

RESEARCH ARTICLE

Correlating conductivity and Seebeck coefficient to doping within crystalline and amorphous domains in poly(3-(methoxyethoxyethoxy)thiophene)

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Funding information

Argonne National Laboratory; U.S. Department of Energy, Grant/Award Number: DE-AC-02-06CH11357; NSF DMREF, Grant/Award Number: 1922259

Abstract

Molecular doping of conjugated polymers (CPs) plays a vital role in optimizing organic electronic and energy applications. For the case of organic thermoelectrics, it is commonly believed that doping CPs with a strong dopant could result in higher conductivity (σ) and thus better power factor (PF). Herein, by investigating thermoelectric performance of a polar side-chain bearing CP, poly(3-(methoxyethoxyethoxy)thiophene) (P3MEET), vapor doped with fluorinated-derivative of tetracyanoquinodimethane F_nTCNQ ($n = 1, 2, 4$), we show that using strong dopants can in fact have detrimental effects on the thermoelectric performance of CPs. Despite possessing higher electron affinity, doping P3MEET with F4TCNQ only results in a σ (27.0 S/cm) comparable to samples doped with other two weaker dopants F2TCNQ and F1TCNQ (26.4 and 20.1 S/cm). Interestingly, F4TCNQ-doped samples display a marked reduction in the Seebeck coefficient (α) compared to F1TCNQ- and F2TCNQ-doped samples from 42 to 13 μ V/K, leading to an undesirable suppression of the PF . Structural characterizations coupled with Kang-Snyder modeling of the α - σ relation show that the reduction of α in F4TCNQ-doped P3MEET samples originates from the generation of low mobility carrier within P3MEET's amorphous domain. Our results demonstrate that factors such as dopant distribution and doping efficiency within the crystalline and amorphous domains of CPs should play a crucial role in advancing rational design for organic thermoelectrics.

KEYWORDS

charge transport, conjugated polymers, electrical conductivity, molecular doping, Seebeck coefficient, thermoelectrics

1 | INTRODUCTION

Molecularly doped semiconducting conjugated polymers (CPs) have been increasingly explored to enable organic electronics and energy applications.^{1–9} The use of

molecular dopants allows for effective control of the charge carrier concentration (n), and in turn, the electronic transport properties of CPs. In the case of organic thermoelectrics, key physical properties that define the thermoelectric material performance include Seebeck

coefficient (α), electronic conductivity (σ), and thermal conductivity (κ).¹⁰ These properties are functions of n and are highly interrelated. The thermal-to-electrical energy conversion efficiency of thermoelectrics is characterized by the dimensionless figure of merit, $ZT = \alpha^2 \sigma T / \kappa$, where T is the temperature in Kelvin and $\alpha^2 \sigma$ is the power factor (PF).¹¹ Organic materials have a potential advantage because of their comparatively low κ , and the community has put a concerted effort in optimizing PF while not sacrificing low κ in order to improve TE performance.

Doping process of CPs is typically achieved via the addition of a molecular dopant to either oxidize (p -type doping) or reduce (n -type doping) the polymer backbone.^{4,12–14} For the case of thiophene-based polymers, p -type acceptors are introduced as oxidant molecules, leading to charge transfer between the host polymer and dopant molecule. This process results in negatively charge dopant anion and positively charged polymers (polarons) after doping. Optimal charge transport properties in CPs require doping methods that maintain their underlying hierarchical structure. Specifically, sequential doping methods where the dopant is infiltrated into the polymer matrix either from an orthogonal solvent-dopant mixture or from the dopant's vapor phase are promising approaches to preserve the underlying local ordering and morphology.^{15–19} In contrast to the solution co-processing method where the formation of aggregation leads to films with poor quality,^{15,16} the sequentially doping of the polymer maintains the crystalline order and long-range connectivity, which results in high charge carrier mobility μ , σ and thus higher PF .

In addition to changing doping methods, improving charge transport can be achieved by permitting efficient polymer-dopant charge transfer by selecting dopants having lowest unoccupied molecular orbital (LUMO) or electron affinity (EA) level close to or deeper than the highest occupied molecular orbital (HOMO) or ionization energy (IE) level of the polymer (p -type doping). For example, Li et al. investigated the doping efficiency of poly(3-hexylthiophene) (P3HT) doped with F4TCNQ and its ester analogues with lower EA levels.²⁰ Interestingly, σ of P3HT doped with ester-substituted dopants is higher than P3HT doped with F4TCNQ, which indicates weaker dopants can also lead to efficient doping and thus improvement in σ . In another study, Keifer et al. demonstrated that F4TCNQ and a comparatively stronger dopant, 1,3,4,5,7,8-hexafluoro-tetracyanonaphthoquinodimethane (F6TCNNQ), can transfer two electrons from the CP to the dopant, leading to double doping and an ionization efficiency close to 200%.²¹ As for weaker dopants, Patel et al. has shown that the weaker F2TCNQ dopant does not significantly sacrifice σ compared to the stronger F4TCNQ dopant and in turn yields a larger PF .²² Recently, our group has shown that the values σ

are within the same order of magnitude for poly 3-(methoxyethoxyethoxy) thiophene (P3MEET) when doping with three different fluorinated tetracyanoquinodimethane dopants (FnTCNQ, $n = 1, 2, 4$), while the values of σ for poly (3-(methoxyethoxyethoxymethyl)thiophene) (P3MEEMT) decrease significantly with the decreasing fluorination level of the dopants.²³ In this regard, organic dopants such as FnTCNQ are considered to be model dopants since the EA levels of FnTCNQ can be easily tuned by changing the number of fluorine atoms.²⁴

In principle, PF is related to both α and σ as the magnitude of σ increases as function of n while, in contrast, the magnitude of α decreases with n .^{11,25} Fundamentally, studies of thermoelectric properties of semiconducting polymers have been investigated in the context of charge transport mechanisms where researchers have been exploring the correlation between α and σ .^{25–35} In 2014, Glauddell et al. presented an empirical relation where $\alpha \sim \sigma^{-1/4}$ by compiling studies of doped thiophene-based polymers. The authors, however, did not provide physical explanation of this relationship.²⁵ More recently, Kang and Snyder have proposed a charge transport model with an energy-dependent parameter s and an energy-independent transport coefficient σ_{E0} , which fits well with the α - σ relationship of conducting polymers over a wide range of σ .²⁶ Particularly, the authors stated that the transport parameter s is related to energetic disorder of different polymers and thus determine the mechanism of charge transport. However, the factors that affect the value of s in the Kang-Snyder model are still unclear. Gregory et al. have developed a semi-localized transport (SLoT) model modified from the Kang-Snyder model where they treat σ_{E0} as a function of temperature and carrier concentration.²⁹ The SLoT model captures a large spectrum including both hopping-like and metal-like transport in CPs and helps tailor thermoelectric properties of doped CPs more accurately. Moreover, Boyle et al. examined the effect of dopant distribution on CPs' electronic structure, charge transport and the α - σ relationship. They found that CPs having non-uniform dopant distribution led to a heavy tailed DOS, resulting in a flattened α - σ profile and where the suppressed α is due to the high degree of disorder.²⁸ The results highlighted the importance of controlling dopant distribution for high performing organic thermoelectrics, and thus motivating further investigations on the role of polymer-dopants interaction, dopant distribution on CPs' thermoelectric properties.

Of particular interest in the field of CPs is studying the role of crystalline (or aggregate) and amorphous phases on charge transport properties. Specifically, understanding how doping occurs within the crystalline and amorphous

phases in CP films and the resulting effects on α – σ relationships and thermoelectric performance still remain poorly understood. To explore this question, in this work we investigate the correlation between σ and α of a polythiophene derivative with a polar, oligoethylene glycol side-chain, P3MEET (chemical structure shown in Figure 1 (A)) vapor-doped with fluorinated-derivatives of tetracyanoquinodimethane (FnTCNQ, $n = 1, 2$, and 4). P3MEET belongs to a new class of *p*-type semiconducting polymers possessing oligoethylene glycol polar side chains which has been increasingly used due to its enhanced processability and thermal stability.^{21,23,36–41} Additionally, choosing dopants with varying EA not only enables the study of polymer-dopant energy mismatch on charge transport properties but can also systematically change the doping efficiency within the crystalline and amorphous domains.

In the first part of the paper, we study the charge transport and thermoelectric properties of P3MEET thin films vapor doped with FnTCNQ. P3MEET exhibits a maximum σ as high as 27.0 ± 3.7 S/cm upon doping with F4TCNQ, which matches our previous study.²³ Despite having higher EA levels, F2TCNQ/F1TCNQ-doped P3MEET have a comparable maximum σ at 26.4 ± 3.1 S/cm and 20.1 ± 0.77 S/cm, respectively. However,

a deviation in α is observed at the high σ region from 42 ± 1 μ V/K in F1TCNQ-doped sample to 13 ± 1 μ V/K in F4TCNQ-doped sample, which leads to a significant suppression of *PF*. In the second part of the paper, origin of this observation is explored by using a combination of spectroscopy techniques (UV–vis–NIR and Raman) and grazing incidence wide angle X-ray scattering (GIWAXS). In the last part, we discuss the α – σ relationship of our FnTCNQ-doped P3MEET thin films using Kang-Snyder charge transport model, which provides insight into the role of crystalline and amorphous domains on charge transport and thermoelectric properties of doped P3MEET polymer thin films.

2 | RESULTS AND DISCUSSION

2.1 | Fabricating P3MEET:FnTCNQ films through vapor doping

In this work, thermoelectric properties of P3MEET were investigated upon doping with three dopants, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane (F2TCNQ) and 2-fluoro-7,7,8,8-tetracyanoquinodimethane (F1TCNQ) with different electron affinity (EA). P3MEET having M_w of 9.2 kg/mol and D of 1.4 was synthesized by the Kumada catalyst transfer polymerization (KCTP) method as described in our previous publication.⁴² Figure 1(A) summarizes the EA values of FnTCNQ ($n = 1, 2$, or 4) and the ionization energy (IE) of P3MEET determined by solution CV measurements. The IE of P3MEET is found to be 4.92 eV, whereas the EA values of F4TCNQ, F2TCNQ and F1TCNQ are determined to be 5.25, 5.10, and 5.01 eV, respectively (see details of CV measurements in ref. 23). As expected, the EA level decreases with decreasing fluorination level for three dopants. All dopants have a lower EA than the IE of P3MEET. To introduce molecular dopant into the polymer, we employed sequential vapor doping method where one first casts a neat thin film and then the dopant is infiltrated into the polymer matrix from the vapor phase as shown in Figure 1(B). For consistency, all neat P3MEET thin films are processed in the same manner in this study: spin-coated from chloroform solution and soft annealed at 80 °C to remove residual solvents within the polymer films (thin films of c.a. 40 nm). Figure 1(B) shows a schematic of our home-built apparatus for controlled vapor doping of polymer thin films in an argon atmosphere glovebox. More details are provided in the methods section and our previous publication.⁴³

UV–vis–NIR absorption spectra (Figures 2 and S1) indicate efficient charge transfer between P3MEET and all three dopant. For neat P3MEET, the primary

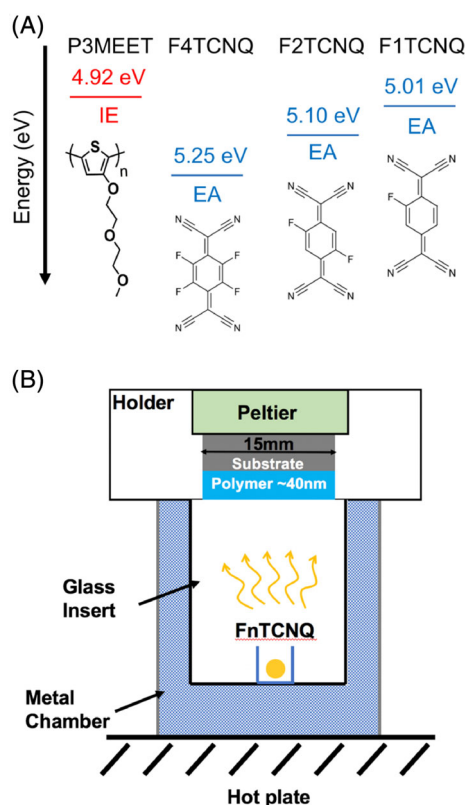


FIGURE 1 (A) HOMO level of P3MEET together with LUMO levels of the three dopants, F1TCNQ, F2TCNQ, and F4TCNQ used in this work. (B) Schematic of vapor doping chamber

absorption peak is observed at 2 eV. Notably, there is significant evidence of polaron absorption peaks at around 0.6 and 1.5 eV in neat P3MEET, which indicates the presence of intrinsic charge carriers in the neat thin film. Upon introducing dopant vapor, charge transfer process can be observed between P3MEET and F_nTCNQ as the neutral absorption peak intensity decreases while the F_nTCNQ anion absorption peaks appear and increases near ~1.4 eV together with the neutral F_nTCNQ absorption peak near 3.25 eV. Note that for thin films doped

beyond 10 min, the neutral F_nTCNQ peak becomes significantly pronounced while the polaron and dopant anion peak intensities remain constant, indicating accumulation of neutral dopants on the polymer surface after vapor doping beyond 10 min.

2.2 | Seebeck coefficient and conductivity as function of vapor doping time

The values of α , σ , and the corresponding PF of P3MEET as a function of F_nTCNQ vapor doping time are summarized in Figure 3. Neat P3MEET already processes a σ of ca. 0.1 S/cm, which is significantly higher than other thiophene-based polymers. This observation is consistent with our UV-Vis-NIR results indicating the presence of intrinsic charge carriers in the film. The electron-donating ability of the oxygen atom next to the polythiophene backbone results in the low IE for P3MEET. Thus, the polymer is prone to oxidation from any remaining catalyst and ambient air during the synthesis and handling processes.⁴² This condition leads to much higher “intrinsic” n and σ at the neat state. The high σ generated simply by ambient doping could open up the door for more simple doping methods of CPs via engineering their IE. For all dopants, the conductivity of P3MEET films increases over two orders of magnitude before saturating after doping for 5 min. The difference in σ between the neat and doped films originates from the differences in both n and μ . Note that n does not linearly scale with σ at high doping level as mobile carriers with higher mobility are generated. Conductivity of films doped with F1TCNQ reach the maximum sooner than the other two dopants which is likely due to its faster sublimation rate at a fixed temperature. The values of σ of 10 min F4TCNQ, F2TCNQ, and F1TCNQ doped P3MEET thin films are 27.0 ± 3.7 , 26.4 ± 3.1 , and 20.1 ± 0.77 S/cm, respectively. As expected, α for the doped films show an inverse correlation with doping time compared to σ . The values of α decrease with increasing vapor doping time and reaches a plateau after 5 min of doping (Figure 3(B)). The values of α of 10 min F4TCNQ, F2TCNQ, and F1TCNQ doped P3MEET thin films are 13 ± 1 , 23 ± 1 , and 42 ± 1 μ V/K, respectively. It is clearly shown that thin films doped by F4TCNQ have much smaller α compared to doping with F1TCNQ and F2TCNQ at the same doping time.

The PF s of all samples are also calculated and plotted in Figure 3(C). It is worth noting that at the saturated doping time (10 min), PF of F1TCNQ doped film (3.5μ W m⁻¹ K⁻²) is higher than those doped by F2TCNQ (1.4μ W m⁻¹ K⁻²) and F4TCNQ (0.48μ W m⁻¹ K⁻²). In

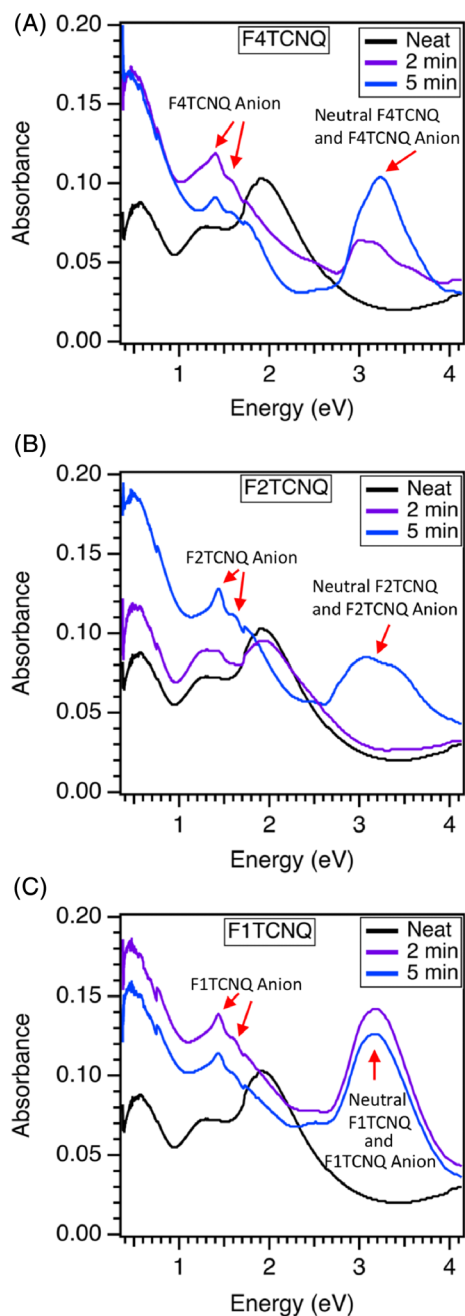


FIGURE 2 UV-vis-NIR spectra of P3MEET thin films as a function of (A) F4TCNQ, (B) F2TCNQ, and (C) F1TCNQ vapor doping time

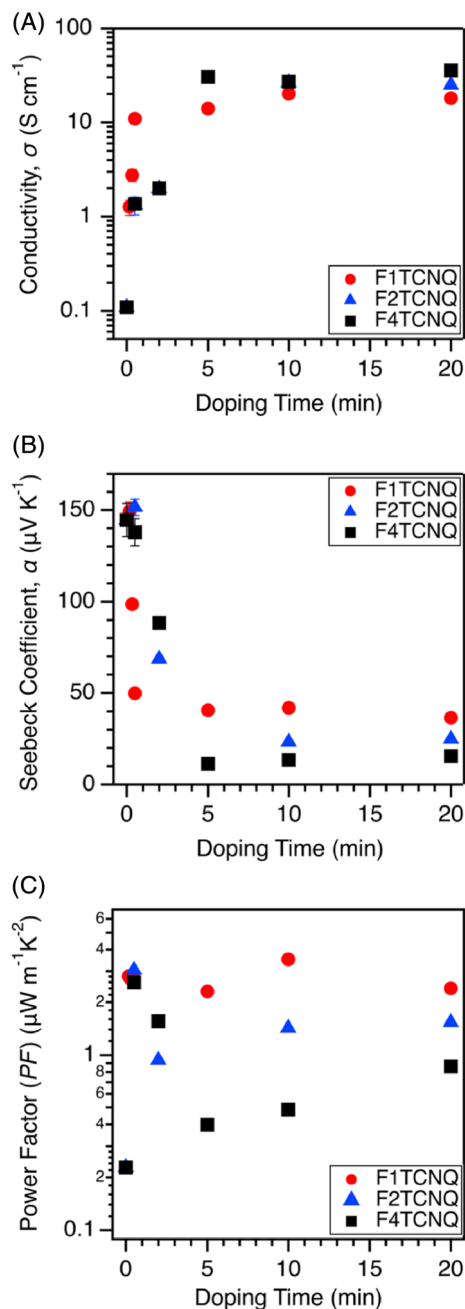


FIGURE 3 (A) Conductivity (σ), (B) Seebeck coefficient (α), and (C) corresponding power factor ($PF = \alpha^2 \sigma$) of P3MEET: F4TCNQ thin films as a function of vapor doping time

particular, F1TCNQ-doped P3MEET has a PF that is an order of magnitude higher than F4TCNQ-doped P3MEET. The difference in PF is due to the dominance of α in the formula of PF where $PF = \alpha^2 \sigma$. Thin films doped by F1TCNQ have larger values of α while the difference in σ is not significant. One possible explanation for the difference in α is the variation in n between the three doped thin films as α is inversely related to n .

To provide further insight on n , electron paramagnetic resonance (EPR) spectroscopy measurements were performed to quantify the spin concentration (N) in

F4TCNQ-doped P3MEET thin films. Here, we take N as a measurement of the polaronic charge carriers generated after doping. The representative continuous wave (CW) EPR spectra for neat and doped thin films recorded at room temperature are shown in Figure S2. The spin concentration in each sample was calculated through double integration of the EPR spectrum divided by the volume of the measured film (Figure S3 and Table 1). The neat P3MEET film has an N of $(1.9 \pm 0.3) \times 10^{19} \text{ cm}^{-3}$, which is relatively high, indicating the polymer is intrinsically doped as suggested by the UV–Vis–NIR and conductivity measurements (Figures 2 and 3(A)). After doping with F4TCNQ for 10 min, the maximum N of doped P3MEET is $(1.9 \pm 0.3) \times 10^{20} \text{ cm}^{-3}$, an order of magnitude higher than neat sample. Note that EPR measurements capture the unpaired electrons that interacted with the applied magnetic field. A decrease in EPR spin concentration could be observed at high doping level when bipolarons are formed, which could lead to underestimation in the calculated carrier concentration.⁴⁴ However, the maximum carrier concentrations measured using other techniques (AC Hall effect,⁴⁵ XPS,^{46,47} and UV–Vis spectroscopy^{19,48}) all lie in the order of 10^{20} to 10^{21} cm^{-3} , which is in agreement with our value calculated from EPR, indicating reasonable and commensurable carrier concentrations in this study. As shown in Figure S3, the N in the 10 min F4TCNQ-doped film is more than 50% higher than that in F1TCNQ/F2TCNQ-doped films. This difference indicates greater extent of doping with F4TCNQ compared to other two dopants. However, the larger N does not lead to a significantly higher σ . We posit that a portion of charge carriers generated in F4TCNQ-doped thin films are trapped in the amorphous region of P3MEET, which possesses lower μ and thus leads to an apparent suppression of σ . Therefore, values of σ for F1TCNQ- and F2TCNQ-doped thin films are comparable with those of F4TCNQ-doped thin films. To investigate our hypothesis, we carried out structural characterization experiments to probe dopant distribution and polymer chain conformational order in P3MEET thin films.

2.3 | Influence of molecular doping on the local molecular order

Grazing incidence wide angle X-ray scattering (GIWAXS) experiments were performed to investigate how molecular doping influences the local molecular order in crystalline domains of P3MEET. 2D GIWAXS images of neat and F4TCNQ-doped P3MEET thin films were shown in Figure S4. The scattering pattern of neat P3MEET suggests face-on orientation of P3MEET as the side-chain stacking peak (100) lies along in-plane direction and the

TABLE 1 Summary of experimental values for conductivity (σ), Seebeck coefficient (α), power factor (PF), spin concentration (N), and Kang-Snyder modeling results for the reduced chemical potential (η) and the transport coefficient (σ_{E0})

Sample	σ^a (S/cm)	α^a ($\mu\text{V/K}$)	PF^a ($\mu\text{Wm}^{-1}\text{K}^{-2}$)	N (cm^{-3}) ^a from EPR	η^a ($s = 1$)	σ_{E0} ($s = 1$) (S/cm)	σ_{E0} ($s = 3$) (S/cm)
F1TCNQ-doped	20.1 ± 0.77	42 ± 1	3.5	9.5×10^{19}	6.8	2.3 ± 0.2	$(1.7 \pm 0.2) \times 10^{-3}$
F2TCNQ-doped	26.4 ± 3.1	23 ± 1	1.4	1.1×10^{20}	12.2	2.0 ± 0.2	$(5.7 \pm 0.3) \times 10^{-4}$
F4TCNQ-doped	27.0 ± 3.7	13 ± 1	0.42	1.9×10^{20}	21.2	1.4 ± 0.1	$(9.7 \pm 2.0) \times 10^{-5}$

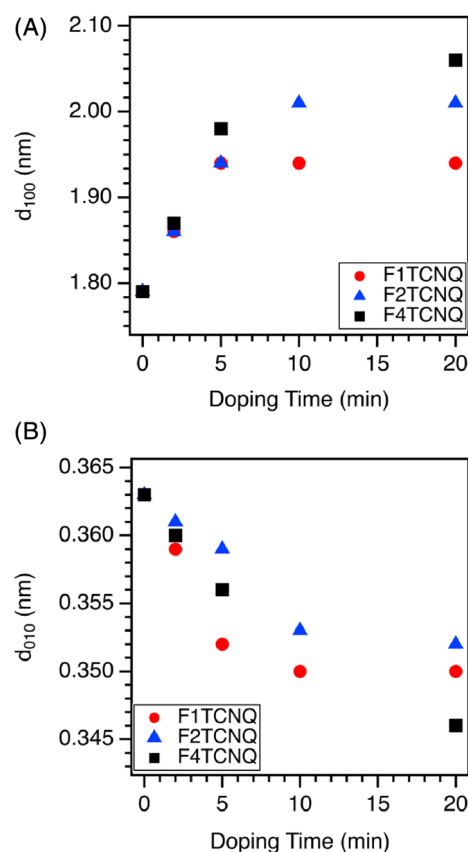
^aTaken at 10 min doping time.

π -stacking peak (010) along out-of-plane direction. In addition, the lack of higher order side-chain scattering reflections together with the broad, diffuse diffraction peaks in GIWAXS patterns indicates a more disordered structure in P3MEET, consistent with our prior studies. Upon introducing dopant into polymer, the GIWAXS patterns appear similar to the neat sample, indicating that doping with vapor F4TCNQ induces minimal changes to molecular order and orientation.

Quantitative changes upon vapor doping by F4TCNQ are seen through the side-chain stacking and π - π stacking distances. We calculate side-chain distance $d_{100} = 2\pi/q_{100}$ as a function of F4TCNQ doping time, the result of which is shown in Figure 4(A). Upon introducing F4TCNQ we observe an increase in d_{100} for all three dopants due to the intercalation of dopant into the side-chain spacing, a widely observed phenomenon in polythiophene-based polymers.^{17,22,43,49,50} Specifically, d_{100} increases initially from 1.79 nm for neat P3MEET to 1.94 nm, 2.01 nm and 2.06 nm for F1TCNQ, F2TCNQ and F4TCNQ-doped thin films, respectively. For all three dopants, d_{100} follow the same trend and reach plateaus beyond ca. 10 min of vapor deposition. Along with the increase in d_{100} , we also observe a decrease in the π -stacking distance, d_{010} during the vapor doping process, as illustrated in Figure 4(B). Notably, decrease in d_{010} is 4.7% in P3MEET after 20 min of doping with F4TCNQ, which is more prominent than with F1TCNQ (3.5%) and F2TCNQ (3.1%), consistent with higher doping efficiency by F4TCNQ.

2.4 | Raman spectroscopy reveals charge transfer between dopants and the amorphous phase

We performed Raman spectroscopy to preferentially investigate the chain conformational order in the amorphous regions of neat and F4TCNQ-doped P3MEET thin films. Note that because F1TCNQ sublimated much faster than other two dopants, the accumulation of neutral F1TCNQ on polymer thin film surface is more rapid as indicated in the UV-Vis-NIR spectra. Therefore, we

**FIGURE 4** (A) Side-chain stacking (d_{100}) and (B) π -stacking distance (d_{010}) of P3MEET:F4TCNQ thin films as a function of vapor doping time

chose to compare Raman spectra of 5 min F1TCNQ-doped thin film with 10 min F2TCNQ- and F4TCNQ-doped thin films as they possess similar amount of dopant during vapor doping time. The excitation wavelength was chosen to be in resonance with the amorphous fraction of the P3MEET thin film,⁵¹ which is 532 nm based on the UV-Vis absorption spectra of solution and thin film (Figure S5). The normalized Raman spectra of the neat and F4TCNQ-doped P3MEET thin films are shown in Figure 5. For neat P3MEET, two strong peaks are observed at 1390 and 1445 cm^{-1} , which are assigned to thiophene C-C bond stretching and the symmetric C=C bond stretching, respectively. In addition, the shoulder at $\approx 1415\text{ cm}^{-1}$ corresponds to polymer chains with higher conformational order. We

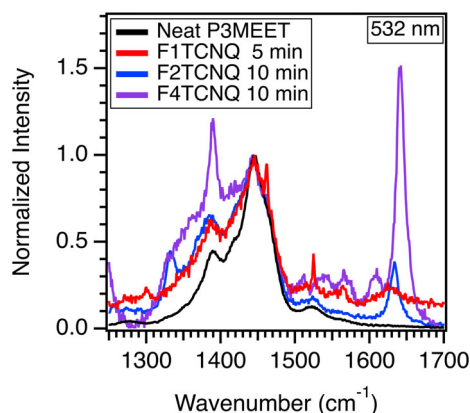


FIGURE 5 Raman spectra of neat and F4TCNQ-doped P3MEET thin films at the excitation wavelength of 532 nm. This excitation wavelength is preferentially in resonance with the amorphous regions of the P3MEET thin film

attribute the appearance of this shoulder to the stiffening of disordered polymer chains arising from the planar polaronic molecular structure in neat P3MEET, which is consistent with previous reports.^{48,52,53} Upon vapor doping by all three dopants, the characteristic peak positions remain unchanged compared with the neat P3MEET while the peaks of doped films are slightly broader than the neat peaks with a relative intensity change of the C–C bond stretching peak. The relative intensity changes upon introducing dopants into the polymer indicates the formation of additional positive charge carriers (polarons) in P3MEET. These features are consistent among F4TCNQ-doped films, which means that amorphous region of P3MEET can be doped by all three dopants to a certain extent. However, the shoulder at 1415 cm^{−1} in Raman spectrum of F4TCNQ-doped P3MEET has a much higher intensity, indicating a more efficient charge transfer between F4TCNQ and amorphous P3MEET. The more efficient charge transfer results in more charge carriers in amorphous region when doped by F4TCNQ compared to the other two dopants, which can be confirmed by a much larger F4TCNQ anion peak around 1650 cm^{−1} compared to F1TCNQ and F2TCNQ anion peaks.⁵⁴ This difference can be explained as the more disordered polymer chains in the amorphous domain of P3MEET has a lower HOMO level compared to crystalline P3MEET, which can limit the charge transfer with F1TCNQ or F2TCNQ.

2.5 | Modeling α – σ relation reveals charge transport mechanism in P3MEET: F4TCNQ

To study the charge transport relation in F4TCNQ-doped P3MEET thin films, we plotted α as a function of σ and

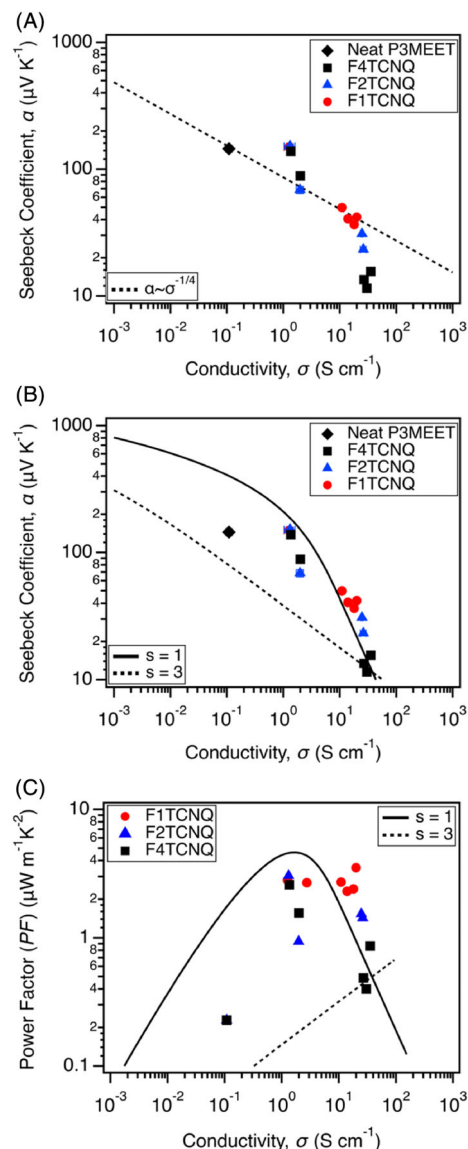


FIGURE 6 Compilation of Seebeck coefficient (α) vs conductivity (σ) data from this study: (A) power law relation ($\alpha \sim \sigma^{-1/4}$) from Glaudell et al.²⁵ (dashed line) and (B) Kang-Snyder charge transport model; (C) compilation of PF vs σ from this study. [$s = 1$ (solid curve) or $s = 3$ (dashed curve)]

compared with previous relations observed for numerous doped CPs. Figure 6(A) represents an empirical fitting (dash line) proposed by Glaudell et al.,²⁵ where the α vs. σ was fit to a power law relation:

$$\alpha = \frac{k_B}{e} \left(\frac{\sigma}{\sigma_\alpha} \right)^{-1/4} \quad (1)$$

where k_B/e is the Boltzmann constant divided by unit charge, or the natural unit of thermopower 86.17 $\mu\text{V/K}$. The parameter σ_α is an empirical constant and fit to

approximately 1 S/cm. The magnitude of σ_α is independent of carrier concentration in the range covered. It is clearly shown in Figure 6(A) that α continuously decreases with increasing σ at low doping regime following this relation. In the higher doping regime, however, we found deviations from the power law relation (Equation 1), similar to the observation by Muller et al. in a molecularly-doped glycolated side chain bearing CP p (g42T-T).³⁶

Recently, the charge transport model proposed by Kang and Snyder has been increasingly used to model α - σ relation for understanding the charge transport mechanism of conducting polymers.^{26,30,32,33} In that model, the transport edge, E_t , was introduced where the hopping transport was also taken into account. E_t is similar to the mobility edge model but does not require metal-like transport above the edge while still accounting for hopping conduction between localized states. Fundamentally, α and σ can be described using the following equations:

$$\sigma = \int \sigma_E \left(-\frac{\partial f}{\partial E} \right) dE \quad (2)$$

$$\alpha = \frac{k_B}{e} \int \frac{E - E_F}{k_B T} \frac{\sigma_E}{\sigma} \left(-\frac{\partial f}{\partial E} \right) dE \quad (3)$$

where σ_E is the transport function, $f(E)$ is the Fermi-Dirac distribution, E_F is the Fermi energy level and T is the temperature. In the Kang-Snyder model, σ_E is assumed to have a power law energy dependence above the transport edge, E_t , with a power of s as shown in Equation 4:

$$\begin{aligned} \sigma_E(E, T) &= \sigma_{E0}(T) \times \left(\frac{E - E_t}{k_B T} \right)^s \quad (E > E_t) \\ &= 0 \quad (E < E_t) \end{aligned} \quad (4)$$

where σ_{E0} is called the transport coefficient, which is an energy-independent parameter. s is the transport parameter, which is determined by fitting experimental data. α and σ of samples can be calculated in terms of s and η , where $\eta = \left(\frac{E_F - E_t}{k_B T} \right)$ is defined as reduced chemical potential and represents the relative position of the Fermi level with respect to E_t . α - σ relations of F4TCNQ-doped P3MEET are fitted using Kang-Snyder model for $s = 1$ or 3 and are summarized in Figures 6(B) and S6. Overall, $s = 1$ model gives better fits than $s = 3$ for all dopants. In particular, F4TCNQ-doped thin films have the largest deviation using the $s = 3$ model.

This deviation is also observed when we fit all data of three dopants together (Figure 6(B)). As stated in Kang and Snyder's work, the $s = 1$ case was only considered for PEDOT-based materials where they suggested that charge transport in this type of materials is mainly affected by acoustic-phonon scattering rather than impurity scattering ($s = 3$). More recently, Lee et al. also proposed $s = 1$ model for α - σ relation of FeCl₃-doped thiophene-based polymers.³³ They assigned the $s = 1$ mechanism with materials possessing a narrow density of states (DOS) which results from high crystallinity and/or degenerate energy states ($\eta \gg 1$) due to high carrier concentration generated by FeCl₃. As seen in Figure 6(B), fitting with $s = 1$ gives the better fit than $s = 3$ for our thin films which might suggest a narrow DOS in the P3MEET-F4TCNQ systems. In addition, the relationship between PF and σ is summarized in Figure 6(C), which follows $s = 1$ better than $s = 3$.

The values of η for F4TCNQ-doped thin films are determined using $s = 1$ model and summarized in Figure S7 and Table 1. The neat P3MEET thin film has an η of 1.2. It is clear that η increases with charge carrier as approximated through EPR measurements, which is consistent with previous study on PBTTC-F4TCNQ by Kang et al.³² η represents the relative energetic difference between the Fermi level and the transport edge and serves as an indicator of the electronic bandwidth of the polymer. The largest η in our system is around 20 ($E_F - E_t = 0.5$ eV), which is physically reasonable, as the full electronic bandwidth of CPs reported in the literature is 0.5–1 eV.^{26,55–58} In our system, F4TCNQ-doped thin film has a larger η ($\eta = 21.2$) than F2TCNQ ($\eta = 12.2$) and F1TCNQ ($\eta = 6.8$) doped thin films, indicating more carriers generated in F4TCNQ-doped P3MEET. However, despite the difference in η and charge carrier concentration, there is little variation in the maximum conductivity for three dopants. We attribute this to the difference in μ as σ is affected by both charge carrier concentration and μ . Importantly, the value of transport coefficient σ_{E0} is directly related to μ and determines the magnitude of σ . As determined by fitting our data, F1TCNQ-doped thin films have the largest value of σ_{E0} (2.3 ± 0.2 S/cm) whereas F4TCNQ-doped thin films have the lowest σ_{E0} (1.4 ± 0.1 S/cm) in the $s = 1$ model. The trend in σ_{E0} indicates that doping with F4TCNQ leads to lower overall average mobility. We note that while $s = 1$ gives better fits than $s = 3$ for all dopants, we observe the same trend in σ_{E0} among the 3 dopants regardless of the value of s (Table 1). This trend is consistent with our hypothesis as thin films doped by F4TCNQ generate more charge carriers in the amorphous regions, which naturally have lower mobility due to the short conjugation length and more disordered structure compared to

the charge carriers generated in crystalline domain. As F4TCNQ dopes the amorphous region more than the other two dopants, the overall charge carriers generated by F4TCNQ is higher and thus leads to a lower α value. However, a larger portion of charge carriers are in the amorphous regions when doped by F4TCNQ, which does not contribute significantly to σ due to the inherently lower μ in the amorphous regions. This explains that there is little variation in σ for P3MEET doped by different dopants at their highest doping level.

Balancing the contribution of charge transport between the crystalline and amorphous regions is a promising strategy in controlling thermoelectric properties. Specifically, our study indicates preferential doping of the crystalline regions through weaker dopants is needed to achieve high PF in P3MEET. A recent study by Liang et al. have demonstrated how to control the sign of α by balancing charge carrier concentration and charge-carrier mobilities in the crystalline and amorphous regions of a doped CP film.⁵⁹ Therefore, going forward, strategies towards proper CP and dopant pairing need to consider the doping level between the crystalline and amorphous regions to balance the correlation between α and σ , and the ultimate PF .

3 | CONCLUSION

In summary, we investigated the charge transport and thermoelectric properties of a polythiophene derivative with a polar side-chain, P3MEET, doped with p -type molecular dopants F n TCNQ ($n = 1, 2$, and 4). Upon doping, electronic conductivity (σ) increased and plateaus to a similar value ($20\text{--}27\text{ S/cm}$) for all three dopants at the maximum doping level. On the other hand, the Seebeck coefficient (α) for F1TCNQ-doped P3MEET thin film ($\alpha = 42 \pm 1\text{ }\mu\text{V/K}$) was threefold higher than the F4TCNQ-doped P3MEET thin film ($\alpha = 13 \pm 1\text{ }\mu\text{V/K}$). We assigned this variation to the difference in doping efficiency, which results in larger carrier concentration in F4TCNQ-doped P3MEET thin film. A combination of X-ray scattering and spectroscopy (UV-Vis-NIR and Raman) indicated extent of doping between the crystalline and amorphous regions. F4TCNQ possess the highest doping efficiency among three dopants within both crystalline and amorphous domains while F1TCNQ and F2TCNQ primarily doped the crystalline regions. Lastly, we modeled the α - σ relationship of our F n TCNQ-doped P3MEET thin films using the Kang-Snyder model where $s = 1$ (transport parameter) was found to give the best fit. Despite having the lowest electron affinity, P3MEET thin films doped with F1TCNQ were found to have the highest transport coefficient ($2.3 \pm 0.2\text{ S/cm}$) which is indicative of higher charge carrier mobility. This results from less carriers generated in the

amorphous region, which allows for an optimized PF . Our findings illustrate the importance of understanding the role of doping in the crystalline and amorphous domains when considering the thermoelectric transport properties of existing and newly synthesized semiconducting CPs.

4 | EXPERIMENTAL METHOD

4.1 | Materials

Poly 3-(methoxyethoxyethoxy) thiophene (P3MEET) was synthesized by first synthesizing the monomers 2,5-dibromo-3-(methoxyethoxyethoxy) thiophene [3MEET], then polymerizing using Kumada Catalyst Transfer Polymerization (KCTP). Additional synthetic details are provided in our previous publication.⁴² Tetracyanoquinodimethane derivatives (F n TCNQ, $n = 1, 2$, and 4) were purchased from TCI Chemicals. Anhydrous chloroform was purchased from Sigma Aldrich and was used as received.

4.2 | Thin film preparation

Thin film samples for GIWAXS experiments were prepared on silicon with native oxide wafer substrates ($15\text{ mm} \times 15\text{ mm} \times 0.5\text{ mm}$, University Wafer). Thin film samples for UV-Vis-NIR spectroscopy, Raman spectroscopy, and electrical characterization were prepared on quartz substrates ($15\text{ mm} \times 15\text{ mm} \times 0.5\text{ mm}$, University Wafer). All substrates were cleaned by ultrasonication in acetone and isopropanol for 10 min each, followed by plasma-cleaning for 3 min. For neat P3MEET thin film preparation, P3MEET was dissolved in anhydrous chloroform (10 mg/ml), and the solution was stirred overnight to fully dissolve the polymer. Then thin films were spin-coated using an SCS G3P spin coater using a two-step spin condition of 2000 rpm for 40s followed by 3000 rpm for 25 s. All solution preparation and spin-coating steps were performed in an Argon glovebox. Thickness of neat films were measured via ellipsometry using the α -SE variable angle spectroscopic ellipsometer (J.A. Woollam Co.). The film thickness was determined to be approximately 40 nm after fitting the raw data to a Cauchy model within the transparent range of P3MEET (800–900 nm).

4.3 | Vapor doping process

Vapor doping was performed in an argon glovebox. Approximately 2 mg of F n TCNQ powder was pressed into a pellet (approximately 3 mm in diameter) and

placed in an aluminum oxide crucible (OD 6.8 mm $\times$ H 4 mm from Government Scientific Source Inc.), which was in turn placed in a glass insert (diameter $\sim$ 5 cm, height $\sim$ 4.5 cm). A stainless-steel container was then preheated for 30 min on a hot plate to allow the chamber to reach a steady temperature (200°C for F4TCNQ, 180°C for F2TCNQ and 160°C for F1TCNQ). The glass insert with the dopant inside was put into the metal chamber to produce dopant vapor. The Peltier on top of the holder is used to keep the substrate temperature at 30 °C during the vapor doping process.

The following experiments (UV-Vis-NIR, EPR, GIWAXS, Raman, conductivity and Seebeck coefficient measurements) were all performed near room temperature.

4.4 | UV-VIS-NIR absorption spectroscopy

UV-Vis-NIR spectra of neat P3MEET and vapor-doped thin films on quartz substrates were obtained using the Shimadzu UV-3600 Plus UV-VIS-NIR Dual Beam Spectrophotometer housed in the Soft Matter Characterization Facility (SMCF) (Pritzker School of Molecular Engineering, University of Chicago). Measurements were taken within a wavelength range of 300–3300 nm.

4.5 | Electron paramagnetic resonance spectroscopy

CW X-band (9–10GHz) EPR experiments were carried out with a Bruker ELEXSYS II E500 EPR spectrometer (Bruker Biospin, Rheinstetten, Germany), equipped with a TE102 rectangular EPR resonator (Bruker ER 4102ST). Measurements were performed at room temperature ($T = 295$ K). Thin films on the substrate with dimensions 2 mm $\times$ 15 mm were placed in the EPR quartz tubes with 4 mm i.d. For spin quantification a single crystal of $\text{CuSO}_4\cdot\text{H}_2\text{O}$ with known spin concentration was used as a reference sample. Spin quantifications were done by comparing double integrals of the experimental and reference EPR signals. For EPR measurement, we estimate a relative error of ca. 20% for each sample due to variations from experimental conditions.

4.6 | Grazing incidence wide angle X-ray diffraction

GIWAXS experiments were conducted at the Advanced Photon Source (Argonne National Laboratory) at beamline

8-ID-E. The energy of the incident beam was at 10.91 keV, and a Pilatus 1MF pixel array detector (pixel size = 172 μm) was used.⁶⁰ The measurement time for one image was 10 s. All samples were placed and measured in a low vacuum chamber (10^{-3} mbar) to reduce the air scattering as well as to minimize beam radiation damage. There are multiple rows of inactive pixels between the detector modules when the images were collected at one position. To fill these inactive gaps, the detector was moved down to a pre-set new position along the vertical direction after each measurement. After the image was collected at the new spot, the data from these two detector positions were combined using the GIXSGUI package for MATLAB to fill the inactive gaps.⁶¹ The absence of artifacts in the combined image demonstrates that the scattering from the sample does not change during the exposure. The GIXSGUI package was also used to output the GIWAXS signals as intensity maps in (q_r , q_z) space, and take the line-cuts along out-of-plane (q_z) and in-plane directions (q_r).

4.7 | Raman spectroscopy

Raman spectroscopy experiments were performed under ambient conditions using the Horiba LabRAM HR Evolution NIR confocal Raman microscope housed in the University of Chicago Materials Research Center. Raman spectra of neat and doped P3MEET thin films were collected using a 100x objective at excitation wavelength of 532 nm. The spatial resolution of each measurement is dependent on the numerical aperture of the microscope objective, the wavelength of the laser used, and the pin-hole size of the confocal imaging mode. In our configurations, the spatial resolution of each Raman spectrum is calculated to be $\sim$ 0.65 μm . Laser power and accumulation time was set to 1% and 20 s to minimize local heating and material degradation.

4.8 | Conductivity and Seebeck measurements

Gold electrical contacts (75 nm thick) for electronic conductivity (σ) and Seebeck coefficient (α) measurements were deposited onto P3MEET thin films via thermal evaporation through shadow masks designed in our lab. Electronic conductivity was measured in the in-plane direction using four probe geometry with a 0.2 mm spacing between electrodes and electrodes length of 1 mm. Seebeck coefficient was measured with two 1 mm² gold pads, which are 3 mm apart. A detailed schematic is provided elsewhere.⁴³ Four probe conductivity measurements were performed using a custom-designed probe station in an Argon

glovebox. Voltage and current measurements were performed using a Keithley 2400 source meter and Keithley 6221 precision current source. A constant current was applied to the outer contacts, and the resultant steady-state voltage response was recorded from the two inner contacts. The resistance (R ; ohms) of the sample was extracted from the slope of the IV sweep using Ohm's law ($V = IR$). The thin film conductivity σ was then calculated using the following equation:

$$\sigma = \frac{\ln 2}{\pi h R}$$

where h is the thickness of the thin film.

The Seebeck coefficient measurements were performed on the same probe station. Two Peltier elements were placed 5 mm apart to provide the temperature difference ($\Delta T = T_H - T_C$). Two thermocouples were used to collect the hot and cold side temperatures, and two probes were used to measure the corresponding voltage value. A minimal amount of thermally conductive silicone paste was applied to the tips of the thermocouple to ensure good thermal contact between the thermocouple and the gold pads. A delay of 200 s was used for voltage measurements to ensure that a steady-state temperature gradient and voltage was reached. The measurements were taken within an approximate ΔT of ± 3 K around 300 K so that the Seebeck coefficient did not change significantly over $T \pm \Delta T$. The Seebeck coefficient was then calculated as $\alpha = -\frac{\Delta V}{\Delta T}$.

ACKNOWLEDGMENTS

The authors acknowledge funding support from NSF DMREF 1922259 (Jonathan W. Onorato, Ban Xuan Dong, Christine K. Luscombe). This research used resources of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) by Argonne National Laboratory under Contract No. DE-AC-02-06CH11357. Parts of this work were carried out at the Soft Matter Characterization Facility of the University of Chicago. The EPR work at Argonne National Laboratory was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under Contract no. DE-AC-02-06CH11357. This work made use of the shared facilities at the University of Chicago Materials Research Science and Engineering Center, supported by National Science Foundation under award number DMR-2011854.

DATA AVAILABILITY STATEMENT

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

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REFERENCES

- [1] I. Salzmann, G. Heimel, M. Oehzelt, S. Winkler, N. Koch, *Acc. Chem. Res.* **2016**, *49*, 370.
- [2] S. Fratini, M. Nikolka, A. Salleo, G. Schweicher, H. Sirringhaus, *Nat. Mater.* **2020**, *19*, 491.
- [3] B. Lüssem, C. M. Keum, D. Kasemann, B. Naab, Z. Bao, K. Leo, *Chem. Rev.* **2016**, *116*, 714.
- [4] T. L. D. Tam, J. Xu, *J. Mater. Chem. A* **2021**, *9*, 5149.
- [5] H. Yan, J. G. Manion, M. Yuan, F. P. García de Arquer, G. R. McKeown, S. Beaupré, M. Leclerc, E. H. Sargent, D. S. Seferos, *Adv. Mater.* **2016**, *28*, 6491.
- [6] M. Goel, M. Thelakkat, *Macromolecules* **2020**, *53*, 3632.
- [7] F. Zhang, C. Di, *Chem. Mater.* **2020**, *32*, 2688.
- [8] M. Sommer, in *Organic Flexible Electronics* (Eds: P. Cosseddu, F. E. Cairaoni), Woodhead Publishing, Cambridge, England **2021**, p. 27.
- [9] Y. Zhang, H. Zhou, J. Seifter, L. Ying, A. Mikhailovsky, A. J. Heeger, G. C. Bazan, T.-Q. Nguyen, *Adv. Mater.* **2013**, *25*, 7038.
- [10] B. Russ, A. Glauddell, J. J. Urban, M. L. Chabiny, R. A. Segalman, *Nat. Rev. Mater.* **2016**, *1*, 50.
- [11] G. J. Snyder, E. S. Toberer, *Nat. Mater.* **2008**, *7*, 105.
- [12] W. Zhao, J. Ding, Y. Zou, C. A. Di, D. Zhu, *Chem. Soc. Rev.* **2020**, *49*, 7210.
- [13] R. Kroon, D. A. Mengistie, D. Kiefer, J. Hynnen, J. D. Ryan, L. Yu, C. Müller, *Chem. Soc. Rev.* **2016**, *45*, 6147.
- [14] I. E. Jacobs, A. Moulé, *J. Adv. Mater.* **2017**, *29*, 1703063.
- [15] D. T. Scholes, S. A. Hawks, P. Y. Yee, H. Wu, R. Jeffrey, S. H. Tolbert, B. J. Schwartz, J. R. Lindemuth, S. H. Tolbert, B. J. Schwartz, *J. Phys. Chem. Lett.* **2015**, *6*, 4786.
- [16] I. E. Jacobs, E. W. Aasen, J. L. Oliveira, T. N. Fonseca, J. D. Roehling, J. Li, G. Zhang, M. P. Augustine, M. Mascal, A. J. Moulé, *J. Mater. Chem. C* **2016**, *4*, 3454.
- [17] J. Hynnen, D. Kiefer, L. Yu, R. Kroon, R. Munir, A. Amassian, M. Kemerink, C. Müller, *Macromolecules* **2017**, *50*, 8140.
- [18] S. N. Patel, A. M. Glauddell, D. Kiefer, M. L. Chabiny, *ACS Macro Lett.* **2016**, *5*, 268.
- [19] E. Lim, K. A. Peterson, G. M. Su, M. L. Chabiny, *Chem. Mater.* **2018**, *30*, 998.
- [20] J. Li, G. Zhang, D. M. Holm, I. E. Jacobs, B. Yin, P. Stroeve, M. Mascal, A. Moulé, *J. Chem. Mater.* **2015**, *27*, 5765.
- [21] D. Kiefer, R. Kroon, A. I. Hofmann, H. Sun, X. Liu, A. Giovannitti, D. Stegerer, A. Cano, J. Hynnen, L. Yu, Y. Zhang, D. Nai, T. F. Harrelson, M. Sommer, A. J. Moulé, M. Kemerink, S. R. Marder, I. McCulloch, M. Fahlman, S. Fabiano, C. Müller, *Nat. Mater.* **2019**, *18*, 149.

- [22] S. N. Patel, A. M. Glaudell, K. A. Peterson, E. M. Thomas, K. A. O'Hara, E. Lim, M. L. Chabinyc, *Sci. Adv.* **2017**, 3, e1700434.
- [23] B. X. Dong, C. Nowak, J. W. Onorato, T. Ma, J. Niklas, O. G. Poluektov, G. Grocke, M. F. DiTusa, F. A. Escobedo, C. K. Luscombe, P. F. Nealey, S. N. Patel, *Chem. Mater.* **2021**, 33, 741.
- [24] P. Hu, K. Du, F. Wei, H. Jiang, C. Kloc, *Cryst. Growth Des.* **2016**, 16, 3019.
- [25] A. M. Glaudell, J. E. Cochran, S. N. Patel, M. L. Chabinyc, *Adv. Energy Mater.* **2015**, 5, 1401072.
- [26] S. Dongmin Kang, G. Jeffrey Snyder, *Nat. Mater.* **2017**, 16, 252.
- [27] S. Watanabe, M. Ohno, Y. Yamashita, T. Terashige, H. Okamoto, J. Takeya, *Phys. Rev. B* **2019**, 10, 201.
- [28] C. J. Boyle, M. Upadhyaya, P. Wang, L. A. Renna, M. Lu-Díaz, S. Pyo Jeong, N. Hight-Huf, L. Korugic-Karasz, M. D. Barnes, Z. Aksamija, D. Venkataraman, *Nat. Commun.* **2019**, 10, 2827.
- [29] S. A. Gregory, R. Hanus, A. Atassi, J. M. Rinehart, J. P. Wooding, A. K. Menon, M. D. Losego, G. J. Snyder, S. K. Yee, *Nat. Mater.* **2021**.
- [30] E. M. Thomas, B. C. Popere, H. Fang, M. L. Chabinyc, R. A. Segalman, *Chem. Mater.* **2018**, 30, 2965.
- [31] N. F. Mott, E. A. Davis, *Electronic Processes in Materials*, Vol. 276. OUP Oxford, Oxford, England **1963**.
- [32] K. Kang, S. Schott, D. Venkateshvaran, K. Broch, G. Schweicher, D. Harkin, C. Jellett, C. B. Nielsen, I. McCulloch, H. Sirringhaus, *Mater. Today Phys.* **2019**, 8, 112.
- [33] Y. Lee, J. Park, J. Son, H. Y. Woo, J. Kwak, *Adv. Funct. Mater.* **2021**, 31, 6900.
- [34] A. Abutaha, P. Kumar, E. Yildirim, W. Shi, S. W. Yang, G. Wu, K. Hippalgaonkar, *Nat. Commun.* **2020**, 11, 1737.
- [35] H. Tanaka, K. Kanahashi, N. Takekoshi, H. Mada, H. Ito, Y. Shimoi, H. Ohta, T. Takenobu, *Sci. Adv.* **2020**, 6, e8065.
- [36] R. Kroon, D. Kiefer, D. Stegerer, L. Yu, M. Sommer, C. Müller, *Adv. Mater.* **2017**, 29, 1700930.
- [37] J. Li, C. W. Rochester, I. E. Jacobs, E. W. Aasen, S. Friedrich, P. Stroeve, A. Moulé, *J. Org. Electron. Phys. Mater. Appl.* **2016**, 33, 23.
- [38] L. Q. Flagg, C. G. Bischak, J. W. Onorato, R. B. Rashid, C. K. Luscombe, D. S. Ginger, *J. Am. Chem. Soc.* **2019**, 141, 4345.
- [39] B. Meng, J. Liu, L. Wang, *Polym. Chem.* **2020**, 11, 1261.
- [40] P. A. Finn, I. E. Jacobs, J. Armitage, R. Wu, B. D. Paulsen, M. Freeley, M. Palma, J. Rivnay, H. Sirringhaus, C. B. Nielsen, *J. Mater. Chem. C* **2020**, 8, 216.
- [41] P. Schmode, A. Savva, R. Kahl, D. Ohayon, F. Meichsner, O. Dolynchuk, T. Thurn-Albrecht, S. Inal, M. Thelakkat, *ACS Appl. Mater. Interfaces* **2020**, 12, 13029.
- [42] B. X. Dong, C. Nowak, J. W. Onorato, J. Strzalka, F. A. Escobedo, C. K. Luscombe, P. F. Nealey, S. N. Patel, *Chem. Mater.* **2019**, 31, 1418.
- [43] T. Ma, B. X. Dong, G. L. Grocke, J. Strzalka, S. N. Patel, *Macromolecules* **2020**, 53, 2882.
- [44] B. Wegner, D. Lungwitz, A. E. Mansour, C. E. Tait, N. Tanaka, T. Zhai, S. Duhm, M. Forster, J. Behrends, Y. Shoji, A. Opitz, U. Scherf, E. J. W. List-Kratochvil, T. Fukushima, N. Koch, *Adv. Sci.* **2020**, 7, 1322.
- [45] D. T. Scholes, P. Y. Yee, G. R. McKeown, S. Li, H. Kang, J. R. Lindemuth, X. Xia, S. C. King, D. S. Seferos, S. H. Tolbert, B. Schwartz, *J. Chem. Mater.* **2019**, 31, 73.
- [46] M. P. Gordon, S. A. Gregory, J. P. Wooding, S. Ye, G. M. Su, D. S. Seferos, M. D. Losego, J. J. Urban, S. K. Yee, A. K. Menon, *Appl. Phys. Lett.* **2021**, 118, 301.
- [47] S. A. Gregory, J. F. Ponder, S. L. Pittelli, M. D. Losego, J. R. Reynolds, S. K. Yee, *ACS Appl. Polym. Mater.* **2021**, 3, 2316.
- [48] E. Lim, A. M. Glaudell, R. Miller, M. L. Chabinyc, *Adv. Electron. Mater.* **2019**, 5, 1.
- [49] D. T. Scholes, P. Y. Yee, J. R. Lindemuth, H. Kang, J. Onorato, R. Ghosh, C. K. Luscombe, F. C. Spano, S. H. Tolbert, B. Schwartz, *J. Adv. Funct. Mater.* **2017**, 27, 1.
- [50] T. Ma, W. Kent, B. X. Dong, G. L. Grocke, S. N. Patel, *Appl. Phys. Lett.* **2021**, 119, 902.
- [51] S. Wood, J. R. Hollis, J.-S. Kim, *J. Phys. D Appl. Phys.* **2017**, 50, 3001.
- [52] W. C. Tsoi, D. T. James, J. S. Kim, P. G. Nicholson, C. E. Murphy, D. D. C. Bradley, J. Nelson, J. S. Kim, *J. Am. Chem. Soc.* **2011**, 133, 9834.
- [53] A. R. Chew, R. Ghosh, Z. Shang, F. C. Spano, A. Salleo, *J. Phys. Chem. Lett.* **2017**, 8, 4974.
- [54] R. Fujimoto, Y. Yamashita, S. Kumagai, J. Tsurumi, A. Hinderhofer, K. Broch, F. Schreiber, S. Watanabe, J. Takeya, *J. Mater. Chem. C* **2017**, 5, 2023.
- [55] D. M. DeLongchamp, R. J. Kline, E. K. Lin, D. A. Fischer, L. J. Richter, L. A. Lucas, M. Heeney, I. McCulloch, J. E. Northrup, *Adv. Mater.* **2007**, 19, 833.
- [56] J. Northrup, *Phys. Rev. B - Condens. Matter Mater. Phys.* **2007**, 76, 5202.
- [57] P. Pingel, L. Zhu, K. S. Park, J. O. Vogel, S. Janietz, E. G. Kim, J. P. Rabe, J. L. Brédas, N. Koch, *J. Phys. Chem. Lett.* **2010**, 1, 2037.
- [58] J. L. Bredas, G. B. Street, *Acc. Chem. Res.* **1985**, 18, 309.
- [59] Z. Liang, H. Ho Choi, X. Luo, T. Liu, A. Abtahi, U. Shantini Ramasamy, J. Andrew Hitron, K. N. Baustert, J. L. Hempel, A. M. Boehm, A. Ansary, D. R. Strachan, J. Mei, C. Risko, V. Podzorov, K. R. Graham, *Nat. Mater.* **2021**, 20, 518.
- [60] Z. Jiang, X. Li, J. Strzalka, M. Sprung, T. Sun, A. R. Sandy, S. Narayanan, D. R. Lee, J. Wang, *J. Synchrotron Radiat.* **2012**, 19, 627.
- [61] Z. Jiang, *J. Appl. Cryst.* **2015**, 48, 917.

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How to cite this article: T. Ma, B. X. Dong, J. W. Onorato, J. Niklas, O. Poluektov, C. K. Luscombe, S. N. Patel, *J. Polym. Sci.* **2021**, 59 (22), 2797. <https://doi.org/10.1002/pol.20210608>