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Quantitative Measurements of the Temperature-Dependent Microscopic and Macroscopic Dynamics of a Molecular Dopant in a Conjugated Polymer

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S Supporting Information

ABSTRACT: Understanding the nature of dopant dynamics in the solid state is critical for improving the longevity and stability of organic electronic devices and for optimizing the doping-induced solubility control (DISC) patterning method. In this work, we use quasi-elastic neutron scattering (QENS) and fluorescence quenching techniques to develop a comprehensive picture of both the microscopic and macroscopic dynamics of the soluble p-type molecular dopant tetrafluoromethyloxycarbonyltricyanoquinodimethane (F4MCTCNQ) in the conductive polymer poly(3-hexylthiophene-2,5-diyl) (P3HT). Specifically, fast dynamics (ps–ns) of the dopant, such as the methyl and the methoxycarbonyl group rotations, are observed in QENS experiments. From confocal fluorescence microscope experiments, longer-range/slower dopant diffusion (ms–days) is captured. However, in order to fit these data, it is necessary to incorporate a Langmuir isotherm equilibrium between the neutral and ionized dopant molecules. Ionized F4MCTCNQ is strongly favored by the equilibrium, but it diffuses 3 orders of magnitude slower than neutral species. Moreover, the macroscopic diffusion is found to depend mostly on the minority concentration of neutral dopant molecules in the film. Finally, the global diffusion coefficient of the monoester-substituted dopant F4MCTCNQ is shown to be more than 1 order of magnitude smaller than that of the widely used dopant F4TCNQ.

INTRODUCTION

The successful development of organic electronic devices, such as organic photovoltaics (OPVs),^{1,2} organic light-emitting diodes (OLEDs),^{3,4} and organic field-effect transistors (OFETs),^{5,6} is largely attributable to the tunability of their electrical properties. Like inorganic semiconductors, organic semiconductors (OSCs) can be doped to facilitate increased charge transport^{7,8} as well as decreased injection or extraction barriers via changes in the Fermi energy.⁹ However, the undesired diffusion of dopants in organic electronic architectures has been known to cause serious stability and longevity issues.^{10–12} Controlling dopant diffusion is also an important aspect of doping-induced solubility control (DISC), a new patterning method recently developed which allows the solubility of a conductive polymer to be switched on and off by doping and dedoping, respectively.^{13–15} It has also been demonstrated that DISC is capable of using both vapor and

solution processes to achieve micrometer and submicrometer resolution, respectively, in a method that is compatible with roll-to-roll solution processing.^{13,16} For DISC patterning, the lateral diffusion of the dopant limits the ultimate resolution of the pattern. Therefore, for both the stability of completed organic devices and for fabrication of these devices using solution compatible methods, understanding the dynamics of the dopants is extremely important to further application development.

The measurement of small molecular dopant diffusion is particularly challenging because dopants are present in trace quantities and composed of the same light elements (C, H, O, N, S) as the host OSCs. Most of these studies so far have

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chemical structures of the materials investigated in this paper are shown in Figure 1. F4MCTCNQ was also chosen because

Figure 1. Chemical structures of F4TCNQ, F4MCTCNQ, P3HT, *d*-P3HT, and the simplified P3HT analogue (M8) investigated in this work.

its methyl group carries three identical protons that can be used as a unique isotopic label in neutron scattering experiments. Quasi-elastic neutron scattering (QENS) is a well-established nondestructive technique to probe dynamic processes in soft matter.³⁷ In the first part of this article, we use QENS to measure the dynamics of F4MCTCNQ at the molecular scale in a sample of fully deuterated P3HT (*d*-P3HT). The protons on the F4MCTCNQ are the only hydrogen sites in the system, and ¹H has a much larger inelastic scattering cross section than any other isotope in the sample, allowing us to track the temperature-dependent motions of the dopant molecule only. The diffusion rate and jump distance for various microscopic motions are measured, and the motions are assigned with the aid of density functional theory (DFT) calculations. In the second part of the article, we use confocal fluorescence spectroscopy to spatially and temporally track the F4MCTCNQ concentration in patterned P3HT films, which allows us to quantify the macroscopic diffusion of the dopant. We show that macroscopic diffusion is principally dependent on the minority concentration of neutral dopant molecules in the film. This multiscale investigation gives an unprecedented mechanistic insight into dopant diffusion in OSCs.

EXPERIMENTAL SECTION

Materials. P3HT (regioregular >98%, M_n = 54–75 kDa), chlorobenzene, deuterated chlorobenzene, and molybdenum oxide (MoO_3) were purchased from Sigma-Aldrich. *d*-P3HT (regioregular >97%) and F4MCTCNQ were synthesized using the methods reported in the literature.^{36,38} All chemicals were used as received unless otherwise indicated. PELCO TEM grids (1GN400, nickel) were purchased from Ted Pella, Inc.

Sample Preparation and Measurements. Neutron Scattering. To prepare the blend sample for QENS measurements, solutions of F4MCTCNQ and *d*-P3HT in deuterated chlorobenzene were first mixed to achieve a 17% mole fraction of dopant to polymer. The blend solution was then drop-cast onto a clean glass slide. The sample was placed into a vacuum chamber to completely evaporate the solvent. The resulting blend layer was scraped from the glass slide using a clean razor blade. Both blend and neat samples were ground to a power using a mortar and pestle for 15 min and then weighed prior to being loaded into a 0.5 mm thick flat aluminum container for further analysis.

QENS measurements were performed on the backscattering spectrometer called BASIS at the Spallation Neutron Source (SNS) 169

focused on the diffusion of dopants from one layer to another in a vertical layer stack. These samples are prepared by either vacuum evaporating or laminating doped and undoped layers of materials. Secondary ion mass spectrometry (SIMS) is by far the most commonly used technique for diffusion studies due to its high spatial and depth resolution in differentiating molecules. A recent study shows that SIMS can be utilized to monitor the diffusion of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), which is a widely used p-type molecular dopant, in the hole transport layer of OLEDs.¹⁷ The SIMS signal from the fluorine atoms gives a unique isotopic label. Similar work using SIMS was also performed more recently on the diffusion of the soluble p-dopant molybdenum tris[1-(methoxycarbonyl)-2-(trifluoromethyl)-ethane-1,2-dithiolene] ($\text{Mo}(\text{tfd-CO}_2\text{Me})_3$) into polymer and polymer blend films using the Mo label.¹⁸ Likewise, excellent work was conducted by Treat et al. where the diffusion of phenyl-C₆₁-butyric acid methyl ester (PCBM) in poly(3-hexylthiophene-2,5-diyl) (P3HT) was quantified using SIMS and a deuterium-labeled PCBM (*d*-PCBM).¹⁹ The same group also quantified the lateral diffusion of *d*-PCBM in P3HT using dynamic SIMS, yielding a one-dimensional diffusion coefficient using Fick's second law.²⁰ However, SIMS is a destructive technique, and additional etching steps are needed. In addition, a unique atom or isotopic labeling is required in order to use SIMS. Other measurement techniques, such as X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), neutron/X-ray/visible light scattering, and photoluminescence, have also been used to measure the diffusion of dopants in layered samples.^{21–29} Most of these studies reported whether dopants diffused beyond their original layer and at which temperature threshold. Although some were able to quantify dopant concentration at an interface or surface, only one study was able to measure diffusion as a function of distance and time. Thus, Fischer et al. quantified the temperature dependence of the diffusion coefficient in a vertical geometry using a time-resolved optical technique.²⁴ Finally, a series of articles have reported the observation of dopant diffusion (or lack thereof) by creating bi- or trilayers and subsequently measuring changes in the electronic properties of layer stack.^{30–34} For these electronic measurements, the movement of dopants is inferred but cannot be quantified.

Previous studies have shown that dopant molecules can diffuse in a small molecule or polymer OSC host. It is known that larger dopant molecules diffuse more slowly but also have been shown to disturb the packing of the OSC and thereby to increase disorder in the local density of states.³⁵ Very few studies have quantified the diffusion rate of dopants. It has been assumed that the onset of diffusion occurs as a result of heating to above the glass transition temperature (T_g) of host OSC. However, one study showed that F4TCNQ diffuses at room temperature in P3HT²³ and another showed that PCBM diffuses into P3HT at 50 °C, which is below the T_g of P3HT.¹⁹ To the best of our knowledge, no molecular level studies have looked into the mechanism for dopant binding or investigated how the properties of the host material affect the onset of dopant diffusion.

In this article, we investigate the temperature-dependent microscopic and macroscopic dynamics of the soluble p-type molecular dopant tetrafluoromethyloxycarbonyltricyanoquinodimethane (F4MCTCNQ) in P3HT. F4MCTCNQ is chosen due to its superior solubility/miscibility and thereby increased doping efficiency compared with F4TCNQ.³⁶ The

170 at Oak Ridge National Laboratory (ORNL) with an energy resolution
171 of 3.5 μeV (full width at half-maximum, fwhm), a dynamic range of
172 $\pm 170 \mu\text{eV}$, and a scattering wavevector Q range from 0.3 to 2.0 $\text{\AA}^{-1}$.³⁹
173 The elastic scans were obtained from 50 to 375 K at a heating rate of 1
174 K/min, and the high statistical QENS spectra were recorded at 273,
175 323, and 373 K. The spectra collected at 50 K were used as the
176 instrument resolution function, and all the data were corrected for
177 detector efficiency using a vanadium standard.

178 **Confocal Spectroscopy.** To prepare samples for the macroscopic
179 diffusion measurements, P3HT films of ~ 50 nm thickness were first
180 obtained by spin-coating 10 mg/mL P3HT from a chlorobenzene
181 solution onto clean glass substrates (cleaned in ultrasonic baths of
182 acetone, 5% Mucosol detergent, and deionized water, followed by
183 drying with nitrogen and exposure to UV/ozone for 30 min). A TEM
184 grid (400 mesh; hole width 38 μm ; bar width 26 μm) was
185 subsequently placed onto the P3HT film using Kapton tape. Next, a
186 2.2 nm F4MCTCNQ layer was deposited onto the P3HT film using
187 an MBraun thermal evaporator at a deposition rate $\sim 0.1 \text{\AA}/\text{s}$ at ~ 80
188 $^{\circ}\text{C}$, followed by the deposition of 50 nm MoO_3 and 100 nm Ag, also
189 via evaporation. Prior to deposition, the evaporation chamber was
190 pumped down to a pressure of 5×10^{-6} mbar. Finally, the samples
191 were encapsulated in an epoxy resin under a glass coverslip to ensure
192 complete isolation from O_2 and H_2O . All fabrication steps were
193 performed inside a nitrogen glovebox.

194 The confocal fluorescence (FL) microscope images were obtained
195 on a Zeiss LSM 700 microscope equipped with a 488 nm laser and a
196 20 $\times$ objective with 0.6 numerical aperture. These confocal FL images
197 (16-bit, 2048 $\times$ 2048 pixels of 320 μm size) were captured at the same
198 position before and after annealing at various temperatures (298, 323,
199 348, and 373 K) for various time steps by tracking the position of the
200 marked center of the TEM grid.

201 **Data Analysis. Neutron Data Analysis.** For the data analysis, the
202 dynamic range was from -120 to $+120 \mu\text{eV}$. The relevant momentum
203 transfer range in this study was limited to 0.5 – $1.3 \text{\AA}^{-1}$ given the signal-
204 to-noise ratio, the flat-plate geometrical limit, and the uncertainty of
205 the background subtraction. DAVE software was used for data
206 reduction and analysis.⁴⁰ The neat *d*-P3HT spectra were subtracted
207 from the F4MCTCNQ doped *d*-P3HT spectra for all the QENS data
208 analyses to ensure that the signal from F4MCTCNQ could be isolated.

209 In general, the experimentally observed scattering intensity
210 $S_{\text{exp}}(Q, \omega)$ at each Q and temperature is expressed as the convolution
211 of the model function $S_{\text{model}}(Q, \omega)$ and the resolution function $R(Q, \omega)$,
212 plus a linear background term $B(Q, \omega)$:⁴¹

$$213 \quad S_{\text{exp}}(Q, \omega) = S_{\text{model}}(Q, \omega) \otimes R(Q, \omega) + B(Q, \omega) \quad (1)$$

214 Here, the model function can be separated into an elastic component
215 (a delta function $\delta(\omega)$) and a quasi-elastic contribution $S_{\text{qe}}(Q, \omega)$:

$$216 \quad S_{\text{model}}(Q, \omega) = \text{DWF}(Q)[A_0(Q)\delta(\omega) + (1 - A_0(Q))S_{\text{qe}}(Q, \omega)] \quad (2)$$

217 where $\text{DWF}(Q)$ is the Debye–Waller factor due to the vibrational
218 motions and $A_0(Q)$ is the elastic incoherent structure factor (EISF)
219 defined as the fraction of elastic scattering. The proposed expression
220 for $S_{\text{qe}}(Q, \omega)$ will be addressed in detail in the **Results and Discussion**
221 section.

222 **Macroscopic Diffusion Model.** The location of dopants within the
223 P3HT films was determined by measuring the fluorescence intensity of
224 P3HT as a function of position using a confocal microscope and 488
225 nm excitation. The concentration of the dopants was determined by
226 comparing to a calibration curve of fluorescence intensity in P3HT as a
227 function of known doping density and assuming that there is no
228 vertical doping gradient (reasonable for diffusion over μm in an ~ 50
229 nm thick film). A two-dimensional two-species (2D2S) diffusion
230 model was developed to fit the 2D doping profiles. The two diffusing
231 species in this model were treated using a Langmuir isotherm
232 equilibrium,⁴² which was preceded for P3HT/dopants in a previous
233 publication.¹⁴ In terms of detailed fits, the 2D concentration profile
234 images were initially evolved based on the above-mentioned diffusion
235 model and then evolved using a stepwise solution to Fick's second law.

The finite-difference method using a forward time-centered difference
scheme was used to evolve the model in time. After each profile was
evolved one time step into the future, the ratio of doped to undoped
F4MCTCNQ was re-equilibrated as a function of position and
concentration using the Langmuir equilibrium. In this rapid
equilibration, it is assumed that the reaction rate between two species
is much faster than the rate of diffusion. In doing so, the diffusion
coefficients for the two species could be treated as fitting parameters
and optimized based on minimization of the sum of squared residuals.

Computational Method. An eight-unit methyl-substituted oligo-
thiophene (M8) oligomer was used as a model for a P3HT chain. The
oligomer was optimized in isolation at the B3LYP/6-31G* level of
theory with Grimme D2 dispersion correction (B3LYP-D).^{43,44} In the
absence of a dielectric medium, two of these optimized oligomers were
then placed at two distinct intermolecular separations (6.30 and 6.96
 $\text{\AA}$), and a F4MCTCNQ molecule was placed midway between and
parallel with the two M8 chains. These two intermolecular separations
were chosen based on the optimized M8/F4TCNQ system.⁴⁵ The
chains were fixed while the F4MCTCNQ was free to relax during a
geometry optimization at the B3LYP-D/6-31G* level. A dielectric
constant of 3.0 was used as it has been shown to be appropriate for
organic semiconductors.^{46–49} The lowest energy geometry was found
to be that with the ring of the F4MCTCNQ stacked over the central
inter-thiophene bond and the ester methyl group on the opposite side
of the M8 chain methyl groups. The two separations were chosen as
twice the distance between a single M8 chain and F4MCTCNQ
molecule from an unconstrained geometry optimization using B3LYP
with and without the dispersion correction, respectively. The two M8
oligomers were constrained in the optimization of the full system to
prevent unphysical wrapping of the chains around the F4MCTCNQ
molecule. These two intermolecular separations were used to give an
estimate of possible variations in the energy barriers to rotation and
translation due to variations in the interchain separation. Since it was
found that introducing solvent into this system does not affect the
intermolecular separation, the values from systems without the
dielectric continuum were used.

To calculate the potential energy barrier for F4MCTCNQ
translation along the polymer backbone axis, atoms in the M8 chains
were fixed while the F4MCTCNQ was free to relax in a set of
optimizations, subject to a position constraint applied by fixing one
atom in the F4MCTCNQ. This set of translation optimizations
spanned up to two thiophene units.

To calculate the potential energy barrier for F4MCTCNQ methyl
rotation between the two M8 chains for both interchain separations, all
atoms in the system excluding the ester methyl hydrogens were fixed,
and these hydrogens were free to relax in a set of optimizations subject
to dihedral angle constraints spanning 120° . In addition, calculations
on an isolated F4MCTCNQ molecule were performed, in which no
atom positions were fixed. Solvent was used in these calculations.
Similar calculations were performed to calculate the barrier for the
F4TCNQ methoxycarbonyl rotation, but only for the isolated
molecule and for the molecule between M8 chains separated by 6.96
 $\text{\AA}$.

228 ■ RESULTS AND DISCUSSION 229

Part One: Microscopic Dynamics of Molecular
Dopant. Elastic Incoherent Neutron Scattering. The micro-
scopic dynamics of the F4MCTCNQ molecule were
investigated using neutron scattering. To determine the
temperature range at which the dynamic transitions of protons
take place and become observable on BASIS, facile elastic
incoherent neutron scattering experiments were performed
first. The elastic scans of the F4MCTCNQ doped *d*-P3HT
blend measured from 50 to 375 K at various Q values are
shown in Figure 2a. Generally, the elastic intensity decreases
monotonically with temperature due to Debye–Waller thermal
factors, while any observed dynamics of the species lead to
further reduction of the elastic intensity.⁵⁰ The divergence from 302

Figure 2. (a) Normalized elastic scattering intensity at various Q and (b) mean-square displacement (MSD) as a function of temperature for the F4MCTCNQ doped d -P3HT blend.

Representative neutron scattering spectra of subtracted 331 doped d -P3HT at $Q = 0.9 \text{ \AA}^{-1}$ at three temperatures (273, 332 323, and 373 K) are shown in Figure 3. The experimental 333

Figure 3. Representative BASIS spectra of subtracted doped d -P3HT at $Q = 0.9 \text{ \AA}^{-1}$ at 273 K (orange), 323 K (dark cyan), and 373 K (purple), along with the resolution function obtained at 50 K (gray dashed line). Both unnormalized (top) and normalized (bottom) data with respect to their intensity at $\hbar\omega = 0$ are shown.

resolution functions collected at 50 K are also plotted. In 334 general, the spectra can be described as a superposition of two 335 contributions: (1) a Gaussian distribution corresponding to the 336 elastic portion and (2) a broad shoulder in the quasielastic 337 region. The broadening of the quasi-elastic components with 338 increasing temperature seen from Figure 3 (it is more obvious 339 in their normalized spectra) provides clear evidence of the 340 occurrence of dynamic processes, which is consistent with the 341 MSD results from elastic scans. Similar broadening features are 342 also observed at other Q ranges (Supporting Information 343 Figures S2 and S3). 344

In order to extract diffusive information from QENS, the 345 experimental spectra were fit using a model function discussed 346 in the Data Analysis section (eqs 1 and 2). Again, since two 347 dynamic processes are observed above 254 K, two stretched 348 exponential relaxation (or Kohlrausch–Williams–Watts, 349 KWW) functions were included in the quasi-elastic term 350 $S_{qe}(Q, \omega)$ in eq 2, expressed as 351

$$S_{qe}(Q, \omega) = P \int \exp \left[- \left(\frac{t}{\tau_1} \right)^{\beta_1} \right] \exp \left(i \frac{E}{\hbar} t \right) dt + (1 - P) \int \exp \left[- \left(\frac{t}{\tau_2} \right)^{\beta_2} \right] \exp \left(i \frac{E}{\hbar} t \right) dt \quad (3) \quad 352$$

where τ and β are the characteristic time and stretching 353 exponent, respectively, while the subscripts 1 and 2 represent 354 different dynamic components. The parameter P is defined as 355 the fraction of the first Fourier-transformed stretched 356 exponential relaxation term. E is the energy change of the 357 neutrons, and $\hbar$ is the reduced Planck constant. Using this 358 model, we expect that the rotations of methyl group can be 359 captured by the faster stretched exponential term (set $\tau_1 < \tau_2$), 360

Figure 4. (a) Relative weight of the first KWW term (eq 3) as a function of Q at various temperatures. (b) Representative QENS spectrum and fit with a single KWW function of subtracted doped d -P3HT at a Q of $0.9\text{ \AA}^{-1}$ and temperature of 273 K . (c) Representative QENS spectrum and fits with two KWW functions of subtracted doped d -P3HT at a Q of $0.9\text{ \AA}^{-1}$ and temperature of 373 K .

while the other motion of the hydrogen sites can be captured using the slower stretched exponential term.

We performed fits to all the spectra and found that a single stretched exponential term was sufficient for satisfactory fits of the 273 K data (the fit weight P values converge to unity, shown in Figure 4a), but at 323 and 373 K , fitting $S_{\text{qe}}(Q, \omega)$ required incorporating two KWW terms for all data except $Q = 1.3\text{ \AA}^{-1}$. Examples of these one and two KWW fits are presented in Figures 4b and 4c, respectively. As can be seen, the fits capture the experimental spectra reliably over the entire energy range in both cases. We attribute the successful fit using only one KWW term at 273 K to the fact that the dynamics of methyl group rotations dominate at a temperature that is just slightly above 254 K . Reduced P values, therefore, are expected once temperature increases, which is exactly what is observed. The P values follow a clear decreasing trend upon heating. At 373 K , an average of $\sim 20\%$ of the total inelastic hydrogen scattering is due to the second dynamic process. The full experimental spectra and fits at all conditions are shown in Supporting Information Figures S4–S6.

The successful fits of QENS spectra using a stretched exponential model allow us to further explore the nature of the dynamic motions. Normally, the mean relaxation time $\langle \tau_i \rangle$ of process i is extracted by

$$\langle \tau_i \rangle = \frac{\tau_i}{\beta_i} \Gamma\left(\frac{1}{\beta_i}\right) \quad (4)$$

where τ_i and β_i are fitting parameters from the stretched exponential model in eq 3, and $\Gamma(x)$ is the gamma function. The Q^2 dependence of calculated values in the form of $\langle \tau_i \rangle^{-1}$ is plotted in Figure 5. The comparison of absolute $\langle \tau_i \rangle^{-1}$ values clearly implies that two distinct diffusive motions are observed as expected. In addition, Figure 5 shows that for both fast and slow processes the $\langle \tau_i \rangle^{-1}$ values exhibit a quadratic behavior at low Q values and then a saturation trend at high Q values. This nonlinear variation of $\langle \tau_i \rangle^{-1}$ as a function of Q^2 indicates noncontinuous diffusion of hydrogen sites,⁵⁴ which is particularly true for the case of methyl group rotations. Therefore, a well-studied jump diffusion model (Singwi–Sjölander model) was employed to describe both dynamic processes, given by⁵⁵

$$\frac{1}{\langle \tau \rangle} = \frac{DQ^2}{1 + DQ^2\tau} \quad (5)$$

Figure 5. Inverse of mean relaxation time (symbols) of the fast process (a) and slow process (b) obtained from KWW fits as a function of Q^2 at various temperatures. The corresponding solid lines are the best representative fits to the jump diffusion model.

where τ is the residence time between jumps of a diffusive particle and D is the diffusion coefficient. The mean-square jump length can also be determined by $\langle L^2 \rangle = 6D\tau$ in this model. As can be seen from the solid lines in Figure 5, these fits yield a reasonable agreement with the data, and the resulting diffusion parameters at each temperature are summarized in Table 1.

By comparing the two dynamic processes, we notice that the observed diffusion coefficients of the faster process are approximately 1 order of magnitude greater than those of the

Table 1. Model Parameters Obtained from Fits of the Q^2 -Dependent $\langle\tau_1\rangle^{-1}$ and $\langle\tau_2\rangle^{-1}$ Using a Jump Diffusion Model

	temp (K)	diffusion coeff D ($\times 10^{-6}$ cm ² /s)	residence time τ (ps)	mean jump length $(\langle L^2 \rangle)^{1/2}$ (Å)
fast process	273	3.13 ± 1.05	34.38 ± 8.50	2.54 ± 0.74
	323	5.90 ± 0.90	20.23 ± 1.62	2.68 ± 0.31
	373	10.17 ± 0.89	12.13 ± 0.64	2.72 ± 0.19
slow process	273			
	323	0.86 ± 0.12	100.15 ± 18.01	2.27 ± 0.26
	373	1.68 ± 0.15	46.57 ± 10.22	2.17 ± 0.34

slower process. Also, the residence time values are factor of 5 lower at the same temperature for the faster process. The mean jump lengths, on the other hand, are comparable at 2–3 Å. With respect to the individual process, the rotational diffusion coefficient of the methyl group increases from 3.13×10^{-6} cm²/s at 273 K to 10.2×10^{-6} cm²/s at 373 K. Although we are unable to capture the slower motion process at 273 K, the diffusion coefficient of the second dynamic process still exhibits a 2-fold increase from 323 to 373 K.

Further analysis of the temperature dependence of the diffusion coefficients and residence time was performed. Here, Arrhenius behavior was assumed to fit the data (seen in Figure 6) and an activation energy E_A associated with each process was

Figure 6. Diffusion coefficient (top) and residence time (bottom) as a function of $1000/T$ for the first dynamic (purple circles) and second dynamic (dark cyan squares). The corresponding solid lines are fits to an Arrhenius behavior.

determined, which is summarized in Table 2. As can be seen, the activation energy of the slow process (~ 14 kJ/mol) is slightly higher than that of the fast process (~ 10 kJ/mol).

Table 2. Activation Energy E_A (kJ/mol) Obtained from Arrhenius Fits of Diffusion Coefficient D and Residence Time τ Associated with Dynamics of Hydrogen Atoms^a

	E_A from diffusion coeff (kJ/mol)	E_A from residence time (kJ/mol)	E_A from elastic scattering (kJ/mol)
fast process	10.4 ± 0.5	9.6 ± 0.8	7.0 ± 0.3
slow process	13.4 ± 2.8	14.9 ± 4.4	

^aThe E_A value derived from elastic scattering is also shown for comparison.

Generally, the E_A of methyl group rotation is reported to be 6–12 kJ/mol for small molecules^{56–58} and polymers.^{51,59–61} To more accurately determine the E_A for this specific sample, we first performed density-functional theory (DFT) calculations on an isolated dopant molecule. The F4MCTCNQ methyl hydrogens were rotated through 120° in 30° increments with the rest of the atoms in the system fixed. As can be seen in Figure 7b (orange curve), the energy barrier to methyl rotation occurs at a 60° offset from the global minimum energy configuration. The calculated barrier of ~ 4 kJ/mol is roughly consistent with the experimental barrier of ~ 10 kJ/mol. However, since this calculated energy barrier could also be affected by the P3HT chains, the barrier in the presence of fixed chains was investigated, and the actual barrier is likely to be between these values. We assumed here, based on the published geometry of P3HT in the presence of F4TCNQ^{62,63} that a F4MCTCNQ molecule is sandwiched between two M8 chains as seen in Figure 7a. Given the possible sensitivity to the M8 chain distance, calculations at two distinct intermolecular separations (6.30 and 6.96 Å) were performed. Figure 7b shows that the magnitude of the rotational barrier increases slightly with increasing interchain separation. In both cases, the barrier to methyl rotation was determined to be 8–10 kJ/mol, yielding a linear distance of 1.8 Å and arc length of 2.1 Å for moved hydrogen atom in this rotation. Given the typical errors of this type of calculation of at least 1 kcal/mol (~ 4 kJ/mol), this result is consistent with the QENS experiments. The value of the jump length, however, is a slightly lower than that determined experimentally, which could be due to the approximations made in the calculations, which were performed in vacuum at zero temperature and with fixed positions for the thiophene backbone. The good match between QENS experiments and DFT calculations validate the assignment of the fast dynamic process to the methyl rotation of F4MCTCNQ.

With regard to the slower observed motion, we can confidently rule out based on DFT calculations that it is due to the translational diffusion of F4MCTCNQ along the polymer backbone. Figure 7c shows the calculated energy profile for the translation of a F4MCTCNQ molecule for one thiophene unit (~ 4 Å) in each direction from its lowest energy position for the 6.96 Å separation and half a thiophene unit (~ 2 Å) in each direction for the 6.30 Å separation. The closer interchain distance between thiophene chains yields substantially higher energy barriers to translation in both directions (~ 60 kJ/mol). However, even calculation using a larger interchain separation still yields a large energy barrier of ~ 30 kJ/mol. Extending the translation for the larger interchain distance to one thiophene unit demonstrates local minima at every half-thiophene unit translation, corresponding to F4MCTCNQ ring stacking directly over a thiophene ring. In any case, the calculated translational barriers are considerably higher than what were measured experimentally from QENS (~ 14 kJ/mol).

Given the small activation energy and jump length of the slower motion, it seems more reasonable that this motion is associated with a localized motion that is internal to the F4MCTCNQ molecule. Closer inspection of the translation calculations in Figure 7c implies that low-energy vibrational motion around the position minima may be responsible for the slower motion. In other words, the whole F4MCTCNQ molecule might move back and forth within a potential well. However, further calculations using a simple harmonic

Figure 7. (a) Sandwich geometry comprising two M8 oligomers and a F4MCTCNQ molecule. The corresponding diffusive motions of each DFT calculations are also described schematically. (b) Rotation energy of the ester methyl hydrogens through 120° for two interchain separations and the isolated dopant molecule. Inset: calculated hydrogen displacements for the F4MCTCNQ methyl rotation. (c) Translation energy of the monoester molecule over one thiophene unit (6.30 Å interchain separation) and two thiophene units (6.96 Å interchain separation). The dashed gray line is the quadratic fit in order to yield a harmonic potential. (d) Rotation energy of ester group for the isolated dopant molecule (top) and a 6.96 Å interchain separation (bottom).

oscillator model, shown as the dashed gray line in Figure 7c, enable us to disprove this hypothesis. The calculated spacing between vibrational energy levels (~ 2.5 meV, Supporting Information section 6) is significantly higher than the energy spread of the QENS measurements (on the order of μ eV), indicating that it is impossible to capture this dynamic motion in the energy window on BASIS. Other possible sources of the slower motion are the localized rotation of methoxycarbonyl group ($-\text{COOCH}_3$) or the rotation of methoxy group ($-\text{OCH}_3$) in F4MCTCNQ. We can safely rule out the methoxy rotation assignment because of its high rotation barrier (>50 kJ/mol) in the literature calculations even for an isolated molecule.^{64,65} On the other hand, DFT calculations of the methoxycarbonyl rotation of an isolated F4MCTCNQ molecule (Figure 7d) yields a barrier of ~ 16 kJ/mol, which is consistent with the QENS results. Although the calculation on the sandwich geometry (6.96 Å interchain separation) produces a significantly higher barrier, a lower value would be expected if the relaxation of the chains were allowed. In addition, given the fact that the inferred E_A values of the slower motion are in good agreement with reported values for methoxycarbonyl rotations,⁶⁵ we tentatively assign the slower motion to this rotation of the dopant.

Additional insight, particularly into the geometry of the motion, can also be obtained by investigating the elastic incoherent structure factors (EISF). The Q -dependent EISF values at three investigated temperatures are plotted in Figure 8. A 3-fold jump model has been widely used to describe methyl group rotations:^{66,67}

Figure 8. Elastic incoherent structure factor (EISF) obtained for subtracted doped d -P3HT as a function of Q at 273 K (orange), 323 K (dark cyan), and 373 K (purple). The solid lines are product fits to a rotational jump diffusion on a circle model (set $N = 30$ in eq 7) and a methyl group 3-fold jump model. The 3-fold jump model of the methyl group is also shown for comparison. Inset: obtained EISF fit parameters using the product diffusion model in form of eq 7.

$$\text{EISF}_{\text{methyl}}(Q) = f_1 + (1 - f_1) \left(\frac{1}{3} [1 + 2j_0(\sqrt{3}Qr)] \right) \quad (6)$$

where j_0 is the spherical zeroth-order Bessel function, f_1 is the fraction of immobile protons, and r is the radius, which was set to 1.03 Å based on the known geometry of methyl group.⁶⁸ However, the fit of methyl group 3-fold jumps (dashed line) shows significant deviation from the EISF values and is also

Figure 9. Schematics of (a) sample preparation and (b) resulting sample geometry and confocal experimental setup. (c) The confocal fluorescence images of patterned films before (top row) and after (bottom row) annealing at various temperatures (298, 323, 348, and 373 K) for time t .

greater in all cases. This clearly indicates that the methyl group rotation is not the only component that contributes to the QENS signal even at 273 K and that the slower motion must also be taken into account, which again is in good agreement with our observations from the elastic QENS data. Therefore, we rewrite eq 6 by including a well-established rotational diffusion model, where it is assumed that the scattering center jumps between N equivalent points on a circle:^{69,70}

$$\text{EISF}(Q) = \left[f_1 + (1 - f_1) \left(\frac{1}{3} [1 + 2j_0(\sqrt{3}Qr)] \right) \right] \times \left[f_2 + (1 - f_2) \left(\frac{1}{N} \sum_{i=1}^N j_0 \left(2QR \sin \frac{\pi i}{N} \right) \right) \right] \quad (7)$$

where f_2 is the fraction of immobile protons involved in the methoxycarbonyl rotation, R is the circle radius, and r is still set to 1.03 Å. The product form means that the whole methyl group moves during the methoxycarbonyl rotation. The detailed derivation is shown in Supporting Information section 1. For $N \rightarrow \infty$, the limiting case of continuous rotational diffusion on a circle is reached. By means of this improved model, the EISF behavior is able to be captured over the whole investigated Q range as seen the solid lines in Figure 8 where N is set to 30 (a satisfactory fit is found for $N \geq 2$). In all cases, the parameter f_1 always converges to 0, revealing that all hydrogen sites are involved in the methyl rotations at any given temperature. The parameter f_2 and R , on the other hand, are found to vary slightly and converge with increasing N (Figure S7), the corresponding converged values of which are summarized in the inset of Figure 8. As can be seen, the values of f_2 follow a clear decreasing trend from 0.86 to 0.29 upon heating, which is consistent with results from Figure 4 that increased scattering from the slower motion is observed as temperature increases. Moreover, the diffusive motion of the

slower motion is restricted on a circle of ~ 2.0 – 3.7 Å radius, which is also consistent with the geometry of the methoxycarbonyl rotation, where the distance from the center of methyl hydrogen sites to the rotation axis is estimated to be ~ 1.7 Å.

Part Two: Macroscopic Dynamics of Molecular Dopants. The previous section demonstrated that two molecular-scale motions of F4MCTCNQ in P3HT can be observed and assigned from QENS experiments. Unfortunately, the energy window of the BASIS spectrometer was insufficient to observe rarer and longer-range diffusive processes that contribute to macroscopic diffusion. Therefore, laser scanning confocal microscopy (LSCM) was used to quantify the macroscopic diffusion of F4MCTCNQ in P3HT.

In order to make this macroscopic measurement possible, a specific sample architecture was required, which was derived from our recently developed dopant-induced solubility control (DISC) patterning method.¹³ Schematics of the sample preparation and resulting sample geometry are shown in Figures 9a and 9b, respectively, and a detailed sample description is provided in the Experimental Section. It is worth emphasizing that it is very important to insert a MoO_3 (or similarly performing oxide) layer between the patterned film and the Ag layer in this experiment because the high work function MoO_3 (WF = 6.8 eV) can act as an insulator to prevent dopant–metal reactions.⁷¹ It is also well-known that the fluorescence (FL) of P3HT is quenched by the presence of dopants or any electron-accepting molecules.^{72–75} By mapping out the FL intensity from LSCM and combining with a calibration curve (Figure S8), we were able to track the dopant concentration in the P3HT film spatially and temporally. We assumed here that there was no vertical concentration gradient of dopants, and thus all diffusion occurs within the two-dimensional plane of the P3HT film. This assumption is valid considering that the P3HT film is only 50 nm thick and fluorescence is measured spatially over ~ 1 – 10 μm. Figure 9c

Figure 10. (a) LSCM fluorescence images of patterned F4TCNQ/P3HT films before (left) and after (right) annealing at 348 K for 50 min. (b) The 2D doping concentration maps converted from LSCM fluorescence images using a calibration curve at $t = 0$ (left) and $t = 50$ min (right). (c) The 2D doping concentration maps for a two-dimensional one-species (2D1S) model fit (left) and its absolute residuals (right). (d) Cross-sectional doping concentration profiles through images in (b) and (c) (indicated by white dashed lines) using a 2D1S diffusion model. (e) The 2D doping concentration maps for a two-dimensional two-species (2D2S) model fit (left) and its absolute residuals (right). (f) Cross-sectional doping concentration profiles through images in (b) and (e) (indicated by white dashed lines) using a 2D2S diffusion model.

show examples of confocal FL images before (top) and after (bottom) annealing for a time t at four different temperatures. The narrowing gaps in the FL intensity clearly indicate that the F4MCTCNQ diffuses from the doped (dark) regions to the undoped (bright) regions in the sample over time, as expected. Preliminary analysis based upon the annealing time at the different temperatures suggests that the macroscopic diffusion rate of the dopant is at least 1 order of magnitude higher for every 25 K temperature increase from 298 to 373 K.

We quantified the macroscopic diffusion rate and mechanism by fitting the dopant concentration as a function of lateral position and diffusion time. The F4TCNQ/P3HT system was used to validate our models. Initially, we attempted to fit the data by using a one-dimensional (1D) Fickian diffusion model that has been used previously to determine the diffusion coefficient of PCBM in a P3HT film,²⁰ the details of which are shown in Figure S9. This 1D model dose not successfully capture the F4TCNQ diffusion behavior. Therefore, we

extended this 1D model to a two-dimensional, one-species (2D1S) diffusion model, which appeared to be more realistic. Images of $60 \times 60 \mu\text{m}$ were used for all the fits in order to save computational time. The experimental confocal FL images before and after annealing at 348 K for 50 min and converted to 2D doping concentration maps are presented in Figures 10a and 10b, respectively, both of which clearly show F4TCNQ diffusion. For this 2D1S model, only one diffusive species was taken into account. The model fit and corresponding residuals are shown in Figure 10c. A direct comparison of cross-sectional profiles from these experimental and fitting images (indicated by the white dashed lines in Figures 10b and 10c, respectively) is also shown in Figure 10d. Again, a single diffusing species model yields an unsatisfactory fit for dopants concentration versus temperature and time, which can be seen from the discrepancy between measured (green line) and fit (red line) doping levels.

Figure 11. (a) A representative F4MCTCNQ diffusion fit at 348 K using a two-dimensional two-species (2D2S) model. 2D doping concentration maps were obtained experimentally from LSCM at $t = 0$ (top left) and $t = 560$ min (top right), 2D2S fit (bottom left), and absolute residuals (bottom right). (b) Cross-sectional doping concentration profiles through images in (a) (indicated by white dashed lines) using a 2D2S diffusion model. (c) Cross-sectional doping concentration profiles using a two-dimensional one-species (2D1S) diffusion model. (d) Determined two diffusion coefficients from 2D2S fits as a function of annealing temperatures for F4MCTCNQ (solid symbols) and F4TCNQ (open symbols) as well as corresponding Arrhenius fits. (e) 2D mole ratio profiles of slower (ionized) species to faster (neutral) species at $t = 560$ min at 348 K for F4MCTCNQ diffusion. (f) Schematic of F4MCTCNQ dopant diffusion derived from 2D2S diffusion model analysis.

We recently showed that an equilibrium between neutral F4TCNQ and ionized F4TCNQ exists in sequentially processed doped P3HT films, which can be described by $\text{F4TCNQ} + \text{P3HT} \rightleftharpoons \text{F4TCNQ}^- + \text{P3HT}^+$.¹⁴ In the cited study, F4TCNQ was added into the P3HT film using an orthogonal solvent. We showed that the orthogonal solvent could not dissolve or deposit F4TCNQ into the crystalline domains of P3HT, but instead only doped the amorphous domains of the polymer. In addition, we quantified the site density versus doping level for doping of the amorphous P3HT using a Langmuir isotherm model. We posit that the same model is very likely to explain the equilibrium for the F4TCNQ dopant in evaporation patterned P3HT films. The Langmuir isotherm model can be expressed as

$$\theta = \frac{C_{\text{ionized}}}{C_{\text{sat}}} = \frac{K_{\text{eq}} C_{\text{neutral}}}{1 + K_{\text{eq}} C_{\text{neutral}}} \quad (8)$$

where θ is the fraction of occupied doping sites in the amorphous domains of the film, C_{ionized} is the film doping concentration, C_{sat} is the saturated film doping concentration, C_{neutral} is the concentration of neutral dopant molecules, and K_{eq} is the equilibrium constant.

Given that both neutral and ionized dopants coexist in this sample, we developed a two-dimensional two-species (2D2S) diffusion model assuming (1) that the neutral and ionized species obey the aforementioned Langmuir isotherm equilibrium and (2) that the rate of equilibration between the two species is much faster than the rate of diffusion. Since increasing the temperature would shift the equilibrium toward a higher population of neutral dopants, the temperature-dependent $K_{\text{eq}} = \exp(-\Delta G^\circ/(k_B T))$, where ΔG° is taken to be the HOMO–LUMO difference between P3HT and the dopant (i.e., roughly the change in energy of the charge transfer process; 0.23 eV for F4TCNQ and 0.14 eV for F4MCTCNQ³⁶), k_B is the constant, 655

656 and T is the temperature. The 2D mapped doping
 657 concentration profiles were then fit with a 2D solution to
 658 Fick's second law, yielding a diffusion coefficient for each
 659 diffusive species (denoted as D_{neutral} and D_{ionized} in order to
 660 differentiate them from the diffusion coefficients obtained from
 661 QENS). The performed 2D2S fit for the F4TCNQ diffusion at
 662 348 K is shown in Figure 10e. By comparing the experimental
 663 and fit doping concentration profiles and inspecting the low
 664 residual between the data and fit in Figures 10b and 10e, it is
 665 clear that this 2D2S model is able to reproduce the lateral
 666 diffusion rates and mechanism in a consistent manner. Cross-
 667 sectional profiles through these images (indicated by the white
 668 dashed lines) are shown in Figure 10f and directly compared
 669 with the 2D2S fit. A full comparison between 2D1S and 2D2S
 670 model fits for F4TCNQ diffusion at other investigated
 671 temperatures can be found in Figures S10 and S11.

672 This 2D2S diffusion model was applied to describe the
 673 diffusion of F4MCTCNQ in the P3HT films. A representative
 674 example of the 2D2S fit for F4MCTCNQ at 348 K is shown in
 675 Figure 11a, and the cross-sectional doping concentration
 676 profiles through these images are provided in Figure 11b.
 677 The fits at other investigated temperatures can be found in
 678 Figure S12. Similar to the case of F4TCNQ, satisfactory fits can
 679 be produced. For consistency, the 2D1S model fits on
 680 F4MCTCNQ were also performed, and the resulting cross-
 681 sectional profiles at the same position are shown in Figure 11c
 682 (corresponding 2D images are presented in Figure S13). The
 683 discrepancy between measured and fit doping levels, especially
 684 in the doped region, using the 2D1S model again shows that a
 685 two species diffusion model is necessary to fit the diffusion data
 686 with sufficient accuracy. Additionally, since the highest doping
 687 ratio of ~ 4.3 mol % in the feature centers is much lower than
 688 the reported saturated doping level (>17 mol %),^{36,62} it is
 689 reasonable to assume that ionized dopants are the majority of
 690 the diffusive species in the system. Also, since the highest
 691 doping ratio is below the C_{sat} determined for the amorphous
 692 domains of P3HT in the previous study,¹⁴ it is likely that most
 693 or all of the dopants are located in and transported through the
 694 amorphous domains of P3HT.

695 The resulting two diffusion coefficients of the faster and
 696 slower species obtained from the 2D2S diffusion model are
 697 plotted as a function of the inverse of the annealing
 698 temperatures ($1000/T$) in Figure 11d. As can be seen, two
 699 distinct diffusion coefficients are observed. The diffusion
 700 coefficient of the faster species D_{neutral} is approximately 2–3
 701 orders of magnitude greater than that of the slower species
 702 D_{ionized} at the same temperature for both the F4MCTCNQ and
 703 F4TCNQ dopants in P3HT. Since the Langmuir isotherm
 704 model tracks the number of available doping sites in the P3HT,
 705 it is reasonable that the ratio of ionized to neutral dopants
 706 increases with reduced doping density. The mole ratio of the
 707 ionized (slower) to neutral (faster) dopant species is therefore
 708 tracked in this diffusion model. A representative 2D map of the
 709 ionized/neutral doping ratio for F4MCTCNQ/P3HT at 348 K
 710 is shown in Figure 11e. It is clear that the concentration of
 711 neutral species is orders of magnitude lower than the ionized
 712 species (also seen in Figure S14) and that this ratio is position-
 713 dependent, reflecting the local equilibrium between unfilled
 714 P3HT sites and dopants. Additionally, the ratio of ionized to
 715 neutral molecules increases as a function of diffusion distance,
 716 from ~ 100 in the initially doped region to ~ 500 in the initially
 717 undoped region (Figure S14). This increased ratio implies that
 718 the neutral dopant can diffuse for longer times in the highly

doped part of the sample, where there are fewer free undoped
 sites on the P3HT. As the dopant leaves the highly doped
 region, the neutral dopant is presented with a large number of
 free doping sites and so readily binds. The two-species diffusion
 processes is illustrated schematically in Figure 11f.

Since the temperature-dependent diffusion coefficients
 follow, within error, Arrhenius behavior (the straight lines in
 Figure 11d), we are able to determine the activation energy E_A
 associated with the diffusion process for each species. In our
 calculations, the D_{neutral} values at 298 K are excluded due to
 their uncertainties, seen from the large error bars in Figure 11d.
 The determined E_A values for translational diffusion are listed
 in Table 3. Interestingly, the E_A values for both neutral and

Table 3. Activation Energy E_A (kJ/mol) for Translational Diffusion Obtained from Arrhenius Fits of Diffusion Coefficients (D_{neutral} and D_{ionized}) of Neutral and Ionized Dopant Molecules, Respectively^a

	$E_{A_{\text{neutral}}}$ (kJ/mol)	$E_{A_{\text{ionized}}}$ (kJ/mol)
F4MCTCNQ	53.8 ± 1.9	55.5 ± 2.4
F4TCNQ	74.2 ± 7.3	55.9 ± 2.6

^a E_A values of F4TCNQ diffusions are also shown for comparison.

ionized F4MCTCNQ (~ 55 kJ/mol) are consistent with the
 translational barriers from DFT calculations in Figure 7c
 (especially for the smaller interchain separation). We note that
 the jump distance for an ionized dopant depends strongly on
 the energy landscape. As can be seen from Figure 7c, an open
 site (no other dopant in the path) and sufficient energy to
 surmount a 50–60 kJ/mol barrier for hopping to the next site
 are required for the ionized species to jump into the nearby
 potential well that is one bond. In addition, Kramer's theory
 was applied to estimate the diffusion coefficient of the dopant
 based on the DFT potential energy curves (Supporting
 Information section 11). The calculation yields a diffusion
 coefficient for ionized F4MCTCNQ of 1.4×10^{-14} cm²/s at
 298 K, which again falls into the range measured in the confocal
 experiments. However, the geometry of the DFT calculations
 depicted a highly simplified ordered P3HT domain, which is
 likely to different from the amorphous P3HT domain in which
 the dopant is expected to reside at the doping density used in
 the experiment. Given this discrepancy between the simulated
 geometry and likely sample geometry, we speculate that the
 measured $E_{A_{\text{ionized}}}$ likely represents an average value and that
 the actual hopping barriers in amorphous domains will be more
 heterogeneous than those estimated in the DFT calculations.

In addition, we can infer from the diffusion model that the
 jump distance for the neutral dopant is considerably larger than
 for the ionized dopant, even though their activation energies are
 similar. We know that the neutral dopant is not Coulombically
 bonded to the P3HT. We also know from the comparison of
 the 2D1S and 2D2S models that the neutral species is needed
 to explain the bulk diffusion profile as a function of time and
 temperature. It can be seen that the jump attempt frequency for
 the neutral and ionized molecules are similar, since since this is
 related to the size of the molecule and the curvature of the
 potential energy surface, which are likely similar of the two
 species. However, the jump distance is not determined from the
 Arrhenius fit but rather by the availability of binding sites. For
 an ionized dopant, the next binding site is one thiophene unit
 away, and thus the jump distance is smaller. For the neutral
 dopant, the next binding site is on average a much larger

distance so although the neutral species is a minority species and has a similar jump attempt frequency to ionized F4MTCNQ, the macroscopic diffusion is largely driven by the diffusive motion of neutral dopant molecules.

Finally, comparing the diffusion coefficients of F4TCNQ to F4MTCNQ, we note that F4TCNQ and F4TCNQ[−] respectively diffuse approximately 10–100 times faster than F4MTCNQ and F4MTCNQ[−] at investigated temperatures (Figure 11d). However, the $E_{A, \text{neutral}}$ of F4TCNQ is shown to be higher than that of F4MTCNQ. The reduced global diffusion of F4MTCNQ, therefore, indicates that the methyl ester side chain on the F4MTCNQ somehow reduces its jump distance. To pin down the reason for the reduced diffusion rate of the substituted dopant, we will present detailed comparisons of temperature-dependent as well as time-dependent diffusion coefficients between F4TCNQ and its soluble analogues in a separate and upcoming paper. In addition, examining reported diffusion studies on PCBM in the P3HT matrix, we can also conclude that the diffusions of molecular dopants F4TCNQ and F4MTCNQ are faster than that of PCBM in the P3HT ($D \approx 10^{-14} \text{ cm}^2/\text{s}$ ^{76–78} and $D \approx 10^{-11} \text{ cm}^2/\text{s}$ ⁷⁹ at around 413 K).

The results and model presented here represent the first detailed mechanistic study of a specific dopant diffusing in a specific semicrystalline semiconducting polymer. The results and model could be applicable to a wider and more general model for dopant diffusion in a wide variety of organic semiconductors. For this model to be generally applicable, a large number of different dopants would need to be investigated in a large number of different semiconductors. Also, a general means to determine the temperature-dependent binding energies for dopants and the energy landscape for OSCs is needed.

CONCLUSION

In conclusion, we have unveiled the diffusion dynamics of the p-type dopant, F4MTCNQ, in the semiconducting polymer P3HT for both microscopic and macroscopic time/distance scales using two different techniques. From QENS experiments, two local motions (<4 Å) are observed: methyl group rotations with $D \approx 10^{-6}$ – $10^{-5} \text{ cm}^2/\text{s}$ and methoxycarbonyl group rotations with smaller $D \approx 10^{-7}$ – $10^{-6} \text{ cm}^2/\text{s}$, both of which exhibit small E_A values (<15 kJ/mol) that are confirmed by DFT calculations. The macroscopic dynamics, on the other hand, are captured by an LSCM imaging technique. A two-dimensional two-species model is developed to interpret this long-range diffusion behavior, which includes a Langmuir isotherm equilibrium between neutral and ionized dopant molecules. As the dominant species, the ionized F4MTCNQ molecules exhibit slower diffusion than the neutral molecules due to a much shorter jump distance. Both the activation energy for diffusion and the jump distance of the ionized species are in good agreement with the estimates from DFT calculations associated with the translational motions of F4MTCNQ along the P3HT backbone (E_A of $\sim 50 \text{ kJ/mol}$ and jump distance of $\sim 2 \text{ Å}$). In contrast, the neutral species has a significantly greater jump distance, which makes the neutral species the dominant diffusing species at the macro scale. Lastly, by comparing the diffusion coefficients between F4MTCNQ and F4TCNQ, we can also conclude that methyl ester substitution in F4MTCNQ not only increases solubility/miscibility and thus doping effectiveness but also helps to anchor dopants into position postdeposition due to

reduced diffusion. In theory, the two-dimensional one-/two-species diffusion developed in this paper could be generalized to determine the diffusion coefficient of any fluorescence quenching species that can be evaporated into a polymer. Studies of the dopant dynamics at both microscopic and macroscopic levels are important for understanding the degradation of organic devices as well as improving DISC patterning methodology.

ASSOCIATED CONTENT

Supporting Information

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Figures S1–S14 (PDF)

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Notes

The authors declare no competing financial interest.

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