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Anion Exchange Doping: Tuning Equilibrium to Increase Doping Efficiency in Semiconducting Polymers

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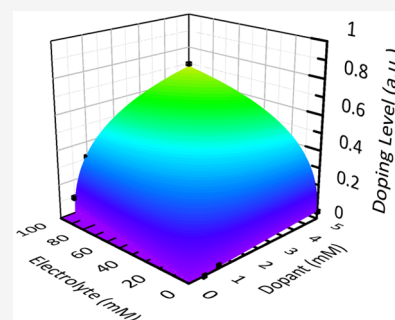
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ABSTRACT: High electron affinity (EA) molecules p-type dope low ionization energy (IE) polymers, resulting in an equilibrium doping level based on the energetic driving force (IE-EA), reorganization energy, and dopant concentration. Anion exchange doping (AED) is a process whereby the dopant anion is exchanged with a stable ion from an electrolyte. We show that the AED level can be predicted using an isotherm equilibrium model. The exchange of the dopant anion (FeCl_3^-) for a bis(trifluoromethanesulfonamide) (TFSI^-) anion in the polymers poly(3-hexylthiophene-2,5-diyl) (P3HT) and poly[3-(2,2-bithien-5-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione-6,5-diyl] (PDPP-2T) highlights two cases in which the process is nonspontaneous and spontaneous, respectively. For P3HT, FeCl_3 provides a high doping level but an unstable counterion, so exchange results in an air stable counterion with a marginal increase in doping. For PDPP-2T, FeCl_3 is a weak dopant, but the exchange of FeCl_3^- for TFSI^- is spontaneous, so the doping level increases by $>10\times$ with AED.



Sequential doping of semiconducting polymers (SPs) is a well studied method for tuning SP film conductivity and solubility while maintaining a film morphology that is ideal for efficient charge transport.^{1–4} Multiple studies have demonstrated that morphology control and sequential doping are essential for obtaining efficient electronic devices, including organic thermoelectrics, organic field effect transistors, and organic electrochemical transistors.^{5–9} Recently, Yamashita et al. demonstrated an improvement to molecular doping efficiency through a process termed anion exchange doping (AED).¹⁰ By immersing a poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene) (PBTfT) film into a solution with the molecular dopant 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) and various electrolytes, they sequentially doped the polymer and exchanged the F4TCNQ⁻ anion for the electrolyte anion. This process yields two advantages. First, the anion exchange enables the choice of a stable counterion. Common p-type dopant anions often react with H₂O and O₂. Thus, AED can be used to create air stable films. Second, AED enables increased film dopant levels compared to conventional doping.^{10,11} Although AED yields significant advantages, there are fundamental knowledge gaps. Currently, there is no method for predicting the equilibrium doping level or the fraction of exchanged anions. Likewise, the link between doping level and carrier density is poorly understood.

In this manuscript, first we study the relationship between solution concentrations of molecular dopants and electrolyte ions on the P3HT film doping level using the dopant FeCl_3 and electrolyte lithium bis(trifluoromethanesulfonyl)imide

(LiTFSI), as developed by Jacobs et al.¹¹ We derive a novel anion exchange isotherm to model equilibrium processes occurring during AED and extract equilibrium constants for both doping and the subsequent anion exchange. This model predicts high p-type doping efficiency is possible in systems with low chemical potential for doping. P-type doping high IE polymers has previously been limited by inherent challenges in the synthesis of stable, high EA dopants.^{1,12} By optimizing the AED process, we reduce the need to develop stable, high EA dopants. We demonstrate that high doping levels are achieved using AED with the high IE donor–acceptor polymer poly[3-(2,2-bithien-5-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione-6,5-diyl] (PDPP-2T).

Figure 1(a)–(c) illustrates the two equilibrium processes occurring during AED. The Langmuir model, when applied to sequential doping, assumes a fixed and finite number of polymer sites are available for doping and simplifies the complex morphologies present in solid state SPs by assuming that all sites have an identical energy landscape. In reality, solid state P3HT contains crystalline and amorphous regions with a variety of configurations. In Figure 1(a), a 180 nm thick P3HT film is immersed in an 8 mL solution of 5 mM FeCl_3 in

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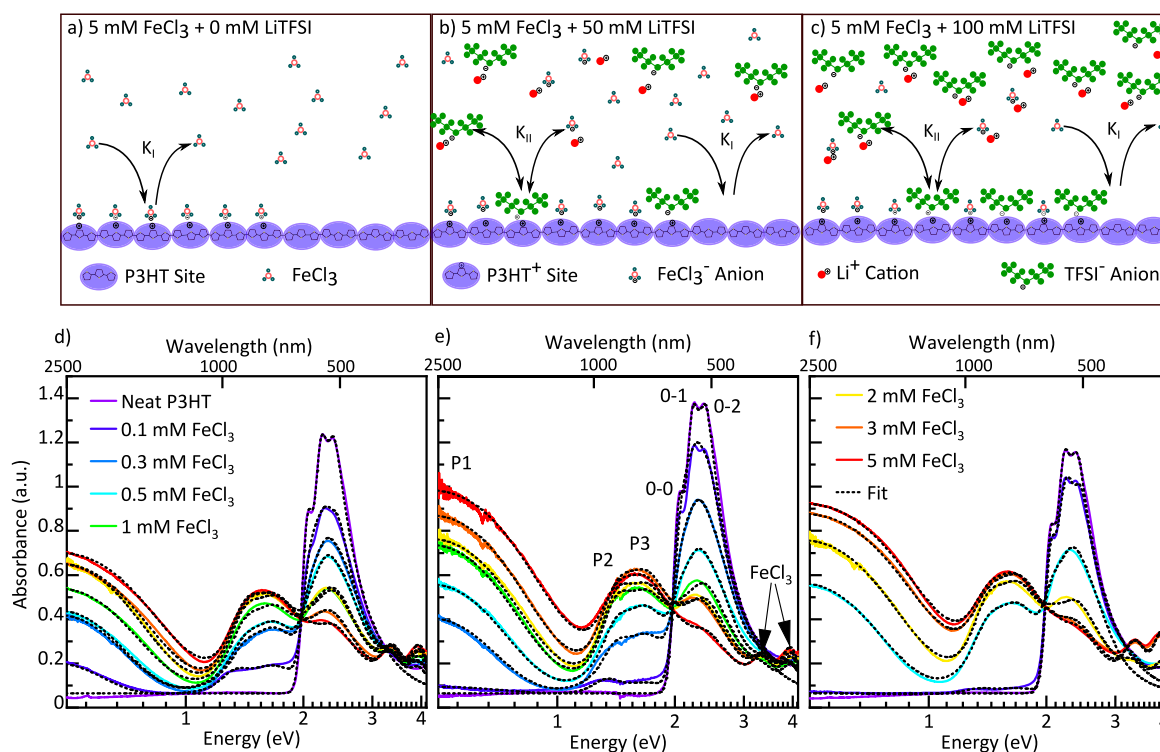


Figure 1. (a) Illustration of FeCl_3 doping P3HT sites with equilibrium constant K_I . (b) and (c) illustrate FeCl_3 doping P3HT sites, where FeCl_3 is subsequently exchanged by TFSI^- with equilibrium constant K_{II} . UV-vis-NIR absorption spectra for P3HT doped with various FeCl_3 solution concentrations and (d) 0, (e) 50, and (f) 100 mM LiTFSI solutions, respectively.

anhydrous *n*-butyl acetate (nBA). The solvent swells the film allowing FeCl_3 to penetrate and undergo charge transfer with P3HT resulting in $\text{P3HT}^+\text{FeCl}_3^-$, with equilibrium constant K_I (eq S3).⁴ In Figure 1(b),(c), a P3HT film is immersed in 8 mL of 5 mM FeCl_3 nBA solution, this time with either 50 mM or 100 mM LiTFSI concentrations, respectively. LiTFSI dissociates into Li^+ and TFSI^- in nBA. FeCl_3 dopes the film with the same equilibrium constant; however, the charged FeCl_3^- anion is now exchanged for the TFSI^- anion with an equilibrium constant K_{II} (Equation S4). LiTFSI is inert toward P3HT, so no third equilibrium is required.

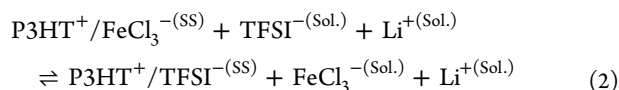
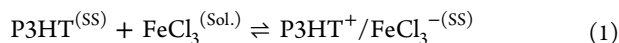


Figure 1d shows ultraviolet-visible-near-infrared spectroscopy (UV-vis-NIR) of sequentially doped P3HT films^{2,3} with various FeCl_3 solutions. Neat P3HT shows three vibronic transitions at ~ 2 eV (0-0), ~ 2.2 eV (0-1), and ~ 2.4 eV (0-2) in accordance with the literature.¹³ As P3HT is doped to higher doping levels, the neat 0-0, 0-1, and 0-2 peaks bleach and broaden, while three broad P3HT⁺ absorbance peaks grow in at 0.47 (P1), 1.25 (P2), and 1.5 (P3) eV.¹⁴⁻¹⁷ As the doping level is increased, an FeCl_3 peak becomes apparent at ~ 3.9 eV, and an FeCl_3^- peak appears at ~ 3.4 eV.¹⁸ UV-vis-NIR of P3HT films sequentially doped with mixtures of FeCl_3 and 50 or 100 mM LiTFSI shows similar trends (Figure 1e,f). Key differences are observed in the extent of bleaching of the neat P3HT vibronic transitions and corresponding growth of the broad P3HT⁺ polaron peaks (P1, P2, and P3) with anion

exchanged films yielding a 10–50% higher doping level with respect to FeCl_3 solutions without an electrolyte present.

Since the P3 absorbance at 1.5 eV (780 nm) overlaps the neutral P3HT absorbance, we deconvoluted overlapping peaks by globally fitting the spectral signatures between 0.5 and 4.2 eV. The cumulative fits for the 0, 50, and 100 mM LiTFSI series are shown in Figure 1(d)–(f), and their corresponding individual peak fits and the remaining fits for the 0.1, 1.0, 10.0, 25.0, and 75.0 mM LiTFSI concentrations are in Figures S2–S9. Similar to previous studies,¹⁶ we constrained the peak positions to remain constant across all studied samples. Our discussion of the UV-vis-NIR peak fitting is in Supporting Information Section S4.

To simplify these spectral changes with respect to doping level, we define Θ as the fraction of doped P3HT sites over the total available P3HT sites. Θ is linearly approximated from optical absorbance by $\theta = \frac{A_p}{A_p + A_N}$, where A_N is the integral of the neutral P3HT absorption peaks and A_p is the integral of P1. The calculated Θ from the UV-vis-NIR data is shown in Figure 2(a),(b). In films sequentially doped with a 5 mM FeCl_3 concentration and no LiTFSI present, $63 \pm 3\%$ of the polymer sites are doped ($\Theta = 0.63 \pm 0.03$). As the LiTFSI concentration increases to 100 mM at a constant 5 mM FeCl_3 concentration, the doping level increases to 75% ($\Theta = 0.75 \pm 0.04$).

To determine the equilibrium coefficients K_I and K_{II} , we derive a generalized anion exchange isotherm (eq 3) in terms of known quantities. This model represents the fraction of doped sites over total sites (Θ) for a polymer undergoing charge transfer with a molecular dopant, followed by a subsequent exchange of anions with a monovalent electrolyte. Further description of the extracted Θ and isotherm

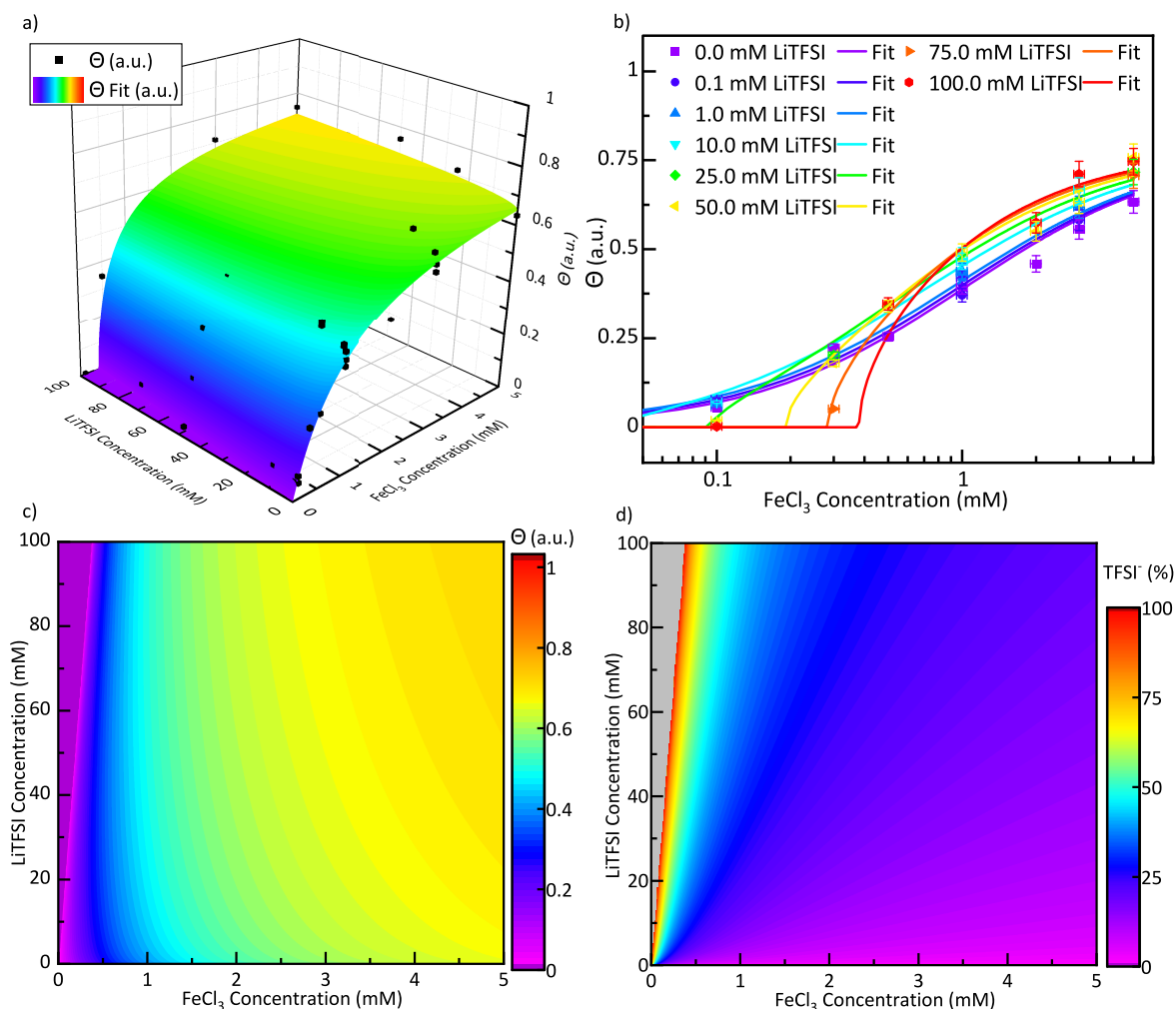


Figure 2. (a) 3D and (b) 2D scatter plots of Θ extracted from UV–vis–NIR and the corresponding anion exchange isotherm fit; (c) shows the Θ fit contour with respect to the prepared FeCl_3 and LiTFSI concentrations, and (d) depicts the percentage of doped P3HT sites with TFSI^- anions. The gray region in (d) corresponds to the range in which no P3HT sites are doped.

parameters are in Supporting Information Section S6. The isotherm derivation is in the Supporting Information eqs S3–S25.

$$\Theta = S \frac{K_1([D] - w[C^+A^-]) + \frac{K_1 K_{II}([D] - w[C^+A^-])([C^+A^-] - w[C^+A^-])}{\Theta_c^0 - K_1([D] - w[C^+A^-])(1 - \Theta)c_t^0}}{1 + K_1([D] - w[C^+A^-]) + \frac{K_1 K_{II}([D] - w[C^+A^-])([C^+A^-] - w[C^+A^-])}{\Theta_c^0 - K_1([D] - w[C^+A^-])(1 - \Theta)c_t^0}} \quad (3)$$

The anion exchange isotherm was fit to the concentration dependent data.^{19,20} The best fit is shown in Figure 2a,b, with residuals displayed in Figure S13. The extracted K_I and K_{II} are 971 ± 85 and $0.2 \pm 0.06 \text{ M}^{-1}$ corresponding to ΔG_I° and ΔG_{II}° of -0.177 ± 0.002 and $0.04 \pm 0.007 \text{ eV}$, respectively. As expected, charge transfer between FeCl_3 and P3HT is spontaneous. At room temperature, the anion exchange process is nonspontaneous, but a new equilibrium is established between FeCl_3^- and LiTFSI^- counterions. Figure 2c shows the contour of the anion exchange isotherm fit. Θ reduces to zero at low FeCl_3 and high LiTFSI concentrations, because the water contamination ($w = 0.0038 \pm 2.3 \times 10^{-4}$) exceeds the prepared FeCl_3 concentration. At the maximum combined dopant/electrolyte concentrations of 5 mM FeCl_3 and 100 mM LiTFSI, the calculated Θ approaches a saturation doping level of 79%, meaning that $\sim 20\%$ of the neutral P3HT

sites cannot be sequentially doped, likely due to disordered dihedral bends along the polymer backbone and/or excluded volume interactions at the substrate or air interfaces. The percent of doped sites occupied by TFSI^- is shown in Figure 2d. Interestingly, in films exposed to 100 mM LiTFSI solutions, the percent of sites with TFSI^- anions remains below $\sim 50\%$ for all FeCl_3 concentrations above $\sim 1 \text{ mM}$. At 1 mM FeCl_3 and 100 mM LiTFSI, approximately half of the doped sites are occupied by TFSI^- .

Figure S18 demonstrates that AED can be used to effectively dope SPs with a relatively weak chemical potential for doping. We tested this prediction by attempting the doping of PDPP-2T with FeCl_3 in the presence of LiTFSI. PDPP-2T has a higher IE ($\text{IE}^{\text{CV}} = 5.4 \text{ eV}$)²¹ than P3HT ($\text{IE}^{\text{CV}} = 5.0 \text{ eV}$), reducing the chemical potential for doping with FeCl_3 . As a result, doping PDPP-2T with FeCl_3 yields low doping efficiency. Figure 3(a) shows raw unnormalized UV–vis–NIR of $80 \pm 5 \text{ nm}$ thick PDPP-2T films sequentially doped at room temperature with 0.5, 1, and 5 mM FeCl_3 solutions. As the doping level is increased, the neutral vibronic (0–0) and (0–1) transitions at 1.3 and 1.5 eV slightly bleach, and polaron transitions P1, P2, and P3 grow in at 0.33, 0.75, and 0.98 eV. An unknown feature grows in with increasing FeCl_3 concentration at 1.13 eV; this is discussed in Supporting

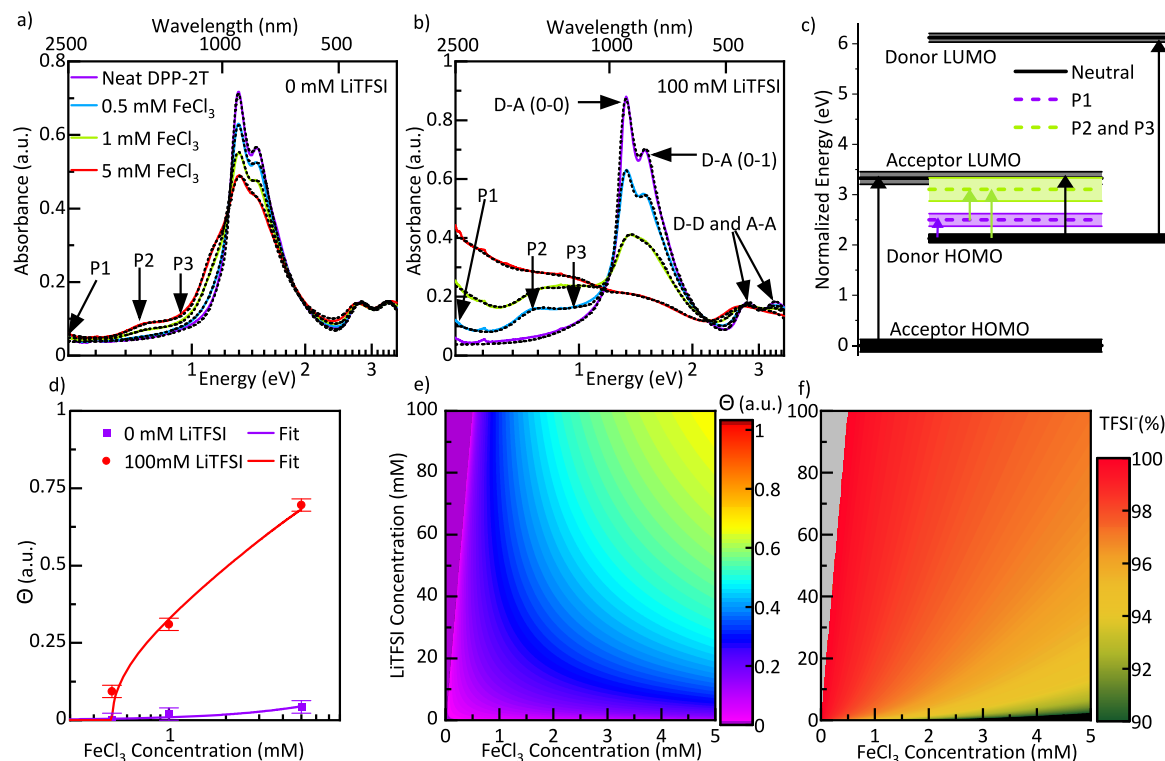


Figure 3. UV-vis-NIR absorption spectra of PDPP-2T films sequentially doped with varying FeCl_3 concentrations and either 0 (a) or 100 mM (b) of LiTFSI. All spectra are fit with with cumulative Gaussian fits (dashed lines) to determine state populations. (c) depicts energy transitions for p-doped alternating D/A copolymers. (d) depicts a 2D scatter plot of Θ extracted from the absorption data and the corresponding anion exchange isotherm fit. (e) shows fit Θ for PDPP-2T as a function of the FeCl_3 and LiTFSI concentrations, and (f) depicts the percentage of doped polymer sites with TFSI^- anions. The gray region in (f) corresponds to the range in which no polymer sites are doped.

Information Section S5. The two high energy D–D and A–A transitions at 2.8 and 3.3 eV mildly broaden. On the other hand, Figure 3(b) shows UV-vis-NIR of PDPP-2T films sequentially doped with the same 0.5, 1, and 5 mM FeCl_3 with the addition of 100 mM LiTFSI. The D–A (0–0) and (0–1) transitions bleach more significantly, and only the P1, P2, and P3 polaron transitions grow in. At the highest doping level, the high energy D–D and A–A transitions quench and broaden, with an increased red-shifted absorbance. Figure 3(c) depicts the corresponding energy transitions.

Discussion of the spectral and isotherm fitting of PDPP-2T is in Supporting Information Section S6.1. The cumulative fits are shown as the dashed line in Figure 3(a),(b). We calculate Θ from the absorption data (Figure 3(d)). As expected, with no LiTFSI present, the higher energetic barrier for charge transfer limits the doping efficiency, reaching a 4.3% doping level ($\theta = 0.043$) with a 5 mM FeCl_3 solution. However, in the presence of 100 mM LiTFSI, PDPP-2T reached a 70% doping level ($\theta = 0.70$) at 5 mM FeCl_3 . We fit Θ for the PDPP-2T samples with the anion exchange isotherm model (Figure 3(d), (e)). The extracted K_I and K_{II} are 9.41 ± 1.62 and $2.92 \pm 0.61 \text{ M}^{-1}$ corresponding to ΔG_I° and ΔG_{II}° of -0.058 ± 0.004 and $-0.028 \pm 0.005 \text{ eV}$, respectively. Unlike P3HT, PDPP-2T approaches a saturated doping level of $\sim 100\%$. Figure 3(f) shows the calculated % TFSI^- anions in the PDPP-2T film after AED. Unlike the P3HT sample, $>90\%$ of doped sites have exchanged FeCl_3^- with TFSI^- .

We performed four-point probe collinear sheet resistance measurements on P3HT films with respect to FeCl_3 concentration at various LiTFSI concentrations (Figure 4(a)). P3HT films doped with only FeCl_3 ranged in

conductivity from $0.066 \pm 0.002 \text{ S/cm}$ at 0.1 mM FeCl_3 up to $140 \pm 20 \text{ S/cm}$ at 5 mM FeCl_3 . Anion exchanged P3HT films doped with 0.1 mM FeCl_3 and 100 mM LiTFSI have the lowest conductivity at $\sim 10^{-3} \text{ S/cm}$, due to traces of water in LiTFSI. The presence of LiTFSI led to the largest enhancement in conductivity at 1 mM FeCl_3 , where the measured conductivity increased from $31 \pm 6 \text{ S/cm}$ at 0 mM LiTFSI to $80 \pm 6 \text{ S/cm}$ at 100 mM LiTFSI. For this sample, 43% of the P3HT^+ sites have TFSI^- and 57% have FeCl_3^- counterions. Discussion of conductivity enhancement is in Supporting Information Section S13.

Carrier density is proportional to the fraction of polymer sites that possess a hole (Θ). To estimate the hole density from Θ , we estimate the minimum site size, which we define as the minimum number of monomer units that can hold a hole state. For the PDPP-2T polymer, we assume that each monomer T-DPP-T is a single site. This assumption is justified by recent first-principle simulations of alternating copolymers.²² Using a film density of 1.1 g/cm^3 , we estimate a maximum hole density (p_{max}) of $8.2 \times 10^{20} \text{ holes/cm}^3$ for PDPP-2T. A 10% uncertainty in film mass density translates to a 10% uncertainty in maximum carrier density. For P3HT, we assume the minimum site size is a four thiophene (4T) monomer section and yields an estimated maximum hole density of $8.5 \times 10^{20} \text{ holes/cm}^3$, nearly identical to that of PDPP-2T. We recognize that more accurate estimates of the minimum site size and maximum carrier density will improve our model's predictive power. Discussion of carrier density is in Supporting Information Section S14.

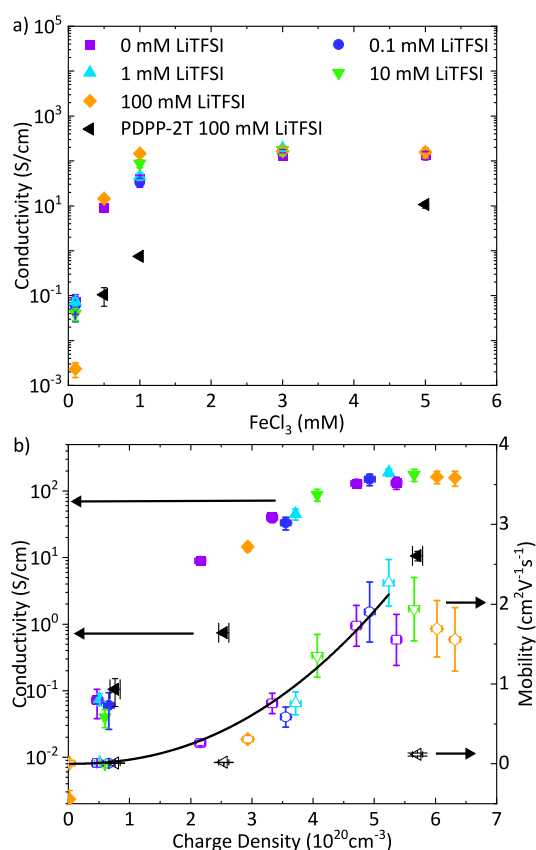


Figure 4. (a) Four-point probe conductivity of P3HT films with respect to FeCl₃ solution concentration at various LiTFSI concentrations, and one conductivity series of PDPPP-2T films with respect to FeCl₃ solution concentrations with 100 mM LiTFSI. (b) Conductivity (filled symbols) and mobility (empty symbols) as a function of charge density.

Scaling these maximum hole densities by the fraction of sites that are doped (Θ) allows us to compare film conductivity (σ) to hole density and estimate hole mobility (eq 4)

$$\mu = \frac{\sigma}{p_{\max} \Theta e} \quad (4)$$

where e is the elemental charge (Figure 4(b)). The P3HT hole mobility is fit to the variable range hopping model (VRHM) (Equation S27),^{23–25} where the prefactor for conductivity ($\sigma_0 = 1.6$ S/m), the effective overlap parameter between localized states ($\alpha^{-1} = 0.16$ nm), and the critical number for the onset of percolation ($B_c = 2.8$) are identical to those of previous P3HT mobility studies.^{23,26} Our sample has an increased width of the exponential density of states ($T_0 = 665$ K) compared to previous fits to P3HT. This analysis shows that μ_h increases with doping density until it saturates at 2.3 cm² V⁻¹ s⁻¹ at a doping density of $\sim 5 \times 10^{20}$ cm⁻³. At higher doping levels, μ_h deviates from the VRHM due to increased structural disorder induced by the presence of counterions.⁸

We were unable to measure the conductivity of the PDPPP-2T films doped with only FeCl₃, because it was below the detection limit of our equipment ($<10^{-3}$ S/cm). The conductivity of PDPPP-2T films anion exchange doped at 100 mM LiTFSI ranged from 0.1 ± 0.05 S/cm with 0.5 mM FeCl₃ up to 10.7 ± 1.8 S/cm with 5 mM FeCl₃ (Figure 4 (a)). IV curves are in Figure S22. The estimated hole density and mobility are in Figure 4(b). The estimated PDPPP-2T mobility

increased from 0.009 to 0.117 cm² V⁻¹ s⁻¹ at 0.5 mM and 5 mM FeCl₃, respectively.

In summary, we demonstrate sequential AED of P3HT and PDPPP-2T films with the dopant FeCl₃ and electrolyte LiTFSI. In P3HT, AED is nonspontaneous, and doping efficiency increases by 10 to 50% in the presence of LiTFSI. We demonstrate control over the exchange of FeCl₃⁻ for TFSI⁻ on P3HT⁺ sites between 0 and 100%. Sheet resistance measurements reveal record P3HT film conductivities of ~ 140 S/cm can be obtained at high FeCl₃ doping levels and remain the same in AED P3HT. In PDPPP-2T, AED is spontaneous, doping efficiency increases $>10\times$ in the presence of LiTFSI, and conductivity increases by >4 orders of magnitude. Therefore, AED enables high p-type doping efficiency in systems with low chemical potential for doping. Future research is needed on AED polymers to address the effects that anion exchange has on polaron delocalization, the stability of doping density in the presence of external stimuli, and how anion exchange affects the polymer film morphology.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcclett.0c03620>.

Molecular Structure of Materials, Experimental Methods, PDPPP-2T Synthesis, UV–vis–NIR Full Gaussian Fits, PDPPP-2T FeCl₃ Absorption Discussion, Fractional Doping Level (Θ) and Isotherm Fitting, Discussion of ΔG° , P3HT Anion Exchange (Assuming one monomer site), Anion Exchange Isotherm Site Size Comparison, Discussion of Θ : Is $\Theta \propto P1$ or $\propto \sum(P1, P2, P3)$?, Anion Exchange Simulations, Extra UV–vis–NIR Tests, Sheet Resistance IV Curves and Discussion of Conductivity Enhancements, Discussion of Carrier Density, X-ray Photoelectron Spectroscopy (PDF)

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Notes

The authors declare no competing financial interest.

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