Doping-related broadening of the density of states governs integer-charge transfer in P3HT

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Abstract: Molecular p-doping allows increasing the conductivity of organic semiconductors, which is regularly exploited in thermoelectric devices. Upon doping, integer and fractional charge transfer have been identified as the two competing mechanisms to occur, where the former is desired to promote the generation of mobile holes in the semiconductor host. In general, high dopant electron affinity is expected to promote integer charge transfer, while strong coupling between the frontier molecular orbitals of dopant and host promotes fractional charge transfer instead. Here, we investigate the role the width of the density of states (DOS) plays in the doping process by doping the conjugated polymer poly(3-hexylthiophene) (P3HT) with tetracyanoquinodimethane (TCNQ) derivatives of different electron affinities at 2% dopant ratio. Cyclic voltammetry confirms that only the electron affinity of F4TCNQ exceeds the ionization energy of P3HT, while TCNQ and FTCNQ turn out to have significantly lower but essentially identical electron affinities. From infrared spectroscopy we learn, however, that ca. 88% of FTCNQ is ionized while all of TCNQ is not. This translates into P3HT conductivities that are increased for F4TCNQ and FTCNQ doping, but surprisingly even reduced for TCNQ doping. To understand the remarkable discrepancy between TCNQ and FTCNQ we calculated the percentage of ionized dopants and the hole densities in the P3HT matrix resulting from varied widths of the P3HT HOMO-DOS via a semi-classical computational approach. We find that broadening of the DOS can yield the expected ionization percentages only if the dopants have significantly different tendencies to cause energetic disorder in the host matrix. In particular, while for TCNQ the doping behavior is well reproduced if the recently reported width of the P3HT HOMO-DOS is used, it must be broadened by almost one order of magnitude to comply with the ionization ratio determined for FTCNQ. Possible reasons for this discrepancy lie in the presence of a permanent dipole in FTCNQ, which highlights that electron affinities alone are not sufficient to define the strength of molecular dopants and their capability to perform integer charge transfer with organic semiconductors.

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Thermoelectric organic-semiconductor (OSC) devices are of particular interest because they are based on cheap constituents from abundant elements, provide large-area scalability and processability at low temperatures, and exhibit superior mechanical flexibility as compared to their inorganic counterparts.[1–3] Conjugated polymers are promising in this field as they exhibit low *thermal* conductivities while molecular doping can be used to achieve high *electrical* conductivities, and both properties are key for thermoelectric applications because they promote the thermoelectric figure of merit (ZT).[2,4–8] In a simplified view of the fundamental processes at work in the molecular p-doping of OSCs, the dopant molecule, typically a strong electron acceptor, receives an electron from the surrounding OSC host and thus populates it with holes as potentially mobile charge carriers. Energetically, this requires the electron affinity of the dopant (EA) to exceed the ionization energy of the OSC host material (IE). This process is commonly referred to as integer-charge transfer (ICT) or ion-pair formation in literature and has been found to stand in competition with fractional charge transfer (FCT), which happens through the formation of supramolecular ground state charge-transfer complexes between the OSC and dopant species.[9–11] We note that the designation of these two competing processes is not always consistent in pertinent literature, where (spatially separated) ion-pairs and charge-transfer complexes are sometimes being used as synonymous for ICT and FCT, respectively. In the following we use ICT and FCT to address the question as to whether integer charge is being transferred or not. The parameters favoring one process over the other are still under debate and gaining control over FCT is of high application-related relevance. In principle, suppressing FCT is desired to maximize the doping efficiency,[11] while, in turn, the presence of a moderate fraction of FCT has recently been found beneficial for maintaining the performance of thermoelectric devices over time.[5,6]

Notably, although FCT does not entail immediate ionization, significant increases in conductivity have been reported for this scenario as well.[9–11] The necessary precondition for FCT is the overlap between the highest occupied molecular orbital (HOMO) of the OSC and the lowest unoccupied molecular orbital (LUMO) of the p-dopant, which results in intermolecular rehybridization. This leads to an energy level splitting into a doubly occupied bonding, and an empty anti-bonding orbital in the FCT complex (i.e. the dopant-OSC pair performing FCT). The latter orbital is the LUMO of the complex and exhibits an electron affinity EA_{CPX} lower than that of the pristine p-dopant, which makes the complex a weaker electron acceptor than the pristine (non-hybridized) dopant species.[11,12] This view is not least based on the inherent disorder inferred by the weak non-covalent interaction of organic molecules in the solid state. It entails that the density of

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states (DOS) follows a Gaussian distribution with a non-zero probability of finding states deep in-between the ground-state HOMO and LUMO, which is in marked contrast to the sharp cut-off at the band edges in inorganic semiconductors.[13] Then, the tail of the semiconductor HOMO-DOS can still experience ionization due to the disorder-governed width of the Gaussian DOS and (potentially) mobile holes can be generated in this scenario as well, albeit to limited extent. This is likely the same reason as to why also weak p-dopants of $EA < IE$ can still directly generate holes in the OSC via ICT and increase the OSC conductivity, however, less efficiently than for $EA \geq IE$. Knowing the limits of charge transfer in one and the other scenario is of practical importance as it can promote the use of weaker dopants whose decreased reactivity can lead to higher environmental stability of OSC devices.[14] In that regard, the OSC poly(3-hexylthiophene) (P3HT) p-doped with tetrafluorotetracyanoquinodimethane (F4TCNQ) has been widely investigated as it was found that both ICT and FCT can occur under some circumstances,[5–7,15–17] and that regio-random (rra) P3HT is more prone to FCT than its regio-regular (rr) variety[16] which has been ascribed to a higher IE.[18] However, (semi)crystalline rr-P3HT and amorphous rra-P3HT are structurally and energetically only comparable to a limited extent, in particular if we assume that disorder may play a crucial role in the doping process. Therefore, structurally more similar OSCs of different IE, or such dopants of different EA, are required to elaborate the role of EA and IE.

In the present study, we probe the prevalence of FCT versus ICT for rr-P3HT by using dopants of different EA at an application-relevant low molar ratio of 2%. This is done for thin films by using 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its derivatives of increasing degree of fluorination (FxTCNQ with x = 0,1,4) with increasing EA.[19] We are particularly interested in this system as, only recently, a very narrow HOMO-DOS of only 63 meV (Gaussian standard deviation σ) has been reported for rr-P3HT by using energy resolved–electrochemical impedance spectroscopy by the groups of Bässler and Köhler,[20] which is at least four times narrower than that inferred from photoemission. By combining cyclic voltammetry (CV), Fourier-transform infrared spectroscopy (FTIR), conductivity measurements on thin films with theoretical modeling on a semi-classical level, we investigate the interplay between the width of the HOMO-DOS and doping-related charge transfer and show that $EA > IE$ is not a strict condition for ICT in p-type doping. Rather, we argue that doping-related microstructural changes induce a broadening of the DOS which must be considered alongside the common EA-IE relation in order to assess the doping efficiency.
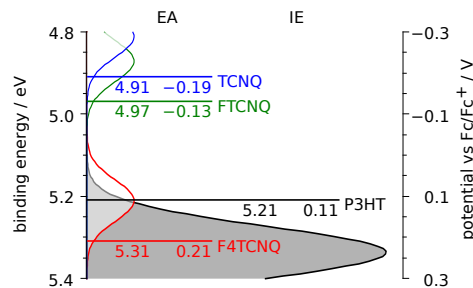
FIG. 1. Ionization energy (*IE*) of rr-P3HT and electron affinity (*EA*) of F4TCNQ, FTCNQ, and TCNQ, as determined by cyclic voltammetry (CV; voltammograms in Supplementary Material Fig. S1). For each material both the binding energy for electrons (in eV) is given versus the vacuum level (left value) together with the according potential (in V) versus ferrocene/ferrocenium (Fc/Fc$^+$) (right value). Gaussian curves in the background symbolize the density of states (DOS) of the P3HT HOMO (grey) and the dopant LUMO (filled white-transparent) plotted with σ of 63 meV for P3HT[20] and 50 meV for the dopants.

As thoroughly investigated in a recent publication by Wegner et al. (Ref. 21) CV-derived redox potentials V_{redox} of dopant and host materials offer a reliable resource for the prediction of ICT; our CV results are depicted in Fig. 1. For TCNQ, FTCNQ, and F4TCNQ we find an *EA* ($V_{\text{redox}}^{\text{LUMO}}$ versus ferrocene/ferrocenium (Fc/Fc$^+$)) of 4.91 eV (-0.19 V), 4.97 eV (-0.13 V), and 5.31 eV (0.21 V), respectively, and an *IE* ($V_{\text{redox}}^{\text{HOMO}}$) of 5.21 eV (0.11 V) for P3HT in the solid state (thin film on ITO). Compared to literature values for the dopants[21] as well as for P3HT[22] (where Fc/Fc$^+$ has been used as an external standard as well), our V_{redox} values are in agreement within ± 0.1 V, which is in the expected error margin of energy levels derived from CV;[23] see the Supplementary Material for plots and details of the data treatment. Strictly following the precondition $EA > IE$ for ICT these results would predict ICT to occur with F4TCNQ only. As the *EA* values of TCNQ and FTCNQ lie few hundred meV below the *IE* of the host, these two dopant species appear well suited to probe the role of the tailing of the Gaussian HOMO-DOS of P3HT in the doping process.

To quantify the occurrence of ICT we examine the dopant responses in FTIR absorbance for drop-cast films of P3HT doped with FxTCNQ from common solution. We thereby exploit that some vibrational modes of TCNQ derivatives undergo a softening which can be related to the degree of charge transfer δ.[5–7,10,11,15,16,24–28] Especially, the C≡N stretch modes from the FxTCNQ
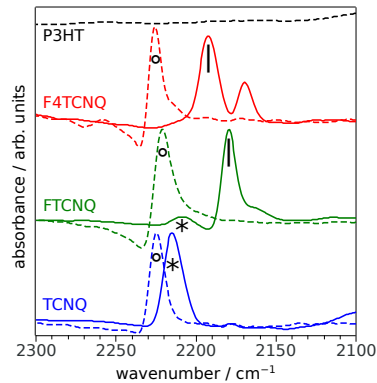
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FIG. 2. FTIR spectra of rr-P3HT thin films doped with F4TCNQ, FTCNQ, and TCNQ at 2% dopant molar ratio (solid lines) and the according pristine compounds (dashed lines); range is focused on C≡N stretch modes of the dopants (full range in Supplementary Material Fig. S2); normalized to the highest absorbance within the range. Rings (○) mark the peaks of neutral dopant species at v_0, bars (|) mark their anions at v_1, and asterisks (∗) dopants undergoing fractional charge transfer.

series (occurring around $2200\,\mathrm{cm}^{-1}$) offer unambiguous insights into the charged state of the dopant without masking by vibrational modes of P3HT (see black curve in Fig. 2). With the wavenumbers v_0 of the neutral dopant ($\delta = 0$) and v_1 of its anion ($\delta = 1$) known from alkali salts, the displacement Δv from the neutral position is correlated to the degree of charge transfer $\delta = 2\Delta v/v_0 \left(1 - v_1^2/v_0^2\right)^{-1}$.[25] Values of $v_0 = 2227\,\mathrm{cm}^{-1}$ and $v_1 = 2194\,\mathrm{cm}^{-1}$ have been reported for F4TCNQ,[26] and $v_0 = 2227\,\mathrm{cm}^{-1}$, $v_1 = 2183\,\mathrm{cm}^{-1}$ for TCNQ;[24] as the F4TCNQ and TCNQ v_0-positions coincide, it is reasonable to expect a similar value for FTCNQ as well. In our data we find the respective positions of the pristine dopant C≡N stretch modes in good agreement (Fig. 2) at 2228, 2224, and $2225\,\mathrm{cm}^{-1}$ for F4TCNQ, FTCNQ, and TCNQ, respectively. For the doped P3HT films, the sample with F4TCNQ (red curve) exclusively shows ICT features as it has been reported before,[26] with its main band in line with the expected v_1 value. Notably, the FTCNQ-doped film (green curve) shows strong vibrational modes highly similar to the ICT-related features found for F4TCNQ. Here, the dominant peak is found at $2180\,\mathrm{cm}^{-1}$ which we assign to v_1 for its proximity to the respective value reported for TCNQ.[24] At the expected ICT position for the latter (blue curve), however, we observe no indication of a v_1 peak above background noise. The dominant mode in TCNQ and the much weaker mode in FTCNQ close-by which lie in-between
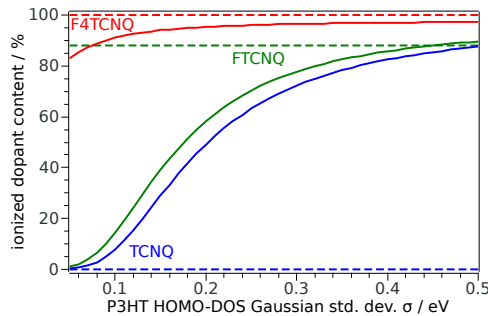
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FIG. 3. Ionized dopant content in P3HT doped with F4TCNQ, FTCNQ, and TCNQ at 2% dopant molar ratio as calculated for varied widths (standard deviations) of the P3HT HOMO-DOS (solid lines) while keeping the width of the dopant DOS fixed (see text); dashed lines mark the ionization percentages as expected from the integrated absorbances in Fig. 2.

the ν_0 and ν_1 are assigned to the dopants in a FCT complex, which is in analogy to our previous findings for quaterthiophene.[10] The peak positions around $2208\,\mathrm{cm}^{-1}$ (FTCNQ) and $2214\,\mathrm{cm}^{-1}$ (TCNQ) translate into δ values 0.36 and 0.27, respectively, while F4TCNQ does not show indications of FCT whatsoever. Since for FCT the value of δ correlates with the interaction strength, these data for FTCNQ versus TCNQ suggest that not only is the ICT fraction higher for dopants with increased EA, but also the dopant-host interaction is stronger.

It is surprising though that with the EA of FTCNQ being over $0.2\,\mathrm{eV}$ lower than the IE of P3HT, the majority of the FTCNQ dopants reside ionized in the polymer matrix, which clearly violates the strict criterion $EA > IE$ for ICT. Therefore, we assume doping-induced disorder to cause significant broadening of the P3HT HOMO-DOS which enables ICT, an assumption which we investigate in the following by semi-classical modeling. Our calculations are based on the assumption that the HOMO/LUMO DOS are well represented by Gaussian distributions, as illustrated in Fig. 1.[20,29] The distribution centers of the P3HT HOMO and the dopant LUMO as the most relevant energy levels are deduced from our experimental IE and EA values, as derived from CV. The distribution onsets then lie off the center by twice the standard deviation σ which has been determined for pristine P3HT in a recent study by Bässler et al. to $63\,\mathrm{meV}$[20] (for more details, see Methods in the Supplementary Material). We further used molecular volume densities taken from the single-crystal structures of P3HT and the FxTCNQ series.[30–32] In our calculations,

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the Fermi level in each system as well as the occupancy of the relevant energy levels (HOMO and LUMO of both the dopants and the host) are then determined by imposing overall charge neutrality. This condition is achieved recursively through the self-consistent solution of the discretized Poisson equation, following the procedure originally described by Oehzelt et al. (Ref. 29) and also detailed in Refs. 10, 11, 33, and 34. We then explored the role of the DOS broadening of the P3HT host by performing these calculations for each P3HT-dopant combination with σ values for the P3HT DOS ranging from 0.05 to 0.5 eV; σ for the dopant LUMO DOS was thereby held constant at the lowest value of 0.05 eV, thus essentially assuming all the broadening occurs in the P3HT DOS. This approach stands in contrast to recent investigations on the facilitation of charge separation between dopant and host through Gaussian broadening. There, both donor and acceptor were small molecules and, therefore, equal broadening was assumed for the DOS prior to doping, as well as for the DOS of the resulting charge-transfer states.[35,36] We stress that, rather than for practical purposes, our approach is based on the argument that small dopant molecules such as FxTCNQ will incur only limited geometrical disorder due to their rigid structure, which is in marked contrast to a polymer such as P3HT which can undergo a plethora of conformational changes[37] and where geometrical disorder is a leading cause of DOS broadening. Still however, the local polarizable environment of the dopant in the blend with the OSC will impact the width of the DOS, e.g., if it is randomly distributed in the alkyl-chain region of P3HT or packed with the polymer backbone. For the low doping concentration of 2% as we target in the present work, this aspect is very difficult to quantify experimentally, e.g., by scattering techniques. The percentages of ionized dopants resulting from our modeling are plotted in Fig. 3 alongside the respective values estimated from the FTIR spectra in Fig. 2 (horizontal dashed lines), which have been derived from ratios between the integrated absorbance in the C≡N stretch mode associated with ICT and the total absorbance.

Generally, we observe that both increased σ and stronger dopants yield higher ionization percentages. The fact that the modeling of F4TCNQ-doping does not reach 100% is expected because our computational approach focuses on the broadening of the host HOMO-DOS. Since the *EA* of F4TCNQ is higher than the *IE* of P3HT, it likely experiences ionization by the next-deeper occupied levels of P3HT as well, which is in line with the shape and position of the occupied states reported in literature,[20] and the landscape of the oxidation states in our P3HT cyclic-voltammogram (Supplementary Material Fig. S1), where the next-to-HOMO peak follows within 0.2 eV. Most notably, while the reported $\sigma = 63$ meV of pristine P3HT,[20] yields <3% ionization for the FTCNQ-

doped sample, the experimentally observed 88% are only met around $\sigma = 450$ meV. At the same σ value, in turn, TCNQ would be expected to exhibit 85% ionization, however, our experimental data tends towards 0%. Again using the pristine-P3HT σ value of 63 meV provides here, indeed, negligible TCNQ ionization of <1%, in line with the experiment. Thus, in contrast to TCNQ, the width of the P3HT HOMO-DOS appears to be significantly altered by the presence of FTCNQ. Our assumption of negligible broadening of the dopant DOS alongside the greater geometrical disorder expected in the polymer might be the reason why our broadening far surpasses the up to 263 meV considered in recent investigations on the facilitation of charge separation between small-molecule acceptors and donors,[35,36] as explained in the previous paragraph.

EA-wise only less than 0.1 eV weaker than FTCNQ, TCNQ thus seems to draw a limit for ICT with P3HT. FCT clearly demands π-π stacking of P3HT and the dopant, hence, reducing disorder and forming even a crystalline lattice.[15] For ICT, it is known that P3HT-F4TCNQ pairs can already form in mixed solution,[38] which lets these "first" active dopants encounter a different energy landscape than those acting upon transition to the solid state. Thus, we hypothesize that the discrepancy between FTCNQ and TCNQ might well originate in a self-amplifying effect. In general, there must be a threshold in energy where the dopant *EA* is close enough to the host *IE* for initial ionization sufficient to cause effective DOS broadening which, as a result, provides even more accessible states for ionization. For P3HT doped with FTCNQ and TCNQ such a threshold lying between their respective EA values would explain their remarkably different doping behavior. For ICT, the distribution of the dopant molecules in the hexyl sidechain region of P3HT has been reported to be crucial for F4TCNQ and ionized dopants have been suggested to pack also with the polymer backbone.[39,40] Thus, P3HT-FxTCNQ systems undergoing ICT have more microstates to mutually arrange than systems performing FCT, hence, such systems can be expected to exhibit more structural disorder. This effect is likely further promoted by a broadening of the dopant LUMO-DOS in the case of ICT, where dopant dispersion in the alkyl chain region provides a complex polarizable environment for the dopant (also in its ground state).[20] As deduced from density functional theory (DFT) calculations (see Supplementary Material for methodology,[41,42]) TCNQ and F4TCNQ both have a negligible dipole moment (<0.001 D, residual due to the accuracy of the method), while FTCNQ carries a significant dipole of 0.908 D. Thus, the presence of a net permanent dipole due to the sole C-F bond makes this species special and even more susceptible to polarization-driven DOS broadening. Recently, dopants with strong quadrupole and dipole moments have also been identified to improve charge separation.[35,36] A further relevant ef-
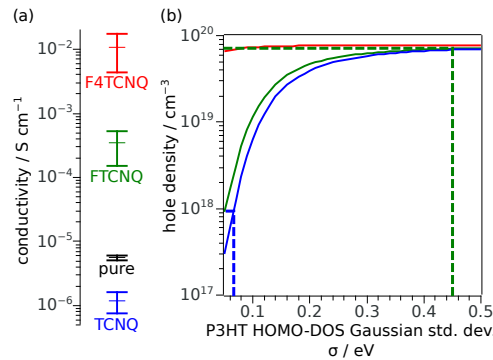
FIG. 4. (a) Conductivity of P3HT pure and doped with F4TCNQ, FTCNQ, and TCNQ at 2% dopant molar ratio. (b) Charge-carrier density (holes) as calculated for varied widths (standard deviations) of the P3HT HOMO-DOS. Dashed lines mark the DOS width that provides the same ionization percentage as deduced from the FTIR data (Fig. 3), and the corresponding hole density.

fect might be added by the reduced symmetry of FTCNQ which effectively induces more disorder than TCNQ (or F4TCNQ, for that matter) for exhibiting only one instead of three planes of symmetry, thus, yielding more possibilities of distinguishable spatial arrangements. In turn, this might promote regular packing of TCNQ with the polymer backbone and, thus, exclusive FCT-complex formation in this case, as we observe experimentally.

Being aware that ICT does not automatically imply the generated charge carriers to be mobile, we chose electrical conductivity of spin-cast P3HT:FxTCNQ thin films (on patterned ITO electrode structures on glass) as an application-directed indicator for the impact of FCT and ICT. As shown in Fig. 4 (a), 2% of F4TCNQ-doping provides an increase of more than three orders of magnitude, from $(5.59 \pm 0.49)\,10^{-6}\,\mathrm{S \cdot cm^{-1}}$ for pristine P3HT to $(1.08 \pm 0.64)\,10^{-2}\,\mathrm{S \cdot cm^{-1}}$. For FTCNQ, the conductivity only increases to $(3.4 \pm 1.9)\,10^{-4}\,\mathrm{S \cdot cm^{-1}}$ and TCNQ even brings a significant reduction to $(1.18 \pm 0.43)\,10^{-6}\,\mathrm{S \cdot cm^{-1}}$. Alongside, we calculated the doping-related charge-carrier (hole) densities for varied P3HT HOMO-DOS widths (Fig. 4 (b)). (Note that our calculations cannot discriminate between mobile holes and those trapped at the dopant site.) While hole densities for TCNQ and FTCNQ doping increase over two orders of magnitude within the investigated σ range of the P3HT HOMO-DOS, F4TCNQ-doped P3HT is virtually unaffected in this sense and yields a charge-carrier density between 6.7 and $7.8 \times 10^{19}\,\mathrm{cm^{-3}}$. For the σ values

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that provide the same ionization percentages as deduced from the FTIR data (marked by dashed lines), the hole density upon FTCNQ doping gives around 7.0×10^{19} cm^{-3} ($\sigma = 450$ meV) while that due to TCNQ doping stays below 10^{18} cm^{-3} ($\sigma = 63$ meV). With practically two orders of magnitude difference, this is well-reflected in the conductivities of the FTCNQ- and TCNQ-doped films. We note though that the conductivities of F4TCNQ and FTCNQ are still one order of magnitude apart while the calculated hole densities are very similar. Further, the addition of TCNQ highly reproducibly *decreases* the conductivity by over one order of magnitude, as compared to pure P3HT. This is remarkable in our view, since the related oligomer quaterthiophene doped with F4TCNQ, which exclusively exhibits FCT, still sees an increase in conductivity.[10] We cannot explain this observation without ambiguity on the basis of the present data, as conductivity hinges on the microstructure of the films which will be characterized in a forthcoming study. However, both trends can be well linked to FCT as well. Going with the idea that the LUMO of the FCT complex (for strong dopants) can effectively act as an electron-accepting level of EA_{CPX}, thus, rendering the FCT complex a p-dopant to the surrounding OSC host matrix,[10,11] the complex LUMO resulting from FCT with a weak dopant such as TCNQ would yield EA_{CPX} too low to significantly ionize P3HT. The spatial vicinity of dopant and host that is required for FCT can then make the neutral complex act as trap for hole transport along the polymer backbone. Such a detrimental influence of the presence of FCT complexes would also explain why FTCNQ-doping yields lower conductivity than F4TCNQ despite a similar charge-carrier density, as, in contrast to F4TCNQ, FTCNQ does experience both ICT and FCT, as it is evident from our FTIR data.

In summary, we have investigated the validity of the perception that for ICT the EA of a p-dopant must exceed the IE of an OSC. We focused on rr-P3HT doped with TCNQ derivatives where only the EA of F4TCNQ exceeds the IE of P3HT. We first employed CV to precisely determine the IE of rr-P3HT and the EA of F4TCNQ, FTCNQ, TCNQ, and deduced from FTIR data to which extent ICT occurs for P3HT doped with these species at a ratio 2%. Via a semi-classical modeling we then calculated the percentages of ionized dopants that result from varying the width of the P3HT HOMO-DOS while keeping that of the dopant fixed. Finally, we compared the calculated hole densities in P3HT which result for these widths, with experimental conductivity data. While F4TCNQ doping of P3HT exclusively resulted in ICT, FTCNQ-doping showed ICT for 88% of the dopants in the film. Our calculations demonstrate that this ionization percentage cannot be achieved without significant broadening of the P3HT HOMO-DOS. In marked contrast, despite an EA almost identical to that of FTCNQ, TCNQ-doping resulted in no indication of ICT

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whatsoever, which emerges naturally from our calculations if the reported σ value for the HOMO-DOS of P3HT of 63 meV is used. For this very system we observed that exclusive occurrence of FCT can even lead to a decrease in conductivity, which we ascribe to charge carrier trapping through the formation of the neutral FCT complexes. Our study indicates that different molecular dopants of similar structural properties and almost identical *EA* may show largely different doping behavior, which we explain by different tendencies for inducing disorder and, thus, for broadening the DOS to promote ICT. The markedly different behavior of TCNQ and FTCNQ might be due to anisotropy and the presence of a strong permanent dipole moment present in the latter, the role of which we plan to investigate in more detail in a forthcoming study.

SUPPLEMENTARY MATERIAL

See Supplementary Material for details on experimental and computational methods, cyclic voltammograms corresponding to energy levels in Fig. 1 (Fig. S1), and the full-range version of the FTIR spectra in Fig. 2 (Fig. S2).

DATA AVAILABILITY

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

REFERENCES

[1] J. Pope and C. Lekakou, "Thermoelectric polymer composite yarns and an energy harvesting wearable textile," Smart Materials and Structures **28**, 095006 (2019).

[2]O. Zapata-Arteaga, A. Perevedentsev, S. Marina, J. Martin, J. S. Reparaz, and M. Campoy-Quiles, "Reduction of the Lattice Thermal Conductivity of Polymer Semiconductors by Molecular Doping," ACS Energy Letters **5**, 2972–2978 (2020).

[3]N. Okada, K. Sato, M. Yokoo, E. Kodama, S. Kanehashi, and T. Shimomura, "Thermoelectric Properties of Poly(3-hexylthiophene) Nanofiber Aerogels with a Giant Seebeck Coefficient," ACS Applied Polymer Materials **3**, 455–463 (2021).

[4]O. Bubnova and X. Crispin, "Towards polymer-based organic thermoelectric generators," Energy & Environmental Science **5**, 9345 (2012).

[5]K. E. Watts, B. Neelamraju, E. L. Ratcliff, and J. E. Pemberton, "Stability of Charge Transfer States in F_4TCNQ-Doped P3HT," Chemistry of Materials **31**, 6986–6994 (2019).

[6]O. Zapata-Arteaga, B. Dörling, A. Perevedentsev, J. Martín, J. S. Reparaz, and M. Campoy-Quiles, "Closing the Stability–Performance Gap in Organic Thermoelectrics by Adjusting the Partial to Integer Charge Transfer Ratio," Macromolecules **53**, 609–620 (2020).

[7]S. E. Yoon, Y. Kang, G. G. Jeon, D. Jeon, S. Y. Lee, S.-J. Ko, T. Kim, H. Seo, B.-G. Kim, and J. H. Kim, "Exploring Wholly Doped Conjugated Polymer Films Based on Hybrid Doping: Strategic Approach for Optimizing Electrical Conductivity and Related Thermoelectric Properties," Advanced Functional Materials , 2004598 (2020).

[8]A. Hamidi-Sakr, L. Biniek, J.-L. Bantignies, D. Maurin, L. Herrmann, N. Leclerc, P. Lévêque, V. Vijayakumar, N. Zimmermann, and M. Brinkmann, "A Versatile Method to Fabricate Highly In-Plane Aligned Conducting Polymer Films with Anisotropic Charge Transport and Thermoelectric Properties: The Key Role of Alkyl Side Chain Layers on the Doping Mechanism," Advanced Functional Materials **27**, 1700173 (2017).

[9]H. Méndez, G. Heimel, A. Opitz, K. Sauer, P. Barkowski, M. Oehzelt, J. Soeda, T. Okamoto, J. Takeya, J.-B. Arlin, J.-Y. Balandier, Y. Geerts, N. Koch, and I. Salzmann, "Doping of Organic Semiconductors: Impact of Dopant Strength and Electronic Coupling," Angewandte Chemie International Edition **52**, 7751–7755 (2013).

[10]H. Méndez, G. Heimel, S. Winkler, J. Frisch, A. Opitz, K. Sauer, B. Wegner, M. Oehzelt, C. Röthel, S. Duhm, D. Többens, N. Koch, and I. Salzmann, "Charge-transfer crystallites as molecular electrical dopants," Nature Communications **6** (2015), 10.1038/ncomms9560.

[11]I. Salzmann, G. Heimel, M. Oehzelt, S. Winkler, and N. Koch, "Molecular Electrical Doping of Organic Semiconductors: Fundamental Mechanisms and Emerging Dopant Design Rules," Accounts of Chemical Research **49**, 370–378 (2016).

[12]I. Salzmann, G. Heimel, S. Duhm, M. Oehzelt, P. Pingel, B. M. George, A. Schnegg, K. Lips, R.-P. Blum, A. Vollmer, and N. Koch, "Intermolecular Hybridization Governs Molecular Electrical Doping," Physical Review Letters **108** (2012), 10.1103/PhysRevLett.108.035502.

[13]G. Horowitz, "Validity of the concept of band edge in organic semiconductors," Journal of Applied Physics **118**, 115502 (2015).

[14]Y. Karpov, T. Erdmann, I. Raguzin, M. Al-Hussein, M. Binner, U. Lappan, M. Stamm, K. L. Gerasimov, T. Beryozkina, V. Bakulev, D. V. Anokhin, D. A. Ivanov, F. Günther, S. Gemming, G. Seifert, B. Voit, R. Di Pietro, and A. Kiriy, "High Conductivity in Molecularly p-Doped Diketopyrrolopyrrole-Based Polymer: The Impact of a High Dopant Strength and Good Structural Order," Advanced Materials **28**, 6003–6010 (2016).

[15]I. E. Jacobs, C. Cendra, T. F. Harrelson, Z. I. Bedolla Valdez, R. Faller, A. Salleo, and A. J. Moulé, "Polymorphism controls the degree of charge transfer in a molecularly doped semiconducting polymer," Materials Horizons **5**, 655–660 (2018).

[16]B. Neelamraju, K. E. Watts, J. E. Pemberton, and E. L. Ratcliff, "Correlation of Coexistent Charge Transfer States in F$_4$TCNQ-Doped P3HT with Microstructure," The Journal of Physical Chemistry Letters **9**, 6871–6877 (2018).

[17]K. E. Watts, B. Neelamraju, M. Moser, I. McCulloch, E. L. Ratcliff, and J. E. Pemberton, "Thermally Induced Formation of HF$_4$TCNQ$^-$ in F$_4$TCNQ-Doped Regioregular P3HT," The Journal of Physical Chemistry Letters **11**, 6586–6592 (2020).

[18]H. Aarnio, P. Sehati, S. Braun, M. Nyman, M. P. de Jong, M. Fahlman, and R. Osterbacka, "Spontaneous charge transfer and dipole formation at the interface between p3ht and pcbm," Advanced Energy Materials **1**, 792–797 (2011).

[19]K. Kanai, K. Akaike, K. Koyasu, K. Sakai, T. Nishi, Y. Kamizuru, T. Nishi, Y. Ouchi, and K. Seki, "Determination of electron affinity of electron accepting molecules," Applied Physics A **95**, 309–313 (2009).

[20]H. Bässler, D. Kroh, F. Schauer, V. Nádaždy, and A. Köhler, "Mapping the Density of States Distribution of Organic Semiconductors by Employing Energy Resolved–Electrochemical Impedance Spectroscopy," Advanced Functional Materials , 2007738 (2020).

[21]B. Wegner, L. Grubert, C. Dennis, A. Opitz, A. Röttger, Y. Zhang, S. Barlow, S. R. Marder, S. Hecht, K. Müllen, and N. Koch, "Predicting the yield of ion pair formation in molecular electrical doping: Redox-potentials *versus* ionization energy/electron affinity," Journal of Materials Chemistry C **7**, 13839–13848 (2019).

14

[22]S. Sweetnam, K. R. Graham, G. O. Ngongang Ndjawa, T. Heumüller, J. A. Bartelt, T. M. Burke, W. Li, W. You, A. Amassian, and M. D. McGehee, "Characterization of the Polymer Energy Landscape in Polymer:Fullerene Bulk Heterojunctions with Pure and Mixed Phases," Journal of the American Chemical Society **136**, 14078–14088 (2014).

[23]C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, and G. C. Bazan, "Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications," Advanced Materials **23**, 2367–2371 (2011).

[24]J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler, and D. O. Cowan, "Degree of charge transfer in organic conductors by infrared absorption spectroscopy," Journal of the American Chemical Society **103**, 2442–2443 (1981).

[25]E. Kampar and O. Neilands, "Degree of Charge Transfer in Donor–Acceptor Systems of the π–π Type," Russian Chemical Reviews **55**, 334–342 (1986).

[26]M. Meneghetti and C. Pecile, "Charge–transfer organic crystals: Molecular vibrations and spectroscopic effects of electron–molecular vibration coupling of the strong electron acceptor $TCNQF_4$," The Journal of Chemical Physics **84**, 4149–4162 (1986).

[27]N. L. Haworth, J. Lu, N. Vo, T. H. Le, C. D. Thompson, A. M. Bond, and L. L. Martin, "Diagnosis of the Redox Levels of $TCNQF_4$ Compounds Using Vibrational Spectroscopy," ChemPlusChem **79**, 962–972 (2014).

[28]J. T. Liu, H. Hase, S. Taylor, I. Salzmann, and P. Forgione, "Approaching the Integer-Charge Transfer Regime in Molecularly Doped Oligothiophenes by Efficient Decarboxylative Cross-Coupling," Angewandte Chemie International Edition **59**, 7146–7153 (2020).

[29]M. Oehzelt, N. Koch, and G. Heimel, "Organic semiconductor density of states controls the energy level alignment at electrode interfaces," Nature Communications **5** (2014), 10.1038/ncomms5174.

[30]N. Kayunkid, S. Uttiya, and M. Brinkmann, "Structural Model of Regioregular Poly(3-hexylthiophene) Obtained by Electron Diffraction Analysis," Macromolecules **43**, 4961–4967 (2010).

[31]Y. Krupskaya, M. Gibertini, N. Marzari, and A. F. Morpurgo, "Band-Like Electron Transport with Record-High Mobility in the TCNQ Family," Advanced Materials **27**, 2453–2458 (2015).

[32]R. Shukla, C. Ruzié, G. Schweicher, A. R. Kennedy, Y. H. Geerts, D. Chopra, and B. Chattopadhyay, "Insight from electron density and energy framework analysis on the structural features of F_x-TCNQ (x = 0, 2, 4) family of molecules," Acta Crystallographica Section B Structural

15

Science, Crystal Engineering and Materials **75**, 71–78 (2019).

[33] J. C. Blakesley and N. C. Greenham, "Charge transfer at polymer-electrode interfaces: The effect of energetic disorder and thermal injection on band bending and open-circuit voltage," Journal of Applied Physics **106**, 034507 (2009).

[34] M. Oehzelt, K. Akaike, N. Koch, and G. Heimel, "Energy-level alignment at organic heterointerfaces," Science Advances **1**, e1501127 (2015).

[35] M. L. Tietze, J. Benduhn, P. Pahner, B. Nell, M. Schwarze, H. Kleemann, M. Krammer, K. Zojer, K. Vandewal, and K. Leo, "Elementary steps in electrical doping of organic semiconductors," Nature Communications **9** (2018), 10.1038/s41467-018-03302-z.

[36] M. Schwarze, C. Gaul, R. Scholz, F. Bussolotti, A. Hofacker, K. S. Schellhammer, B. Nell, B. D. Naab, Z. Bao, D. Spoltore, K. Vandewal, J. Widmer, S. Kera, N. Ueno, F. Ortmann, and K. Leo, "Molecular parameters responsible for thermally activated transport in doped organic semiconductors," Nature Materials **18**, 242–248 (2019).

[37] F. Panzer, H. Bässler, and A. Köhler, "Temperature Induced Order–Disorder Transition in Solutions of Conjugated Polymers Probed by Optical Spectroscopy," The Journal of Physical Chemistry Letters **8**, 114–125 (2017).

[38] J. Gao, E. T. Niles, and J. K. Grey, "Aggregates Promote Efficient Charge Transfer Doping of Poly(3-hexylthiophene)," The Journal of Physical Chemistry Letters **4**, 2953–2957 (2013).

[39] H. Hase, K. O'Neill, J. Frisch, A. Opitz, N. Koch, and I. Salzmann, "Unraveling the Microstructure of Molecularly Doped Poly(3-hexylthiophene) by Thermally Induced Dedoping," The Journal of Physical Chemistry C **122**, 25893–25899 (2018).

[40] M. G. Voss, D. T. Scholes, J. R. Challa, and B. J. Schwartz, "Ultrafast transient absorption spectroscopy of doped P3HT films: Distinguishing free and trapped polarons," Faraday Discussions **216**, 339–362 (2019).

[41] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin,

16

R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, "Gaussian 09 Revision E.01," Gaussian Inc. Wallingford CT 2009 (2009).

[42]J.-D. Chai and M. Head-Gordon, "Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections," Physical Chemistry Chemical Physics **10**, 6615 (2008).
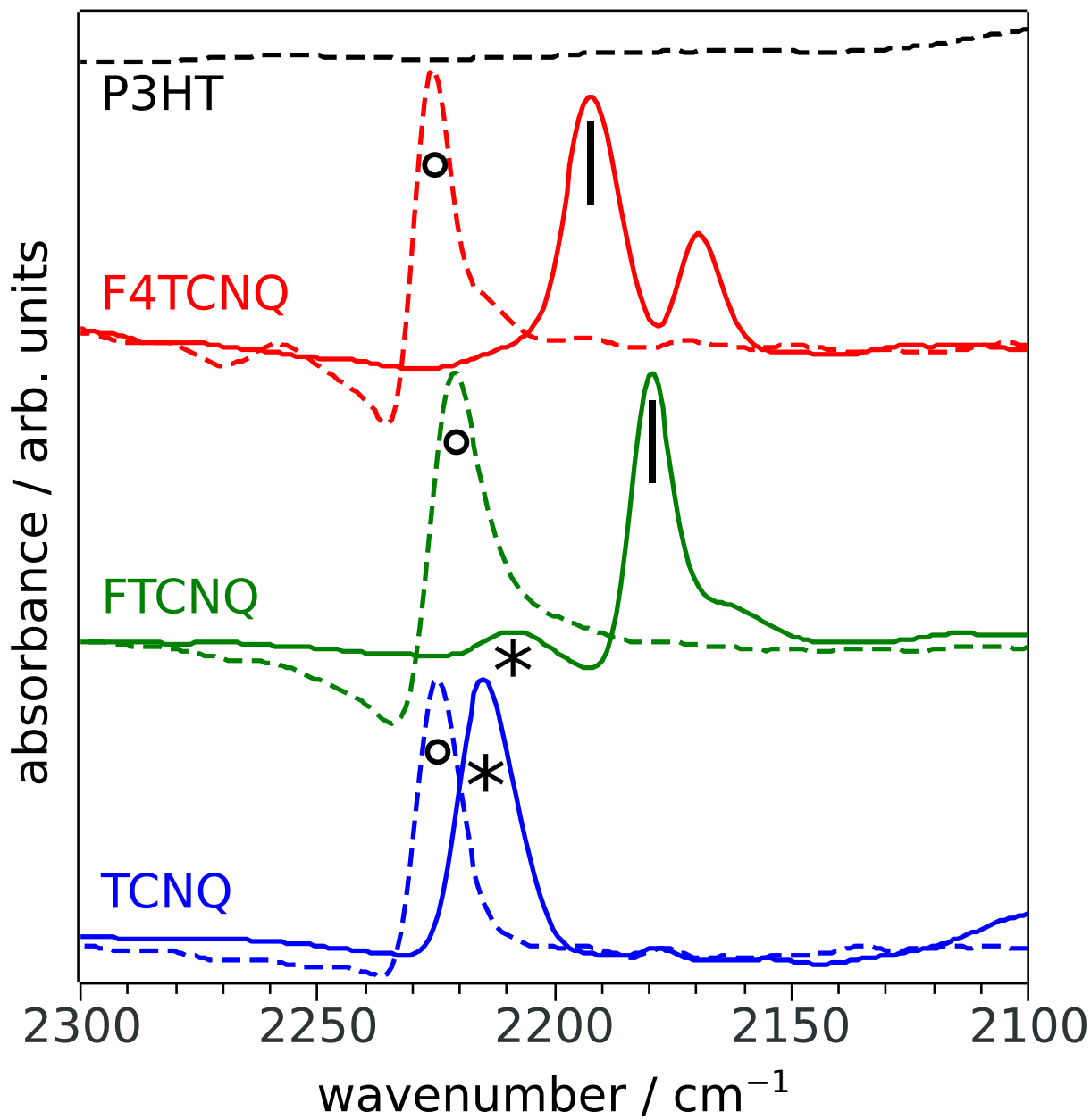
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