

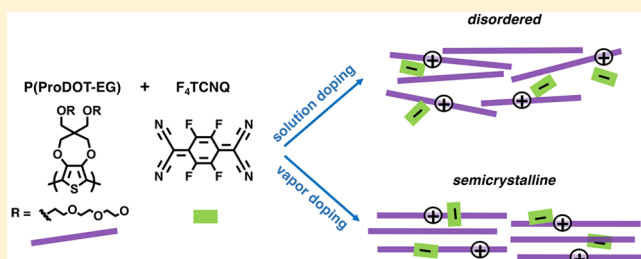
Nonaggregating Doped Polymers Based on Poly(3,4-Propylenedioxythiophene)

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Supporting Information

ABSTRACT: Electrical doping of organic semiconductors is critical for their use in electrical devices. However, many high-performance semiconductors exhibit drastically reduced solubilities when doped in solution, making it difficult to deconvolute the roles of doping and morphological changes on their electrical properties. Here, we report the synthesis of a semiconducting polymer based on poly(3,4-propylenedioxythiophene) (ProDOT) substituted with oligo(ethylene glycol) (EG) side chains that is designed to solvate dopant molecules. When doped with F₄TCNQ in solution, the polymer P(ProDOT-EG) undergoes efficient charge transfer while remaining soluble with no indication of aggregation. The electrical conductivity of thin films cast from heavily doped solutions is ~1 S/cm; optical spectroscopy reveals that the doping efficiency is reduced upon formation of the solid film. Diffusion of F₄TCNQ from the vapor phase into films of neutral P(ProDOT-EG) yields comparable conductivities to films cast from doped solutions. Absorption spectroscopy and X-ray diffraction of doped films reveal that the doping efficiency and nature of charge carriers (polaron or bipolaron) are strongly affected by the processing route. The lack of the localized polaron signature for films doped by infiltration of the dopant from the vapor phase indicates that morphology has a large role in determining the nature of the charge carriers in semiconducting polymers.



INTRODUCTION

Doping semiconducting polymers is critical for controlling their electrical conductivity, filling trap states that impede transport in transistors, and tuning the alignment of transport states at interfaces in organic electronic devices.^{1,2} The charge carriers in doped polymers must be compensated by a species with the opposite charge, which is often an ionized derivative of the dopant. The introduction of charge on the backbone of semiconducting polymers stiffens them and changes the solvent quality, leading to precipitation. In the solid state, the counterion to the charged backbone of the polymer can sometimes disrupt the molecular ordering that aids charge transport. Designing semiconducting polymers to incorporate dopants while maintaining both solution processability and high electrical conductivity remains challenging.

We present here the results of an investigation into the electrical conductivity and processability of a derivative of poly(3,4-propylenedioxythiophene) (PProDOT). The addition of oligo(ethylene glycol) side chains improves the solubility of the polymer in both neutral and doped forms. This design allowed us to compare two common processing routes to dope semiconducting polymers without the complicating role of aggregation in solution.

Semiconducting polymers are oxidized or reduced with dopants to increase their electrical conductivity.¹ Dopants for both *p*-type¹ and *n*-type conduction^{2,3,4} have been developed

and operate by similar mechanisms. Electrical doping of semiconducting polymers can be achieved using molecular charge transfer dopants that donate electrons to the polymer (reduction) or accept electrons from the polymer (oxidation). In this case the counterion to the charge carrier on the polymer backbone is the dopant itself. There can be either integer charge transfer (ICT) or partial charge transfer leading to a charge transfer complex (CTC) between the molecular dopant and polymer.⁵ For *p*-type polymers, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) is a widely used dopant because of its favorable electron affinity for charge transfer from a wide range of semiconducting polymers and its stability in the reduced state.^{6–12} Another doping route relies on dopants that undergo electron transfer with the semiconducting polymer and change composition. For example, the charge transfer reaction of NO⁺PF₆[−] with semiconducting polymers liberates NO gas, leaving PF₆[−] as the counterion to the charge carrier.¹³ In either case, a counterion must be incorporated in the solid polymer to balance the charge carrier on the backbone.

The method by which a dopant is introduced into a semiconducting polymer plays a critical role in determining the

Received: November 7, 2018

Revised: January 27, 2019

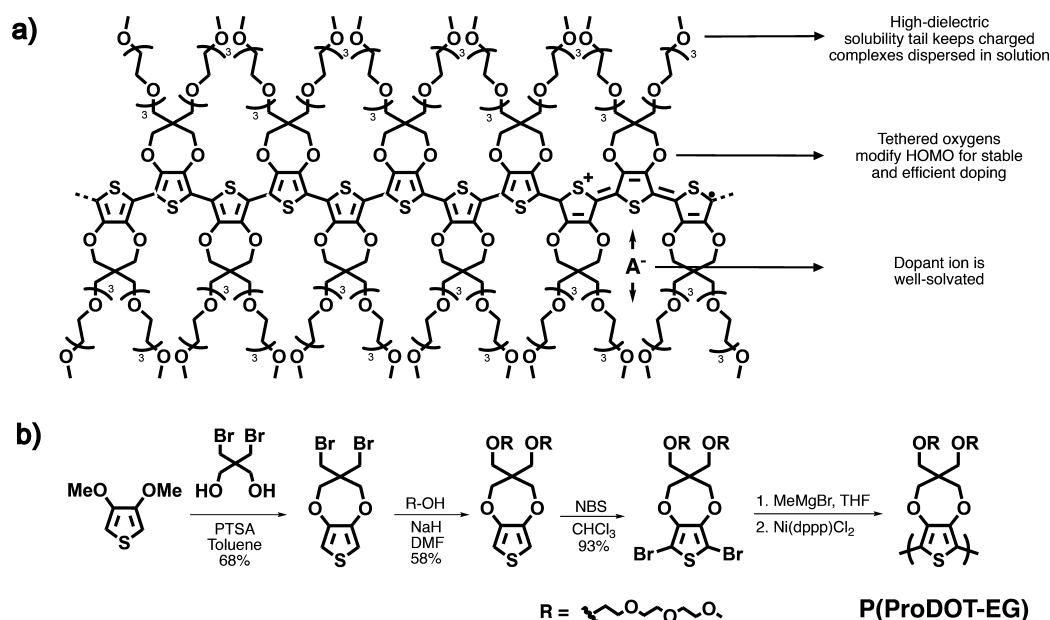


Figure 1. (a) Schematic illustrating chemical structure and system design choices for P(ProDOT-EG). (b) Synthesis of P(ProDOT-EG).

efficacy of doping by charge transfer. Sequential doping, in which a polymer film is cast in its neutral form and then exposed to a vapor of the dopant or a solution of the dopant,^{10,12,14} tends to lead to higher electrical conductivities than solution doping, in which polymers are doped in solution prior to casting.^{8,11,12,14–17} The origin of this difference has been attributed to precipitation and/or aggregation^{1,11,14,18–21} during oxidation of the polymer in solution due to changes in the solvent quality for the charged polymer. To prevent precipitation and to enable casting films, solutions of doped polymers are frequently kept at high temperatures and dilute concentrations.^{14,21} Casting doped solutions leads to morphologies in films that exhibit low effective carrier mobilities even at relatively high carrier concentration. In contrast, casting from the neutral form allows the polymer film to maintain the morphology that allows for effective charge transport, such as local orientational alignment of ordered domains.²² In materials such as poly(3-hexylthiophene) (P3HT) and the thienothiophene-based polymer PBTBT, the observance of the Hall effect in sequentially processed films attests to their higher electronic quality than solution-doped films.^{12,17,23}

The influence of aggregation in solution on the resulting electrical conductivity in thin films has been most widely studied using regioregular and regiorandom P3HT.^{1,11,18,24} Reducing aggregation of P3HT in solution has been shown to improve the morphology and conductivity of the cast films.^{12,14,19} At the same time, aggregation in solution can be an important condition to efficient doping.¹¹ The conjugation length of well-solvated P3HT is low due to its flexible backbone, thereby increasing its ionization energy relative to that of its aggregated form. As a result, aggregated solutions of regioregular P3HT show effective doping from F₄TCNQ whereas solutions of less ordered regiorandom P3HT do not.^{18,11} These studies suggest that delicate optimization is needed for solution doping: too little aggregation and the polymer chains will not undergo efficient electron transfer in solution, whereas with too much aggregation and the polymer chains will form inhomogeneities in cast films. The detailed

role of aggregation is still not well understood in P3HT, particularly with the recent observation of the formation of charge transfer states with F₄TCNQ in the solid state rather than integer charge transfer by changing the casting conditions.²⁵

PProDOT is an especially soluble substituted polythiophene with efficient and stable doping in solution,^{26–31} which makes it ideal for understanding the relative roles of aggregation and doping in solution on electrical conductivity. PProDOT is similar to the highly conductive poly(3,4-ethylenedioxythiophene) (PEDOT) system. The cyclic dialkoxy group attaches to the 3- and 4-positions of the thiophene monomer in PEDOT, allowing high intrachain order in the solid state and adding electron density to reduce the ionization energy for doping.^{27,30,32,33} However, in PProDOT an extra carbon in the dialkoxy ring attached to thiophene allows for symmetric and orthogonal substitution of two side chains per monomer, which increases its solubility without disrupting the intrachain order.^{29–31,34} Since its inception, the ProDOT system has been demonstrated to be adaptable to a wide variety of polymerization chemistries³⁵ and side-chain motifs,^{26,29,30,36} with promising conductivities in ambient settings.³¹ While these exceptionally processable polythiophenes have been widely used in electrochromic and electrochemical settings, they have not been employed to investigate the consequences of processing methods on the conductivity of thin films.

Herein, we report a soluble ProDOT derivative with relatively polar side chains that undergoes complete oxidative doping in solution without any aggregation. The lack of aggregation upon doping allows us to gain information about the conjugation length of doped chains in solution and how the structural ordering in the solid state is affected by the method used to introduce the dopant F₄TCNQ. We find that this polymer has an electrical conductivity of ~1 S/cm when doped in solution prior to casting or when dopants are infiltrated after casting. Surprisingly, the introduction of dopants induces structural order in vapor-doped films and leads to a different balance of the type of charge carriers,

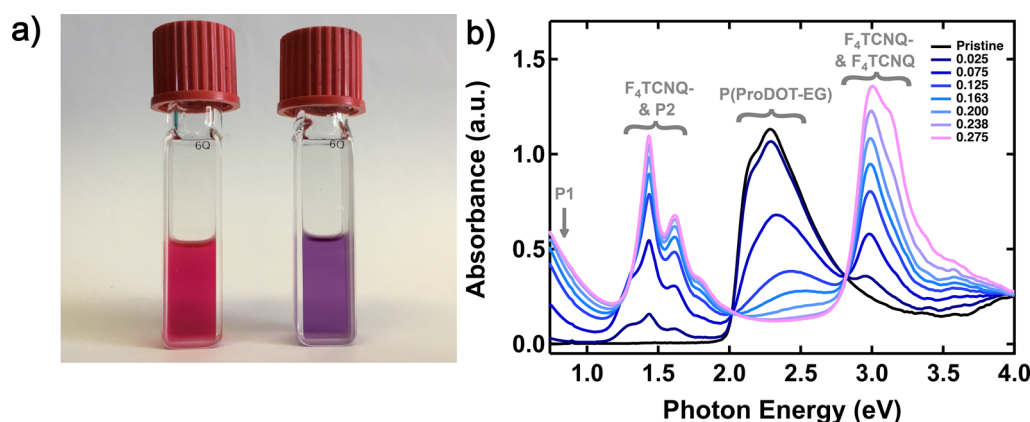


Figure 2. (a) Photograph of P(ProDOT-EG) in DCE (left) and methanol (right) at a concentration of 0.05 mg/mL showing solvatochromism. (b) UV-vis-NIR solution spectra of P(ProDOT-EG) in DCE at 0.05 mg/mL, with varying amounts of F₄TCNQ per monomer subunit of polymer. The spectra show complete oxidative doping via the bleaching of the polymer peak at 2.3 eV.

providing a means to understand the role of structural ordering in their formation.

RESULTS

System Design and Synthesis. To better understand the role of processing on the electrical conductivity of semi-conducting polymers, we designed a polymer that allowed for high levels of doping while maintaining stability and solubility (Figure 1a). Polythiophene was selected as the backbone and was modified to tune its electronic structure and solubility. First, oxygen-containing propylene rings were tethered directly to the thiophene rings to lower the ionization energy and facilitate doping experiments; ProDOT-based polymers are relatively stable when doped and show reversible electrochemical doping to high levels.^{26–28} Then, the propylene rings were substituted with oligo(ethylene glycol) (EG) side chains to keep the charged polymer in solution at high concentrations.³⁷ While EG-based systems are widely used to solvate cations,^{38–40} anionic dopants/counterions should be better solvated by these polar side chains than alkyl substituents, preventing ionic aggregates in solution.^{37,41} The polymer, denoted P(ProDOT-EG), was synthesized by adapting procedures detailed in the literature to prepare the brominated ProDOT-EG monomer and subsequently polymerize it via Grignard metathesis (Figure 1b).^{30,31} Details of the synthetic procedure and characterization of intermediates and final product are given in the Supporting Information. The synthetic procedure yielded ProDOT-EG with a polystyrene-equivalent molecular weight $M_n = 16.6$ kDa with a polydispersity of 1.6 (see the Supporting Information for details of the synthesis and NMR spectra of the precursors and polymer, Figures S1–S6).

Optical Spectroscopy Shows Solubility of Neutral and Doped P(ProDOT-EG). P(ProDOT-EG) is soluble in neutral form in a wide variety of solvents without aggregation. The polymer dissolves in both nonpolar solvents (toluene, benzene, chlorobenzene, dichloromethane, and chloroform) and polar solvents (THF, ethyl acetate, acetonitrile, and methanol) at concentrations of 10 mg/mL. It is also soluble in dichloroethane without any visible sign of precipitation, allowing doping in solution with F₄TCNQ (*vide infra*). The color of solutions of the polymer shows a solvatochromic effect (Figure 2a), suggesting strong chain-solvent interactions. Ultraviolet-visible-near-infrared (UV-vis-NIR) absorption

spectroscopy of the polymer in solution verifies this solvatochromism and reveals changes in the vibronic progression in the spectra as the solvent becomes more polar (Figure S8).⁴² In the most polar solvent employed, methanol, P(ProDOT-EG) shows the strongest vibronic character in conjunction with a bathochromic shift by ~90 meV. To confirm that the vibronic peaks were not due to aggregation, the absorbance was measured after serial dilution (Figure S9).⁴³ The spectral features and extinction coefficient remained constant with increasing dilution, verifying that the vibronic character was not due to aggregation (Figure S10). This vibronic and solvatochromic character is not observed in well-solvated poly(alkylthiophenes) that usually show a single solvent-independent broad peak for the polymer $\pi-\pi^*$ transition. In contrast, PProDOT and PEDOT analogues with long side chains do show vibronic peaks. These spectral features indicate that P(ProDOT-EG) adopts a more planar conformation leading to longer conjugation lengths aided by interactions with polar solvents.^{29,34,40,44,45}

The conjugation length of P(ProDOT-EG) in solution can be estimated to at least 12 subunits by comparison to ProDOT oligomers. Soluble ProDOT oligomers have progressively lower absorption edges with increasing number of subunits with the 12-mer showing a similar value of 2.0 eV.⁴⁶ The conjugation length can be roughly estimated from the absorption edge and is comparable to values of 10–20 typically estimated for polythiophenes.⁴⁷ This behavior likely proceeds from both solvent and intramolecular S–O interactions that promote longer conjugation lengths.^{32,41} Therefore, unlike sterically hindered polythiophenes that avoid aggregation by adopting nonplanar conformations,^{42,43} P(ProDOT-EG) avoids aggregation through strong chain-solvent interactions while maintaining a more planar conformation which will impact the efficacy of doping in solution.^{42,43}

P(ProDOT-EG) can be oxidatively doped in solution to the fully charged state without aggregation. Figure 2b shows the UV-vis-NIR absorbance taken in dichloroethane (DCE) of P(ProDOT-EG) doped with increasing molar equivalents of F₄TCNQ.^{8,10–12,14–16,18} The bleaching of the absorption of the neutral polymer (2.3 eV) with increasing concentration of F₄TCNQ occurs simultaneously with the growth in intensity of the absorption of the P(ProDOT-EG) cation (1.2–1.8 eV and monotonic increase below 1 eV)^{13,31,46,48} and the growth of the absorption of the anion of F₄TCNQ (1.4, 1.6, and 3.0

eV).^{8,15} There is an isosbestic point at 2.0 eV that indicates that the neutral polymer is converted directly to the oxidized form by F₄TCNQ. The appearance of the F₄TCNQ anion indicates efficient integer charge transfer (ICT) between the two compounds. Remarkably, oxidative doping can be taken to completion without aggregation—the absorption of the neutral polymer is completely bleached after adding 0.28 mol equiv of F₄TCNQ. Above this concentration, the peaks for the anion of F₄TCNQ at 1.4 and 1.6 eV no longer increase, signifying that additional F₄TCNQ is not further oxidizing the polymer. This clear observation of complete oxidation of the backbone is not observed with many semiconducting polymers.^{6,11,21,49} For example, solutions of P3HT:F₄TCNQ show a peak near ~2.0 eV assigned to aggregates of the polymer that can obscure the change in the neutral absorbance.^{15,37} Because of the solubility of P(ProDOT-EG) in DCE even when highly oxidized (at polymer concentrations of 12 mg/mL), there is no spectral signature of aggregation of the polymer.

Aggregation in solution is not necessarily a prerequisite for efficient doping of polythiophenes if the conjugation length is long enough to promote charge transfer. ICT commonly occurs in poly(alkylthiophenes) that aggregate upon doping; for example, well-solvated regiorandom P3HT does not undergo the efficient doping observed in solution for regioregular P3HT.¹⁸ We nonetheless observe highly efficient doping of P(ProDOT-EG) with F₄TCNQ, even in the absence of aggregation. Cyclic voltammetry gives estimated ionization energy (IE) for P(ProDOT-EG) (4.8 eV) in solution that is also consistent with the energetics for ICT (Figure S11). This lower IE is consistent with previous reports of ProDOT polymers with low oxidation potentials³⁰ and likely proceeds from the intramolecular S–O interactions that promote longer conjugation lengths.⁵⁰ Thus, because P(ProDOT-EG) already exhibits long conjugation lengths in solution, aggregation is not required to lower the ionization energies for ICT. For comparison, the value for well-solvated P3HT can be estimated to be ~5.3 to 5.4 eV, and P3HT cannot undergo ICT in the absence of aggregation that increases its conjugation length.²⁴ Finally, the favorable solubility of P(ProDOT-EG)⁺:F₄TCNQ[−] relative to P3HT⁺:F₄TCNQ[−] may also drive the reaction equilibrium toward the doped state,¹¹ consistent with observations for more soluble analogues of F₄TCNQ.⁷

The doping efficiency of P(ProDOT-EG) decreases at higher concentrations of F₄TCNQ. The doping level was determined by the molar ratio of F₄TCNQ[−] to P(ProDOT-EG) repeat units (Figure 2b; see the Supporting Information and Figures S12 and S13). The addition of F₄TCNQ after the absorption of the neutral polymer is fully bleached does not lead to significant increases in the concentration of F₄TCNQ[−] (Table S1). By comparing the doping level to the equivalents of dopant added, we find that the efficiency of charge transfer remains at ~70% until a loading of 0.125, after which it begins to fall (Table S1). This fall in efficiency can also be confirmed in the spectra in Figure 2b, based on the growth of the neutral F₄TCNQ peak (3.2 eV),⁸ which becomes more prominent at higher dopant concentrations. These results are consistent with previous reports on alkyl- and EG-substituted polythiophene/F₄TCNQ systems showing reduced efficiency of charge transfer at higher equivalents of dopant.^{11,37}

The number of carriers on the backbone of P(ProDOT-EG) at the highest levels is consistent with the longer conjugation lengths observed for this polymer. The neutral absorption of the polymer is bleached above addition of 0.24 equiv of

F₄TCNQ per monomer subunit, and the corresponding doping level is ≈0.11, or 1 F₄TCNQ anion per 9 ± 1 thiophene units (Table S1). This result indicates that charge carriers can occupy up to 8–10 subunits along the P(ProDOT-EG) backbone and is consistent with the estimated conjugation length of the neutral species. For comparison, when P3HT is doped in solution with F₄TCNQ at ratios of 4–6 per monomer, the neutral absorbance is not fully bleached.¹⁵ While such a ratio is consistent with theory that suggests localization of the charge transfer complex,⁵¹ the presence of aggregated and solvated P3HT makes it difficult to determine if the residual absorption is due to one population or the other. Here the longer conjugation length of P(ProDOT-EG) likely allows the charge carrier to spread over more repeat units on the backbone.

The spectral features of the P(ProDOT-EG) suggest a large population of singly oxidized subunits (polarons) with a minor shift toward bipolarons at higher doping levels. Upon doping, the absorption spectrum has features between 1.2 and 1.8 eV that overlap the F₄TCNQ anion peaks as well as a monotonic increasing absorbance below 1 eV. We denote the lower energy feature as P1 and the higher energy feature as P2, in accordance with assignments in previous literature.¹ To compare the intensities between these features, the absorbance of F₄TCNQ[−] was subtracted from the P2 region (Figure S13), leaving behind a peak shape very similar to previous reports of oxidized PProDOT.^{26,31} Assigning these spectral features to specific charge carriers is challenging because polarons (i.e., ProDOT⁺) and bipolarons (i.e., ProDOT²⁺) in polythiophenes have both been assigned to energies near the P1 and P2 features,^{13,48,52} and the interpretation of these assignments is still discussed.^{15,53} We can compare the spectra of P(ProDOT-EG) with literature data for ProDOT oligomers where the redox state was systematically varied. Oxidation of a ProDOT 12-mer, which is at a similar conjugation length as P(ProDOT-EG), to the +1 state showed a prominent spectral feature near 1.4 eV with a weak feature into lower energies.⁴⁶ Further oxidation of the 12-mer to the +2 state showed an absence of the 1.4 eV feature and a broader red-shifted peak at 0.6 eV. Progressive electrochemical doping of ProDOT polymers yields similar features.^{26,27,31} Based on these systems, the spectral features of P(ProDOT-EG) are consistent with a large population of ProDOT¹⁺ with a small fraction of ProDOT²⁺. When comparing the intensity of P1 to P2 (Table S2), we see an increasing intensity ratio as the dopant loading is increased (from 0.9 to 1.9 as the number of equivalents of F₄TCNQ changes from 0.025 to 0.24), confirming a shift in oxidation state toward ProDOT²⁺. We therefore propose that the charge carriers on P(ProDOT-EG) chains in solution are primarily composed of polarons, with a small fraction of bipolarons that increases with dopant loading.

It is important to point out that the solubility of P(ProDOT-EG) allows for the detailed analysis of the changes in spectral features with oxidation. For comparison, previous reports with P3HT doped with F₄TCNQ show a heterogeneous mixture of aggregates and dissolved polymer that both obfuscate the absorption spectra and prevent such definitive examinations of oxidation states and charge carrier sizes, especially at doping saturation. In contrast, the spectra of P(ProDOT-EG) unambiguously display complete bleaching of the main absorption of well-dispersed, homogeneous polymer chains.

Electrical Conductivity of Films Cast from Doped Solutions. P(ProDOT-EG) does not aggregate or precipitate

from doped solutions. Aggregation and precipitation in solution have been observed to lead to inhomogeneities in films of polymers cast at high doping levels and polymer concentrations above $\sim 1\text{--}2$ mg/mL.^{12,16,21} After the concentration of the P(ProDOT-EG) solutions in DCE was increased to 10 mg/mL for casting, there was no precipitation even at high doping levels of F₄TCNQ allowing casting of homogeneous films (Figure 3). We are not aware of similar

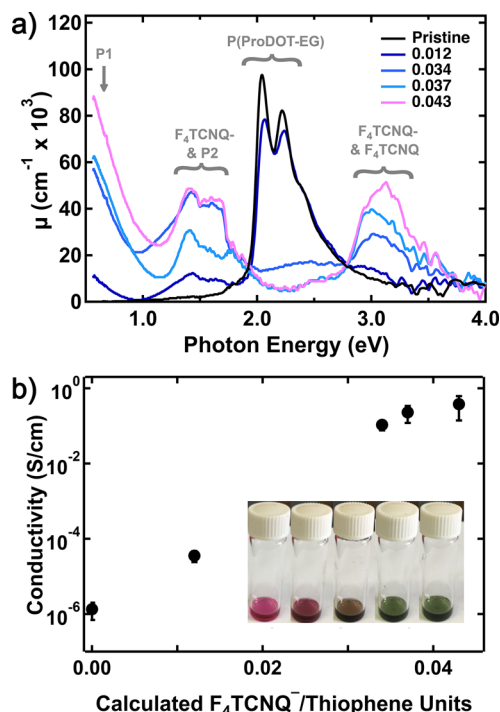


Figure 3. (a) UV-vis-NIR spectra of thin films cast from solutions of P(ProDOT-EG) at 10 mg/mL mixed with various molar equivalents of F₄TCNQ per monomer subunit prior to casting; each spectrum is labeled with the doping level calculated based on F₄TCNQ⁻ absorbance near 1.4 eV (section VI of the Supporting Information). The absorbance of the neutral polymer between 2 and 3 eV is bleached with increasing concentration of dopant. (b) Electrical conductivity of thin films as a function of calculated doping level in DCE. The inset shows photographs of the solutions corresponding to the doping levels measured. Error bars indicate 1 standard deviation from triplicate measurements; the error in the ratio of F₄TCNQ⁻/thiophene units is similar to the size of the symbol in the plot.

observations for polythiophenes at such concentrations—even short EG-substituted polythiophenes show precipitation after a dopant loading of 0.10 as well as an aggregation peak in the UV-vis spectra at more dilute concentrations.³⁷

Thin films formed from doped solutions exhibit a reduction in doping efficiency and a shift in the dominant charge carrier. The absorption edge of the neat thin film has a small red-shift of ~ 90 meV relative to the solution and a pronounced vibronic structure, characteristic of solution-state to solid-state phase transitions of conjugated polymers. Doped solutions of P(ProDOT-EG) were cast into films after adding various concentrations of F₄TCNQ (Figure 3). Analysis of the absorbance of doped P(ProDOT-EG) films reveals a lower doping efficiency relative to the solutions (Figure 3a and Table S3) and a similarly decreasing efficiency with increasing dopant loading. This trend is consistent with previous reports of EG-substituted polythiophenes doped with F₄TCNQ.⁵⁷ The lower

efficiency in the solution-doped film is further verified by the strong absorbance of neutral F₄TCNQ that remains after subtracting the spectrum of F₄TCNQ⁻ from the spectrum of the doped film (see Figure S12). For example, in films cast from solutions with 0.18 equiv of F₄TCNQ, the residual neutral F₄TCNQ peak ($\epsilon = 56000$ L mol⁻¹ cm⁻¹)¹² indicates that the concentration of neutral is more than 3 times higher than that of the anion (Table S3). We note that an exact concentration of neutral F₄TCNQ is difficult to calculate because residual neutral F₄TCNQ is present in the solid-state spectrum of F₄TCNQ⁻ used for the subtraction.⁵⁴ The UV-vis-NIR absorbance (Figure 3a) of the films also exhibits a much higher P1:P2 ratio compared to the solution spectra, suggesting a relative shift in the electronic structure of charge carriers during film formation. This increased P1:P2 ratio, despite a lower doping level, could arise from a change in chain conformation to longer conjugation lengths during film formation or an increased proximity of charged and neutral polymer chains to each other in the solid state.^{53,55} Furthermore, the significant changes in the P1:P2 ratio occur as the concentration of F₄TCNQ in the casting solution changes, for example, when comparing the 0.034 to 0.037 doping level (Figure 3a).

The conductivity of solution-doped P(ProDOT-EG) thin films (thicknesses 30–70 nm) increased with increasing concentration of F₄TCNQ as expected. The maximum conductivity of 0.6 S/cm was reached at a loading of 0.25 equiv of F₄TCNQ per thiophene subunit (Figure 3b and Table S3). The carrier mobility at the highest carrier concentration (estimated from the concentration of F₄TCNQ⁻) for P(ProDOT-EG) is ~ 0.2 cm²/(V s). The conductivity is lower than that reported for P3HT/F₄TCNQ solution-doped films in the literature cast under varying conditions from solvent (~ 1 to 10 S/cm).^{10,11,12,14,19} The carrier concentrations of doped P(ProDOT-EG) films (Table S3) are lower by a factor of 5–10 compared to literature values for P3HT/F₄TCNQ, which have some variation with the method of analysis.^{8,10,15} Our results suggest that aggregation in solution alone is not the only limiting factor for the electrical conductivities of solution-doped polythiophenes. The decreased doping efficiency (and therefore higher concentration of neutral F₄TCNQ) in the film state and changes in chain shape/charge-carrier types may be more critical factors.

The solubility of oxidized P(ProDOT-EG) does help to avoid the sharp drop in electrical conductivity with increasing charge concentration observed in many polymers due to precipitation and inhomogeneities.^{11,56,57} For comparison, the trend in conductivity for P(ProDOT-EG) systems with dopant loading is markedly different from the most widely studied polymer P3HT. The conductivity of solution-doped P3HT:F₄TCNQ sharply increases up to 0.18 mol equiv and then drops precipitously at higher concentrations,^{7,11} attributed to aggregation in solution that leads to heterogeneity in the cast films. Here, the conductivity of films of P(ProDOT-EG) increases linearly after the sharp enhancement in conductivity between 0 and 0.11 equiv of F₄TCNQ per monomer subunit. We attribute this difference to the increased solubility of P(ProDOT-EG)⁺ and F₄TCNQ⁻ relative to P3HT. These results complement recent reports whereby increasing the solubility of substituted tetracyanoquinodimethane-based dopants allows further conductivity gains from doping past $\sim 18\%$.⁷ The favorable interactions of P(ProDOT-EG) and F₄TCNQ are further supported by the

fact that no changes are observed when the doped films were heated at 130 °C for 2 h, a treatment which is known to remove F₄TCNQ from films of P3HT but not EG-substituted polythiophenes.³⁷ Without aggregation, we thus observe the expected conductivity trend for doped organic semiconductors: at low dopant concentrations the filling of traps leads to large gains in mobility and conductivity, while at higher concentrations the mobility remains constant leading to relatively linear gain in conductivity with increasing carrier concentration.

Once the neutral polymer has been initially bleached, further doping mainly changes the distribution of charge carriers and does not lead to significant increases in the carrier mobility. The absorption of the neutral polymer in the films is significantly bleached relative to that of the solutions at 0.11 equiv (Figure 3a), and calculated doping levels do not substantially increase past this point (Table S3). The absence of absorbance of the neutral polymer, coupled with the lower doping levels relative to the doped solutions, suggests that removal of solvent changes the population of carriers. Because we expect the polymer chain to extend in the solid state, this difference could be due to an increased conjugation length in the solid, consistent with the increased P1:P2 ratio noted above. Further increases in the concentration of F₄TCNQ do not lead to any significant reduction of the π - π^* absorption of the polymer and mainly lead to changes in the distribution of charge carriers, based on changes in the P1:P2 absorption ratio.^{13,15,31,46,48}

Electrical Conductivity of Vapor-Doped Films. While the high solubility of P(ProDOT-EG) allows for processing of the doped polymer from solvent, it is difficult to know if the resulting morphology revealed the limit of electrical conductivity. Sequential doping from solution, i.e., casting a dopant from a solvent onto a solid film using a nonsolvent for the polymer, was not possible because of the high solubility of P(ProDOT-EG).¹² P(ProDOT-EG) films exposed to a vapor of F₄TCNQ in a sealed vessel for various time durations showed ICT. As the film is exposed to F₄TCNQ vapor for longer times, the pristine polymer peak becomes fully bleached and the neutral F₄TCNQ peak becomes prominent (Figure 4a). The bleaching of the absorbance of neutral polymer chains in the solid state is a result of diffusion into the film leading to well-solvated F₄TCNQ⁻ in the polar side chains of the P(ProDOT-EG). Again, the full bleaching of the neutral absorbance is unusual compared to other *p*-type polymers, such as P3HT and PBTTT,^{10,17,23,58} that have a residual absorption near the neutral peak after doping with F₄TCNQ.

The electrical conductivity of P(ProDOT-EG) doped with F₄TCNQ introduced from the vapor phase is similar to solution-doped films. Similar to solution-doped films, vapor-doped films show increases in conductivity by over 6 orders of magnitude relative to the pristine state (Figure 4b). However, the maximum conductivity of 0.8 S/cm occurs at a doping level that is a factor of ~ 1.2 lower based on the concentration of F₄TCNQ⁻ extracted from the respective spectra (Tables S3 and S4).⁸ The estimated charge carrier mobility is ~ 0.8 cm²/(V s), similar to values observed for heavily doped P3HT.⁵⁹ These values are at the limit of the differences in standard error of the two doping methods suggesting that both routes lead to comparable values. This result contrasts that of PBTTT where $\sim 100\times$ increases in electrical conductivity with vapor doping are observed^{17,22} and P3HT where $\sim 10\times$ differences have been reported.¹⁰ The different behavior for P(ProDOT-EG)

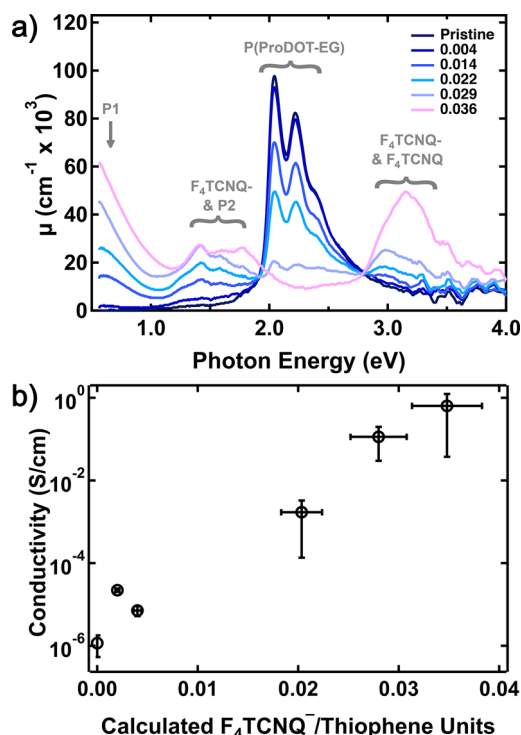


Figure 4. (a) UV-vis-NIR spectra of films of P(ProDOT-EG) exposed to F₄TCNQ vapor for various times, leading to progressively higher molar equivalents of F₄TCNQ anions (shown in the legend). The films show complete doping in the solid phase, seen by the bleaching of the polymer peak at 2.3 eV. (b) Electrical conductivity as a function of molar equivalents of F₄TCNQ⁻ to repeat units of P(ProDOT-EG) for vapor-phase doping of films from polymer P(ProDOT-EG). Horizontal error bars correspond to error from the fitting procedure, and vertical error bars correspond to 1 standard deviation from triplicate measurements.

suggests that avoiding aggregation during solution minimizes the differences in the conductivity observed between solution and solid-state doping. We proceeded to investigate whether the morphology of the films plays a significant role in the resulting electrical conductivities.

Role of Processing in Electrical Conductivity. Differences in the optical spectra and diffraction patterns upon doping of P(ProDOT-EG) provide a means to understand how the electrical conductivity varies between processing methods as a function of carrier concentration. Sequential doping of semiconducting polymers is believed to be favorable to casting of doped solutions because the infiltration does not disrupt the morphology of the pristine polymer film that is important for charge transport.^{10,12,14,17,58} In contrast, solution doping leads to aggregation of the polymer, leading to a less ordered morphology in cast films and therefore lower conductivity relative to the sequentially doped films. P(ProDOT-EG) does not aggregate in solution at concentrations used for casting films, allowing us to determine how changes in the charge carrier distribution of the polymer influence the resulting properties in films. Analysis of optical absorbance spectra and grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements shows significant differences in the two processing routes that both yield comparable electrical conductivity in thin films.

The evolution of the optical spectra of P(ProDOT-EG) upon doping shows that introduction of F₄TCNQ from the

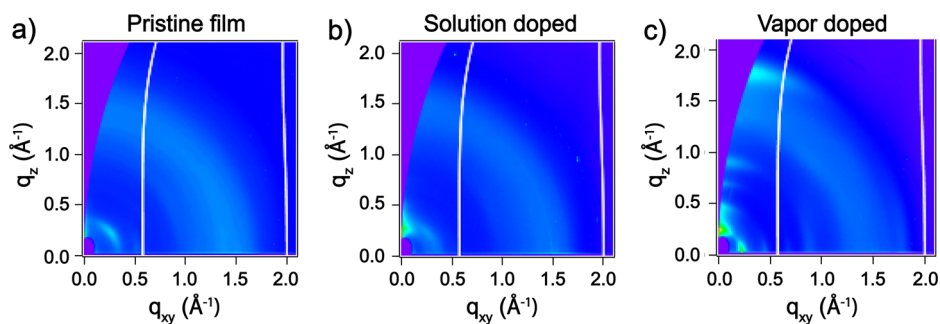


Figure 5. GIWAXS patterns for the (a) pristine, (b) solution-doped, and (c) vapor-doped films of P(ProDOT-EG). The pristine film and the initial sample for vapor-doping were cast at room temperature and then annealed 130 °C for 2 h.

vapor phase is uniform in the films and that the neutral regions of the films have good ordering through both doping routes. The absorption spectra of films of P(ProDOT-EG) can be interpreted using Spano's H–J aggregate model.⁶⁰ The ratio of intensities of the $0 \rightarrow 0$ and $0 \rightarrow 1$ vibronic transitions in films of undoped P(ProDOT-EG) is larger than 1, indicating dominantly J-aggregate character (Figure 4a); J-aggregate character is also observed in films of alkylated ProDOT polymers³⁴ and dispersed nanofibers of P3HT.⁶¹ J-aggregate character is indicative of good intrachain ordering and planarity of the backbones. The J-aggregate character of the neutral absorbance is maintained as the doping level is increased from 0 to 0.029 equiv in the vapor-doped films. There is a small change in the ratio $I_{0 \rightarrow 0}/I_{0 \rightarrow 1}$ (1.17 to 1.09) during doping, but no new features appear near the neutral absorbance. The solution-doped films show an intensity ratio of 1.05 at a doping level of 0.012 also indicating J-aggregate character.

The structural order determined by X-ray scattering shows distinct differences for vapor- and solution-doped films. 2D grazing incidence wide-angle X-ray scattering (GIWAXS) patterns of films of neat P(ProDOT-EG) do not show significant crystalline order (Figures 5 and 6). This observation is surprising considering the strong J-aggregate vibronic character in the absorbance spectrum that indicates the

pristine polymer film is composed of polymer chains with long conjugation lengths. Donor–acceptor polymers with stiff backbones and long, branched side chains, such as the indacenodithiophene–benzothiadiazole-based polymer IDTBT, show similar optical and structural behavior.^{62–64} It is likely that conformational disorder of the long side chains in P(ProDOT-EG) causes disorder in the intermolecular layering. Films doped from solution similarly show weak scattering, but a feature at low q in the out-of-plane direction is observed (Figures 5 and 6). Remarkably, vapor-doped films have scattering features indicating crystalline ordering with significant texturing relative to the substrate. A progression of three peaks at low q ($d = 25.8 \text{ \AA}$) is assigned to stacking by the side chains, and the in-plane peak at high q ($d = 3.50 \text{ \AA}$) is assigned to π -stacking of the chains (Figure 6). There are both edge-on and face-on crystallites in the films based on the in-plane and near out-of-plane scattering (Figure 5). The π -stacking distance of 3.50 \AA is lower than that reported for sequentially doped P3HT:F₄TCNQ at 3.64 \AA ^{10,11} and similar to that in other cyclic alkoxy-substituted polythiophenes such as PEDOT.^{65–67} We do not observe scattering peaks that correspond to crystallites of neutral F₄TCNQ¹¹ or a diffuse scattering ring for aggregates indicating that the dopants are well-dispersed in the polar side-chain regions.

Overall, the X-ray scattering and absorbance spectra reveal that the neutral P(ProDOT-EG) chains are extended, but have glassy interchain ordering, and that introduction of the dopant from the vapor phase into the neat films improves structural registry between the chains. The changes in ordering of the vapor-doped films likely proceeds from π -cation interactions and steric driving forces. Stronger π – π interactions are induced by the presence of π -cations^{68–70} and have been implicated in the ordering observed in doped P3HT.⁷¹ While it is difficult to uncover the kinetics of the formation of differences in ordering between the solution- and vapor-doped films, we can consider the interactions during the doping process. While π -cations are present in the solution, the P(ProDOT-EG) chains are dispersed and surrounded by dopants, making it difficult to form longer range order when solvent is quickly removed (Figure 7). In contrast, P(ProDOT-EG) chains in neutral films are already in close proximity with one another while π -cations form during vapor doping. The GIWAXS pattern of neat films shows weak scattering, suggesting that the separation of the pristine polymer chains fluctuates due to disorder in the long side chains (Figure 5). As F₄TCNQ infiltrates the free volume in the neat film, it provides a steric driving force to reduce the fluctuation in the interchain separation (Figure 7). We expect that F₄TCNQ resides in the

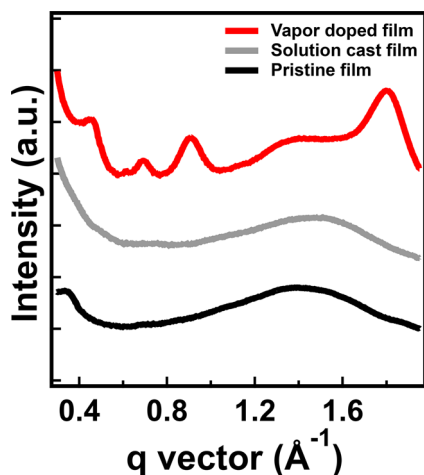


Figure 6. Out-of-plane line profiles for pristine, solution-, and vapor-doped films (at saturation) obtained from 2D GIWAXS measurements. The vapor-doped film shows significant ordering with a strong side chain-stacking progression at low q as well as a π -stacking signature at high q .

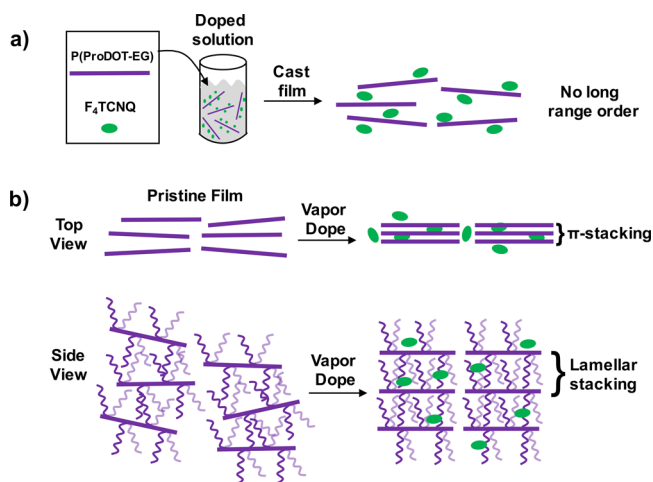


Figure 7. Schematic and summary of the ordering during doping of (a) solution and (b) sequentially doped P(ProDOT-EG). The chains in solution can be doped to high levels without aggregation, but are dispersed in solution and unable to form ordered film structures upon solvent drying. The backbones in the solid state do not possess long-range order due to conformational disorder in the long side chains that splay out from the backbone. However, because they are already in close proximity, they can respond to the steric and π -cation driving forces and upon doping to form ordered, stacked structures.

side chains similar to other doped polymers;^{22,54,71} if it resided in the π -stack of the polymer chains, we would expect to see signatures of a charge transfer state in the optical absorption spectra which are not observed.^{25,72} We note that the P(ProDOT-EG) film heats to ~ 80 °C during vapor-doping which may assist in the structural rearrangement,¹⁰ but heat itself is not sufficient because the neat films are already annealed at 130 °C without signs of similar crystallization.

The optical spectra reveal significant differences between the nature of carriers in solution- and vapor-doped films that is related to the structural ordering. The P1:P2 ratio in the absorbance of vapor-doped films (Figure 4a) is unusually high—both compared to that of the solution doped films (Figure 3a) and polythiophene films at low doping levels.^{7,8,10–15,19,37,48} Because the P2 absorbance is usually associated with polarons, this has one of two implications: (1) there are effectively no polarons at relatively low doping levels in these P(ProDOT-EG) films, which is unusual at room temperature,¹⁵ or (2) polarons can exist with exceedingly weak P2 absorbances. In either case, the nature of the charge carriers changes significantly based on the structural order in the film; despite comparable doping levels (~ 0.04), the vapor-doped film, which exhibits both high intrachain and interchain order relative to the solution-doped film, shows a much higher P1:P2 ratio. It is therefore possible that the P2 absorbance is a signature of localized polarons, and the structural disorder in the solution-doped films leads to localization of the charge carriers. In contrast, the higher level of order in the vapor-doped films facilitates charge-carrier delocalization reducing the population of localized polarons (P2) and increasing delocalized carriers (P1). The slightly higher conductivity of the vapor-doped film at a lower carrier concentration than the solution-doped films is consistent with this hypothesis.

CONCLUSION

In summary, we have designed and synthesized a polythiophene derivative with polar side chains to examine the role

of aggregation in solution on the electrical properties of thin films. While aggregation is generally a prerequisite for efficient doping for homopolymers like P3HT that have short conjugation lengths when well-solvated, P(ProDOT-EG) exhibits efficient doping despite avoiding aggregation and can remain soluble even at high doping levels. This ability likely proceeds from long conjugation lengths leading to a lower ionization energy in conjunction with strong chain–solvent interactions. The charge carriers introduced in solution by doping with F₄TCNQ can occupy up to nine thiophene subunits, and the carriers are primarily composed of polarons with a small subset of bipolarons.

The electrical conductivities of solution- and vapor-doped films of P(ProDOT-EG) are comparable. These doped films, however, show significant differences in the nature of the charge carriers and in their structural ordering. The films doped with F₄TCNQ vapor show crystalline ordering that arises from infiltration of the dopant. The ordering leads to an increase in conductivity and in the population of bipolarons (or delocalized polarons) at carrier concentrations where (localized) polarons are observed in other polythiophenes. The solution-doped films show signatures of polarons, suggesting that the structural order of the polymer backbone plays a large role in determining the type of charge carrier.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b02389.

Experimental details; Figures S1–S13 and Tables S1–S4 (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge a grant from Department of Energy Office of Basic Energy Sciences (Grant DE-SC0016390) for materials synthesis, characterization, and analysis. We also gratefully acknowledge the use of equipment in the UCSB Materials Research Laboratory Shared Experimental Facilities, supported by the MRSEC Program of the NSF under Award DMR 1720256, a member of the NSF-funded Materials Research Facilities Network. Diffraction experiments were performed at the Advanced Light Source, supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract DE-AC02-05CH11231.

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