

RESEARCH ARTICLE

On the Origin of Polymer-Specific Polarity Inversion in Heavily Doped Conjugated Polymers

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ABSTRACT

Polarity inversion of conjugated polymers, the switching of electrical polarity with increasing doping level, is considered a promising approach for achieving *n*-type polymeric materials. Previous studies have attempted to explain this phenomenon, particularly in terms of changes in the band structure at different doping levels. However, polarity inversion has only been observed in a limited number of conjugated polymers, and the reasons why it does not occur universally remain unclear. Herein, the origin of the polymer-specific occurrence of polarity inversion is investigated through a systematic comparative analysis of a series of isoindigo-based conjugated polymers doped with gold(III) chloride (AuCl₃). When the concentration of AuCl₃ in the polymer film exceeds a certain threshold, an *n*-type doping pathway involving chlorination of the conjugated backbone emerges, contributing to a transition from *p*- to *n*-type behavior. The critical gold atomic density at which inversion occurs is estimated to be ~0.4 atoms nm⁻³. Importantly, the dopant uptake capability of each polymer film depends on its chemical structure; this structural dependency determines whether the dopant concentration in the film can exceed the threshold required for polarity inversion, thereby accounting for the polymer-specific differences in polarity inversion behavior.

1 | Introduction

Polarity inversion of a doped conjugated polymer (CP) refers to the phenomenon in which the dominant charge carrier polarity in a CP switches as a function of doping level. Since the early reports of this unusual inversion behavior [1–3], several subsequent studies have followed, gradually revealing its implications

and potential [4–13]. Research on polarity inversion has attracted attention due to its two major significances. First, it offers a route to understand how the electronic band structure and charge transport mechanisms of CPs evolve with increasing doping level, thereby expanding the understanding of the electrical properties of heavily doped CPs. Second, systematic understanding of polarity inversion can enable the utilization of this phenomenon

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in a controlled and efficient manner in various applications to enhance material performance. A representative example is exploiting polarity inversion to obtain a highly conductive *n*-type CP by heavily doping a *p*-type CP with a *p*-dopant [7, 10, 14]. This approach offers a promising alternative to traditional *n*-type CPs and *n*-dopants, which often suffer from poor environmental stability [15–17].

Previous studies that have sought to uncover the underlying mechanisms of heavily doped CPs have primarily focused on the evolution of the electronic band structure and the filling of density of states (DOS) as doping levels increase. For example, J. Liu et al. showed that doping-induced charge transfer complex states are formed during the *n*-doping of naphthalenediimide (NDI)-based *n*-type CPs, which are energetically located below the neutral band in the DOS of the CPs [5]. They observed polarity inversion from *n*-type to *p*-type and attributed it to charge transport through these charge transfer complex states, which causes the transport energy to lie below the Fermi level of the doped CPs. Wang and coworkers investigated *p*-to-*n* polarity inversion in diketopyrrolopyrrole (DPP)-based *p*-type CPs upon *p*-doping with FeCl₃. Based on ultraviolet photoelectron spectroscopy (UPS) measurements, they observed a downward shift of the Fermi level upon doping and attributed the polarity inversion to the crossing of the Fermi level from above to below the highest occupied molecular orbital (HOMO) energy level of the CPs [6, 10]. Liang et al. showed that the convergence of occupied and unoccupied states of CPs under heavy doping leads to a reduction of the transport gap and the emergence of a semi-metallic DOS [7]. They suggested that both positive and negative charge carriers can contribute to the overall charge transport of heavily doped CPs, via hopping transport and band-like transport, respectively, and that the polarity is determined by the balance between these two conduction mechanisms. W. Choi et al. proposed that the formation and broadening of localized DOS within the bandgap at high doping levels account for the *p*-to-*n* polarity inversion of *p*-type CPs, as the localized DOS serves as an efficient electron pathway and induces the transition of majority carriers from holes into electrons [11].

In a recent study by our group, we elucidated for the first time the chlorination-induced *n*-doping mechanism underlying the doping-induced *p*-to-*n* polarity inversion of a CP [18]. In that work, we doped indacenodithiophene-co-benzothiadiazole (IDTBT), a representative *p*-type CP, with the strong oxidizing agent gold(III) chloride (AuCl₃) and observed a transition in charge transport from *p*-type to *n*-type as the AuCl₃ concentration increased. This transition was attributed to doping-induced chemical and structural modifications of the polymer; in particular, chlorination of the IDTBT backbone by chloride ions generated from excess AuCl₃ played a critical role in driving the polarity inversion toward *n*-type charge transport in heavily doped IDTBT.

These findings, along with numerous other studies, have advanced the understanding of doping-induced polarity inversion in CPs. However, polarity inversion is not universally observed; depending on the polymer, doping may or may not result in polarity inversion. Despite this, little in-depth investigation has addressed why different polymers display distinct polarity inversion behaviors. In the present study, we extend our previous

research to elucidate the origins of such variations across different CPs. Through a comparative investigation of isoindigo-based CPs, we show that each polymer exhibits a distinct capability for dopant incorporation under identical doping conditions. Furthermore, we demonstrate that polarity inversion occurs only when the dopant number density within the polymer film exceeds a critical threshold. Because dopant uptake capability differs among polymers, their ability to surpass this threshold varies accordingly, leading to polymer-dependent polarity inversion behavior.

2 | Results and Discussion

2.1 | Chemical and Electronic Structures of Isoindigo-Based CPs

To investigate the polymer-dependent doping-induced polarity inversion behavior of CPs, we performed a comparative study on a series of isoindigo (IID)-based CPs incorporating different donor units: thiophene-vinylene-thiophene (TVT), selenophene-vinylene-selenophene (SVS), and TVT with a cyano group on the vinyl linkage (CNTVT). For convenience, the polymers with SVS, TVT, and CNTVT units are hereafter called P(IID-SVS), P(IID-TVT), and P(IID-CNTVT), respectively. Figure 1a illustrates the key concept of this study. Each polymer exhibits a different capability for dopant uptake, which leads to variations in the degree of polarity inversion. During sequential doping of polymer films with a dopant solution, the polymer that effectively incorporates the dopant undergoes substantial formation of delocalized electrons, resulting in polarity inversion from *p*-type to *n*-type. In contrast, the polymer that exhibits poor dopant uptake fails to generate sufficient delocalized electrons, even when treated with a high-concentration dopant solution, and thus remains *p*-type. Further details on this phenomenon will be discussed in the following sections. The molecular structures of the three IID-based CPs are shown in Figure 1b. The polymers were synthesized according to the synthetic routes and procedures described in the Supporting Information (Scheme S1 and Figures S1–S6). The thermal properties and molecular weight data of the synthesized polymers are also provided in the Supporting Information (Figures S7–S11). The polymers were designed to possess long and branched alkyl side chains with a six-carbon-long alkyl spacer between the branching point and the polymer backbone. Such a side chain structure provides the polymer film with sufficient lamellar spacing to accommodate dopant molecules, thereby contributing to efficient doping of CPs [19, 20]. Selenium (Se) atoms have greater polarizability and a smaller ionization potential than sulfur atoms; consequently, selenophene-containing CPs usually exhibit lower-lying lowest unoccupied molecular orbital (LUMO) energy levels and similar HOMO energy levels compared to their thiophene-containing counterparts [21, 22]. In addition, the higher polarizability of Se atoms leads to stronger Se–Se interactions between adjacent polymer chains, resulting in stronger interchain interactions and enhanced crystallinity [21–24]. This is often accompanied by a smaller bandgap in selenophene-containing CPs compared to thiophene-containing counterparts [21, 23, 24]. On the other hand, in the case of CNTVT unit, the introduction of a cyano group on the vinyl linkage of TVT decreases both the HOMO

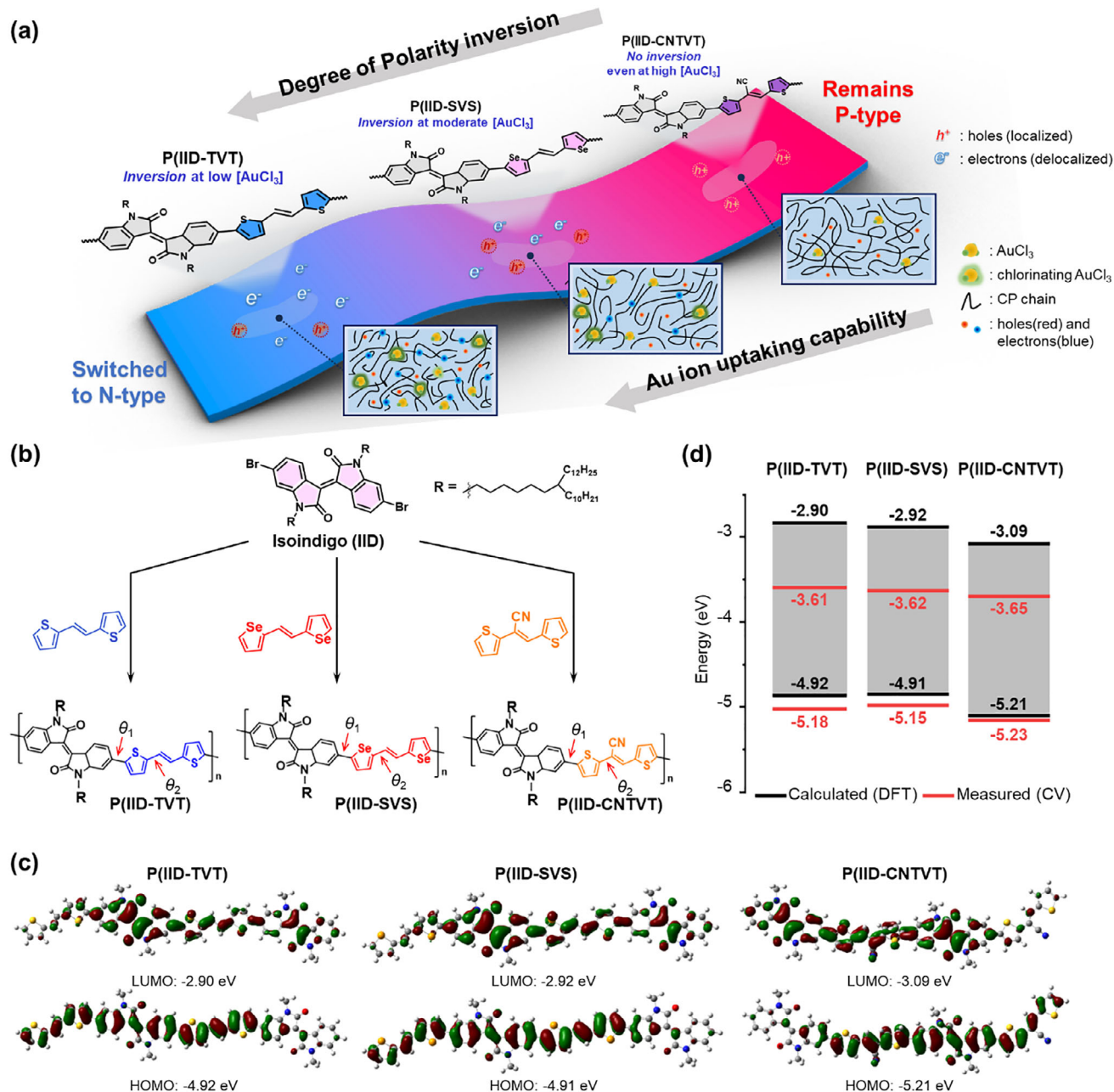


FIGURE 1 | Overview of this study and the materials investigated. (a) Schematic illustration of polymer-dependent, doping-induced polarity inversion behavior. The occurrence of polarity inversion and the doping concentration at which it occurs are determined by the specific polymer. (b) Molecular structures of P(IID-TVT), P(IID-SVS), and P(IID-CNTVT). (c) DFT-calculated HOMO and LUMO of the CPs. (d) DFT-calculated and experimentally measured frontier molecular orbital energy levels.

and LUMO energy levels of the TVT moiety due to the strong electron-withdrawing characteristics of the cyano group [19].

The density functional theory (DFT)-calculated HOMO and LUMO energy levels of the TVT, SVS, and CNTVT units are provided in Figure S12, and these results are consistent with previous reports. DFT calculations on the dimers of donor-acceptor units, namely di(IID-TVT), di(IID-SVS), and di(IID-CNTVT), yielded HOMO/LUMO energy levels of -2.90/-4.92, -2.92/-4.91, and -3.09/-5.21 eV, respectively (Figure 1c,d). The frontier orbital energy levels were nearly identical for the dimers containing TVT and SVS, while they were slightly lower for the dimer containing

CNTVT. DFT-calculated dihedral angles (θ_1 and θ_2) of the dimers suggested that P(IID-SVS) and P(IID-TVT) would have nearly similar backbone planarity ($\theta_1 = 19.4^\circ$, $\theta_2 = 1.3^\circ$ for P(IID-TVT); $\theta_1 = 18.3^\circ$, $\theta_2 = 1.3^\circ$ for P(IID-SVS)), whereas P(IID-CNTVT) would have a much more twisted backbone ($\theta_1 = 22.3^\circ$ and $\theta_2 = 16.4^\circ$) due to the large steric hindrance between the thiophene and cyano group in the CNTVT unit. This difference in backbone torsion affected the molecular packing of the polymer films, as will be further discussed in the section on crystalline structure. The HOMO and LUMO energy levels of the polymer films experimentally determined by cyclic voltammetry (CV) exhibited trends consistent with the DFT results (Figure 1d; Figure S13).

TABLE 1 | Summary on the DFT-calculated and experimentally determined frontier orbital energy levels of CPs.

Polymer	E_{HOMO} (calc.) ^a	E_{LUMO} (calc.) ^a	E_{HOMO} (exp.) ^b	E_{LUMO} (exp.) ^c	$E_{\text{g,opt}}$ ^d
P(IID-TVT)	−4.92	−2.90	−5.18	−3.61	1.57
P(IID-SVS)	−4.91	−2.92	−5.15	−3.62	1.53
P(IID-CNTVT)	−5.21	−3.09	−5.23	−3.65	1.58

^aDFT-calculated;^bExperimentally determined from CV measurements;^cEstimated from E_{HOMO} and $E_{\text{g,opt}}$;^dOptical bandgap determined from the absorption edge of UV–vis spectra.

The differences in the HOMO energy levels determined by CV among the polymers were smaller than those predicted by DFT; the HOMO energy level difference of less than 0.1 eV was considered unlikely to cause a significant variation in charge transfer efficiency from these polymers to the dopant. The results of both DFT calculations and CV measurements are summarized in Table 1.

2.2 | Doping of IID-Based CP Thin Films

Thin films of the CPs were doped with AuCl_3 using a sequential doping method. AuCl_3 is one of the most widely used *p*-type dopants for CPs due to its strong oxidizing ability [25, 26]. To control the amount of dopant incorporated into the CP films, and thereby the doping level, the concentration of AuCl_3 in the doping solution (hereafter referred to as “doping concentration”), denoted as $[\text{AuCl}_3]$, was varied from 0.1 to 10 mg mL^{−1}. With increasing doping concentration, the UV–vis–NIR absorption spectra of the CP films exhibited a progressive depletion of the π – π^* absorption in the visible region (400–800 nm) and the emergence of new broad absorption bands around ~1000 and 1500–2500 nm (Figure 2a), indicative of polaron and bipolaron formation [27, 28]. The spectral evolution continued with increasing doping concentration and reached near saturation beyond 3 mg mL^{−1}. The saturated absorption intensity of the polaronic/bipolaronic bands followed the order P(IID-TVT) > P(IID-SVS) > P(IID-CNTVT), implying that doping generated more polaronic states in P(IID-TVT), followed by P(IID-SVS) and P(IID-CNTVT).

The increase in the doping level of the CP film with increasing $[\text{AuCl}_3]$ was further confirmed by Kelvin probe force microscopy (KPFM). It is well known that, as the *p*-doping level of a CP increases, its work function (WF) increases, that is, the Fermi level shifts downward with respect to the vacuum level [6, 7, 11]. We performed KPFM measurements on undoped and doped P(IID-SVS) films to examine changes in the WF of the CP film as a function of doping concentration. As a result, the WF was observed to increase monotonically with increasing doping concentration (Figure S14), which is in good agreement with previous reports.

The charge transport properties of the three undoped CPs were evaluated using field-effect transistor (FET) measurements, and all devices exhibited typical *p*-type transfer characteristics (Figure S15). The electrical characteristics of the doped CPs were then examined as a function of doping concentration,

revealing distinct doping-dependent charge transport behaviors (Figure 2b). Along with electrical conductivity (σ), the Seebeck coefficient (S) was measured to determine the dominant charge carrier type, as the sign of S indicates charge carrier polarity: positive for hole-dominated (*p*-type) transport and negative for electron-dominated (*n*-type) transport [8]. Note that although the samples contain ionic species originating from the dopant, their influence on the measured Seebeck coefficient is expected to be negligible. This is because thermovoltage arising from ion migration generally requires sufficiently high ion mobility within the matrix, whereas in this case the samples are dry solid polymer films, in which ion motion is highly suppressed [29–34]. For P(IID-TVT), sequential doping at low doping concentrations ($[\text{AuCl}_3] \leq 0.1$ mg mL^{−1}) resulted in low σ and an unmeasurable S . Upon increasing $[\text{AuCl}_3]$ to 0.3 mg mL^{−1}, σ increased sharply and S became measurable. Notably, S remained negative for all doping concentrations, indicating that polarity inversion from *p*-type to *n*-type occurred already at doping concentrations below 0.3 mg mL^{−1}. P(IID-SVS) exhibited a different behavior. σ increased sharply at low $[\text{AuCl}_3]$, peaked, and slightly decreased at higher concentrations, similar to P(IID-TVT). The S value was positive at $[\text{AuCl}_3] = 0.3$ mg mL^{−1} but decreased progressively with increasing doping concentration, inverting to negative values at $[\text{AuCl}_3] \geq 1$ mg mL^{−1}. This indicates polarity inversion at an intermediate doping concentration range of 0.3–1.0 mg mL^{−1}. P(IID-CNTVT) displayed yet another distinct trend. σ increased steeply up to $[\text{AuCl}_3] = 1$ mg mL^{−1} and then plateaued. The S remained unmeasurable up to this concentration, likely due to insufficient charge density resulting from low doping efficiency. At $[\text{AuCl}_3] \geq 3$ mg mL^{−1}, S became measurable with positive values that decreased with increasing doping concentration, but the sign remained positive even at 10 mg mL^{−1}. Thus, P(IID-CNTVT) did not exhibit polarity inversion within the measured range. The doping concentration-dependent electrical properties of the three CPs are summarized in Table 2. To highlight the differences in doping-induced polarity inversion, the variation of S with doping concentration is presented in Figure 2c. The power factor (PF), defined as $\text{PF} = S^2\sigma$, was also calculated at each doping concentration and is shown in Figure 2b and Table 2.

The polarity inversion behavior of the polymers was further confirmed by AC Hall-effect measurements (Figure 2d). In Hall effect experiments, the sign of the Hall voltage reflects the dominant charge carrier type: for coherent charge carriers, a positive Hall voltage indicates hole-dominated (*p*-type) transport, while a negative Hall voltage indicates electron-dominated (*n*-type) transport. In contrast, incoherent carriers such as hopping carriers are known to contribute a Hall voltage of opposite

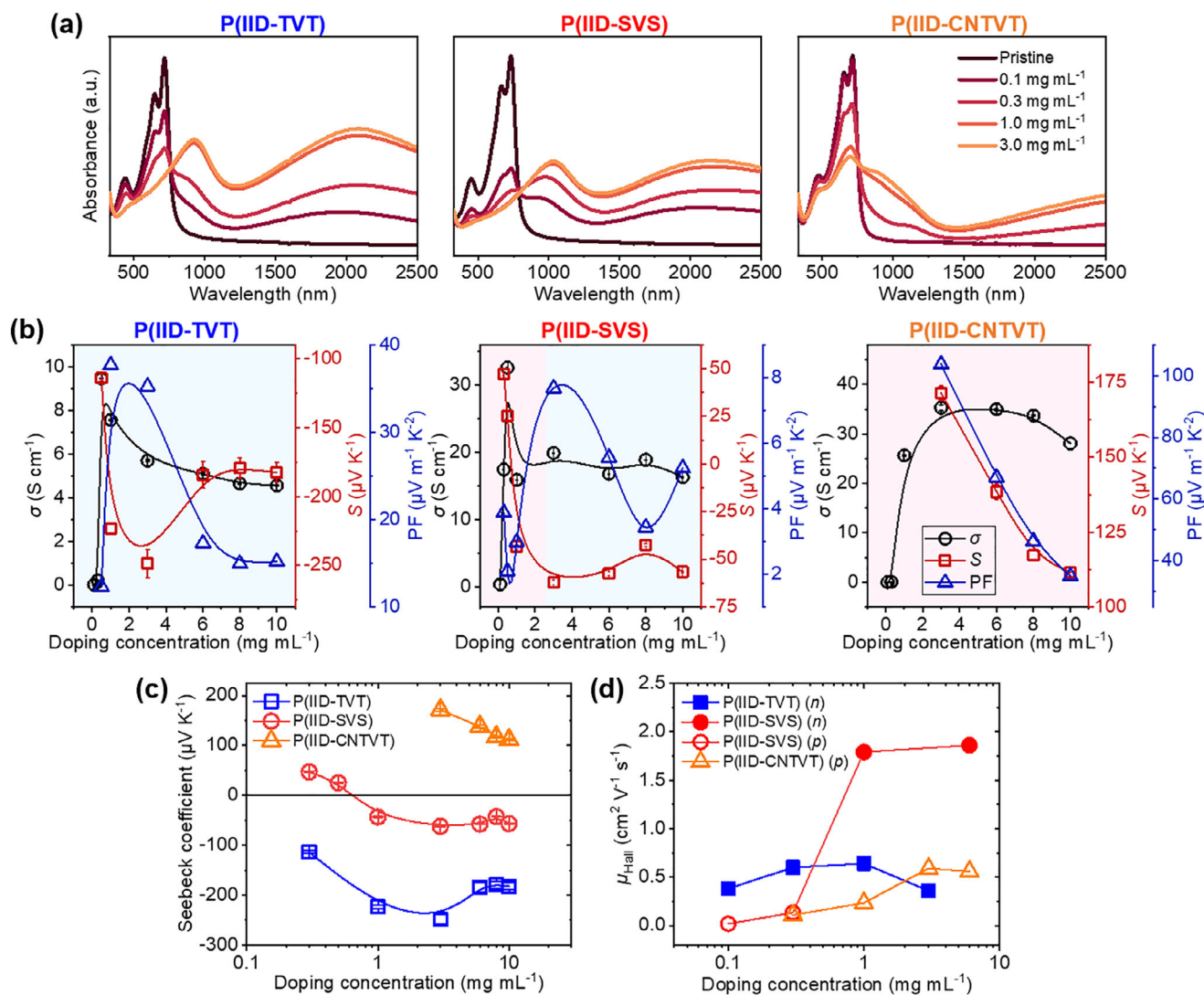


FIGURE 2 | Characterization of CP films upon doping. (a) UV-vis-NIR absorption spectra of CP films as a function of doping concentration. (b) Electrical conductivity, Seebeck coefficient, and power factor of doped CP films as a function of doping concentration. P(IID-TVT) and P(IID-SVS) show polarity inversion at very low and intermediate doping concentrations, respectively, while P(IID-CNTVT) does not exhibit polarity inversion. (c) Plot showing the Seebeck coefficient variation of each polymer with doping concentration, restructured from (b) for improved readability. (d) Charge carrier type and Hall mobility of the samples at different doping concentrations, determined by AC Hall-effect measurements. Open symbols represent p -type carriers, while closed symbols indicate n -type carriers.

sign due to their response to the transverse Hall electric field [35, 36]. In our study, the charge carrier polarities determined from Hall measurements were consistent with those from the Seebeck coefficients. That is, doped P(IID-TVT) exhibited n -type carriers, doped P(IID-CNTVT) exhibited p -type carriers across all doping concentrations, and doped P(IID-SVS) underwent polarity inversion from p -type to n -type between 0.3 and 1.0 mg mL⁻¹, in agreement with Seebeck coefficient results. As doping is expected to increase the population of delocalized charge carriers, these results suggest that in P(IID-TVT) and P(IID-SVS), coherent charge carriers generated by doping become the primary contributors to their n -type transport. Notably, the Hall mobility of P(IID-SVS) increased significantly as the major carrier type switched from p -type to n -type (Figure 2d). This trend aligns with the abrupt decrease in activation energy for charge transport (E_a), determined from the temperature dependence of σ (Figure S16), upon the onset of polarity inversion. Together, these observations

point to the emergence of a doping-induced n -type transport mechanism that progressively dominates charge transport with increasing doping concentration.

In summary, Seebeck coefficient and AC Hall-effect measurements consistently demonstrate polymer-specific polarity inversion behavior: P(IID-TVT) undergoes inversion at very low doping concentration, P(IID-SVS) at intermediate doping concentrations, and P(IID-CNTVT) shows no inversion even at the highest doping concentration tested.

An interesting final point regarding the polarity inversion behavior is that the observed polarity inversion is reversible. In other words, the polarity can be reversibly switched between p -type and n -type through repeated doping and dedoping cycles. This was experimentally confirmed by doping, dedoping, and re-doping P(IID-SVS) and measuring the Seebeck coefficient at each step.

TABLE 2 | Electrical properties of doped CPs as a function of doping concentration.

Polymer	Doping concentration [mg mL ⁻¹]	Electrical conductivity [S cm ⁻¹]	Seebeck Coefficient [μ V K ⁻¹]	Power factor [μ W m ⁻¹ K ⁻²]
P(IID-TVT)	0.1	3.7×10^{-3}	—	—
	0.3	9.46 (± 0.01)	-114.0 (± 2.6)	12.3
	1	7.56 (± 0.03)	-223.2 (± 3.6)	37.7
	3	5.70 (± 0.03)	-248.6 (± 10.2)	35.2
	6	5.09 (± 0.07)	-184.3 (± 9.6)	17.3
	8	4.65 (± 0.04)	-179.3 (± 7.2)	14.9
	10	4.56 (± 0.03)	-182.5 (± 7.3)	15.2
P(IID-SVS)	0.1	0.34 (± 0.01)	—	—
	0.3	17.4 (± 0.05)	47.1 (± 0.7)	3.9
	0.5	32.6 (± 0.06)	25.3 (± 0.2)	2.1
	1	15.9 (± 0.04)	-43.3 (± 1.2)	3.0
	3	19.9 (± 0.05)	-62.1 (± 1.3)	7.7
	6	16.8 (± 0.06)	-57.5 (± 1.0)	5.6
	8	18.9 (± 0.02)	-42.6 (± 0.6)	3.4
	10	16.3 (± 0.09)	-56.7 (± 0.5)	5.2
P(IID-CNTVT)	0.1	1.5×10^{-5}	—	—
	0.3	0.04 (± 0.001)	—	—
	1	25.6 (± 0.04)	—	—
	3	35.3 (± 0.6)	171.4 (± 2.3)	103.6
	6	35.0 (± 0.1)	138.4 (± 2.5)	67.0
	8	33.7 (± 0.1)	117.2 (± 1.8)	46.3
	10	28.1 (± 1.1)	111.5 (± 1.9)	34.9

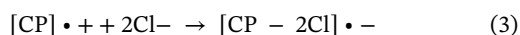
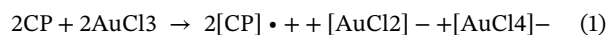
P(IID-SVS) was selected as a representative polymer because, among the three polymers studied, it most clearly exhibits both *p*-type and *n*-type characteristics before and after inversion, allowing the polarity change to be easily and unambiguously monitored via Seebeck coefficient measurements. To completely dedope the doped P(IID-SVS) film, the film initially doped at $[\text{AuCl}_3] = 1.0 \text{ mg mL}^{-1}$ was immersed in pure acetonitrile at 80°C for 30 min. The dedoped polymer film was then re-doped using an acetonitrile-based AuCl_3 solution at either 0.3 or 1.0 mg mL⁻¹. Successful dedoping and re-doping were verified by UV-vis-NIR absorption spectra (Figure S17a). The dedoped film, like the pristine film, showed no polaronic absorption above 1000 nm, indicating complete dedoping of the polymer. After re-doping at $[\text{AuCl}_3] = 0.3$ or 1.0 mg mL⁻¹, broad polaronic absorption bands reappeared in the 1000–2500 nm region, confirming successful re-doping. Seebeck coefficient measurements of these doped/re-doped films are shown in Figure S17b. The polymer doped once at $[\text{AuCl}_3] = 1.0 \text{ mg mL}^{-1}$ exhibited a Seebeck coefficient of approximately $-40 \text{ } \mu\text{V K}^{-1}$, indicating *n*-type behavior. After dedoping and re-doping at $[\text{AuCl}_3] = 0.3 \text{ mg mL}^{-1}$ (below the inversion threshold), the re-doped film exhibited a Seebeck coefficient of $\sim 31 \text{ } \mu\text{V K}^{-1}$, demonstrating *p*-type behavior. In contrast, when re-doped again at $[\text{AuCl}_3] = 1.0 \text{ mg mL}^{-1}$, the film recovered a Seebeck coefficient of $\sim -37 \text{ } \mu\text{V K}^{-1}$, nearly identical to its initial value, confirming *n*-type behavior. These results clearly demonstrate that the polarity inversion observed in this study is

a reversible process and can be repeatedly controlled via doping and dedoping.

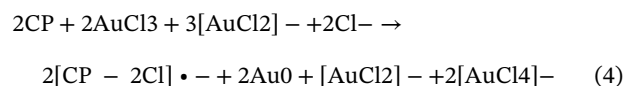
2.3 | Mechanistic Origin of Polymer-Specific Polarity Inversion

In our previous study, we showed that doping CPs with high-concentration AuCl_3 can lead to *n*-doping of the CPs via chlorination of their conjugated backbone [18]. According to that study, *n*-doping by AuCl_3 proceeds through a series of chemical reactions as follows. First, AuCl_3 that penetrates into the CP film accepts an electron from the CP backbone, resulting in *p*-type doping of the polymer and the formation of AuCl_2^- and AuCl_4^- (Equation (1)) [37–40]. When the amount of AuCl_3 incorporated into the film is sufficiently high, the local concentration of AuCl_2^- also becomes high. Then, some AuCl_2^- can be reduced and precipitate in its most stable form, Au^0 , releasing Cl^- ions during the process (Equation (2)) [37–41]. The generated Cl^- ions then can react with $[\text{CP}]^{+}$ to form a chlorinated CP backbone, which results in the generation of negative charge carriers on the CP, that is, *n*-doping of the CP (Equation (3)). These processes are expected to occur at sufficiently high AuCl_3 concentrations within the solid-state CP film, and during these processes, AuCl_2^- , AuCl_4^- , and Cl^- ions is likely to serve as counterions that stabilize the positively charged CP segments

[37, 42], although their precise roles remain unclear and require further investigation [18].



By adding Equation (1) through (3) together with properly balanced coefficients, the net transformation in which a negative charge is introduced onto the CP by Cl^- becomes more clearly apparent, although the intermediate steps are not explicitly shown (Equation (4)):



It is worth noting that previous studies have reported *n*-doping of organic conjugated molecules by anions (primarily halide ions) [43–48]. In those studies, anions were proposed to transfer electrons to the conjugated molecules through “anion- π interactions,” thereby inducing *n*-doping. The *n*-doping of polymers by Cl^- ions in the present work can also be understood as a type of anion-induced *n*-doping, similar to these prior reports. However, unlike these studies, which intentionally employed salts containing anions as *n*-dopants to achieve *n*-doping, the present study is fundamentally different in that we used a *p*-dopant (AuCl_3), yet its excess presence led to the in-situ generation of anions (Cl^-) and the emergence of an *n*-doping pathway. This key distinction differentiates the situation in this work from those in previous reports.

We also note that the *p*-dopant capable of inducing effective *p*-to-*n* polarity inversion is not limited to AuCl_3 . For instance, in our previous work, we confirmed that AuBr_3 or VCl_3 can also induce *p*-to-*n* polarity inversion of IDTBT when present in excess [18]. In addition, the polymer used in the present study, P(IID-SVS), exhibited similar polarity inversion behavior when FeCl_3 was employed as the dopant instead of AuCl_3 (Figure S18a). These results suggest that any metal-halide-based *p*-dopant that (i) possesses a sufficiently high redox potential to enable strong initial oxidation of CPs and the subsequent generation of halide ions, and (ii) provides halide ions that are sufficiently reactive toward the positively charged polymer backbone to form stable covalent C–X (X = halogen) species capable of introducing negative charges to the polymer, has the potential to induce chlorination-induced *n*-doping and *p*-to-*n* polarity inversion in CPs. However, this does not imply that any Cl^- ion source can chlorinate the polymer backbone or induce *n*-doping. For example, treating the polymers studied here with KCl or NaCl did not lead to either *p*-doping or *n*-doping (Figure S18b), likely because their cation possesses no oxidizing capability and therefore cannot *p*-dope the polymers. This outcome further supports our conclusion that the chlorination-induced *n*-doping we observe emerges only when a sequence of redox reactions is triggered by strong *p*-doping of the polymer, and only when the required combination of redox thermodynamics, chloride release,

and backbone reactivity toward chloride ions is simultaneously satisfied. A more detailed discussion of chlorination-induced *n*-doping of CPs under excess AuCl_3 can be found in our previous study [18].

To confirm whether the same chlorination-induced *n*-doping mechanism we established in our previous study also operates in the IID-based CPs examined in the present study, we performed x-ray photoelectron spectroscopy (XPS) analysis on doped P(IID-TVT), P(IID-SVS), and P(IID-CNTVT). To verify whether the above chemical reactions also occur in these CPs, the oxidation states of Au were examined using the Au 4f XPS spectra (Figure 3a; Figure S19). The Au 4f spectrum consisted of $4f_{5/2}$ and $4f_{7/2}$ peaks, which were further deconvoluted into sub-peaks corresponding to different oxidation states of Au^0 , Au^+ , and Au^{3+} [49–51]. The presence of these oxidation states strongly supports the generation of Cl^- ions as described in Equations (1) and (2). The relative proportions of each oxidation state were calculated by integrating the corresponding sub-peaks, and the results are presented as bar graphs in Figure 3a. Au^+ consistently accounted for the smallest fraction in nearly all samples, while Au^0 or Au^{3+} was the most dominant. In P(IID-TVT) and P(IID-CNTVT), Au^0 was the predominant species, whereas in P(IID-SVS), Au^{3+} was the most abundant. These differences among the polymers are likely attributed to variations in their chemical properties; however, the exact reasons remain unclear and require further investigation.

A notable difference among the three CPs is the significant variation in the amount of dopant incorporated into the CP films. The amount of AuCl_3 that penetrated into the doped polymer films was quantified by integrating the total area under the Au 4f XPS spectrum. To determine the absolute atomic density of Au within the samples, we measured a reference spectrum from a pure Au film and used it to calibrate the Au atomic density in our samples. More details on the calibration procedure are provided in the Experimental Section. The variation in Au atomic density with doping concentration in doped CP films is presented in Figure 3b. The results showed that for all three polymers, the density of Au atoms present in the doped polymer films increased with increasing doping concentration. Among them, P(IID-TVT) exhibited the highest Au atomic density, while P(IID-CNTVT) showed the lowest when treated under identical doping conditions. The difference in Au atomic density among the polymers, despite being treated at the same doping concentration, was attributed to their varying affinities for AuCl_3 . Specifically, DFT calculations revealed that the interaction energy between the monomer unit of P(IID-TVT) and an AuCl_3 molecule is more than twice that between the monomer unit of P(IID-CNTVT) and an AuCl_3 molecule (Figure S20), suggesting that the greater AuCl_3 uptake capability of P(IID-TVT) arises from its stronger affinity for AuCl_3 .

Interestingly, when considering the onset doping concentrations at which polarity inversion occurs in each polymer, we can infer that a threshold Au atomic density of approximately $0.3\text{--}0.4$ atoms nm^{-3} is required to induce the inversion. More specifically, in the case of P(IID-TVT), this threshold was exceeded even at very low doping concentrations ($[\text{AuCl}_3] \leq 0.1 \text{ mg mL}^{-1}$), leading to early polarity inversion. For P(IID-SVS), the threshold was surpassed at intermediate doping concentrations ($0.1 \leq [\text{AuCl}_3]$

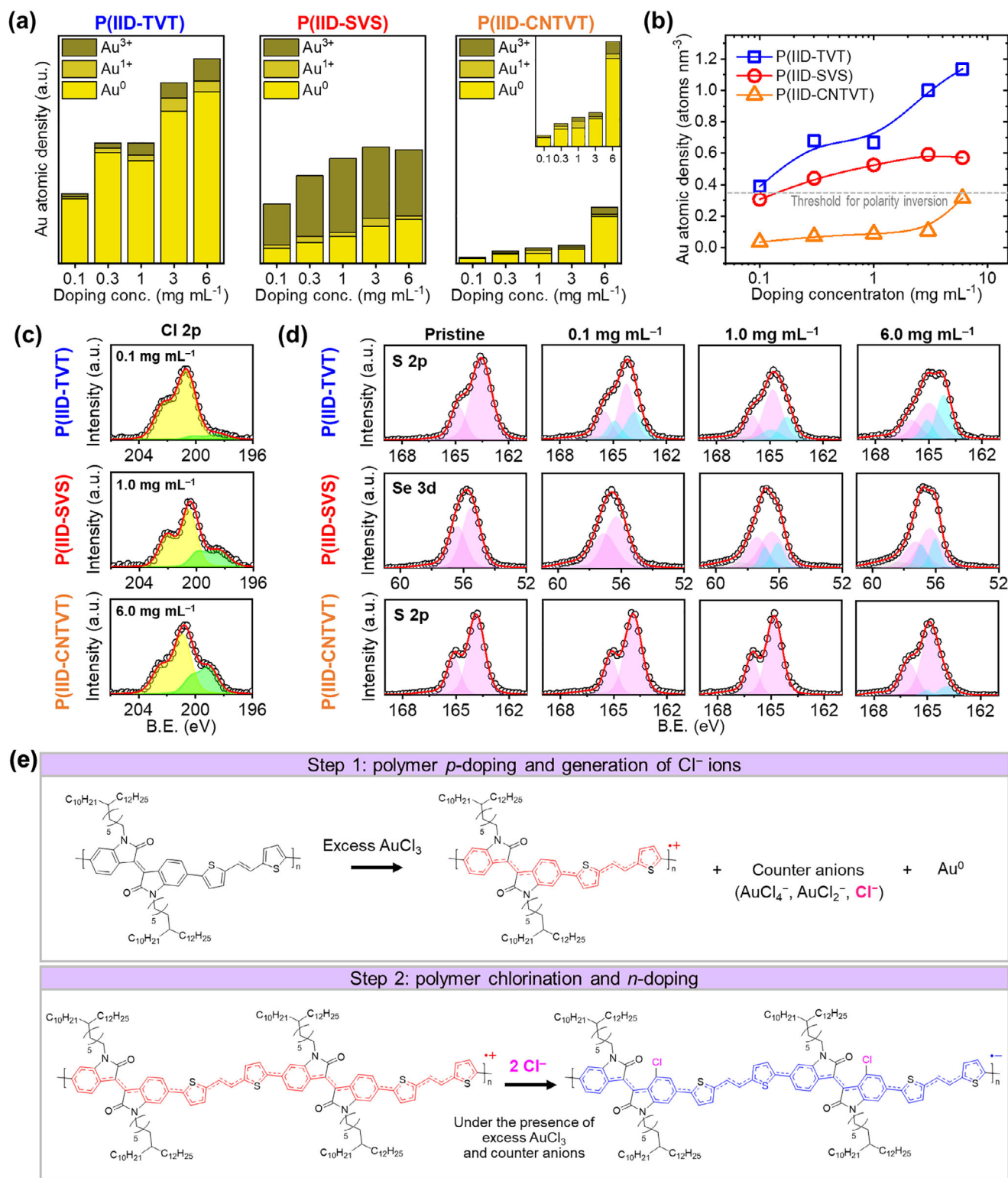


FIGURE 3 | Elucidation of polymer-specific polarity inversion behavior. (a) Relative amounts of Au atoms in different oxidation states (Au^0 , Au^{+1} , and Au^{+3}) within the doped CP films, determined by deconvolution of the Au 4f XPS spectra and integration of the corresponding peak areas. (b) Number density of Au atoms in doped CP films as a function of doping concentration. (c) Cl 2p XPS spectra of doped CP films. Each spectrum is deconvoluted into high- and low-binding-energy peaks, assigned to organic Cl (yellow) and inorganic chloride (green), respectively. (d) S 2p spectra (for P(IID-TVT) and P(IID-CNTVT)) and Se 3d spectra (for P(IID-SVS)) of pristine and doped CP films. Each spectrum is deconvoluted into high-binding-energy (pink) and low-binding-energy (cyan) peaks, with the latter attributed to chlorination-induced *n*-doping of the CP. (e) Molecular-structure representation of the mechanism in Equations (1–3): Step 1 shows polymer *p*-doping under excess AuCl_3 , where gold chloride species and Cl^- ions act as counterions. Step 2 illustrates Cl^- reacting with positively charged segments, explicitly showing chlorine substitution at the IID(1) position.

$\leq 1.0 \text{ mg mL}^{-1}$), corresponding to the onset of inversion. In contrast, P(IID-CNTVT) did not reach this threshold even at the highest doping concentration tested ($[\text{AuCl}_3] = 10 \text{ mg mL}^{-1}$), and consequently, no polarity inversion was observed.

The manifestation of the abovementioned *n*-doping mechanism (Equations (1–4)) is further supported by the Cl 2p XPS spectra. Figure 3c shows the Cl 2p XPS spectra of P(IID-TVT) doped at 0.1 mg mL^{-1} , P(IID-SVS) doped at 1.0 mg mL^{-1} , and P(IID-CNTVT) doped at 6.0 mg mL^{-1} . Each spectrum can be deconvoluted into a pair of $2p_{3/2}$ and $2p_{1/2}$ peaks at relatively high binding energies (~ 201 and 202 eV for the $2p_{3/2}$ and $2p_{1/2}$ peaks, respectively) and another pair at lower binding energies (~ 199 and 200 eV for the $2p_{3/2}$ and $2p_{1/2}$ peaks, respectively). The high-binding-energy peaks are attributed to organic chlorine species, while the low-binding-energy peaks originate from inorganic chlorides [52, 53]. The presence of organic Cl peaks provides direct evidence of chemical reactions between Cl^- ions and the CPs. Notably, despite being doped at the lowest doping concentration among the three, P(IID-TVT) exhibits the largest proportion of organic Cl peaks. This reflects the highest degree of AuCl_3 penetration into P(IID-TVT), as previously confirmed by the Au 4f XPS results (Figure 3a,b), which results in the greatest Cl^- generation. In the case of P(IID-CNTVT), although polarity inversion does not occur at a doping concentration of 6.0 mg mL^{-1} , its Cl 2p XPS spectrum still shows a small but detectable contribution from organic Cl peaks. This suggests that some Cl^- generation and subsequent chlorination of the polymer does take place in P(IID-CNTVT), but to an extent insufficient to induce polarity inversion.

The S 2p XPS spectra (for P(IID-TVT) and P(IID-CNTVT)) and Se 3d XPS spectra (for P(IID-SVS)) also exhibit consistent trends (Figure 3d). In the pristine polymers, the S $2p_{3/2}$ and S $2p_{1/2}$ peaks are observed around 163 and 165 eV, and the Se $3d_{5/2}$ and Se $3d_{3/2}$ peaks appear around 55 and 56 eV. As the doping concentration increases, these peaks gradually shift to higher binding energies, likely due to the formation of positive charges induced by *p*-doping [54–58]. At sufficiently high doping concentrations, however, new peaks emerge at lower binding energies than the original ones, which can be interpreted as the result of negative charges introduced into the polymer backbone through its interaction with Cl^- ions [57, 58]. These low-binding-energy peaks begin to clearly appear at doping concentrations that approximately coincide with the onset of polarity inversion in P(IID-TVT) and P(IID-SVS). In the case of P(IID-CNTVT), although no polarity inversion is observed, weak low-binding-energy peaks are seen at a high doping concentration of 6.0 mg mL^{-1} . This observation is consistent with the presence of organic Cl signals in the Cl 2p XPS spectra of P(IID-CNTVT).

By integrating the above results, we conclude that the origin of the polymer-specific polarity inversion behavior lies in the varying ability of each CP to incorporate AuCl_3 under a given doping process. In other words, the occurrence of polarity inversion, as well as the specific doping concentration at which it takes place, is essentially determined by the amount of AuCl_3 that the CP film can incorporate. When a CP film incorporates a sufficient quantity of AuCl_3 , a series of chemical reactions occurs alongside the *p*-type doping process, leading to the formation of Cl^- ions.

These Cl^- ions chlorinate the polymer backbone, thereby contributing to the development of *n*-type transport characteristics in the doped CP film. If the amount of incorporated AuCl_3 is large enough to produce a sufficient concentration of Cl^- ions, and the resulting chlorination-induced *n*-doping is substantial, the charge transport polarity of the CP film is inverted from *p*-type to *n*-type. Among the three polymers studied, P(IID-TVT), which incorporates the largest amount of AuCl_3 , undergoes polarity inversion even at low doping concentrations. P(IID-SVS), with a lower AuCl_3 uptake capability, exhibits polarity inversion at intermediate doping concentrations. In the case of P(IID-CNTVT), due to its limited ability to incorporate AuCl_3 , it does not reach the threshold required for polarity inversion, even at the highest doping concentration tested.

Finally, we further elaborate on the chlorination-induced *n*-doping mechanism by discussing the specific locations along the polymer backbone where chlorination occurs. When we dedoped the AuCl_3 -doped P(IID-TVT) film by heating it at a high temperature (180°C) under an inert nitrogen atmosphere [59], we observed that the maximum of the polymer's π – π^* transition peak in the UV–vis–NIR absorption spectrum of the dedoped film was slightly red-shifted by $\sim 5 \text{ nm}$ compared to that of the pristine polymer (Figure S21). To identify the specific site along the P(IID-TVT) backbone at which chlorination produces such a spectral change, we performed time-dependent DFT (TD-DFT) calculations (Figures S22–S24). UV–vis–NIR absorption spectra were simulated using TD-DFT for each case in which chlorine was substituted or added at different positions along the backbone. The results revealed that chlorine substitution at the IID(1) position (see Figure S23) could account for the small red-shift of the π – π^* transition peak maximum observed in the dedoped film. To the best of our knowledge, this study represents the first report of doping-induced polarity inversion of a donor–acceptor copolymer in which the polarity inversion mechanism is mediated by the acceptor unit. This contrasts with our previous study [18], in which AuCl_3 induced *p*-to-*n* polarity inversion in IDTBT through chlorine substitution at the donor unit, indacenodithiophene (IDT). The distinct chlorination behaviors of P(IID-TVT) and IDTBT suggest that the molecular-level mechanism of chlorination-induced *n*-doping by AuCl_3 can vary considerably depending on the polymer's molecular structure.

Reflecting our identification on the specific chlorination site on the polymer backbone, the steps of chlorination-induced *n*-doping process are illustrated in Figure 3e, using P(IID-TVT) as a representative example. Note that Figure 3e provides a molecular-structure representation of the same mechanism described in Equations (1–3). Step 1 represents the polymer *p*-doping process occurring in the presence of excess AuCl_3 , during which positively charged segments are generated on the polymer backbone, and various gold chloride species in different oxidation states, as well as Cl^- ions, serve as counterions, accompanied by the formation of some metallic Au. Step 2 in Figure 3e illustrates the reaction between Cl^- ions and the positively charged polymer segments, explicitly depicting chlorine substitution at the IID(1) position, which cannot be conveyed by Equation (3) alone. This reaction is also noted to occur under conditions where excess AuCl_3 and the aforementioned counterions are present.

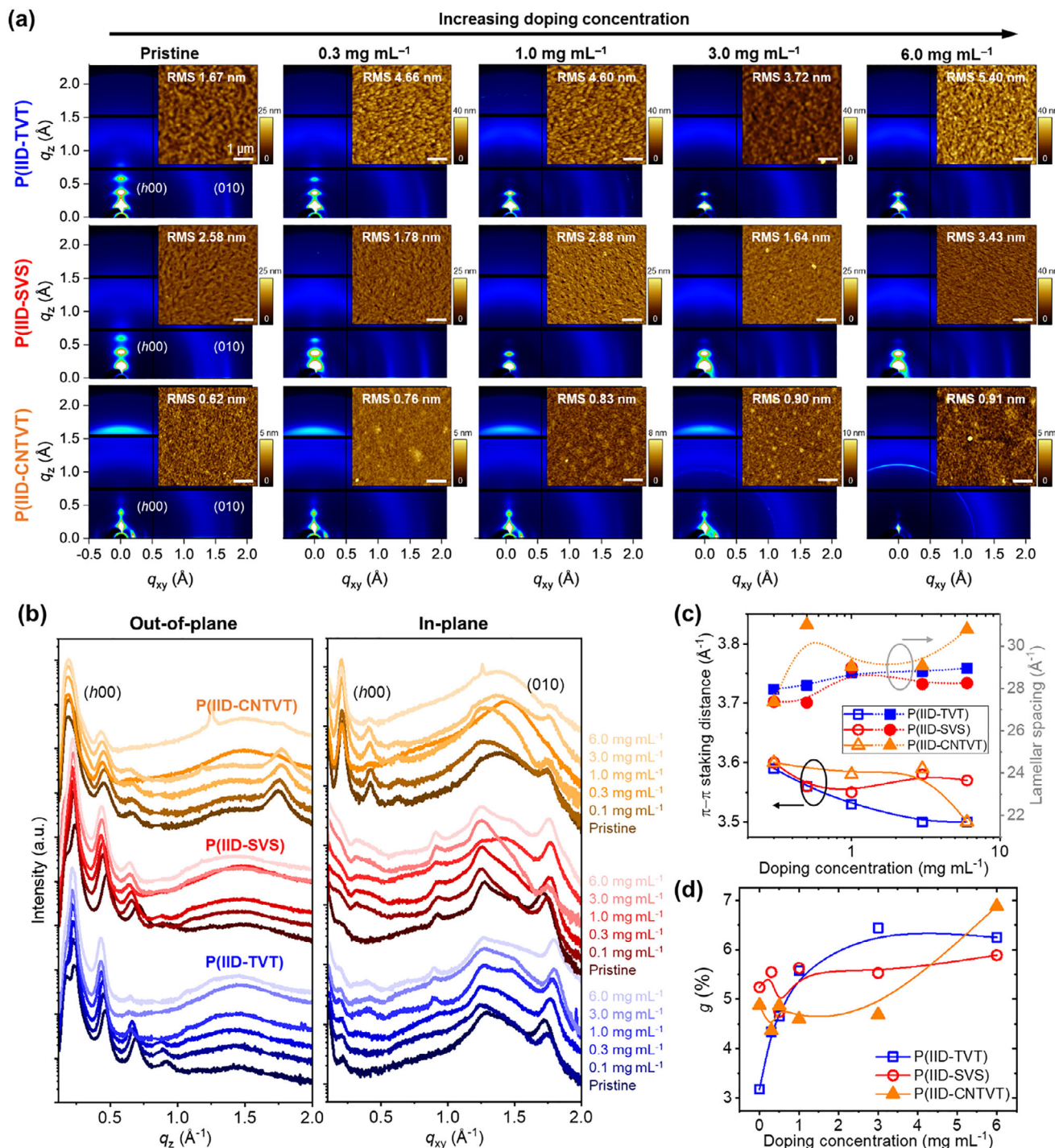


FIGURE 4 | Analysis of the structural evolution in CP films upon doping. (a) 2D GIXD images of pristine and doped CP films. Inset: AFM height images of the corresponding films. (b) 1D line-cut profiles of the diffraction patterns shown in (a), taken along the out-of-plane and in-plane directions. (c) Changes in lamellar spacing and π - π stacking distance of CP crystals as a function of doping concentration. (d) Evolution of the paracrystalline disorder parameter (g) with increasing doping concentration.

2.4 | Microstructural Changes of CP Films Upon Doping

To investigate the changes in the crystalline structure of CP films upon doping, 2D grazing-incidence X-ray diffraction (2D GIXD) was conducted on pristine and doped CP films (Figure 4a,b). In the GIXD patterns, pristine P(IID-TVT) and P(IID-SVS) exhibited a series of strong ($h00$) reflections along the out-of-plane direction

and a pronounced (010) peak in the in-plane direction, indicative of a preferential edge-on orientation. In contrast, pristine P(IID-CNTVT) displayed ($h00$) peaks in both the out-of-plane and in-plane directions, along with the (010) peak appearing in both directions, suggesting a bimodal orientation comprising both edge-on and face-on packing. The lamellar stacking distances were similar for P(IID-TVT) (26.4 Å) and P(IID-SVS) (26.3 Å), while P(IID-CNTVT) exhibited a slightly longer spacing (28.4

Å). The π - π stacking distances were comparable across the three polymers, measured at 3.64, 3.65, and 3.62 Å for P(IID-TVT), P(IID-SVS), and P(IID-CNTVT), respectively. Diffraction intensities were stronger for P(IID-TVT) and P(IID-SVS) than for P(IID-CNTVT), and the crystalline coherence lengths calculated from the full width at half maximum (FWHM) of the (100) and (010) peaks were also greater for P(IID-TVT) and P(IID-SVS). These results indicate higher crystallinity in P(IID-TVT) and P(IID-SVS) films compared to P(IID-CNTVT), consistent with our DFT calculation results showing a larger dihedral angle in the P(IID-CNTVT) backbone. The presence of cyano group induces greater backbone twisting in P(IID-CNTVT), thereby disrupting its molecular packing relative to the other two polymers. Detailed crystallographic parameters extracted from the GIXD patterns are summarized in Tables S1–S3. Meanwhile, surface morphologies of the films, obtained via atomic force microscopy (AFM), revealed that P(IID-TVT) exhibited the highest surface roughness, followed by P(IID-SVS) and then P(IID-CNTVT) (Figure 4a, inset). This trend, when considered in relation to the crystallinity of the polymers, suggests that higher crystallinity is associated with increased surface roughness.

In the doped CP films, increasing doping concentration resulted in a gradual decrease in diffraction intensity, an increase in lamellar stacking distance, and a decrease in the π - π stacking distance. These trends are commonly observed in doped conjugated polymers and suggest that the dopant molecules are preferentially located within the lamellar stacking regions of the polymer chains [60–64]. The orientation distribution of the polymer crystals remained unchanged upon doping. Changes in the lamellar and π - π stacking distances as a function of doping concentration are presented in Figure 4c. Meanwhile, consistent with the decrease in diffraction peak intensities, the paracrystalline disorder parameter (g), which quantifies the degree of structural disorder in partially ordered materials [65], increased with doping concentration (Figure 4d). Notably, the rate of increase in g with doping concentration varied depending on the polymer. For P(IID-TVT), g exhibited the steepest increase with doping concentration, beginning from relatively low doping concentrations. For P(IID-CNTVT), g remained nearly constant up to relatively high doping concentrations and began to increase only when the concentration reached 6 mg mL⁻¹. P(IID-SVS) showed an intermediate rate of increase in g with doping concentration, falling between the behaviors of the other two polymers.

Based on the above microstructural analysis, the differences in structural changes of the polymer films induced by dopant incorporation appear to be closely related to the amount of AuCl₃ taken up by each polymer. In all three polymers, the crystalline structure becomes increasingly disrupted as AuCl₃ is incorporated. P(IID-TVT) appears to undergo structural breakdown more readily upon interaction with AuCl₃, allowing it to accommodate a greater amount of dopant. In contrast, P(IID-CNTVT) shows greater resistance to structural disruption by AuCl₃, resulting in the lowest dopant uptake among the three. P(IID-SVS) exhibits an intermediate behavior between these two polymers. A schematic summary of these findings is presented in Figure 5. For reference, the microstructural changes induced by AuCl₃ incorporation in these three IID-based CPs differ from those observed in our previous study on IDTBT [18]; in IDTBT, which is a nearly amorphous

CP, increased AuCl₃ incorporation led to enhanced crystallinity and a transition in crystalline orientation from predominantly face-on to predominantly edge-on. These observations suggest that the effect of dopant incorporation on polymer microstructure may vary significantly depending on the molecular structure of the polymer, indicating a promising direction for future research.

Finally, we discuss the structural changes of the doped CP films in relation to their charge transport characteristics. In general, an increase in charge carrier density upon doping leads to the filling of trap states in CPs, and such trap filling is known to facilitate charge transport [66, 67]. Trap filling is expected to occur in all three polymers, P(IID-TVT), P(IID-SVS), and P(IID-CNTVT). However, as discussed above, the amount of AuCl₃ incorporated into each polymer and the extent of the resulting structural changes differ significantly. These structural differences lead to variations in charge transport characteristics among the polymers, as observed in Figure 2d, for example. For P(IID-TVT), a large amount of AuCl₃ is incorporated even at low doping concentrations, which is accompanied by a substantial increase in structural disorder. This disorder hinders charge transport, limiting the extent to which charge mobility can be improved. P(IID-SVS) incorporates a smaller amount of AuCl₃ compared to P(IID-TVT), but shows a relatively modest increase in disorder. As a result, a more pronounced enhancement in charge mobility is observed upon doping. In the case of P(IID-CNTVT), both AuCl₃ incorporation and structural changes remain limited, even at high doping concentrations. Consequently, only gradual and relatively small improvements in mobility are observed with increasing doping concentration.

3 | Conclusion

In this work, we investigated the polymer-specific nature of polarity inversion in CPs upon doping, focusing on a series of IID-based CPs with different donor units. Through combined electrical, spectroscopic, and structural analyses of the CPs doped with the *p*-type dopant AuCl₃, we demonstrate that polarity inversion is not a universal property of CPs but is instead highly dependent on the polymer's ability to incorporate the dopant. Polarity inversion was observed at low doping concentrations for P(IID-TVT), at intermediate concentrations for P(IID-SVS), and was not observed for P(IID-CNTVT) within the studied doping concentration range. XPS analysis revealed that these differences arise from varying degrees of AuCl₃ incorporation and the subsequent generation of Cl⁻ ions, which lead to chlorination-induced *n*-doping and contribute to the polarity inversion. A critical threshold Au atomic density of 0.3–0.4 atoms nm⁻³ was identified as necessary for the onset of polarity inversion. Structural analysis on the CP films further showed that structural changes upon doping correlate with the degree of dopant incorporation. Specifically, higher AuCl₃ uptake led to greater increases in structural disorder, which in turn influenced the charge transport properties.

These findings address a critical knowledge gap in understanding why polarity inversion occurs only in certain polymers under specific doping conditions. This work reveals that the ability to incorporate dopants is a key factor in determining whether and

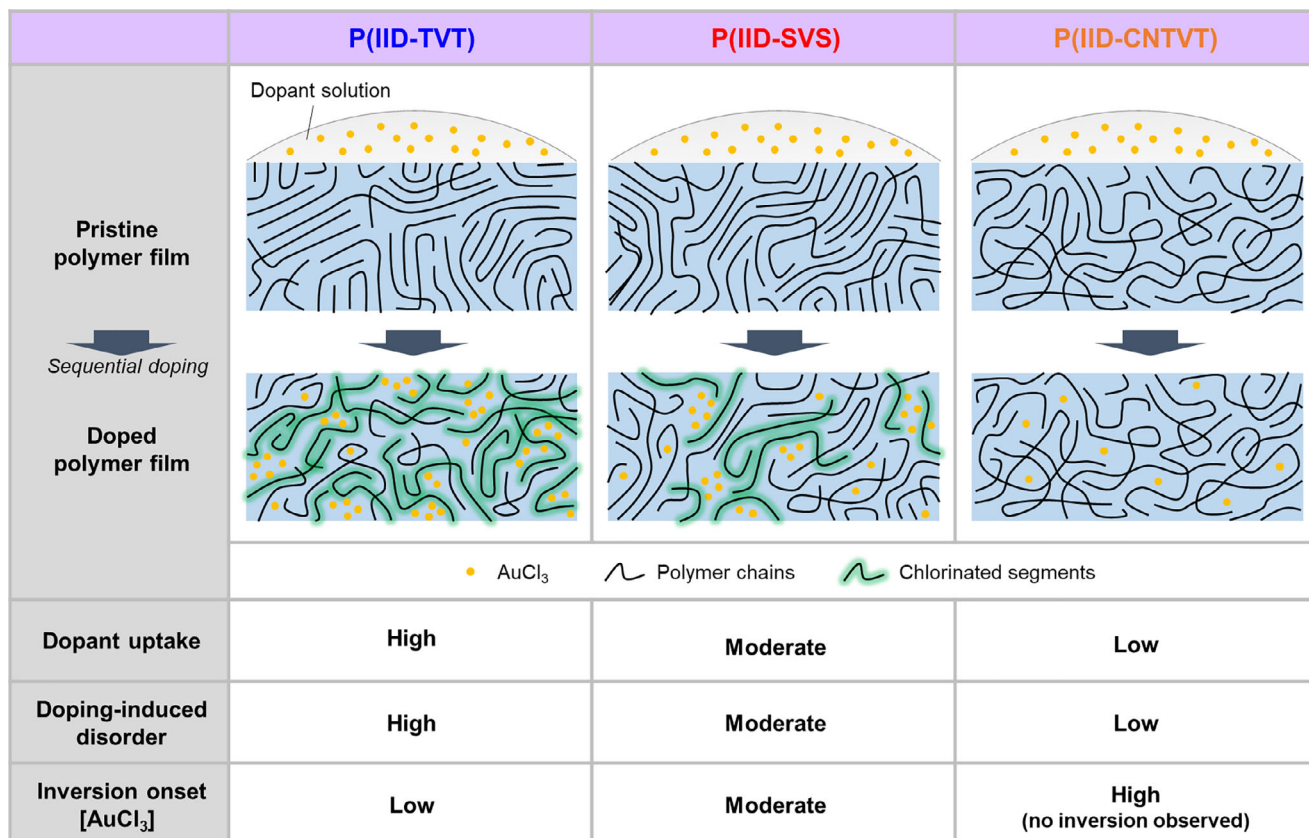


FIGURE 5 | Schematic illustration of polymer-dependent dopant incorporation and the resulting structural changes. The degree of AuCl_3 uptake varies among the CPs, increasing from P(IID-CNTVT) to P(IID-TVT). Greater AuCl_3 incorporation is accompanied by a more pronounced increase in structural disorder. Green-highlighted segments represent chlorinated regions of the polymer chains, which appear in areas with high local concentrations of AuCl_3 . This chlorination contributes to the *p*-to-*n* polarity inversion observed in the CPs.

when polarity inversion takes place, and that polarity inversion is governed by a complex interplay of polymer-dopant interactions. Overall, this study sheds light on the underlying principles governing polarity inversion in CPs and is expected to provide valuable guidelines for designing CPs with controlled and reliable polarity inversion.

4 | Experimental Section

4.1 | Materials

P(IID-TVT), P(IID-SVS), and P(IID-CNTVT) were synthesized as described in the Supporting Information. The dopant materials and processing solvents were purchased from Tokyo Chemical Industry (Japan) and used without further purification.

4.2 | Preparation of Pristine and Doped Polymer Films

Polymer solutions were prepared by dissolving the polymers in anhydrous chlorobenzene at a concentration of 7 mg mL^{-1} . Glass substrates ($1.5 \times 1.5 \text{ cm}^2$) were sequentially cleaned via ultrasonication in acetone, isopropyl alcohol, and deionized water, and then thoroughly dried. A surface treatment was subsequently performed using UV-ozone exposure for 20 min. The polymer

films were fabricated by spin-coating the prepared solutions onto the cleaned substrates under a nitrogen atmosphere, resulting in films with a thickness of $\sim 40 \text{ nm}$. To introduce dopants, acetonitrile-based AuCl_3 solutions were drop-cast onto the polymer films and left for 1 min before spin-coating was employed to remove any excess solution. The doped films were then subjected to mild thermal annealing at $\sim 80^\circ\text{C}$ for 10 min to ensure complete drying.

4.3 | Fabrication of OFETs

OFET devices were fabricated on SiO_2/Si substrates. A heavily doped *p*-type silicon wafer functioned as the gate electrode, while a 300 nm-thick thermally grown SiO_2 layer served as the gate dielectric. For surface preparation, the substrates underwent piranha treatment using a 7:3 mixture of sulfuric acid and hydrogen peroxide, followed by the formation of an octadecyltrichlorosilane self-assembled monolayer on the dielectric surface. Polymer thin films were deposited by spin-coating polymer solutions (5 mg mL^{-1} in chloroform), and were subsequently annealed at different temperatures (as-cast, 150°C , and 200°C) for 20 min under a nitrogen atmosphere. Au electrodes (40 nm in thickness) were deposited as source and drain electrodes via thermal evaporation at a rate of $\sim 1 \text{ \AA s}^{-1}$. The device geometry was defined with a channel length (L) of $100 \text{ }\mu\text{m}$ and a channel width (W) of $1000 \text{ }\mu\text{m}$.

4.4 | Electrical Characterizations

Electrical properties of the OFET devices were evaluated under vacuum conditions ($\sim 10^{-3}$ Torr) using a Keithley 4200 semiconductor parameter analyzer. The field-effect hole mobility, $\mu_{h,\text{FET}}$, was extracted in the saturation regime based on the equation: $I_{\text{D,sat}} = (WC_i/2L)\mu_{h,\text{FET}}(V_G - V_{\text{th}})^2$, where $I_{\text{D,sat}}$ was the saturated drain current, C_i (10.8 nF cm^{-2}) is the gate dielectric capacitance, V_G was the gate voltage, and V_{th} is the threshold voltage. The sheet resistance of the polymer films was determined using the van der Pauw method. Electrical conductivity was then calculated from the measured sheet resistance and the film thickness. The Seebeck coefficient was measured using a custom-built system equipped with two Peltier modules to generate a controlled temperature gradient. A thermocouple was used to simultaneously record the temperature difference and the resulting thermovoltage, with measurements performed using a Keithley 6510/7700 Data Acquisition System and a Keithley 2182A nanovoltmeter. AC Hall measurements were conducted using a LakeShore 8404 Hall measurement system. An alternating magnetic field with a frequency of 0.01–0.1 Hz and a root-mean-square field strength of 1.19 T was applied during the measurements.

4.5 | XPS Analysis and Quantification of Au Atomic Density in Doped CP Films

XPS measurements were conducted using a NEXSA G2 system (Thermo Fisher Scientific). To determine the atomic number density of Au in the doped CP films, a reference sample was prepared by depositing a pure Au film with a known bulk density of 19.32 g cm^{-3} at room temperature. The atomic number density of this reference Au film was calculated by dividing its mass density by the molar mass of Au (197.0 g mol^{-1}) and then multiplying by Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$), yielding an estimated value of $\sim 5.91 \times 10^{22} \text{ atoms cm}^{-3}$. The atomic number density of Au in the doped polymer samples was estimated by comparing the integrated area of the Au 4f peak in the XPS spectra of the samples to that of the reference Au film. Specifically, the ratio of the peak areas was multiplied by the atomic number density of the reference film to obtain the Au atomic density in the doped samples.

4.6 | Other Characterizations

^1H and ^{13}C NMR spectra were recorded using a Bruker 300 MHz and Bruker DRX 500 MHz spectrometers, respectively. Thermogravimetric analysis (TGA) was performed using a TA 2050 thermogravimetric analyzer (TA Instruments) under a nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. Differential scanning calorimetry (DSC) was performed using a DSC 2100 differential scanning calorimeter (TA Instruments) under nitrogen flow with a heating rate of $10^\circ\text{C min}^{-1}$ from 0°C to 300°C . UV–vis–NIR absorption spectra were collected using a Jasco V-770 spectrophotometer. FTIR spectra were obtained using a Jasco FT/IR-4700 spectrometer. Cyclic voltammetry (CV) was performed at room temperature using a 0.10 M solution of tetrabutylammonium perchlorate (Bu_4NClO_4) in chloroform with a scan rate of 50 mV s^{-1} . A Pt wire and an Ag/AgCl electrode were used as the counter

and reference electrodes, respectively. 2D GIXD patterns were measured at the 3C and 9A beamlines of the Pohang Accelerator Laboratory (PAL), Korea. Surface morphology of the films was characterized using an NX-10 atomic force microscope (Park Systems) in non-contact mode. Gel permeation chromatography (GPC) was conducted on a Shimadzu LG system using chloroform as the eluent at a flow rate of 1.0 mL min^{-1} to determine the number-average molecular weights (M_n). DFT calculations were performed using the Gaussian 16 software package with the nonlocal hybrid Becke three-parameter Lee–Yang–Parr (B3LYP) functional. The 6–31G(d) basis set was employed for C, H, N, O, S, and Se atoms, and LANL2DZ with an effective core potential (ECP) was applied to Au and Cl atoms.

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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.

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