

RESEARCH ARTICLE

Charge Transport Dynamics in Doped Organic Polymer: Effect of New Split-Functional Dopant on an Amorphous Organic Semiconductor

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ABSTRACT

Understanding the microscopic mechanisms governing charge transport in electronically doped conjugated polymers is important from both fundamental and device perspectives. Here, we investigate an amorphous semiconducting polymer, PTB7-Th, as a suitable host to incorporate a specific organic salt system. The electronically disordered polymer, when doped with a split functional dopant that consists of organic cation 4-(acetyl-amino)-2,2,6,6-tetramethyl-1-oxo-piperidinium (ATOP) and the bulky anion tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (BARF), undergoes a major enhancement in electrical transport. In addition to enhancing solubility, the BARF counterion effectively minimizes the coulombic interaction between the anion and the charge carrier on the polymer backbone, which facilitates efficient ion-pair dissociation. A six-order-of-magnitude enhancement in conductivity and a significant improvement in carrier mobility are observed in optimally doped samples. Temperature-dependent DC conductivity measurements indicate variable-range hopping transport, with improved hopping parameters upon doping. Additionally, AC measurements reveal faster carrier relaxation, systematic activation energy changes, and minimal ionic migration, highlighting improved electronic transport upon doping. Complementary molecular dynamics simulations capture ion–polaron and ion–ion correlations that rationalize the observed transport enhancement. The results highlight the connection from microscopic interactions to macroscopic enhancement in electrical performances while also identifying the origin of saturation beyond a critical dopant concentration.

1 | Introduction

Organic semiconductors (OSCs) combine structural tunability with solution processability, yet their electronic properties remain fundamentally constrained by strong carrier localization, disorder, and deep trap states [1–4]. These factors suppress intrinsic carrier densities, leading to low charge carrier mobilities and

poor electrical conductivity, which can limit device performance. Controlled electronic doping is therefore indispensable not only for enhancing conductivity and mobility or tuning interfacial energetics, but also for understanding how dopant–host interactions dictate charge transport. Early chemical doping strategies employed volatile diatomic halogens such as Cl₂, Br₂, and I₂, which readily diffuse into organic semiconductor

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matrices [4]. While effective at inducing charge transfer, these dopants intrinsically convert into their corresponding counterions rather than allowing independent selection of the ionic species, thereby limiting precise controllability [5]. This constraint, along with poor thermal stability and significant ion migration, ultimately undermines device reliability [6]. To mitigate these effects, alternative approaches have been explored, such as oxygen-induced doping followed by anion exchange with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), which has been shown to significantly enhance conductivity. Nevertheless, lithium-ion migration eventually caused unstable doping levels in these approaches [7, 8]. A major advance was the introduction of strong electron acceptors such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), which became the standard p-type dopant for OSCs [9]. However, despite its effectiveness, F4TCNQ suffers from poor solubility, leading to compromised film quality, undesired interlayer diffusion, and limited stability under ambient and thermal conditions, thereby restricting its applicability in practical devices [10–12]. Beyond these limitations, although crystalline and semicrystalline polymers can tolerate high dopant concentrations through sequential solid-state doping [13], single-step blending of highly crystalline or semicrystalline polymers often causes severe precipitation, preventing uniform film formation [14, 15]. Furthermore, dopant-induced disorder is strongly influenced by the effective distance between charge carriers along the polymer chain and the dopant anions [16]. To overcome these challenges, recent efforts have shifted toward the design of high-molecular-weight dopants with weakly interacting counter-ions that minimize coulombic binding and promote efficient ion-pair dissociation [17–19]. Several studies have demonstrated that the electrostatic interaction between charge carriers and dopant counterions plays a crucial role in determining free-carrier generation in doped conjugated polymers. Large, weakly coordinating anions reduce Coulomb binding and enhance charge dissociation at low doping levels, resulting in higher free-carrier ratios and conductivity [9, 19]. However, it is observed that at high doping levels, smaller anions can achieve similar carrier densities and promote Coulomb potential overlap, thereby lowering the charge-dissociation barrier and maximizing free-carrier generation. This highlights that the optimum counterion size depends on the doping regime and the targeted device performance [20]. The dopant used in this study belongs to the class of oxoammonium compounds that are air-stable and known to be mild oxidizing agents and effective in reactions of converting alcohols to ketones/aldehydes [21, 22]. After one-electron reduction, the dopant forms neutral species such as the TEMPO (4-Acetamido-2,2,6,6-tetramethylpiperidine 1-oxyl) radical. By employing an organic salt (comprising a cation or cation radical and an anion), the doping process can, in principle, be decoupled from the role of the counter anion. In a recent work, we introduced a split-functional doping strategy [23] in which the organic cation part acts exclusively to drive charge transfer, while the sterically demanding counter-anion serves solely to maintain charge neutrality and stabilize the organic semiconductor radical cation. This concept was successfully validated across a variety of donor materials and hole-transporting materials (HTMs), demonstrating its broad applicability to organic electronic systems [23]. In this study, we extend this approach to the amorphous conjugated polymer PTB7-Th, employing an organic cation (ATOP) paired with a bulky anion (BARF).

PTB7-Th was chosen because its amorphous nature enables uniform film formation, making it well suited for large-area, solution-processable roll-to-roll fabrication, where achieving uniform crystallinity is challenging. Uniform film morphology has also been reported for doped PTB7-Th using a one-step coating process from a blended solution [24]. Additionally, with a stable and well-controlled doping strategy to optimize energetics and interfaces, such systems show strong potential for scalable device applications and can serve as efficient transport layers in optoelectronic devices [25]. Moreover, the HOMO orbitals of PTB7-Th are delocalized along the π -conjugated backbone, particularly around double bonds and high electron-density regions, maintaining efficient charge transport (See Figure S7). The dopant was selected considering the favorable energy-level alignment, wherein the ionization potential (IP_{OSC}) of the host [26] closely matches the electron affinity (EA_{Dopant}) of the dopant (Figure S1), thereby facilitating efficient charge transfer upon doping (Figure 1a) [27]. The bulky, electron-withdrawing BARF anion not only enhances dopant solubility (500 mg/ml in Acetonitrile) but also reduces ion-polymer coulombic interactions, thereby facilitating transport efficiency [18, 28]. This design strategy allows the doping threshold to be reached at low concentrations while preserving the structural integrity of the polymer matrix. In addition, the presence of strong electron-withdrawing substituents increases the oxidation potential, which can suppress back electron transfer and contribute to improved thermal stability of the doped film (Figure S6). The primary objective of this study is to elucidate the interaction of heavy counterion-based dopant with the amorphous polymer matrix and its influence on the underlying transport dynamics. In this regard, several models have been proposed to explain charge transport in conjugated polymers, drawing parallels with amorphous semiconductors [29, 30]. Due to the absence of long-range order and the presence of diverse structural and electronic defects, no single model fully captures the conduction mechanism. In this context, it is widely accepted that charge transport in both single-component and multicomponent organic disordered semiconductors proceeds via incoherent hopping between localized states that are randomly distributed and typically take up a Gaussian distribution [31]. Other widely applied models include fluctuation-induced tunnelling (FIT) [32], describing charge delocalization via tunnelling between conducting domains, and Mott's variable-range hopping (VRH) [33], which dominates when carriers hop to energetically favorable distant sites. VRH has been extensively used to rationalize dc conductivity in a broad range of conjugated polymers, including polyacetylene, polyaniline, polypyrrole, and polythiophenes, and is regularly used to describe the conductivity-mobility relations in disordered organic semiconductors and low-dimensional polymer systems [34–36]. Efros and Shklovskii showed that random electric potentials from charged donors and acceptors in disordered semiconductors create a coulomb gap, a power-law suppression of electronic states near the Fermi level [37, 38]. Additionally, AC measurements provide detailed information on relaxation dynamics, trap-state information, and ionic effects within the material [39, 40]. In parallel, molecular dynamics (MD) simulations are employed to probe molecular-level interactions between the polymer backbone and the ionic species. MD effectively captures ionic diffusivity and transport behavior, revealing how ion incorporation modulates local structure, charge delocalization, and carrier mobility, thereby dictating the

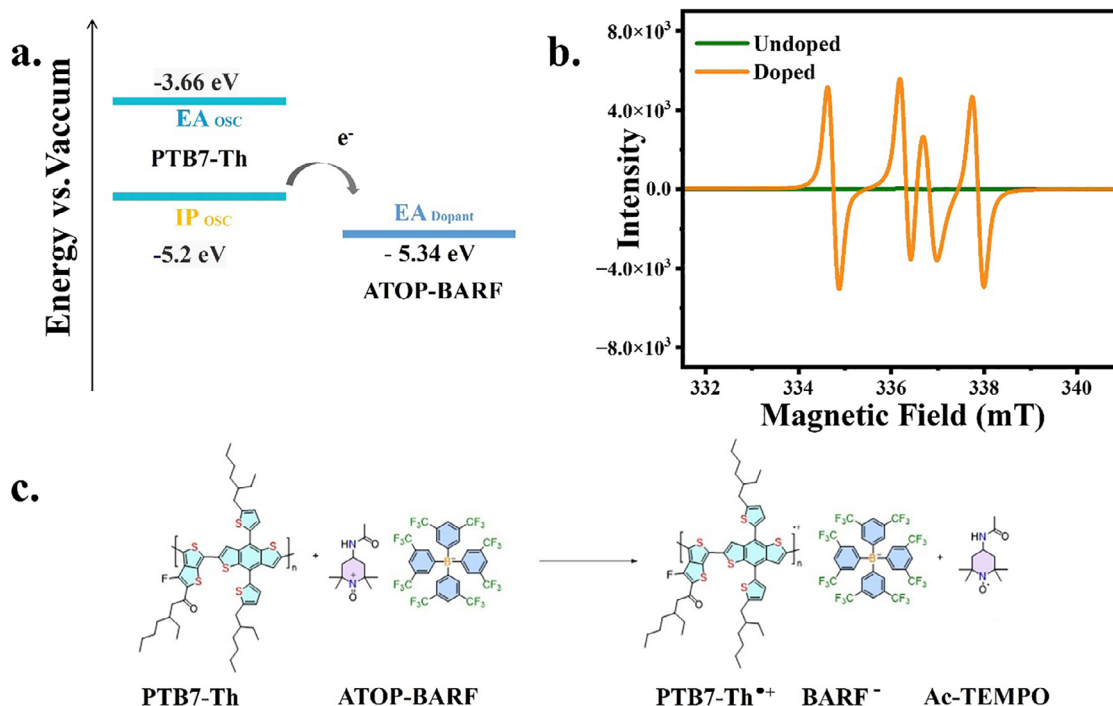


FIGURE 1 | Charge Transfer Mechanism (a) Schematic illustration of the energy level alignment between the host (Value derived from UPS measurements) [26] and dopant system (from Cyclic voltammetry measurements, Figure S1), (b) EPR Spectra of undoped and 10 mol% (w.r.t. the monomer unit) doped PTB7-Th, (c) Schematic of the cation radical generation mechanism.

overall charge-transport mechanism in the doped polymer system [41–44].

Building on this understanding, the goal of this study is to elucidate the origin of enhanced electrical performance by systematically correlating split-functional doping with charge transport dynamics, while identifying the limitations that emerge beyond a critical dopant concentration through comprehensive analysis.

2 | Results and Discussion

The dopant used in this study comprises two components, each with a distinct role during doping. The cation part, 4-(acetylamino)-2,2,6,6-tetramethyl-1-oxo-piperidinium (ATOP), causes charge transfer from the PTB7-Th polymer, resulting in the formation of radical cations along the polymer backbone (see Figure 1b,c and Figure S12). This process, depicted in Figure 1b, gives rise to distinct EPR signals that are characteristic of the doped state (Details, Section S10). The radical cations on the polymer backbone are counterbalanced by tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (BARF) from the dopant. Since the morphology of OSC thin films influences charge-carrier behavior, the effect of doping on film morphology was analyzed using AFM. As shown in Figure 2, surface roughness changes minimally (~ 1 nm) from the pristine film to 10 mol% ATOP-BARF doping, indicating that film uniformity is largely retained at moderate doping levels. However, beyond this concentration, the roughness of the doped films increases sharply, suggesting the onset of morphological distortion due to a high number of intercalants [14] (Figure 2d,h). The presence of the weakly

coordinating anion (BARF) enhances dopant solubility and helps maintain film uniformity at lower to moderate doping levels, effectively suppressing large-scale clustering and preventing channel blockage. In parallel, KPFM measurements show a uniform surface potential, indicating homogeneous doping (Details, Section S5 and Figure S4). Additionally, increasing ATOP-BARF concentration raises the work function of PTB7-Th from 4.78 to 5.0 eV, confirming pronounced p-type doping [45, 46] (Figure 3a).

Beyond this doping level, the work function varies minimally, indicating a saturation level of the doping process. The observed shift reflects an increased charge carrier density introduced by the dopant, consistent with a doping mechanism driven by the redox potential difference between the dopant and the polymer. Additionally, UV-vis-NIR spectroscopy shows that pristine PTB7-Th exhibits a characteristic peak at 775 nm (≈ 1.6 eV), while doped films display an additional sub-bandgap feature at 1127–1140 nm (≈ 0.77 eV), attributed to polaron formation, reflecting a direct microscopic signature of successful doping (See Figure 3b) [24]. X-ray photoelectron spectroscopy (XPS) further provides evidence of doping by tracking the shifts in core-level binding energies. It is observed that F 1s, S 2p_{3/2}, and S 2p_{1/2} peaks shift toward higher binding energies upon doping. (See Figure 3c,d). In parallel, a new high-binding-energy feature (See Figure 3d) is enlarged, possibly due to oxidized sulphur species formed via dopant-induced charge transfer (details Section S2).

The doping effect can be directly read off in the electrical measurements (Figure 3e,f). In the low-field regime (applied voltage < 1 V), it exerts only a small force on charge carriers, resulting in minimal acceleration. Under these conditions, carriers remain uniformly distributed throughout the device, preventing localized

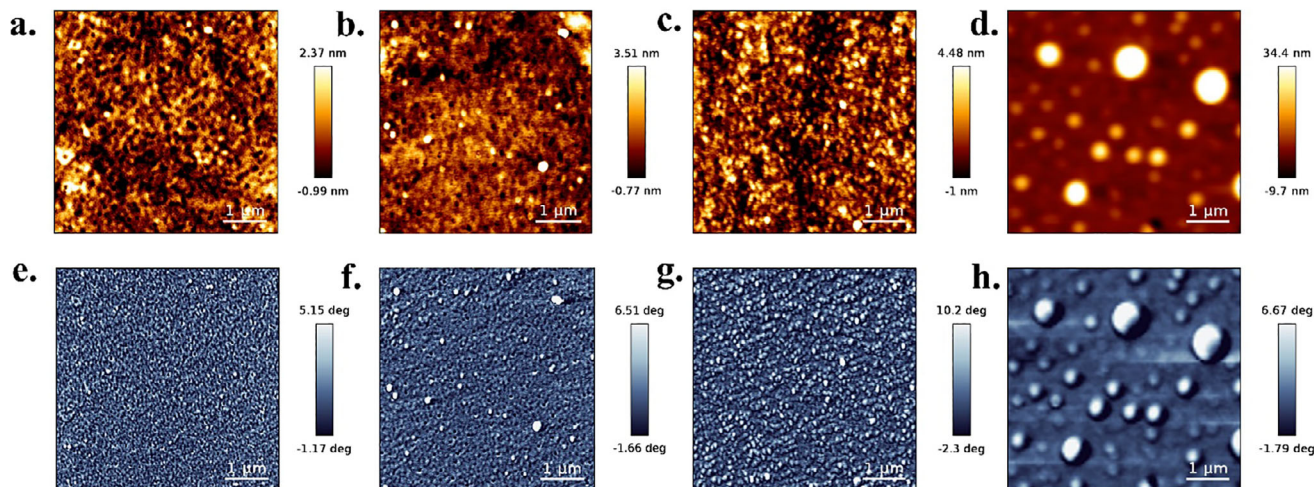


FIGURE 2 | Surface roughness of thin films through AFM height and phase images. (a,e) Pristine PTB7-Th material; (b,f) 1 mol% doping; (c,g) 10 mol% doping; (d,h) 30 mol% doping.

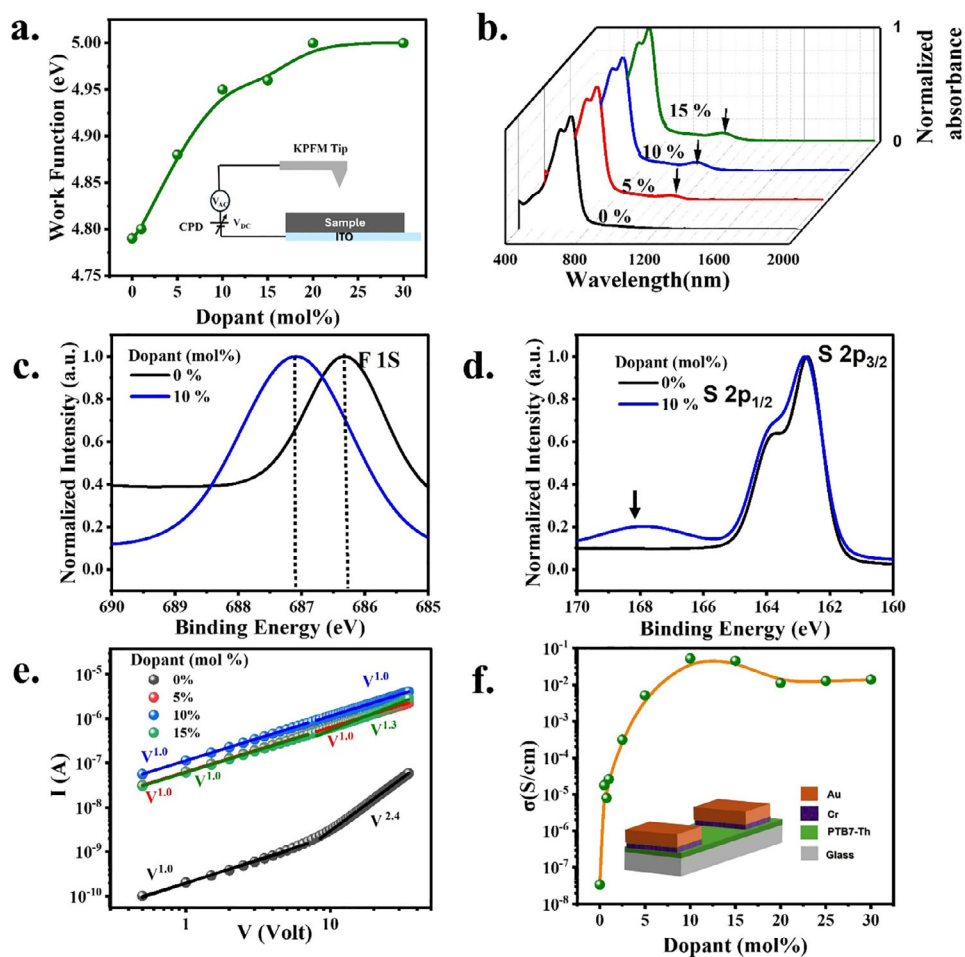


FIGURE 3 | Signatures of doping in the PTB7-Th: ATOP-BARF system obtained from (a) work function measurements (Inset: Schematic of the KPFM measurements), (b) UV-Visible-NIR absorption of undoped and doped films, XPS spectra of (c) C—F and (d) C—S bonding environments, (e) current–voltage (I–V) characteristics of a planer device, and (f) conductivity as a function of dopant concentration (Inset: Schematic of the two-terminal device).

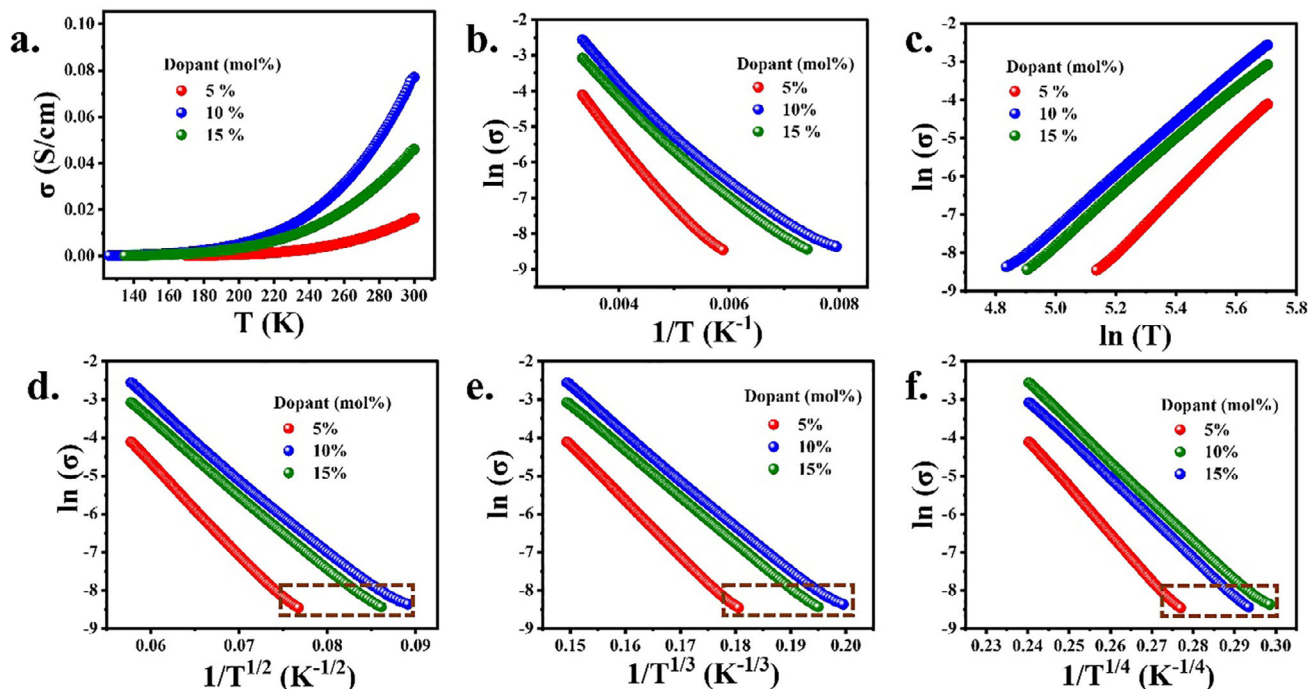


FIGURE 4 | DC Transport Mechanism. (a) Conductivity (σ) versus Temperature in Kelvin (T) (b) $\ln(\sigma)$ versus $1/T$ (c) $\ln(\sigma)$ versus $\ln(T)$ (d) $\ln(\sigma)$ versus $1/T^{1/2}$ (e) $\ln(\sigma)$ versus $1/T^{1/3}$ (f) $\ln(\sigma)$ versus $1/T^{1/4}$.

charge buildup. This results in a linear ohmic current–voltage behavior ($I \propto V$) as observed for undoped and doped films. At high fields, charge conduction is limited by the low intrinsic carrier density of the undoped polymer. When the injection rate exceeds the rate at which carriers can drift or diffuse away, space-charge accumulation occurs, as reflected in the current-voltage curve ($I \propto V^{2.4}$). In contrast, doping introduces additional carriers that mitigate space-charge effects, promote a more ohmic-like response even at higher fields, and significantly enhance charge transport.

The undoped PTB7-Th films exhibited an ohmic conductivity (σ) of $\sim 10^{-8}$ S/cm. At a doping level of 10 mol% (w.r.t. to monomer unit of the polymer), the conductivity exhibits a pronounced rise, reaching $\sim 0.5 \times 10^{-1}$ S cm⁻¹, beyond which it begins to saturate (Figure 3f). This represents a remarkable six-order-of-magnitude enhancement in conductivity, demonstrating the strong doping efficiency of the dopant. To further probe the origin of these improvements and the observed saturation, it is essential to gain a clear understanding of the underlying transport dynamics. In our system, the incorporation of a bulky counterion-based dopant introduces important considerations regarding its interaction with the polymer matrix and its influence on charge transport. In this regard, temperature-dependent DC conductivity analysis may contribute to elucidating the transport mechanisms in doped disordered polymers. The conductivity (σ)–temperature (T) dependence of the doped PTB7-Th system exhibits a trend where σ increases with T (Figure 4a).

This temperature dependence is a key indicator of the underlying charge transport mechanism. In such systems, thermally activated conduction can often be described by the Arrhenius behavior $\sigma = \sigma_0 \exp(E_{a,DC}/kT)$, where $E_{a,DC}$ is the DC activation energy (minimum energy required for a carrier to hop between

localized states), k is the Boltzmann constant. However, the nonlinear behavior observed in the $\ln \sigma$ vs. $1/T$ plot (Figure 4b) deviates from ideal Arrhenius behavior, indicating that a simple band-to-band conduction mechanism does not apply to this broad temperature range [47]. This deviation suggests that transport is dominated by disordered hopping processes, rather than delocalized band conduction. To further probe the transport mechanism in these doped samples, the improved Kivelson inter-polaron hopping model was first employed. According to the modified formulation, the temperature-dependent conductivity follows a power law.

$$\sigma = AT^n$$

where A and n are constants, with $n > 10$ required for the model to be valid. $\ln \sigma$ vs. $\ln T$ plots (Figure 4c) were used to extract the exponent n . The obtained values of n ranged between 6 and 7, which are significantly below the threshold value [48]. This suggests that the improved Kivelson model does not adequately capture the transport behavior in our doped PTB7-Th films. Efros–Shklovskii (ES) law was next applied to describe the conduction mechanism. Experimental verification of the ES law involves plotting $\ln \sigma$ as a function of $T^{-1/2}$ (Figure 4d) and checking for linearity, consistent with the ES expression [37, 38]:

$$\sigma = \sigma_0 \exp \left[- \left(\frac{T_{ES}}{T} \right)^{1/2} \right]$$

In parallel, the Mott Variable Range Hopping (VRH) framework, which models charge transport as hopping between localized states with energy and spatial variation, is also considered by plotting $\ln \sigma$ as a function of $T^{-1/3}$ and $T^{-1/4}$ (Figure 4e,f). The DC

conductivity in the Mott VRH model is expressed as [49]:

$$\sigma = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{\frac{1}{d+1}} \right]$$

where T_0 is the characteristic Mott temperature, and d is the dimensionality of the transport (2D or 3D). Among these, we have observed that the 3D VRH model (Figure 4f) fitting slightly better (Section S4) in this temperature range, considering this, we have observed that the decrease in T_0 with increasing dopant concentration from 5% to 10% implies a reduction of the average hopping distance and energy (W), along with an increase in the density of states at the Fermi level, assuming a constant localization length. These trends confirm the enhanced doping efficiency and increased carrier delocalization with doping. Furthermore, Figure S3 shows a clear reduction in DC activation energy ($E_{a,DC}$) with increasing doping, highlighting easier thermal activation of carriers. At higher doping levels (e.g. 15%), key hopping parameters average hopping energy (W), hopping distance (R), and $E_{a,DC}$ begin to saturate, indicating that the system approaches its optimal doping level (Section S4). At low temperatures, the conductivity becomes less thermally activated, suggesting a transition in the charge transport mechanism from thermally activated hopping to tunnelling transport, a behavior commonly reported in other conjugated polymers (Figure 4d–f box area) [49]. This transition temperature shifts from 188 K (for 5% doping) to ~140 K (for 10% and 15% doping), consistent with enhanced carrier delocalization at higher doping levels [49]. Collectively, temperature-dependent DC measurements indicate that the BARF counterion diffuses its negative charge over a large volume, weakening coulomb binding and enabling carriers to delocalize over multiple sites rather than remain confined near individual counterions, thereby reducing both the hopping distance and the activation energy. The role of the BARF anion is further confirmed by comparison with a smaller counterion (BF_4^-) using the same cation (ATOP). Despite similar doping levels, ATOP–BARF shows significantly higher conductivity than ATOP– BF_4 , as the bulky, weakly coordinating BARF reduces coulomb binding and enhances charge delocalization, whereas BF_4^- promotes carrier localization and limits transport (details Section S3 and Figure S2).

Complementary information about charge carriers' relaxation dynamics was obtained via Impedance Spectroscopy (IS), by applying a small sinusoidal input signal over a wide frequency range. A single semicircular feature appears in the resulting Nyquist plot, which indicates the presence of a dominant relaxation process and reflects that ion migration effects are insignificant under these frequency ranges. With the increase in doping, the impedance value decreases and reaches saturation at a 10%–15% doping level (Figure 5a). The peak of the semicircle serves as an indicator for the characteristic relaxation time (τ), which follows the condition $\omega\tau = 1$ (Figure 5a) [50]. With increasing doping, τ decreases, indicating a faster charge carrier response and more efficient transport pathways (Figure 5b). This reduction in τ underscores the role of doping in promoting charge delocalization and minimizing resistive losses within the polymer matrix however, beyond a doping level of approximately 10%–15%, the decrease in τ becomes less pronounced, implying that further doping yields only marginal improvements in carrier dynamics.

The relaxation time τ varies with temperature and follows Arrhenius-type behavior [39, 50] (Figure 5c):

$$\tau = \tau_0 \exp \left[\left(\frac{E_{a,AC}}{kT} \right) \right]$$

The extracted AC activation energy ($E_{a,AC}$) decreases with increasing doping concentration, from approximately 190 meV at 5% doping to 140 meV at 10% doping. This reduction signifies enhanced charge carrier dynamics and more efficient charge transport processes at moderate doping levels. However, beyond 15% doping, $E_{a,AC}$ increases again with $E_{a,AC} \approx 177$ meV for 15%, suggesting the onset of dopant-induced disorder or aggregation that hinders charge transport. This rise in activation energy at higher doping levels indicates that excessive doping introduces additional trapping or scattering centers, slowing down relaxation dynamics and reducing transport efficiency. Furthermore, the similarity between the activation energies obtained from DC and AC conductivities suggests that the distribution of random energy barriers in the glassy polymer matrix PTB7-Th is isotropic for charge carrier transport [51]. The AC conductivity response exhibits the following features: (a) a nearly constant conductivity in the low-frequency region, (b) a transition to power-law behavior, following $\sigma \propto \omega^s$ ($0 < s < 1$) at higher frequencies, and (c) with increasing doping concentration, the frequency-independent (DC-like) region progressively broadens and eventually saturates (Figure 5d). In the low-frequency region, charges have sufficient time to hop between localized states within each field cycle, resulting in a steady-state (DC-like) conductivity that appears as a flat plateau in the frequency-independent region. This regime corresponds to long-range charge transport through thermally activated hopping. At higher frequencies, the electric field varies too rapidly to sustain long-range motion, and carriers can only undergo localized hopping between nearby trap states. The observed broadening of the low-frequency plateau with increasing doping concentration indicates that the dopant (ATOP–BARF) effectively passivates deep trap states, thereby facilitating enhanced long-range charge transport [39]. The low-frequency region of the AC conductivity spectrum matches the measured DC conductivity, further indicating negligible ionic contributions and confirming that charge transport is predominantly electronic [52]. The bulky BARF anion is largely immobile within the polymer matrix, thereby suppressing ionic migration and minimizing its contribution to overall ionic conductivity.

In parallel with the observed enhancement in conductivity, SCLC-based hole-only devices were fabricated to extract the charge carrier mobility [53–56]. The SCLC region shifts to higher voltages in doped polymers compared to undoped ones, consistent with the increased background carrier concentration reported in the literature [53]. The mobility increased from $2. \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the pristine film to $1.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for 0.12% ATOP–BARF doping, representing a nearly two-order-of-magnitude improvement (Figure 6a,b). However, SCLC probes high-field, vertical bulk limited transport dominated by injected carriers. This trend in the enhancement of mobility was also observed from lateral transport through field-effect transistor (FET) measurements carried out for the low-doping range (Section S7 and Figure S5).

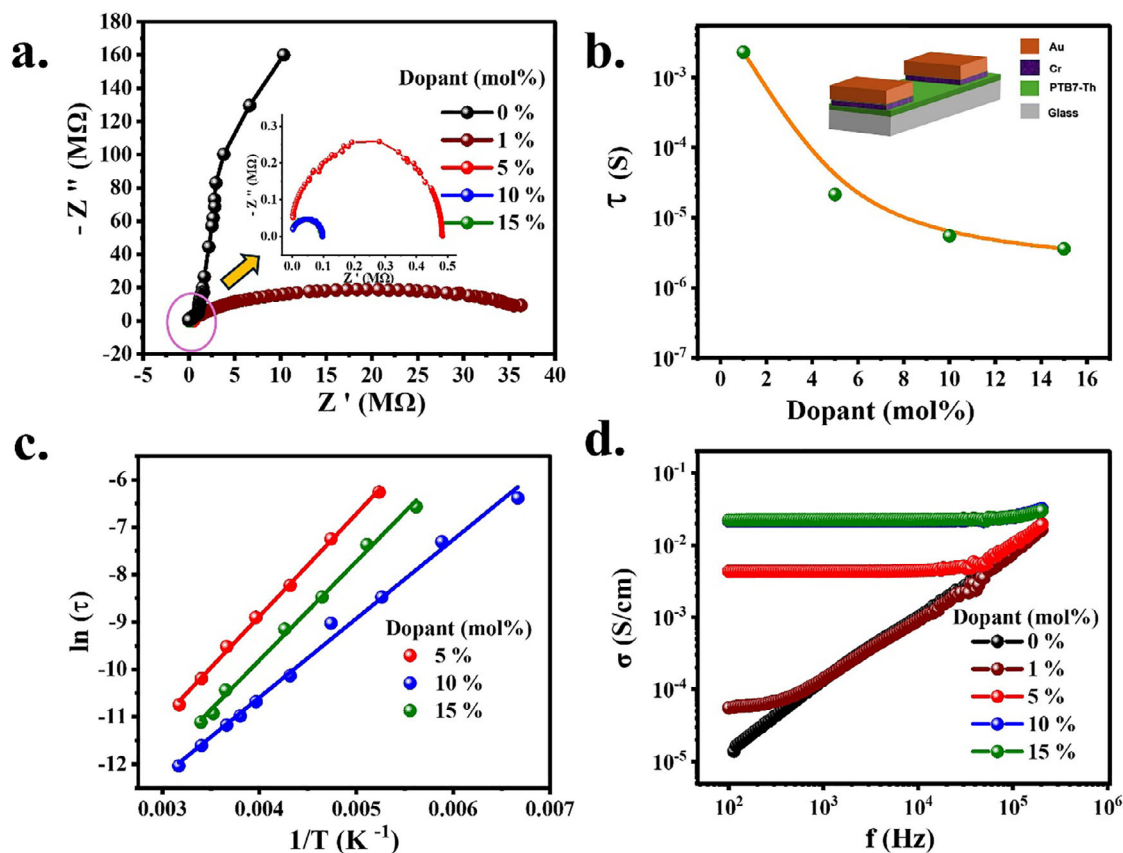


FIGURE 5 | AC Transport Mechanism. (a) Nyquist plot (inset-magnified view of 5, 10, and 15 mol% doped polymer, where the 15 mol% overlaps with 10 mol%) (b) Relaxation time (τ) vs. % Dopant used to dope the polymer, the temperature of measurement is 310 K, the connecting line is the guide to the eye (inset-device architecture) (c) $\ln(\tau)$ vs $1/T$ (d) conductivity dependency on the frequency of AC measurement for different doping concentrations.

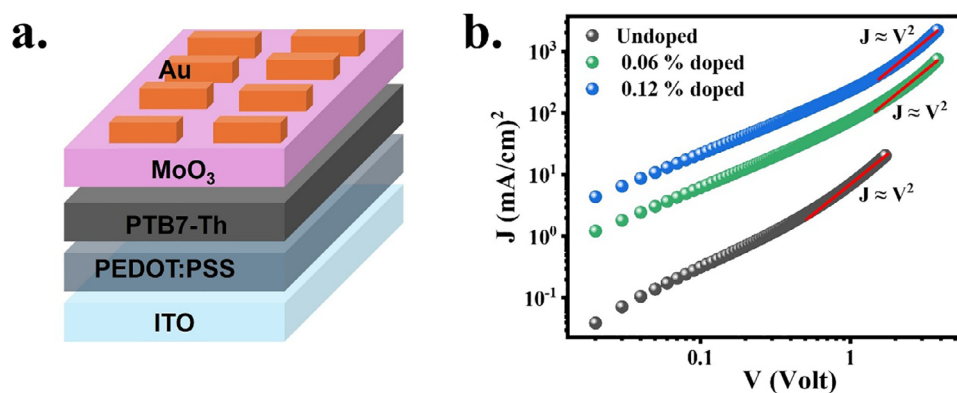


FIGURE 6 | Mobility calculation through space charge-limited current (a) Device configuration (b) Current Density (J) versus voltage (V) characteristics.

To examine the microscopic origin behind the trends of these improvements in electrical performance, we performed molecular dynamics (MD) simulations. In the radial distribution functions (RDFs), at low doping (5%), both backbone-cation and backbone-anion RDFs exhibit sharp primary peaks, signifying localized and strong associations between the polymer and the cationic or anionic part of the dopant. As doping increases (10%–15%), these peaks broaden and shift outward, implying weaker and more diffuse interactions (Figure 7a,b). This trend is

consistent with BARF's bulky, weakly coordinating nature, which reduces coulombic binding, facilitates ion-pair dissociation, and enables delocalized hole transport. The experimental signatures of enhanced conductivity and mobility with increasing doping thus find clear support in the MD results. The cation-anion RDF shows a prominent short-range peak at 5% doping, which diminishes at higher concentrations, signifying the progressive dissociation of tight ion pairs. This trend begins to saturate at 10%–15% doping, supporting the experimental observation

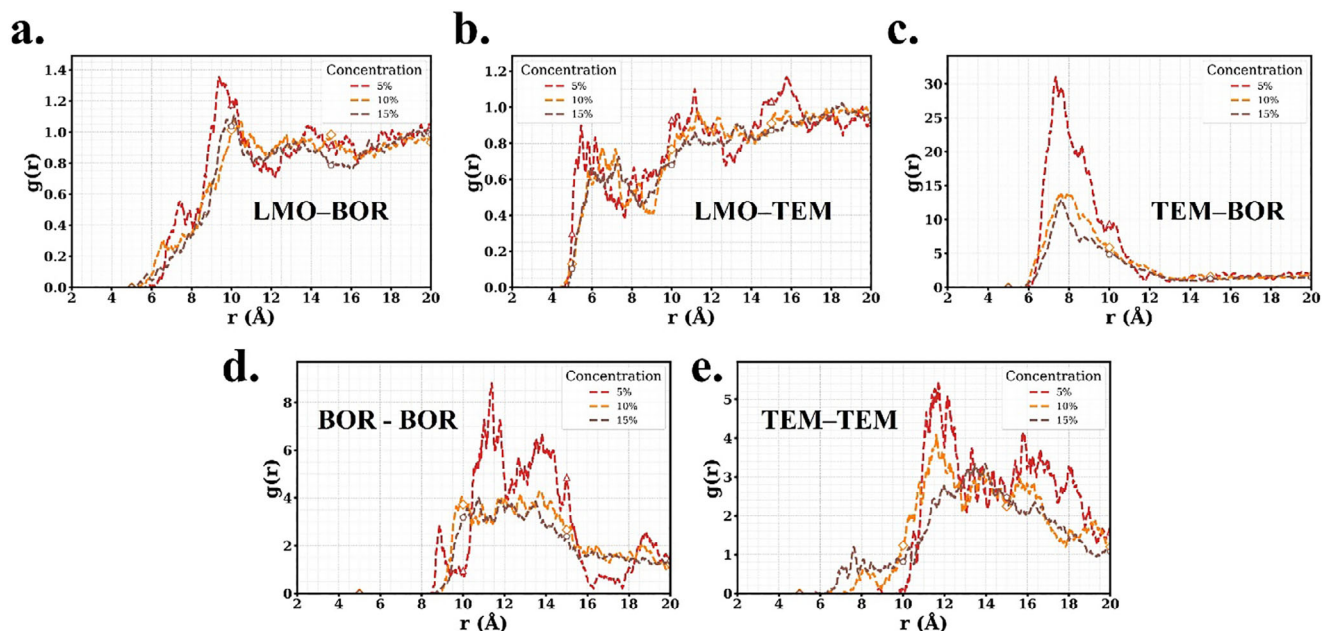


FIGURE 7 | Radial distribution function (RDF) plots of different interaction pairs at varying concentrations (5, 10, and 15 mol%). (a) LMO–BOR represents the interaction between the polymer moiety and the anionic dopant; (b) LMO–TEM represents the interaction between the polymer moiety and the cationic dopant; (c) TEM–BOR corresponds to the cationic–anionic dopant interaction; (d) BOR–BOR shows the anionic–anionic interaction; and (e) TEM–TEM shows the cationic–cationic interaction.

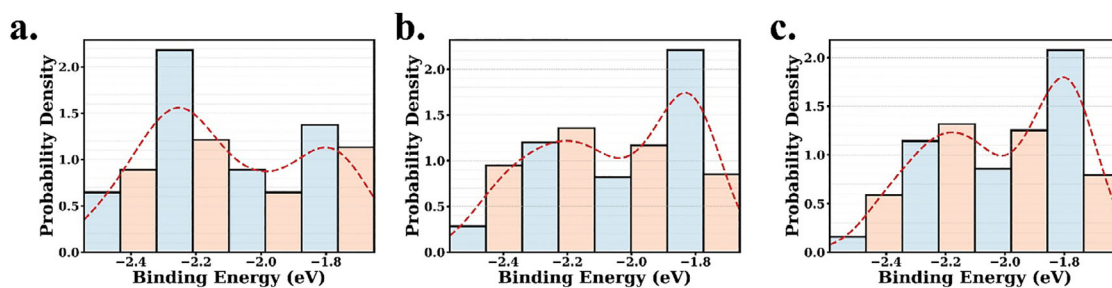


FIGURE 8 | Binding energy landscapes at different concentrations with probability density distributions and smooth trend lines (red dashed). (a) 5 mol% concentration, (b) 10 mol% concentration, and (c) 15 mol% concentration.

that work function enhancements reach a plateau (Figures 3a and 7c). Anion–anion RDFs show intermediate-distance correlations that weaken with doping, leading to a more uniform anion distribution 10%–15% level (Figure 7d).

This dispersal stabilizes the film morphology and underpins the experimental observation of homogeneous charge landscapes in AFM up to moderate doping. In parallel, the cation–cation RDF shifts toward closer separations with increasing doping. At 10%–15%, new short-range peaks emerge, pointing to cation clustering once ion-pairing is no longer the dominant interaction (Figure 7e). This clustering coincides with the experimental onset of morphological inhomogeneities and the saturation of conductivity at high doping, suggesting that polaron–polaron interactions and dopant aggregation begin to limit performance.

Analysis of the cation–anion binding energy distributions further supports the RDF results (Figure 8). At a 5% doping level, the distribution is showing narrow and strongly negative, indicating

that most ion pairs are tightly bound. With increasing doping level to 10% the peak shifts to less negative energies, with a broader distribution suggests a growing fraction of weakly bound or dissociated pairs. The emergence of such weak interactions aligns with the dramatic rise in free carrier density and conductivity (Figure 3f). At higher doping concentration (15%), the binding environments are most diverse, indicating increasing structural disorder that eventually restricts further gains in conductivity.

To further elucidate the origin of these trends, dimensionality reduction analyses using PCA and t-SNE were performed, offering an orthogonal visualization of the evolving ionic environments (Figure 9). At 5% doping, the compact and well-separated clusters for cation–anion pairs indicate a homogeneous population of strongly bound ion pairs, consistent with the sharp RDF peaks and narrow binding energy distributions. As the doping level increases to 10%–15%, these clusters broaden and begin to overlap, reflecting the emergence of diverse coordination environments and a growing population of weakly bound or

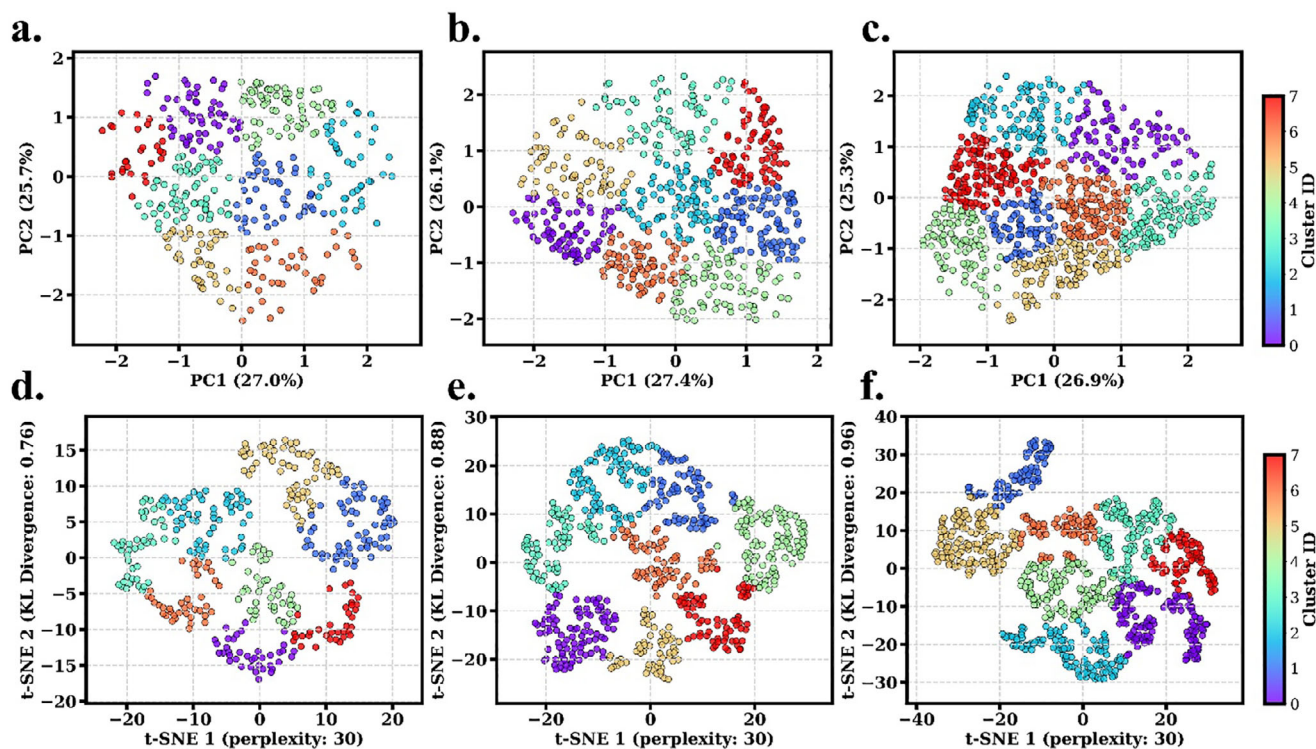


FIGURE 9 | Dimensionality reduction analysis of polymer-dopant systems at 5, 10, and 15 mol% concentrations. The first row shows Principal Component Analysis (PCA) results, while the second row presents the corresponding t-SNE visualizations for the same concentrations.

dissociated pairs—precisely in line with the broadened RDFs and reduced binding energies. For like-charged interactions, PCA and t-SNE reveal the development of new subclusters at higher doping, mirroring the short-range cation and anion aggregation captured in RDFs. These projections thus map the structural evolution from a uniform, strongly associated regime at low doping to a heterogeneous landscape of delocalized and clustered species at higher doping.

In parallel to explicitly account for polaron-counterion interactions, we performed an additional set of MD simulations with a revised representation of the doped state. While the overall simulation protocol remains as described in the Methods section, the key modification is the removal of TEM (ATOP-derived) cations from the system to reflect post-charge-transfer conditions. The doped polymer is instead modeled by introducing effective positive charges along the polymer backbone, distributed over adjacent monomer units to mimic polaron formation. The presence of BARF anions maintains charge neutrality. All other simulation parameters, including force field, equilibration procedure, and production time scales, remain unchanged.

As shown in Figure S9a, which presents the radial distribution function between the positively charged polymer segments (polarons) and the BARF anions, the first peak at short separation is most pronounced for the 5 mol% system (red dashed line) than the 10 mol% (orange) and 15 mol% (grey) cases. This indicates a higher probability of close polaron-anion proximity at lower dopant concentration, consistent with stronger local electrostatic association at 5 mol% compared to higher concentrations. Figure S9b shows the polaron-polaron radial distribution functions. In

the 5 mol% case, the first peak appears at a significantly larger separation (~ 11 – 12 Å), indicating a low probability of finding polarons in close proximity to one another. At higher concentrations, polarons are more frequently found at shorter separations, reflecting increased polaron density and closer spatial packing. The anion-anion radial distribution functions (Figure S9c) show comparatively weaker and less systematic trends. While the 5 and 15 mol% systems exhibit peaks at similar distances, the 10 mol% system displays a slight shift toward larger separations. Overall, these results suggest that anion-anion correlations do not exhibit a clear monotonic dependence on dopant concentration within the present data.

Taken together, the RDF analysis indicates a reduction in local polaron-anion proximity with increasing concentration, accompanied by increased polaron-polaron spatial proximity, while anion-anion organization remains comparatively insensitive. These trends are discussed in relation to the experimentally observed transport behavior, without implying a direct causal relationship. Moreover, Figure S10 presents the distributions of polaron-anion interaction energies at three different concentrations. As shown in Figure S10a–c, the distributions are skewed toward less negative values, indicating that a large fraction of configurations correspond to relatively weak electrostatic interactions. Notably, the 5 mol% system (Figure S10a) exhibits a higher probability of more negative interaction energies compared to the 10 and 15 mol% cases, reflecting a greater prevalence of strongly bound polaron-anion configurations at lower concentration. These results indicate that polaron-anion interactions are, on average, stronger at lower dopant concentration and become progressively weaker with increasing concentration. This trend is consistent with the reduced likelihood of close polaron-anion

proximity observed in the corresponding RDF analysis and is discussed in relation to the experimentally observed transport behavior, without implying a direct quantitative relationship.

Overall, at low doping levels, specifically, at 5 mol%, the system exhibits a higher probability of strongly bound polaron–anion configurations, as reflected in the interaction energy distributions and radial distribution functions. In contrast, at higher concentrations (10 and 15 mol%), these strongly bound configurations become progressively less prevalent, indicating weaker average polaron–anion interactions and increased spatial separation, which promote ion-pair dissociation. As a result, charge carriers become more delocalized, leading to a pronounced increase in electrical conductivity. This coherent structural–energetic–transport correlation highlights the delicate balance achieved by the bulky BARF anion in enabling efficient doping while delineating the intrinsic limits set by dopant-induced aggregation.

3 | Conclusions

In summary, we demonstrate that the rationally designed ATOP-BARF dopant enables efficient, thermally robust, and air-stable molecular doping of amorphous conjugated polymers. The enhanced charge transport originates from reduced hopping distance and activation energy, suppressed ion migration, and effective passivation of deep trap states, as consistently evidenced by DC and AC conductivity measurements. Along with that, the improvement of carrier mobilities were also obtained from FET and SCLC measurements. However, beyond a certain threshold, these enhancements saturate, as reflected in the behavior of key transport parameters. Complementary MD simulations provide molecular-level insights into this behavior, uncovering favorable ion–polymer interactions and binding-energy landscapes that underpin the observed improvements. At higher doping levels, simulations reveal that ion separation from the split functional dopants reaches a limit, constraining effective carrier generation and ultimately leading to performance saturation.

Overall, the combined experimental and computational analyses provide a unified framework for understanding how controlled split-functional doping leverages favorable molecular interactions to enhance charge transport and, ultimately, improve electrical performance in disordered organic semiconductors.

4 | Materials and Methods

4.1 | Materials

The parent semiconductor, Poly{4,8-bis[5-(2-ethylhexyl)-thiophen-2-yl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophene-4,6-diyl} (PTB7-Th), was purchased from Lumtec (Luminescence Technology Corp., Product Code: LT-S9139), Mw = 10 000–100 000 (GPC), CAS NO: 1469791-66-9 and used as received. The dopant, ATOP-BARF, comprises a cationic component, ATOP [4-(acetylamino)-2,2,6,6-tetramethyl-1-oxopiperidinium], and an anionic component, BARF [tetrakis(3,5-bis(trifluoromethyl)phenyl)borate], and for ATOP-BF₄, BF₄ stands for tetrafluoroborate [23]. The solvents

1,2-dichlorobenzene and acetonitrile were purchased from Sigma-Aldrich and used without further purification.

4.2 | Sample Preparation

The PTB7-Th polymer was dissolved in DCB to prepare a solution, while the dopant was separately dissolved in acetonitrile with overnight stirring to form a dopant solution. The two solutions were mixed in appropriate molar ratios to achieve different doping levels. Acetonitrile was used in a very low proportion (more than 30 times lower than 1,2-dichlorobenzene) to minimize co-solvent-induced disruptions. The resulting mixture was further stirred for 7–8 h to ensure homogeneous and uniform mixing. Glass substrates were initially cleaned using a soap solution, thoroughly rinsed with deionized (DI) water, and subjected to a 10-min ultrasonic treatment in a 1:1 mixture of isopropyl alcohol and acetone. To remove organic and ionic contaminants and enhance hydrophilicity, RCA (Radio Corporation of America) cleaning was performed. The substrates were then rinsed again with DI water, dried using a pure nitrogen gas stream, and further treated with plasma cleaning to improve their hydrophilic properties. Thin films with varying dopant concentrations were prepared by spin coating the doped solutions onto the cleaned glass substrates, followed by annealing at 110°C. For two-terminal device fabrication, a thin layer of chromium (3 nm) and gold (55 nm) was deposited using a thermal evaporator under a vacuum pressure of 10^{−6} bar. Samples used in Kelvin Probe Force Microscopy (KPFM) measurements were prepared on indium tin oxide (ITO) substrates cleaned following the procedure outlined earlier.

4.3 | SCLC Device Fabrication

The ITO substrates were cleaned using the same procedure described previously. A thin layer of PEDOT: PSS, filtered through a 0.25 μm syringe filter, was spin-coated onto the ITO surface and annealed at 140°C. Subsequently, a ~185 (± 5) nm thick PTB7-Th film (pristine or doped) was spin-coated on top. Finally, a 3 nm MoO₃ layer was thermally evaporated, followed by the deposition of a gold (Au) layer to form the top contact.

4.4 | FET Fabrication

OFETs were fabricated using Ossila substrates (product code S221) with a channel length of 30 μm and a channel width of 1 mm. The samples were prepared using the thin-film processing methods described above.

4.5 | AFM and KPFM Measurements

The surface morphology was analyzed using a JPK Nano Wizard 3 equipped with Pt-coated cantilever tips (resonance frequency: 300 kHz), while the surface potential was measured in Kelvin Probe Force Microscopy (KPFM) mode using cantilevers with a resonance frequency of 75 kHz. In parallel, the work function was derived from contact potential difference (V_{CPD}) measurements, using highly oriented pyrolytic graphite (HOPG) as the reference.

The estimates were obtained from the standard relation that equates the measured (V_{CPD}) to the known work function of the AFM tip ϕ_{tip} and that of the semiconductor ϕ_s , that is.

$$V_{CPD} = \frac{\phi_{tip} - \phi_s}{-e}$$

The electrical characterization (J–V measurements) was performed using a Keithley 4200 SCS parameter analyzer.

4.6 | I–V Measurements

Current–voltage (I–V) characteristics were measured using a Keithley 4200A-SCS system, with a customized probe station for device connections.

4.7 | IS Measurements

Impedance spectroscopy (IS) measurements were carried out using the Analog Discovery 2 (Digilent) by applying a small periodic signal of 500 mV, averaging 50 repetitions. All measurements were performed inside a properly shielded Faraday cage to minimize external noise.

4.8 | Temperature Dependent Study

Temperature-dependent DC conductivity measurements were performed using a Physical Property Measurement System (PPMS), while AC measurements were conducted using a nitrogen-purged, temperature-controlled stage (Linkam LTS420E-PB4).

4.9 | UV–Vis Spectroscopy

UV–vis measurements were performed using a PerkinElmer system. The samples were prepared on quartz substrates by spin-coating.

4.10 | C–V Measurements

Electrochemical characterization was carried out using a Bio-Logic SP-300 potentiostat controlled through the EC-Lab interface. A glassy carbon electrode (GCE, $\sim 1.6 \text{ mm}^2$ area) was employed as the working electrode, along with a platinum counter electrode and a silver wire functioning as the pseudo-reference. All measurements were taken at room temperature under ambient laboratory conditions. The electrolyte consisted of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6). Cyclic voltammograms were collected using a potential increment of $\pm 0.01 \text{ V}$. Ferrocene (Fc) was introduced as an external calibration marker, and the reported potentials are aligned to the Fc/Fc^+ redox standard.

4.11 | EPR Analysis

Electron paramagnetic resonance (EPR) measurements were carried out on a Magnetech ESR5000 spectrometer operating in the X-band ($\sim 9.4 \text{ GHz}$) under continuous-wave conditions. All spectra were collected at 25°C in ambient atmosphere. A 4 mM PTB7-Th solution (monomer molecular weight: $889.36 \text{ g mol}^{-1}$) was prepared in 1,2-dichlorobenzene and blended with ATOP-BARF at doping levels of 10 mol%. The prepared solutions were transferred into quartz capillaries with an inner diameter of $\sim 50 \text{ }\mu\text{m}$, an outer diameter of $\sim 100 \text{ }\mu\text{m}$, and a length of 25 mm. Each capillary was positioned vertically inside the resonator to maintain uniform filling and achieve a reliable signal response.

4.12 | XPS Analysis

XPS measurements were performed using ULVAC-PHI (PHI 5000 VersaProbe III) system with non-monochromatic Al K α X-rays (1486.70 eV). XPS measurements were carried out in an ultra-high vacuum (UHV) chamber with a base pressure of $< 9 \times 10^{-8} \text{ Pa}$. Undoped and doped solutions were spin-coated at a spin speed of 1000 rpm for 10 sec followed by 4000 rpm for 40 sec on FTO substrates for XPS measurements. High-resolution spectra were recorded at 55 eV pass energy at intervals of 0.05 eV. Survey spectra were recorded at 280 eV pass energy at intervals of 1 eV. CasaXPS software was used for XPS peak fitting.

4.13 | Computational Methodology

To examine the bulk properties of the materials and comprehend how bulk properties change with dopant concentration, molecular dynamics (MD) simulations were performed (Section S9 and Figure S8). In order to understand the trend and saturation behavior seen at higher doping levels (10% and 15%), the analysis was focused on three distinct dopant concentrations: 5%, 10%, and 15%. The GROMACS simulation package was used to perform the molecular packing of the dopant molecules and PTB7-Th polymer [57, 58]. The number of dopant molecules varied with the target concentration, and each system had a total of 1000 polymer units, which provided a statistically representative volume. After packing, the system was carefully considered to ensure that all molecules were properly separated, with no atomic overlaps or close contacts. Energy minimization was then performed using the steepest descent algorithm with the Verlet cutoff scheme for non-bonded interactions, and the Particle Mesh Ewald (PME) method [59] was used to treat long-range Coulombic interactions. Following minimization, an NPT equilibration run (5 ns) was carried out to allow the system to relax and achieve a stable configuration. To obtain a glassy-phase morphology, an annealing protocol was employed. The system was heated for 3 ns and subsequently cooled for another 3 ns. The V-rescale thermostat [60] and Berendsen barostat [61] were used for temperature and pressure coupling, respectively, with a time step of 1 fs for all simulations. During the heating phase, the temperature was ramped from 100 to 800 K at specific time intervals (0 ns $\rightarrow$ 100 K,

0.3 ns → 300 K, 1.3 ns → 800 K) and maintained at 800 K until 3 ns. For the cooling stage, the temperature was decreased sequentially (0 ns → 800 K, 0.2 ns → 600 K, 0.8 ns → 300 K) and maintained at 300 K for an additional 2.2 ns. The density convergence criteria confirmed that the obtained morphology corresponded to a stable glassy state suitable for subsequent analysis. Annealing workflow is well tested in some of the recent works [41, 42].

Post-equilibration analyses included radial distribution function (RDF) calculations to know the spatial organization and intermolecular packing around reference molecules. Additionally, binding energy analyses were carried out using the XTB semi-empirical method implemented in ORCA [62]. The XTB method [63], developed by Grimme's group, provides an efficient and accurate approach for large molecular systems. To further explore structural relationships and support the interpretation of experimental data, dimensionality reduction and clustering analyses were performed using Python 3. The k-nearest neighbors (KNN) algorithm was applied, along with Principal Component Analysis (PCA) and t-distributed Stochastic Neighbor Embedding (t-SNE) methods. Optimal clustering parameters were determined using the elbow method and Calinski–Harabasz index, both of which suggested $k = 8$ as the optimal number of clusters. This clustering information was then used to interpret the PCA and t-SNE results in relation to the experimental observations. This clustering protocol was used in our earlier work [64]. The initial and equilibrated information of the simulation is also provided in Figure S11.

Author Contributions

Chandan Pramanik: conceptualization, writing – original draft, methodology, validation, visualization, writing – review and editing, software, formal analysis, data curation, investigation. **Shubham Gupta:** conceptualization, validation, visualization, data curation. **Brijesh K. Patel:** data curation. **Anirban Mondal:** conceptualization, writing – review and editing, supervision, resources, data curation, formal analysis, funding acquisition. **Pabitra K. Nayak:** conceptualization, writing – review and editing, data curation, supervision, resources, visualization, funding acquisition. **K. S. Narayan:** funding acquisition, investigation, conceptualization, validation, writing – review and editing, resources, supervision, project administration.

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Conflicts of Interest

A patent based on the dopant system has been filed.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: adfm78579-sup-0001-SuppMat.docx.