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The Effect of Electrostatic Interaction on n-Type Doping Efficiency of Fullerene Derivatives

Jian Liu,^{*} Sudeshna Maity, Nathan Roosloot, Xinkai Qiu, Li Qiu, Ryan C. Chiechi, Jan C. Hummelen, Elizabeth von Hauff, and L. Jan Anton Koster^{*}

The molecular doping of organic semiconductors represents a key strategy for advancing organic electronic applications. However, the n-doping of organic materials is usually less efficient than p-doping and strategies toward the design of more efficient n-doping still remain less explored. In this contribution, the impact of electrostatic interaction is explored on the doping efficiency of fullerene derivatives. [6,6]-Phenyl-C₆₁-butyric acid methyl ester (PCBM) and a [60]fulleropyrrolidine with a more polarizable triethylene glycol type side chain (PTEG-1) are employed for a comparative study. It is found that the doping efficiency of lightly doped PCBM layers is limited to a few percent, while doped PTEG-1 films exhibit very high doping efficiency approaching 100%. The enhanced n-doping of PTEG-1 compared with that of PCBM is further substantiated by Raman and Fourier transform infrared spectroscopic studies. The activation energy for charge generation in doped PTEG-1 is much smaller than that of doped PCBM, which confirms a higher probability for dissociation of charge transfer complexes in the former compared to the latter. The enhanced molecular n-doping for PTEG-1 is attributed to the electrostatic interaction between the charge transfer complex and the polar environment offered by the triethylene glycol diether side chain.

The molecular doping of solution-processed organic semiconductors plays a key role in organic electronic devices such as organic solar cells, light-emitting diodes, field-effect transistors, and organic thermoelectrics.^[1–8] Both p-type and n-type

molecular doping is required for practical applications; however, the development of n-type doping of organic semiconductors still lags behind that of their p-type counterparts. One of the key factors is the relatively low doping efficiency (η), i.e., the stoichiometric ratio of free carrier density to dopants. Bao and co-workers developed an air-stable n-type dopant, namely, 4-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)-N,N-dimethylaniline (n-DMBI).^[9] They used this dopant to dope [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and achieved an electrical conductivity of $1.9 \times 10^{-3} \text{ S cm}^{-1}$. They did not calculate the corresponding doping efficiency, but observed microscopic phase segregation. Chabinyc and co-workers reported a maximum conductivity of $\approx 10^{-3} \text{ S cm}^{-1}$ with a η of $\approx 1\%$ for the benchmark n-type polymer poly(naphthalenediimide-*alt*-bithiophene) (N2200) doped with n-DMBI.^[10] The low η was attributed to poor host/dopant

miscibility. By functionalizing the host with polar glycol ether side chains, we achieved a very high electrical conductivity of over 2 S cm^{-1} and η of 18% at a doping concentration of 30 mol% in films of n-doped fullerene derivatives and a η of 20% at a doping concentration of 20 mol% in films of an n-doped naphthalenediimide-*alt*-bithiophene based copolymer, respectively.^[11,12] Very recently, Kiefer et al. obtained an enhanced n-doping efficiency of 13% at a doping concentration of 20 mol% in an n-doped naphthalenediimide-based copolymer through the use of polar side chains.^[13]

All of the previous works focused on n-doped systems with large doping concentrations (>10 mol%), where the host/dopant miscibility is most likely the dominant factor. The inclusion of polar side chains increases the polarity of the host, which improves the miscibility in the doped films and thus promotes higher doping efficiency.^[12–15] However, the effect of polar side chains on the doping mechanism at a molecular level remains unexplored. A lightly doped system, where a very small amount of dopant molecules are typically well dispersed in the host matrix due to entropy, serves as a good platform for exploring the doping mechanism at a quasi-molecular level. However, this type of study has not yet been conducted. Additionally, lightly doped organic semiconductors with relatively high doping efficiencies are very suitable for the charge

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transport/extraction layer in organic/hybrid solar cells and light-emitting diodes.^[1,16,17]

Molecular doping is assumed to be a two-step process: i) ionization of the dopant by transferring a charge (electron/hole) to the host material to form charge transfer complexes (CTCs) and ii) dissociation of these CTCs, eventually generating free charge carriers.^[18] The probability of dopant ionization, which is primarily governed by the energetics of the host and dopant molecules, was considered to be rather efficient in lightly doped systems.^[18–20] The latter process is, however, not straightforward in an organic semiconductor matrix with low dielectric constants ($\epsilon = 3\text{--}4$) due to a strong Coulomb binding energy of several 100 meV between a carrier and the dopant molecule.^[21] At present, the latter process is still not well understood. The doping efficiency usually remains very low at a sub-threshold doping ratio of $\approx 2\%$, which is the so-called “weak regime” doping observed in several doping systems.^[22] In a theoretical study, Arkhipov et al. pointed out that energetic disorder can actually enhance the dissociation of CTCs.^[23] This argument was recently confirmed in a combined experimental and theoretical study conducted by Tietze et al.^[24] However, a large energetic disorder is usually detrimental to charge transport in disordered organic films. Therefore, there is a need for effective strategies to promote the dissociation of CTCs and to further increase the doping efficiency of organic semiconductors.

In this contribution, we explored the impact of electrostatic interaction on the doping efficiency in lightly doped fullerene derivatives. PCBM and a [60]fulleropyrrolidine with a polar triethylene glycol diether side chain (PTEG-1) were employed as the host and n-DMBI as the dopant. The doping concentration was kept below 0.5 mol% to exclude any host/dopant miscibility issues and doping-induced structural disorder. The AFM results indicated that n-DMBI molecules were uniformly dispersed in

the matrix of both fullerene derivatives. The charge generation in both doped fullerene derivatives was temperature dependent. Doped PTEG-1 at a doping concentration of 0.5 mol% rendered an activation energy of 43 meV, which is much smaller than that (92 meV) of doped PCBM (0.5 mol%). A smaller activation energy corresponds to a higher probability of dissociation of the CTCs. As a result, the doping efficiency of lightly doped PTEG-1 was greatly improved to $\approx 100\%$ from a few percent in doped PCBM films. Raman and Fourier transform infrared (FTIR) spectra of the pristine and doped fullerene derivative films confirmed the more efficient n-doping of films of PTEG-1 compared with those of PCBM. The enhanced molecular n-doping of PTEG-1 is attributed to a relatively large electrostatic interaction between CTCs and the surrounding of the polar side chains.

The fullerene derivatives (PCBM and PTEG-1) were respectively blended with various amounts of dopant (n-DMBI) to effect n-doping. The chemical structures of the fullerene derivatives and dopant are displayed in Figure 1a. To take a measure of the n-doping process, metal/insulator/semiconductor (MIS) devices with an architecture of ITO/ Al_2O_3 /doped PCBM or PTEG-1/Al were fabricated as shown in Figure 1b. We employed atomic layer deposition (ALD) to prepare the insulating Al_2O_3 layer to obtain a smooth surface and small leakage currents. Admittance spectroscopy was used to characterize the MIS devices. The band diagram of the MIS device operating in the depletion regime is schematically shown in Figure 1c. Figure 1d,e shows the plots of capacitance (C_p) versus applied DC voltage bias (V_d) in the MIS devices based on doped PCBM and PTEG-1 films, respectively. At a negative bias, the MIS devices operate in the accumulation regime with C_p dominated by the oxide layer. The charge carriers are gradually depleted by modulating V_d from negative to positive. As a result, C_p starts to drop due to additional

Figure 1. a) The chemical structures of host and dopant molecules, b) the architecture of the MIS devices, c) the schematic of the MIS device working at a depletion regime, the $C\text{--}V$ plots of doped PCBM-based devices d), doped PTEG-1-based devices e), and f) their corresponding admittance loss spectra.

Figure 2. The plots of a) carrier densities and b) electrical conductivities as a function of the doping ratio in doped fullerene derivatives.

capacitance from the depleted active layer that is in series with the capacitor from the oxide layer. The carrier density (n) can be extracted according to Equation (1)^[25]

$$n = \frac{2}{e\epsilon_0\epsilon_r A^2} \frac{\partial C_p^{-2}}{\partial V} \quad (1)$$

where e , ϵ_0 , ϵ_r , and A are an elementary charge, the dielectric constant of vacuum, the relative dielectric constant of the active layer and the active layer area, respectively. In addition to carrier density extraction, the MIS device can also be used to measure the electrical conductivity (σ) in the vertical direction via the admittance loss (G_p/ω) spectra as shown in Figure 1e in Equation (2)^[26]

$$\sigma = 2\pi f_p (C_i + C_b) \frac{d}{A} \quad (2)$$

where f_p , C_b , d , and σ are the characteristic frequency in the loss spectra, active layer capacitance, and the thickness and electrical conductivity of the active layer.

Figure 2a displays the carrier densities and doping efficiencies of doped PCBM and PTEG-1 films. The doping efficiency of doped PCBM is rather low at a few percent over the doping range studied. It should be noted that the doping efficiency in this lightly doped PCBM is higher than that (<0.7%) previously reported in the scenario with high doping concentrations (>10 mol%).^[11] This difference indicated that the host/dopant miscibility issue was partially or completely overcome in lightly doped systems, which fulfilled our intention of this study. At the same doping ratio, doped PTEG-1 films showed higher carrier densities compared to doped PCBM. Additionally, the carrier density in the doped PTEG-1 layers rendered a superlinear increase with the doping ratio. At this stage, the reason for the superlinear dependence between carrier density and the doping ratio was unclear. We speculated that it is related to the Coulomb traps from ionized dopants, the individual potential of which gradually overlaps to reduce the trap depth with increasing doping ratio.^[23,27,28] The 0.1 mol% doped PTEG-1 exhibits a doping efficiency of 36%, which increases up to $\approx 100\%$ at a doping ratio of 0.5 mol%. Figure 2b shows a plot of electrical conductivity as a function of the doping ratio in doped PCBM and PTEG-1 films. As observed, the doped PTEG-1 layers exhibit more than one order of magnitude higher electrical conductivity than the doped PCBM films due to a higher doping level.

Figure 3a,b displays the temperature dependence of the electrical conductivity $\sigma(T)$ and carrier density $n(T)$ in the doped layers. The temperature dependence of the conductivity in doped PCBM and PTEG-1 films can be well described by the classic Arrhenius equation. The activation energies (E_A) can be obtained by fitting, giving values of 439 and 212 meV for 0.5 mol% doped PCBM and 0.5 mol% doped PTEG-1, respectively. A smaller activation energy (E_A) in doped PTEG-1 agrees well with its higher doping level according to our previous works.^[11,15] Interestingly, the charge carrier densities also show a temperature dependence in both doped fullerene derivatives. Such a temperature dependence of the carrier density has been only reported in p-doped organic systems with activation energies in the range from several meV to several tens of meV.^[20,24] The first step, i.e., the formation of the CTC, was reported to be almost temperature independent.^[24] As such, the observed thermal activation of charge carrier generation most likely stemmed from the dissociation of CTCs. The doped PTEG-1 layer shows a much smaller activation energy (43 meV at 0.5 mol% doping) for charge generation than the doped PCBM layer (92 meV) at the same doping condition. The reduced activation energy indicates that charge carriers are more easily generated in doped PTEG-1 layers, which explains the increased doping efficiency in doped PTEG-1 films compared with doped PCBM layers. With the knowledge of $\sigma(T)$ and $n(T)$, we are able to extract the temperature dependence of the mobility $\mu(T)$ of doped fullerene derivatives based on the formula $\sigma(T) = e \times \mu(T) \times n(T)$. The characteristics of $\mu(T)$ of doped PCBM (0.5 mol%) and PTEG-1 (0.5 mol%) are displayed in Figure 3c. The extracted activation energies (E_μ) are 374 and 169 meV for 0.5 mol% doped PCBM and 0.5 mol% doped PTEG-1, respectively. How $\sigma(T)$, $\mu(T)$ and $n(T)$ are related to doping and the charge transport process will be discussed later. Our previous study indicated that undoped PTEG-1 has an identical electron mobility to that of undoped PCBM.^[29] However, here we observed that the electron mobility of 0.5 mol% doped PCBM is one order of magnitude higher than that of doped PTEG-1 (0.5 mol%). We argued that the reduced mobility in doped PTEG-1 film may be attributed to the doping process. Since CTCs are more easily dissociated in doped PTEG-1 to generate free charges and dopant cations than in doped PCBM, an increased trapping probability of free electrons by these dopant cations reduces the mobility in the vertical direction in doped PTEG-1 films.

Figure 3. The plots of a) electrical conductivities, b) carrier densities, and c) mobility as a function of the inverse temperature in doped fullerene derivatives (symbols). The solid lines represent fits by the Arrhenius equation.

Figure 4a–d show the topographic (top panel) and current (bottom panel) micrographs for pristine PCBM, pristine PTEG-1, 0.5 mol% doped PCBM, and 0.5 mol% doped PTEG-1 thin films, respectively. We did not observe any differences

in either the topographic or phase micrograph upon lightly doping of these fullerene derivatives. These results indicate that the dopant is uniformly dispersed in the matrix in these samples. Observable phase separation, as observed previously in

Figure 4. The topographic (top panel) and current (bottom panel) AFM micrographs for a) pristine PCBM, b) 0.5% doped PCBM, c) pristine PTEG-1, and d) 0.5% doped PTEG-1 thin films, respectively.

Figure 5. Raman and FTIR spectra for a,b) pristine PCBM (black), 0.5 mol% doped PCBM (red), and 30 mol% doped PCBM (blue) and c), d) pristine PTEG-1 (black), 0.5 mol% doped PTEG-1 (red), and 30 mol% doped PTEG-1 (blue). The prominent Raman modes are indicated by dashed lines. The relevant FTIR modes are highlighted in blue.

moderately or heavily doped systems, did not occur here.^[9,11] As the current measured in conductive AFM was affected by the tip geometry, applied bias, and force load, we used the same type of Pt-Ir-coated tip with a radius of 25 nm under a constant bias of 5 V and a load of 1.6 nN for all measurements reported in this work. The doping sites in the doped films can be easily visualized as white spots in conductive AFM images. As observed, the doped PTEG-1 layer displayed an apparently higher current than the doped PCBM layer, which is consistent with its higher electrical conductivity. This indicates that the doping sites in the doped PCBM layer are more localized and separated from each other while a continuous network is formed by the dense and mutually coupled doping sites in the doped PTEG-1 film.

We performed vibrational spectroscopy to further support our argument that n-DMBI dopes PTEG-1 more efficiently than PCBM. Optical spectroscopy is less sensitive than electrical or microscopic measurements due to the low density and local variations in charged fullerene derivatives. For this reason, we compared spectra taken from pristine fullerene derivative films with those of their doped films at 0.5 and 30 mol%. **Figure 5a,b** shows the Raman and FTIR spectra of pristine PCBM (black), 0.5 mol% doped PCBM (red), and 30 mol% doped PCBM (blue), respectively. **Figure 5c,d** show the Raman and FTIR spectra of pristine PTEG-1 (black), 0.5 mol% doped PTEG-1 (red), and 30 mol% doped PTEG-1 (blue), respectively. The Raman spectra were normalized to the largest peak at 1450 cm⁻¹. The apparent increase in the peak centered at 1100 cm⁻¹ is actually a decrease in the peak centered at 1450 cm⁻¹. Red shifting or a decrease in the intensity of the Raman mode at ≈1460 cm⁻¹ (the pentagonal

pinch mode of the C₆₀ cage) have been recognized before as signatures of doped fullerene solids.^[30,31] We observed a slight decrease in this mode for the 30 mol% doped PCBM film. In contrast, the pentagonal pinch mode was nearly completely suppressed in the 30 mol% doped PTEG-1 film, consistent with a strong electron-phonon coupling that changes the symmetry of the mode, resulting in broadening and splitting of the line.^[31]

C₆₀ has four IR active modes, located at 527, 586, 1183, and 1429 cm⁻¹.^[30] Theoretical calculations of the IR spectrum of PCBM revealed further peaks at higher wavenumbers related to the side chain.^[32] The peak at 1737 cm⁻¹ is characteristic for the C=O stretch of the ester carbonyl group in the PCBM side chain.^[32–34] The sensitivity of this mode toward changes in the dielectric environment has been exploited to monitor the charge transfer processes between polymer donors and PCBM.^[34,35] We did not observe any significant influence of doping on the IR spectrum of PCBM, except for the emergence of a new peak at 1600 cm⁻¹ in the 30 mol% doped sample, which was seen in the neat dopant molecule (not shown here). The fingerprint region of the IR spectrum for PTEG-1 (**Figure 5d**) contains more features than that of PCBM due to the contributions of the ether moieties in the side chain. We observed that the intensity of the fullerene mode centered at 1429 cm⁻¹ decreased upon doping (30 mol% doped sample), consistent with a change in the symmetry of the fullerene cage.

The fullerene derivatives are disordered systems with charge carriers hopping in a Gaussian-shaped energy landscape.^[36] Such a hopping process has been well described by the

Figure 6. a) The schematic of typical density of states (DOS) plot with several important energy levels in a Gaussian system and b) the simulated carrier densities as a function of E_A/E_0 (E_A and E_0 are the activation energies of mobility in doped films and in a typical diode device).

Gaussian disorder model (GDM).^[36] Figure 6a shows a typical density of states (DOS) plot with several important energy levels in a Gaussian system. Based on the GDM, the charge carriers are considered to be thermally activated to the transport energy level (E_T) for charge transport. Another important parameter is the equilibrium energy level (E_{eq}) located at $-\sigma_d^2/kT$.^[37] As the Fermi level (E_F) is below E_{eq} (in this scenario, the E_F is not shown), thermally assisted hopping occurs with E_{eq} as the starting point. As a result, the GDM gives an activation energy of $4\sigma_d^2/9kT$ for the charge carrier mobility.^[38] With increasing charge carrier density, E_F will pass E_{eq} and serves as the new starting point for hopping (marked in brown).

For lightly doped systems, such as 0.5 mol% doped PCBM and 0.1 mol% doped PTEG-1, with carrier densities of less than 10^{17} cm^{-3} , the thermal activation process for charge transport starts from the equilibrium energy level E_{eq} . Based on the GDM, we can calculate the disorder parameter (σ_d) with their activation energies of mobility E_μ , which are 347 meV (0.5 mol% doped PCBM) and 344 meV (0.1 mol% doped PTEG-1). In this way, σ_d of both doped fullerene derivatives was determined to be 100 meV, which is larger than that (75 meV) of their pristine films reported previously.^[39] We attribute the broadening of DOS to the molecular doping effects either from microstructural changes or the Coulomb interaction from ionized dopants.^[28,40]

When the carrier density is sufficiently high, with E_F crossing over E_{eq} , the extended Gaussian disorder model (EGDM) can well explain the effect of charge carrier on the transport process.^[41] Based on the EGDM, the temperature dependence of charge transport not only depends on the disorder of materials but also on the charge density. We recently used this relationship to estimate the carrier density in doped films.^[11,13] By adapting the disorder parameter and activation energy of mobility E_μ (169 meV for 0.5 mol% doped PTEG-1) to this relationship (Figure 6b and details in the Experimental Section), we obtain a carrier density of $4.7 \times 10^{18} \text{ cm}^{-3}$ for the 0.5% doped PTEG-1 layer, which is close to our measured value of $2.5 \times 10^{18} \text{ cm}^{-3}$ in the MIS devices. Interestingly, this method was recently applied to an n-doped conjugated polymer and was found to agree with measurements of the carrier density based on electron paramagnetic resonance.^[13] Our results show that this relatively simple method based on the

EGDM can be used to obtain an estimate of the carrier density in doped films.

As explained in the introduction, free carrier generation by CTC dissociation has to overcome a Coulomb binding of several 100 meV in the doped organic films. Tietze et al. pointed out the crucial role of energetic disorder in favoring the dissociation of CTCs.^[24] However, it was reported that PCBM and PTEG-1 have nearly identical electron affinity, disorder parameter and electron mobility.^[29,42] As such, the differences in the activation energy of carrier generation and doping efficiency for both doped systems should not stem from their energetics and energetic landscapes. Another factor, which has been considered to impact the dissociation of CTCs, is the electrostatic interaction between CTCs and the surrounding molecules. This effect was previously estimated to be on the order of 0.1–0.5 eV.^[24,43] It has been previously inferred that ionized dopant exists primarily within the polar phase created by the glycol ether side chains in the case of PTEG-1.^[11,15] The commensurate phase in PCBM is considerably less polar, as its side chains are aliphatic with only one rather rigid polar ester moiety. This point is supported by the large relative dielectric constant of $\epsilon_r = 5.7$ for PTEG-1 film compared to that ($\epsilon_r = 3.9$) for PCBM film.^[29] A series of C–O bonds in the side chains in a PTEG-1 molecule create four permanent and very flexible dipoles^[44] that can interact with host/dopant ion pairs to screen the electric fields created by n-DMBI⁺, disfavoring microscopic phase segregation. We propose that this overall process may facilitate the creation of free charge carriers, i.e., there is a smaller activation barrier to carrier generation in films of doped PTEG-1 than PCBM. Our study emphasizes the role of electrostatic interactions in molecularly n-doping of fullerene derivatives. However, future efforts on a broader range of organic semiconductors are warranted to generalize these effects.

In summary, we explored the impact of electrostatic interaction on the doping efficiency in relatively lightly doped fullerene derivatives, where n-DMBI molecules were uniformly dispersed in the matrix. It was found that the doping efficiency of lightly doped PCBM layers was only a few percent, but doped PTEG-1 films exhibited a very high doping efficiency approaching 100%. The enhanced n-doping of PTEG-1 compared to that of PCBM was further substantiated by Raman and FTIR spectroscopic studies. These in-depth studies indicate that the CTCs

in doped PTEG-1 are more likely to be dissociated than those in doped PCBM, and the increased doping efficiency in doped PTEG-1 may be attributed to the stabilizing electrostatic interaction between CTCs and the polar surrounding offered by the triethylene glycol diether side chains. Our study might point out a direction for increasing the n-doping efficiency of fullerene derivatives and contributed to the understanding of the doping mechanism, which may be extended to n-type conjugated polymer systems.

Experimental Section

Materials: PCBM and n-DMBI were purchased from Solenne BV and Sigma Aldrich, respectively. PTEG-1 was synthesized according to the previously reported procedure.^[29]

Characterization: The thicknesses of the thin films were measured by ellipsometry. Conductive probe atomic force microscopy (CPAFM) measurements were carried out on a Multimode 8 AFM (Bruker, model MMAFM-2) equipped with a PeakForce TUNA application module. The current was measured by scanning the sample at a bias of 5 V in TUNA mode (contact mode). A Pt-Ir-coated tip (SCM-PIT V2, Bruker, resonant frequency of 75 KHz, spring constant of 0.4 N m⁻¹, radius of 25 nm) was used with a load of 1.6 nN in the measurements. To determine the capacitance, conducted impedance spectroscopy was conducted in the frequency range from 1 Hz to 10 MHz using a Solartron 1260 impedance gain-phase analyzer with an AC drive voltage of 20 mV and an applied DC bias of -4 V to the MIS devices working at an accumulation regime. The capacitance-voltage (C-V) measurements were conducted at drive frequencies of 200 Hz for the Mott-Schottky analysis.

MIS Device: The ITO substrates were sequentially washed using detergent, acetone, and isopropanol. Then, the substrates were dried using a nitrogen gun and treated by UV-ozone for 20 min. 50 nm insulated Al₂O₃ layer was deposited on the ITO substrates by the ALD technique. Doped PCBM and PTEG-1 layers with thickness of ≈100 nm were spin coated on top of the Al₂O₃ layer from their mixed chloroform solution with n-DMBI in a N₂ filled glove box. The resultant active layers were annealed at 120 °C for 30 min and 100 nm Al layer was deposited as top electrodes in a vacuum of 4 × 10⁻⁷ mbar.

Raman and FTIR Spectroscopy: Host (PCBM and PTEG-1) solutions and dopant (n-DMBI) solutions were prepared separately and stirred overnight at room temperature in a nitrogen environment. Chloroform (anhydrous, 99.8%, purchased from Sigma-Aldrich) was used as the solvent for all solutions. To prepare the doped samples, n-DMBI solution was mixed with the host solution and stirred overnight at room temperature.

The glass substrates were cleaned successively in acetone, 2-propanol, and miliQ water in an ultrasonic bath for 10 min each. The substrates were subsequently treated in an ozone/UV cleaner for 15 min and transferred into the glove box. The pristine and doped solutions were spin coated on to the cleaned substrates at 300 rpm for 20 s. For the Raman measurements, a 50 nm layer of Au was evaporated on the fullerene film afterward. All processes were performed in an inert environment. During the measurement, the sample was placed in an airtight sample holder, which was filled with nitrogen.

For the Raman measurements, the films were prepared on glass substrates. The measurements were performed using 532 nm excitation with a 10 s exposure. For the FTIR measurements, the films were prepared on CaF₂ substrates.

Extended Gaussian Disorder Model: The geometry of the model was a cubic grid of regularly spaced points along the cube's x, y, and z axes. 150 grid points were used in each direction, yielding a total of 150³ grid points. The grid points were sites that could be occupied by a carrier. Coulomb repulsion between the carriers disallowed multiple carriers to be present on one grid point. In the model, not individual carriers, but the occupational probability of a grid point was used to calculate the mobility. Each grid point was also assigned an energy at the start of a simulation. This energy was randomly selected from a Gaussian

distribution with a mean value of zero and a standard deviation of σ , where σ is known as the disorder parameter, k_B is the Boltzmann constant, and T is the temperature in Kelvin. The model assumes that the hop rates are of Miller-Abraham type, as in Equation (4). The mobility was calculated by solving the steady-state Pauli master equation

$$\sum_j [W_{i \rightarrow j} n_i (1 - n_j) - W_{j \rightarrow i} n_j (1 - n_i)] = 0 \quad (3)$$

when the system was under the influence of a small electric field. In Equation (3), n_i and n_j are the occupational probabilities of point i and j . W_i and W_j are the Miller-Abrahams hopping rates

$$W_{i \rightarrow j} = \begin{cases} v \exp(-\Delta E_{ij} / k_B T), & \text{if } \Delta E_{ij} > 0 \\ v & \text{otherwise} \end{cases} \quad (4)$$

In Equation (4) v is an intrinsic rate, ΔE_{ij} is the energy difference between site i and j , together with the electric field tilting the Gaussian energy landscape in space, k_B is the Boltzmann constant, and T is the temperature. The formula assumes all hops downward in energy are equally likely and upward hops require thermal energy in order to occur. After solving Equation (1) for n_i , the mobility can be calculated from Equation (5)

$$\mu = \frac{\sum_{ij} W_{i \rightarrow j} n_i (1 - n_j) (\vec{r}_j - \vec{r}_i) \cdot \hat{F}}{N_0 L^3 |\hat{F}|} \quad (5)$$

where $\hat{F} = \vec{F} / |\vec{F}|$ represents a unit vector in the direction of the electric field, with $\vec{F}$ being the electric field vector, $\vec{r}_i$ and $\vec{r}_j$ are the position vectors of points i and j with respect to some point, N_0 is the average carrier density, and L^3 is the total volume simulated in the calculation. From the EGDM, the activation energy of the temperature dependence of the charge carrier mobility can be obtained. This is done by fitting an Arrhenius temperature dependence

$$\mu = \mu_0 e^{-E_a / (k_B T)} \quad (6)$$

to the mobility as a function of temperature and charge carrier density as obtained by the implementation of the EGDM. μ_0 does not influence the activation energy of the charge carrier mobility (μ). k_B and T are the Boltzmann constant and the temperature.

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] B. Lüssem, M. Riede, K. Leo, *Phys. Status Solidi A* **2013**, 210, 9.
- [2] A. M. Glaudell, J. E. Cochran, S. N. Patel, M. L. Chabiny, *Adv. Energy Mater.* **2015**, 5, 1401072.
- [3] M. Culebras, C. Gómez, A. Cantarero, *Materials* **2014**, 7, 6701.
- [4] Y. Zhang, H. Zhou, J. Seifert, L. Ying, A. Mikhailovsky, A. J. Heeger, G. C. Bazan, T.-Q. Nguyen, *Adv. Mater.* **2013**, 25, 7038.
- [5] A. V. Tunc, A. De Sio, D. Riedel, F. Deschler, E. Da Como, J. Parisi, E. von Hauff, *Org. Electron.* **2012**, 13, 290.
- [6] J. Kim, D. Khim, K.-J. Baeg, W.-T. Park, S.-H. Lee, M. Kang, Y.-Y. Noh, D.-Y. Kim, *Adv. Funct. Mater.* **2016**, 26, 7886.
- [7] D. Beretta, N. Neophytou, J. M. Hodges, M. G. Kanatzidis, D. Narducci, M. Martin-Gonzalez, M. Beekman, B. Balke, G. Cerretti, W. Tremel, A. Zevalkink, A. I. Hofmann, C. Müller, B. Döring, M. Campoy-Quiles, M. Caironi, *Mater. Sci. Eng., R* **2018**, <https://doi.org/10.1016/j.mser.2018.09.001>.
- [8] J. Liu, G. Ye, B. van der Zee, J. Dong, X. Qiu, Y. Liu, G. Portale, R. C. Chiechi, L. J. A. Koster, *Adv. Mater.* **2018**, 30, 1804290.
- [9] P. Wei, J. H. Oh, G. Dong, Z. Bao, *J. Am. Chem. Soc.* **2010**, 132, 8852.
- [10] R. A. Schlitz, F. G. Brunetti, A. M. Glaudell, P. L. Miller, M. A. Brady, C. J. Takacs, C. J. Hawker, M. L. Chabiny, *Adv. Mater.* **2014**, 26, 2825.
- [11] J. Liu, L. Qiu, G. Portale, M. Koopmans, G. ten Brink, J. C. Hummelen, L. J. A. Koster, *Adv. Mater.* **2017**, 29, 1701641.
- [12] J. Liu, L. Qiu, R. Alessandri, X. Qiu, G. Portale, J. Dong, W. Talsma, G. Ye, A. A. Sengrrian, P. C. T. Souza, M. A. Loi, R. C. Chiechi, S. J. Marrink, J. C. Hummelen, L. J. A. Koster, *Adv. Mater.* **2018**, 30, 1704630.
- [13] D. Kiefer, A. Giovannitti, H. Sun, T. Biskup, A. Hofmann, M. Koopmans, C. Cendra, S. Weber, L. J. Anton Koster, E. Olsson, J. Rivnay, S. Fabiano, I. McCulloch, C. Müller, *ACS Energy Lett.* **2018**, 3, 278.
- [14] L. Qiu, J. Liu, R. Alessandri, X. Qiu, M. Koopmans, R. W. A. Havenith, S. J. Marrink, R. C. Chiechi, L. J. Anton Koster, J. C. Hummelen, *J. Mater. Chem. A* **2017**, 5, 21234.
- [15] J. Liu, L. Qiu, G. Portale, S. Torabi, M. C. A. Stuart, X. Qiu, M. Koopmans, R. C. Chiechi, J. C. Hummelen, L. J. Anton Koster, *Nano Energy* **2018**, 52, 183.
- [16] C. Momblona, L. Gil-Escrig, E. Bandiello, E. M. Hutter, M. Sessolo, K. Lederer, J. Blochwitz-Nimoth, H. J. Bolink, *Energy Environ. Sci.* **2016**, 9, 3456.
- [17] S. Shao, J. Liu, H.-H. Fang, L. Qiu, G. H. ten Brink, J. C. Hummelen, L. J. A. Koster, M. A. Loi, *Adv. Energy Mater.* **2017**, 7, 1701305.
- [18] A. Mityashin, Y. Olivier, T. Van Regemorter, C. Rolin, S. Verlaak, N. G. Martinelli, D. Beljonne, J. Cornil, J. Genoe, P. Heremans, *Adv. Mater.* **2012**, 24, 1535.
- [19] I. Salzmann, G. Heimel, M. Oehzelt, S. Winkler, N. Koch, *Acc. Chem. Res.* **2016**, 49, 370.
- [20] P. Pingel, D. Neher, *Phys. Rev. B* **2013**, 87, 115209.
- [21] J.-M. Kim, S.-J. Yoo, C.-K. Moon, B. Sim, J.-H. Lee, H. Lim, J. W. Kim, J.-J. Kim, *J. Phys. Chem. C* **2016**, 120, 9475.
- [22] D. T. Duong, H. Phan, D. Hanifi, P. S. Jo, T.-Q. Nguyen, A. Salleo, *Adv. Mater.* **2014**, 26, 6069.
- [23] V. I. Arkhipov, P. Heremans, E. V. Emelianova, H. Bässler, *Phys. Rev. B* **2005**, 71, 1.
- [24] M. L. Tietze, J. Benduhn, P. Pahner, B. Nell, M. Schwarze, H. Kleemann, M. Krammer, K. Zojer, K. Vandewal, K. Leo, *Nat. Commun.* **2018**, 9, 1182.
- [25] P. Pingel, M. Arvind, L. Kölln, R. Steyrlleuthner, F. Krafft, J. Behrends, S. Janietz, D. Neher, *Adv. Electron. Mater.* **2016**, 2, 1600204.
- [26] P. Pingel, R. Schwarzl, D. Neher, *Appl. Phys. Lett.* **2012**, 100, 143303.
- [27] A. Abate, D. R. Staff, D. J. Hollman, H. J. Snaith, A. B. Walker, *Phys. Chem. Chem. Phys.* **2014**, 16, 1132.
- [28] V. I. Arkhipov, E. V. Emelianova, P. Heremans, H. Bässler, *Phys. Rev. B* **2005**, 72, 235202.
- [29] F. Jahani, S. Torabi, R. C. Chiechi, L. Jan, A. Koster, J. C. Hummelen, *Chem. Commun.* **2014**, 50, 10645.
- [30] C. A. Reed, R. D. Bolskar, B. O. Voltammetry, *Chem. Rev.* **2000**, 100, 1075.
- [31] H. Kuzmany, M. Matus, B. Burger, J. Winter, *Adv. Mater.* **1994**, 6, 731.
- [32] J. Maibach, T. Adermann, T. Glaser, R. Eckstein, E. Mankel, A. Pucci, K. Müllen, U. Lemmer, M. Hamburger, T. Mayer, W. Jaegermann, *J. Mater. Chem. C* **2014**, 2, 7934.
- [33] J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, J. Yao, C. L. Wilkins, *J. Org. Chem.* **1995**, 60, 532.
- [34] L. W. Barbour, M. Hegadorn, J. B. Asbury, *J. Am. Chem. Soc.* **2007**, 129, 15884.
- [35] R. D. Pensack, K. M. Banyas, J. B. Asbury, *Phys. Chem. Chem. Phys.* **2010**, 12, 14144.
- [36] S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, A. V. Vannikov, *Phys. Rev. Lett.* **1998**, 81, 4472.
- [37] N. I. Craciun, J. Wildeman, P. W. M. Blom, *Phys. Rev. Lett.* **2008**, 100, 056601.
- [38] H. Bässler, *Phys. Status Solidi B* **1993**, 175, 15.
- [39] V. D. Mihailetschi, J. K. J. van Duren, P. W. M. Blom, J. C. Hummelen, R. A. J. Janssen, J. M. Kroon, M. T. Rispens, W. J. H. Verhees, M. M. Wienk, *Adv. Funct. Mater.* **2003**, 13, 43.
- [40] A. Abate, D. R. Staff, D. J. Hollman, H. J. Snaith, A. B. Walker, B. D. Naab, J. Q. Zhong, J. Park, W. Chen, Y. Cui, *Phys. Chem. Chem. Phys.* **2014**, 16, 1132.
- [41] W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, M. A. J. Michels, *Phys. Rev. Lett.* **2005**, 94, 206601.
- [42] S. Torabi, F. Jahani, I. Van Severen, C. Kanimozhi, S. Patil, R. W. A. Havenith, R. C. Chiechi, L. Lutsen, D. J. M. Vanderzande, T. J. Cleij, J. C. Hummelen, L. J. A. Koster, *Adv. Funct. Mater.* **2015**, 25, 150.
- [43] I. Eisenstein, R. W. Munn, *Chem. Phys.* **1983**, 77, 47.
- [44] H. D. de Gier, F. Jahani, R. Broer, J. C. Hummelen, R. W. A. Havenith, *J. Phys. Chem. A* **2016**, 120, 4664.