face-on orientation demonstrate superior electrical

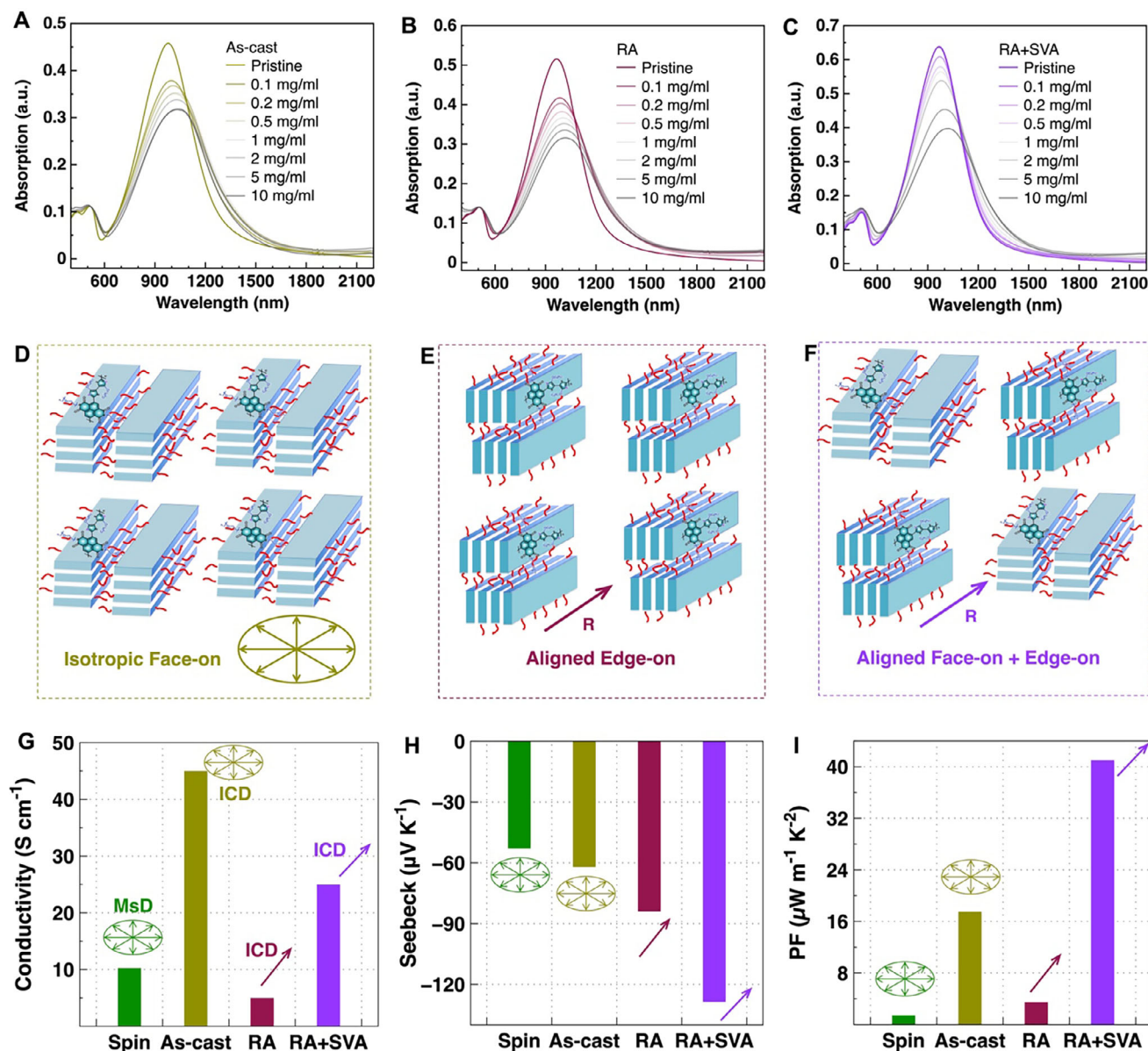


FIGURE 5 | Evolution of the UV-vis-NIR absorbance spectra of P(NDI2OE7-Tz2) films in pristine (A), rub-aligned (B), and rub-aligned after exposure to CHCl₃ vapors for 15 min (C). Dominant contact plane present in the P(NDI2OE7-Tz2) pristine (D), rub-aligned (E), and rub-aligned after exposure to CHCl₃ vapors for 15 min (F) thin films. Summary of best TE performances recorded for P(NDI2OE7-Tz2) films doped with N-DMBI: electrical conductivity (G), Seebeck coefficient (H), and power factor (I).

performance upon doping, because thanks to the accessibility of the polymer backbone, the face-on alignment maximizes the exposure of the reactive sites in the conjugated backbone to the dopant molecules, thereby facilitating effective doping [72]. In addition, it is known that the fibrillar morphology in the analogue polymer P(NDI2OD-T2) corresponds to a so-called form I of the polymer obtained in pristine films cast from chloroform or by epitaxy on 1,3,5-trichlorobenzene [64, 73]. This suggests that, besides the contact plane, the type of morphology of the films and the polymorph must also have an impact on the TE performance. In this regard, if the orientation of the edge-on domains in rub-aligned films could be flipped to face-on while maintaining in-plane chain orientation, one could expect an enhancement in TE properties. Accordingly, we attempted to mitigate the poor TE performance of as-rubbed P(NDI2OE7-Tz2) films by transforming

their edge-on structure using solvent vapor annealing at ambient temperature [74, 75].

As a solvent, we chose chloroform (CHCl₃) as it was used to prepare the pristine P(NDI2OE7-Tz2) films that yielded the beneficial fibrillar morphology with good TE performances in the non-aligned face-on oriented films. Figure S10 shows the sequence of ED patterns for P(NDI2OE7-Tz2) films exposed to CHCl₃ solvent vapors. Upon increasing exposure time, the appearance of new equatorial (h00) reflections (h = 1,2) is observed, indicating the generation of aligned P(NDI2OE7-Tz2) crystallites with face-on contact plane in the initially edge-on rubbed films (Figure 5F). By contrast, the intensity of the broad and intense 010 reflection that is predominant in as-rubbed films was reduced but did not disappear, indicating a mixed orientation

of the resulting films. In parallel, polarized UV-vis spectroscopy demonstrated that the main absorption band at 965 nm increased in absorbance for POL_{//}R (incident light polarization parallel to the rubbing direction) and decreased for POL_⊥R (incident light polarization perpendicular to the rubbing direction), which further translated to an increase of DR upon SVA (see Figure S11). This spectroscopic change implies that SVA effectively re-orientes the initially rub-aligned edge-on P(NDI2OE7-Tz2) chains, thereby facilitating the formation of face-on aligned domains. Based on the intensity of the (h00) reflections ($h = 1, 2$), we determine that films with a majority of face-on crystallites are obtained after 15 min exposure to CHCl₃. Subsequently, SVA-treated films were subjected to ICD with N-DMBI. ED was used to analyze the structure of these films, indicating that both the orientation and the ratio of edge-on vs. face-on domains are maintained upon doping. Only marginal structural changes are observed; i.e., the π -stacking distance was slightly changed, whereas the lamellar periodicity d_{100} was slightly increased from 32.0 Å to 32.6 Å (Figure S12). Remarkably, the SVA-treated aligned films exhibited a dramatic recovery and enhanced TE performance over rub-aligned films. Specifically, $\sigma_{//}$ increased approx. three times, reaching $25 \pm 14 \text{ S cm}^{-1}$, and critically the $S_{//}$ reached a high value of $-129 \pm 1 \text{ } \mu\text{V/K}$ (Figure 4F,I). Furthermore, the anisotropies of the Seebeck coefficient and of the electrical conductivity are now aligned with those observed for classical p-type polymers, both being enhanced in the chain direction. We further considered the thermodynamic implications of the observed anisotropy in the Seebeck coefficient. Fundamentally, the Seebeck coefficient represents the entropy transported per unit charge ($S = \Sigma/q$). Consequently, a higher $S_{//}$ suggests that carriers traveling along the polymer backbone carry a higher average entropy than those hopping in the perpendicular direction. This phenomenon can be understood through two lenses. First is the microscopic model. Scheunemann et al. demonstrated that structural alignment increases the carrier localization length in the parallel direction [76]. This preferential path effectively shifts the transport energy upward. From a thermodynamic perspective, this shift increases the energy, and thus the entropy, associated with each charge carrier. Second is the mesoscopic model. Limelette et al. attribute the anisotropy to the heterogeneous mesostructure of aligned films, consisting of alternating crystalline and amorphous domains [66]. Since these two phases have different thermal and electrical properties, the internal temperature gradient is not uniform. Because these domains are probed in series ($\perp$) vs. parallel ($//$), the resulting internal redistribution of the temperature gradient leads to a macroscopic anisotropy in the measured Seebeck coefficient. Notably, while the microscopic hopping model typically accounts for moderate anisotropy ratios ($S_{//} / S_{\perp} < 1.5$), the heterogeneous model provides a more robust explanation for larger disparities, as it factors in the thermal conductivity mismatch between the crystalline and amorphous phases.

The successful decoupling of $\sigma_{//}$ and $S_{//}$ translates into a significantly improved PF_{//} of $41 \pm 24 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$, one order of magnitude higher than that of the as-rubbed edge-on films. (Figure 4L). With respect to previous results, it turns out that films consisting of exclusively edge-on domains display poor TE properties in general [65]. It is also very interesting to note that it is the first time that an SVA treatment is capable of switching the dominant contact plane from edge-on to face-on in conjugated polymers while maintaining/improving the in-plane orientation

of polymer chains. In the case of conjugated polymers with alkyl side chains, both SVA and thermal annealing tend to induce the reversed transition from face-on to edge-on orientation. The peculiar case observed for P(NDI2OE7-Tz2) is probably related to the OEG side chains that confer a different surface energy to P(NDI2OE7-Tz2) crystallites, hence, different interactions with the substrate as compared to analogous polymers with pure alkyl side chains. Indeed, a previous study shows that the surface energy of the polymer films determines the dominant contact plane, being either edge-on or face-on [77]. In general, these results demonstrate the crucial role of controlling in parallel the dominant contact plane and in-plane alignment of the crystallites in achieving high-performance organic thermoelectric thin film (Figure 5G,H,I).

3 | Conclusion

In conclusion, we presented a detailed investigation into the structure-property relationships governing the n-type thermoelectric performance of P(NDI2OE7-Tz2), utilizing both conventional MsD and the advanced ICD strategies in pristine and rub-aligned thin films. From the study with MsD, a high σ of $\approx 10 \text{ S cm}^{-1}$ was achieved. Initial characterization of the pristine and MsD-doped P(NDI2OE7-Tz2) films via GIWAXS revealed a predominantly face-on orientation, characterized by a short π -stacking distance of 3.47 Å. When doped in solution with the n-dopant N-DMBI, P(NDI2OE7-Tz2) achieved a high electrical conductivity exceeding 10 S cm^{-1} , positioning it as a new benchmark of reported NDI-based polymers. ICD of the non-aligned P(NDI2OE7-Tz2) films yielded significantly enhanced thermoelectric performance with a PF of $17.5 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$, showing its advantage in accommodating the N-DMBI dopants without severe structural disruption. Contrary to previous literature reports, mechanical rubbing of P(NDI2OE7-Tz2) transformed the film from a face-on orientation to a purely edge-on orientation, resulting unexpectedly in a substantial drop in power factor below $4 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$, and highlighting that the pure edge-on contact plane is fundamentally detrimental to TE performances of doped P(NDI2OE7-Tz2). To overcome this limitation, SVA was employed to successfully transform the film structure, introducing a majority of face-on domains in rub-aligned films. Consequently, the coexistence of in-plane aligned face-on and edge-on crystallites induced by SVA effectively decoupled σ and S and led to a substantial enhancement of thermoelectric performance, achieving a superior power factor of $41 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$. These results and insights extend the current understanding of structure-property relationships in organic thermoelectrics, providing a crucial design principle for future high-performance organic thermoelectric materials: in addition to chain alignment, the control of phase coexistence and contact plane orientation appears paramount for maximizing charge transport metrics.

4 | Experimental Section/Methods

4.1 | Materials, Polymer Synthesis, and Basic Characterizations

The materials, synthesis, and basis characterizations (NMR spectrum and SEC chromatogram) are provided in Figures S13 and S14,

respectively) of the polymer, as well as thermal measurements, Cyclic voltammetry, and electrical measurements, are detailed in the [Supporting Information](#).

4.2 | MsD Doping

The P(NDI2OE7-Tz2) solution was formulated by dissolving the polymer in chloroform to achieve a concentration of 10.0 g/L. The dopant solution was prepared by dissolving n-DMBI in chloroform at a concentration of 5 g/L. Doped solutions were subsequently prepared by blending the polymer solution and dopant solution at specific volume ratios to achieve the target molar ratio. Then, the clean substrate was spin-coated with the solutions for 20 s at 1500 rpm/min, followed by a 30-min thermal annealing at temperatures exceeding 100°C. Four-probe electrical conductivity ($L/W = 160\ \mu\text{m}/1000\ \mu\text{m}$ with $40\ \mu\text{m}$ probe spacing) was measured using a Keithley 4200 semiconductor analyzer inside a glovebox. All doping, processing, and subsequent electrical measurements were conducted within an Argon-filled glovebox under an inert atmosphere ($p(\text{O}_2) < 10\ \text{ppm}$, $p(\text{H}_2\text{O}) < 1\ \text{ppm}$).

4.3 | High Temperature Rubbing and ICD Doping

Solutions of P(NDI2OE7-Tz2) were prepared in chloroform (CHCl_3) at a concentration of 30 mg/mL. The polymer films were then deposited using the doctor blade method at 45°C onto the glass substrates covered with the sacrificial NaPSS layer. n-Butyl acetate was employed for doping, while chloroform was used for thin-film preparation and solvent vapor treatment. Sacrificial NaPSS layers were spin-coated at 3000 rpm from a 10 mg/mL aqueous solution onto glass substrates sequentially cleaned by ultrasonication in acetone (15 min), ethanol (15 min), Hellmanex (15 min), and twice in deionized water. Rub-alignment was performed using a custom-built setup, consisting of a rotating cylinder clad in microfiber cloth and a translating thermal stage. The geometry of the four bar electrodes is shown in Figure S15. The thickness of P(NDI2OE7-Tz2) polymer films was extracted from UV-vis absorbance spectroscopy, calibrated against thickness data obtained from Atomic Force Microscopy measurements on non-oriented films (Figure S16). Solutions of N-DMBI in n-butyl acetate were used to dope non-oriented, oriented, and oriented P(NDI2OE7-Tz2) films treated with chloroform vapor at room temperature following a sequential doping protocol. The films were fully immersed in dopant solutions of increasing concentration from 0.1 to 10 mg/mL for 10 s. All rubbing, doping, vapor treatment, and subsequent electrical measurements were conducted in a Jacomex glovebox under an inert atmosphere ($p(\text{O}_2) < 10\ \text{ppm}$, $p(\text{H}_2\text{O}) < 1\ \text{ppm}$).

4.4 | Chloroform Solvent Vapor Annealing

The rub-aligned P(NDI2OE7-Tz2) polymer film was placed in a crystallizer of 100 mL containing 10–20 mL CHCl_3 . To prevent direct contact with the liquid solvent, the film was placed on a glass support. The crystallizer was then closed to generate saturated solvent vapors. The treatment was performed as a function of exposure time. SVA was performed in a Jacomex

glovebox under a nitrogen atmosphere, with $p(\text{O}_2) \leq 10\ \text{ppm}$ and $p(\text{H}_2\text{O}) \leq 1\ \text{ppm}$.

4.5 | ESR Measurements

For electron spin resonance (ESR) analysis, the prepared doped solutions were transferred into paramagnetic-free quartz tubes. After that, the solvent was evaporated within a glovebox with a regulated argon atmosphere to produce dry samples. Following the complete removal of the solvent, the tubes were hermetically sealed to preserve sample integrity. ESR spectra were then acquired at room temperature utilizing a JEOL JES-FA200 ESR spectrometer.

4.6 | UV-Vis-NIR Absorbance Spectroscopy

UV-vis-NIR absorption spectra (350–2500 nm) of oriented P(NDI2OE7-Tz2) films treated as a function of exposure time in chloroform vapor, as well as spectra of doped P(NDI2OE7-Tz2) non-oriented, oriented, and oriented films treated with chloroform vapor, were recorded using a Cary 5000 spectrometer at a spectral resolution of 1 nm. Measurements were conducted with polarized incident light, varying dopant concentration. The incident light polarization was oriented either parallel (0° , POL//R) or perpendicular (90° , POL $\perp$ R) relative to the rubbing direction.

4.7 | DFT Calculations

Density functional theory (DFT) calculations were performed using Gaussian 16 Rev A.03 [78]. Polymer chains with 5 repeat units were constructed using the preferred conformations [34], with each chain end-capped by the bithiophene / bithiazole groups to form symmetrical chains. Polymer chains were relaxed using $\omega\text{B97XD}/6\text{-}31\text{G}^*$, where ω was set to be 0.1 Bohr $^{-1}$ as a representative value for conjugated polymers. After reaching a stationary point, the optimal range separation parameter for each polymer was determined by variation of ω according to the described methods to fulfill Koopmans' theorem. Single-point calculations used this optimal ω value [79]. Polaron distributions were determined by subtraction of the electron densities of the neutral polymer from those of the singly-reduced polymer [80].

4.8 | GIWAXS Measurement

Grazing incidence wide-angle x-ray scattering (GIWAXS) measurements were conducted at the Stanford Synchrotron Radiation Light source, SLAC National Accelerator Laboratory, Beamline 11-3. The energy of the x-ray beam was 12.7 keV. All samples were measured at an incidence angle (α) of 0.12° . Scattering intensity was collected using a Rayonix MX225 CCD 2D area detector. The sample-to-detector distance was calibrated using a LaB_6 polycrystalline standard. All data are reported in terms of the scattering vector, $q = (4\pi/\lambda)\sin(\theta)$, where θ is the scattering angle. Data were processed using a custom Python code [Siemons, N. (2025) "Materials_Data_Analytics". Zenodo. <https://doi.org/10.5281/zenodo.15366819>]. In-plane and out-of-plane linecuts were

integrated over azimuthal angles (χ) in the range 60°–87° and 5°–30°, respectively.

4.9 | Transmission Electron Microscopy

Non-oriented, oriented, and chloroform vapor-treated oriented P(NDI2OE7-Tz2) polymer films were first coated with a thin film of amorphous carbon using an Edwards Auto306 evaporator or a Cressington 108a carbon coater. The coated films were then floated on distilled water and transferred onto copper TEM grids. Chloroform vapor treatment was performed as a function of exposure time on copper grids with oriented P(NDI2OE7-Tz2) films. Doping by dipping in N-DMBI/n-butyl acetate solution was carried out on the copper grids. Both chloroform vapor treatment and doping were performed under an inert atmosphere inside the glovebox. TEM was performed in bright field, high-resolution and diffraction modes using a TECNAI200 FEI microscope operating at 200 kV and equipped with an Eagle 2k CCD camera. To prevent de-doping of the oriented films, beam exposure was carefully minimized using a low-dose setup. Calibration of reticular distances was carried out using the 0 0 2 reflections of oriented poly(3-hexylthiophene) (P3HT) used as a standard reference.

Acknowledgements

S.W. and S.O. contributed equally to this work. S.W. acknowledges the ANR grant (ANR-23-CPJ1-0047-01), Université du Littoral Côte d'Opale (ULCO), and BQR2025 (NCPETEEC) for financial support. A.P., S.O., O.B., and M.B. acknowledge ANR grants THERMOPOLYS (ANR-22-CE50-0020) and TriPODE (ANR-23-CE06-0032). Y.H. thanks the National Natural Science Foundation of China (92577207;62222403). X.S. and S.L. thank DFG for funding within GRK2948. M. Schmutz is acknowledged for technical support with TEM. N. Zimmermann is acknowledged for technical support in pre-patterned device preparation. C. Contal is acknowledged for technical support with Atomic Force Microscopy. The use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515

Open access publication funding provided by COUPERIN CY26.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

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

References

- O. Bubnova and X. Crispin, "Towards Polymer-Based Organic Thermoelectric Generators," *Energy & Environmental Science* 5 (2012): 9345, <https://doi.org/10.1039/c2ee22777k>.
- R. Kroon, D. A. Mengistie, D. Kiefer, et al., "Thermoelectric Plastics: From Design to Synthesis, Processing and Structure–Property Relationships," *Chemical Society Reviews* 45 (2016): 6147–6164, <https://doi.org/10.1039/C6CS00149A>.
- X. Rodríguez-Martínez, F. Saiz, B. Döring, et al., "On the Thermal Conductivity of Conjugated Polymers for Thermoelectrics," *Advanced Energy Materials* 14 (2024): 2401705, <https://doi.org/10.1002/aenm.202401705>.

- M. Berggren, D. Nilsson, and N. D. Robinson, "Organic Materials for Printed Electronics," *Nature Materials* 6 (2007): 3–5, <https://doi.org/10.1038/nmat1817>.
- A. Khasbaatar, Z. Xu, J. H. Lee, et al., "From Solution to Thin Film: Molecular Assembly of π -Conjugated Systems and Impact on (Opto)electronic Properties," *Chemical Reviews* 123 (2023): 8395–8487, <https://doi.org/10.1021/acs.chemrev.2c00905>.
- L. Zhang, X. L. Shi, Y. L. Yang, and Z. G. Chen, "Flexible Thermoelectric Materials and Devices: From Materials to Applications," *Materials Today* 46 (2021): 62–108, <https://doi.org/10.1016/j.mattod.2021.02.016>.
- Y. Chen, Y. Zhao, and Z. Liang, "Solution Processed Organic Thermoelectrics: Towards Flexible Thermoelectric Modules," *Energy & Environmental Science* 8 (2015): 401–422, <https://doi.org/10.1039/C4EE03297G>.
- S. Wang, G. Zuo, J. Kim, and H. Sirringhaus, "Progress of Conjugated Polymers as Emerging Thermoelectric Materials," *Progress in Polymer Science* 129 (2022): 101548, <https://doi.org/10.1016/j.progpolymsci.2022.101548>.
- S. Wang, "New-Era Polymer Thermoelectrics: Material Innovations, Doping Frontiers, Decoupling Strategies, and Unconventional Applications," *Advanced Materials* 38 (2026): 22912, <https://doi.org/10.1002/adma.202522912>.
- W. N. Wu, Q. B. Zheng, and C. L. Liu, "Recent Progress in p-type Doped Conjugated Polymer-Based Thermoelectric Thin Films," *Synthetic Metals* 307 (2024): 117682, <https://doi.org/10.1016/j.synthmet.2024.117682>.
- Z. Ye, M. Zhang, J. Deng, L. Liang, C. Du, and G. Chen, "An Emerging Liquid-Crystalline Conducting Polymer Thermoelectrics: Opportunities and Challenges," *Nanomicro Letters* 18 (2025): 82.
- D. Wang, J. Ding, Y. Ma, et al., "Multi-Heterojunctioned Plastics With High Thermoelectric Figure of Merit," *Nature* 632 (2024): 528–535, <https://doi.org/10.1038/s41586-024-07724-2>.
- O. Bubnova, Z. U. Khan, H. Wang, et al., "Semi-Metallic Polymers," *Nature Materials* 13 (2014): 190–194, <https://doi.org/10.1038/nmat3824>.
- Y. Zhong, V. Untilova, D. Muller, et al., "Preferential Location of Dopants in the Amorphous Phase of Oriented Regioregular Poly(3-hexylthiophene-2,5-diyl) Films Helps Reach Charge Conductivities of 3000 S cm^{−1}," *Advanced Functional Materials* 32 (2022): 2202075, <https://doi.org/10.1002/adfm.202202075>.
- S. N. Patel, A. M. Glaudell, D. Kiefer, and M. L. Chabiny, "Increasing the Thermoelectric Power Factor of a Semiconducting Polymer by Doping From the Vapor Phase," *ACS Macro Letters* 5 (2016): 268–272, <https://doi.org/10.1021/acsmacrolett.5b00887>.
- V. Vijayakumar, Y. Zhong, V. Untilova, et al., "Bringing Conducting Polymers to High Order: Toward Conductivities Beyond 105 S cm^{−1} and Thermoelectric Power Factors of 2 mW M^{−1} K^{−2}," *Advanced Energy Materials* 9 (2019): 1900266, <https://doi.org/10.1002/aenm.201900266>.
- I. E. Jacobs, Y. Lin, Y. Huang, et al., "High-Efficiency Ion-Exchange Doping of Conducting Polymers," *Advanced Materials* 34 (2022): 2102988, <https://doi.org/10.1002/adma.202102988>.
- P. Durand, H. Zeng, T. Biskup, et al., "Single Ether-Based Side Chains in Conjugated Polymers: Toward Power Factors of 2.9 mW m^{−1} K^{−2}," *Advanced Energy Materials* 12 (2021): 2103049.
- N. Chen, T. Mukhopadhyay, Y. Song, et al., "Enhancing Electrical Conductivity and Power Factor in Poly-Glycol-Bithienylthienothiophene With Oligoethylene Glycol Side Chains Through Tris(pentafluorophenyl) Borane Doping," *Advanced Functional Materials* 34 (2024): 2400469, <https://doi.org/10.1002/adfm.202400469>.
- S. E. Yoon, Y. Kang, J. Im, et al., "Enhancing Dopant Diffusion for Ultrahigh Electrical Conductivity and Efficient Thermoelectric Conversion in Conjugated Polymers," *Joule* 7 (2023): 2291–2317, <https://doi.org/10.1016/j.joule.2023.09.002>.
- B. Meng, J. Liu, and L. Wang, "Recent Development of n-type Thermoelectric Materials Based on Conjugated Polymers," *Nano Materials Science* 3 (2021): 113–123, <https://doi.org/10.1016/j.nanoms.2020.10.002>.

22. M. Li and Y. Shi, "Organic Thermoelectric Materials From n-Type Polymer Semiconductors," *Chempluschem* 88 (2023): 202300215, <https://doi.org/10.1002/cplu.202300215>.
23. H. Tang, Y. Liang, C. Liu, et al., "A Solution-Processed n-type Conducting Polymer With Ultrahigh Conductivity," *Nature* 611 (2022): 271–277, <https://doi.org/10.1038/s41586-022-05295-8>.
24. Z. Ke, A. Abtahi, J. Hwang, et al., "Highly Conductive and Solution-Processable n-Doped Transparent Organic Conductor," *Journal of the American Chemical Society* 145 (2023): 3706–3715, <https://doi.org/10.1021/jacs.2c13051>.
25. J. D. Huang, Q. Li, Q. Wang, et al., "Preventing Benzoquinone-Based Catalyst Aggregation Enables the One-Step Synthesis of Highly Conductive Poly(benzodifurandione) Without Post-Reaction Purification," *Advanced Materials* 37 (2025): 2502426, <https://doi.org/10.1002/adma.202502426>.
26. X. Yan, M. Xiong, X. Y. Deng, et al., "Approaching Disorder-Tolerant Semiconducting Polymers," *Nature Communications* 12 (2021): 5723, <https://doi.org/10.1038/s41467-021-26043-y>.
27. S. Deng, Y. Kuang, L. Liu, et al., "High-Performance and Ecofriendly Organic Thermoelectrics Enabled by N-Type Polythiophene Derivatives With Doping-Induced Molecular Order," *Advanced Materials* 36 (2024): 2309679, <https://doi.org/10.1002/adma.202309679>.
28. S. Gamez-Valenzuela, J. Li, S. Ma, et al., "High-Performance n-Type Organic Thermoelectrics With Exceptional Conductivity by Polymer-Dopant Matching," *Angewandte Chemie International Edition* 63 (2024): 202408537, <https://doi.org/10.1002/anie.202408537>.
29. I. E. Jacobs and A. J. Moule, "Controlling Molecular Doping in Organic Semiconductors," *Advanced Materials* 29 (2017): 1703063, <https://doi.org/10.1002/adma.201703063>.
30. A. Dash, S. Guchait, D. Scheunemann, et al., "Spontaneous Modulation Doping in Semi-Crystalline Conjugated Polymers Leads to High Conductivity at Low Doping Concentration," *Advanced Materials* 36 (2024): 2311303, <https://doi.org/10.1002/adma.202311303>.
31. J. F. Ponder Jr., S. A. Gregory, A. Atassi, et al., "Significant Enhancement of the Electrical Conductivity of Conjugated Polymers by Post-Processing Side Chain Removal," *Journal of the American Chemical Society* 144 (2022): 1351–1360, <https://doi.org/10.1021/jacs.1c11558>.
32. J. Shanahan, L. Yan, Y. Olanrewaju, et al., "Acid-Triggered Side Chain Cleavage Leads to Doped Conjugated Polymers of High Conductivity," *Journal of the American Chemical Society* 146 (2024): 32243–32248, <https://doi.org/10.1021/jacs.4c09843>.
33. F. Zhong, Y. Zheng, J. Song, L. Chen, and H. Li, "Side-Chain-Free Benzothiadiazole-Based Thermoelectric Polymers With Enhanced Electrical Conductivity and Thermal Stability by Acid Cleavage," *Advanced Functional Materials* 35 (2025): 2507113, <https://doi.org/10.1002/adfm.202507113>.
34. S. Wang, H. Sun, T. Erdmann, et al., "A Chemically Doped Naphthalenediimide-Bithiazole Polymer for n-Type Organic Thermoelectrics," *Advanced Materials* 30 (2018): 1801898, <https://doi.org/10.1002/adma.201801898>.
35. J. Liu, L. Qiu, R. Alessandri, et al., "Enhancing Molecular n-Type Doping of Donor–Acceptor Copolymers by Tailoring Side Chains," *Advanced Materials* 30 (2018): 1704630, <https://doi.org/10.1002/adma.201704630>.
36. O. Bardagot, Y. Kervella, A. A. Medjahed, et al., "Effect of a Benzothiadiazole Spacer on Transport Properties and N-doping of Naphthalenediimide-Based Copolymers," *Journal of Materials Chemistry C* 11 (2023): 14108–14118, <https://doi.org/10.1039/D3TC02816J>.
37. M. Ma, G. Ye, S. Jang, et al., "Realizing an N-Type Organic Thermoelectric ZT of 0.46," *ACS Energy Letters* 10 (2025): 1813–1820, <https://doi.org/10.1021/acsenenergylett.4c03590>.
38. J. Wang, C. Wu, Z. Ren, et al., "Achieving Ultrahigh n-Type Thermoelectric Power Factor in an Intrinsically Large Transport-Fermi Energy Gap Conjugated Polymer," *Advanced Materials* 38 (2026): 12453.
39. K. Shi, F. Zhang, C. A. Di, et al., "Toward High Performance n-Type Thermoelectric Materials by Rational Modification of BDPVP Backbones," *Journal of the American Chemical Society* 137 (2015): 6979–6982, <https://doi.org/10.1021/jacs.5b00945>.
40. Y. Lu, Z. D. Yu, Y. Liu, et al., "The Critical Role of Dopant Cations in Electrical Conductivity and Thermoelectric Performance of n-Doped Polymers," *Journal of the American Chemical Society* 142 (2020): 15340–15348, <https://doi.org/10.1021/jacs.0c05699>.
41. K. Feng, H. Guo, J. Wang, et al., "Cyano-Functionalized Bithiophene Imide-Based n-Type Polymer Semiconductors: Synthesis, Structure–Property Correlations, and Thermoelectric Performance," *Journal of the American Chemical Society* 143 (2021): 1539–1552, <https://doi.org/10.1021/jacs.0c11608>.
42. R. A. Schlitz, F. G. Brunetti, A. M. Glaudell, et al., "Solubility-Limited Extrinsic n-Type Doping of a High Electron Mobility Polymer for Thermoelectric Applications," *Advanced Materials* 26 (2014): 2825–2830, <https://doi.org/10.1002/adma.201304866>.
43. D. Trefz, A. Ruff, R. Tkachov, et al., "Electrochemical Investigations of the N-Type Semiconducting Polymer P(NDI2OD-T2) and Its Monomer: New Insights in the Reduction Behavior," *The Journal of Physical Chemistry C* 119 (2015): 22760–22771, <https://doi.org/10.1021/acs.jpcc.5b05756>.
44. S. Wang, H. Sun, U. Ail, et al., "Thermoelectric Properties of Solution-Processed n-Doped Ladder-Type Conducting Polymers," *Advanced Materials* 28 (2016): 10764–10771, <https://doi.org/10.1002/adma.201603731>.
45. D. Kiefer, A. Giovannitti, H. Sun, et al., "Enhanced n-Doping Efficiency of a Naphthalenediimide-Based Copolymer Through Polar Side Chains for Organic Thermoelectrics," *ACS Energy Letters* 3 (2018): 278–285, <https://doi.org/10.1021/acsenenergylett.7b01146>.
46. J. Liu, G. Ye, B. V. Zee, et al., "N-Type Organic Thermoelectrics of Donor–Acceptor Copolymers: Improved Power Factor by Molecular Tailoring of the Density of States," *Advanced Materials* 30 (2018): 1804290, <https://doi.org/10.1002/adma.201804290>.
47. J. Liu, G. Ye, H. G. O. Potgieser, et al., "Amphipathic Side Chain of a Conjugated Polymer Optimizes Dopant Location Toward Efficient N-Type Organic Thermoelectrics," *Advanced Materials* 33 (2021): 2006694, <https://doi.org/10.1002/adma.202006694>.
48. X. Yang, G. Ye, K. Tran, et al., "Impact of Oligo(Ethylene Glycol) Side Chains on the Thermoelectric Properties of Naphthalenediimide-Dialkoxybithiazole Polymers," *ACS Materials Letters* 6 (2024): 1207–1215, <https://doi.org/10.1021/acsmaterialslett.4c00068>.
49. X. Peng, G. Ye, L. Zhang, Y. Kuang, S. Shao, and J. Liu, "Enhancing Charge Transport Performance of n-Doped Conjugated Polymers by Customizing Amphipathic Side Chains," *Macromolecules* 57 (2024): 7156–7164, <https://doi.org/10.1021/acs.macromol.4c00837>.
50. C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, and G. C. Bazan, "Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications," *Advanced Materials* 23 (2011): 2367–2371, <https://doi.org/10.1002/adma.201004554>.
51. O. Bardagot, C. Aumaitre, A. Monmagnon, J. Pécaut, P. A. Bayle, and R. Demadrille, "Revisiting Doping Mechanisms of n-type Organic Materials With N-DMBI for Thermoelectric Applications: Photo-Activation, Thermal Activation, and Air Stability," *Applied Physics Letters* 118 (2021): 203904, <https://doi.org/10.1063/5.0047637>.
52. H. Wei, P. A. Chen, J. Guo, et al., "Low-Cost Nucleophilic Organic Bases as n-Dopants for Organic Field-Effect Transistors and Thermoelectric Devices," *Advanced Functional Materials* 31 (2021): 2102768, <https://doi.org/10.1002/adfm.202102768>.
53. J. Kim, J. Guo, G. Sini, et al., "Remarkable Conductivity Enhancement in P-Doped Polythiophenes via Rational Engineering of Polymer-Dopant Interactions," *Materials Today Advances* 18 (2023): 100360, <https://doi.org/10.1016/j.mtadv.2023.100360>.

54. S. Wang, W. Zhu, I. E. Jacobs, et al., "Enhancing the Thermoelectric Properties of Conjugated Polymers by Suppressing Dopant-Induced Disorder," *Advanced Materials* 36 (2024): 2314062, <https://doi.org/10.1002/adma.202314062>.
55. B. J. Kim, S. Chung, S. Sim, H. Lee, J. Lee, and K. Cho, "Boosting Thermoelectric Performance of Doped Conjugated Polymers Through π - π Aggregates-Induced Percolation Pathway," *Nano Energy* 146 (2025): 111547, <https://doi.org/10.1016/j.nanoen.2025.111547>.
56. J. Rivnay, M. F. Toney, Y. Zheng, et al., "Unconventional Face-On Texture and Exceptional In-Plane Order of a High Mobility n-Type Polymer," *Advanced Materials* 22 (2010): 4359–4363, <https://doi.org/10.1002/adma.201001202>.
57. S. Guchait, A. Dash, A. Lemaire, L. Herrmann, M. Kemerink, and M. Brinkmann, "Phase-Selective Doping of Oriented Regioregular Poly(3-hexylthiophene-2,5-diyl) Controls Stability of Thermoelectric Properties," *Advanced Functional Materials* 34 (2024): 2404411, <https://doi.org/10.1002/adfm.202404411>.
58. D. T. Scholes, S. A. Hawks, P. Y. Yee, et al., "Overcoming Film Quality Issues for Conjugated Polymers Doped With F4TCNQ by Solution Sequential Processing: Hall Effect, Structural, and Optical Measurements," *The Journal of Physical Chemistry Letters* 6 (2015): 4786–4793, <https://doi.org/10.1021/acs.jpclett.5b02332>.
59. I. E. Jacobs, E. W. Aasen, J. L. Oliveira, et al., "Comparison of Solution-Mixed and Sequentially Processed P3HT:F4TCNQ Films: Effect of Doping-Induced Aggregation on Film Morphology," *Journal of Materials Chemistry C* 4 (2016): 3454–3466, <https://doi.org/10.1039/C5TC04207K>.
60. S. Wang, T. P. Ruoko, G. Wang, et al., "Sequential Doping of Ladder-Type Conjugated Polymers for Thermally Stable n-Type Organic Conductors," *ACS Applied Materials & Interfaces* 12 (2020): 53003–53011, <https://doi.org/10.1021/acsami.0c16254>.
61. S. Guchait, D. R. Hinojosa, N. J. Pataki, et al., "Thermoelectric Properties of a Family of Benzodifuranone-Based Conjugated Copolymers in Oriented Thin Films Doped Sequentially with NDMBI-H," *Advanced Electronic Materials* 12 (2025): 2500047.
62. V. Vijayakumar, P. Durand, H. Zeng, et al., "Influence of Dopant Size and Doping Method on the Structure and Thermoelectric Properties of PBTTT Films Doped With F6TCNNQ and F4TCNQ," *Journal of Materials Chemistry C* 8 (2020): 16470–16482, <https://doi.org/10.1039/D0TC02828B>.
63. S. Wang, S. Fabiano, S. Himmelberger, et al., "Experimental Evidence That Short-Range Intermolecular Aggregation Is Sufficient for Efficient Charge Transport in Conjugated Polymers," *Proceedings of the National Academy of Sciences* 112 (2015): 10599–10604, <https://doi.org/10.1073/pnas.1501381112>.
64. D. Trefz, Y. M. Gross, C. Dingler, et al., "Tuning Orientational Order of Highly Aggregating P(NDI2OD-T2) by Solvent Vapor Annealing and Blade Coating," *Macromolecules* 52 (2018): 43–54, <https://doi.org/10.1021/acs.macromol.8b02176>.
65. S. Guchait, Y. Zhong, and M. Brinkmann, "High-Temperature Rubbing: An Effective Method to Fabricate Large-Scale Aligned Semiconducting and Conducting Polymer Films for Applications in Organic Electronics," *Macromolecules* 56 (2023): 6733–6757, <https://doi.org/10.1021/acs.macromol.3c01073>.
66. P. Limelette, N. Leclerc, and M. Brinkmann, "Heterogeneous Oriented Structure Model of Thermoelectric Transport in Conducting Polymers," *Scientific Reports* 13 (2023): 21161, <https://doi.org/10.1038/s41598-023-48353-5>.
67. Y. Huang, D. H. Lukito Tjhe, I. E. Jacobs, et al., "Design of Experiment Optimization of Aligned Polymer Thermoelectrics Doped by Ion-Exchange," *Applied Physics Letters* 119 (2021): 111903, <https://doi.org/10.1063/5.0055886>.
68. Y. Tian and F. Molina-Lopez, "Boosting the Performance of Printed Thermoelectric Materials by Inducing Morphological Anisotropy," *Nanoscale* 13 (2021): 5202–5215, <https://doi.org/10.1039/D0NR08144B>.
69. L. Deng and G. Chen, "Recent Progress in Tuning Polymer Oriented Microstructures for Enhanced Thermoelectric Performance," *Nano Energy* 80 (2021): 105448, <https://doi.org/10.1016/j.nanoen.2020.105448>.
70. Y. Wang and K. Takimiya, "Naphthodithiophenediimide-Bithiopheneimide Copolymers for High-Performance n-Type Organic Thermoelectrics: Significant Impact of Backbone Orientation on Conductivity and Thermoelectric Performance," *Advanced Materials* 32 (2020): 2002060, <https://doi.org/10.1002/adma.202002060>.
71. H. Zeng, P. Durand, S. Guchait, et al., "Optimizing Chain Alignment and Preserving the Pristine Structure of Single-Ether Based PBTTT Helps Improve Thermoelectric Properties in Sequentially Doped Thin Films," *Journal of Materials Chemistry C* 10 (2022): 15883–15896, <https://doi.org/10.1039/D2TC03600B>.
72. F. Zhang, E. Mohammadi, G. Qu, X. Dai, and Y. Diao, "Orientation-Dependent Host–Dopant Interactions for Manipulating Charge Transport in Conjugated Polymers," *Advanced Materials* 32 (2020): 2002823, <https://doi.org/10.1002/adma.202002823>.
73. M. Brinkmann, E. Gonthier, S. Bogen, et al., "Segregated versus Mixed Interchain Stacking in Highly Oriented Films of Naphthalene Diimide Bithiophene Copolymers," *ACS Nano* 6 (2012): 10319–10326, <https://doi.org/10.1021/nn304213h>.
74. S. J. Kang, S. Song, C. Liu, D. Y. Kim, and Y. Y. Noh, "Evolution in Crystal Structure and Electrical Performance of Thiophene-Based Polymer Field Effect Transistors: A Remarkable Difference Between Thermal and Solvent Vapor Annealing," *Organic Electronics* 15 (2014): 1972–1982, <https://doi.org/10.1016/j.orgel.2014.05.026>.
75. J. Li, M. Xue, N. Xue, et al., "Highly Anisotropic P3HT Film Fabricated via Epitaxy on an Oriented Polyethylene Film and Solvent Vapor Treatment," *Langmuir* 35 (2019): 7841–7847, <https://doi.org/10.1021/acs.langmuir.9b00402>.
76. D. Scheunemann, V. Vijayakumar, H. Zeng, et al., "Rubbing and Drawing: Generic Ways to Improve the Thermoelectric Power Factor of Organic Semiconductors?," *Advanced Electronic Materials* 6 (2020): 2000218, <https://doi.org/10.1002/aelm.202000218>.
77. J. Kim, X. Ren, Y. Zhang, et al., "Efficient N-Type Organic Electrochemical Transistors and Field-Effect Transistors Based on PNDI-Copolymers Bearing Fluorinated Selenophene-Vinylene-Selenophenes," *Advanced Science* 10 (2023): 2303837, <https://doi.org/10.1002/adv.202303837>.
78. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., *Gaussian 16 Rev A.03* (Gaussian, Inc, 2016).
79. M. Moser, K. J. Thorley, F. Moruzzi, et al., "Highly Selective Chromoionophores for Ratiometric Na⁺-Sensing Based on an Oligoethyleneglycol Bridged Bithiophene Detection Unit," *Journal of Materials Chemistry C* 7 (2019): 5359–5365, <https://doi.org/10.1039/C8TC06000B>.
80. K. J. Thorley, "Estimation of Polaron Delocalization Lengths in Conjugated Organic Polymers," *The Journal of Physical Chemistry B* 127 (2023): 5102–5114, <https://doi.org/10.1021/acs.jpcc.3c00153>.

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