Critical dopant concentrations govern integer and fractional charge-transfer phases in doped P3HT

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Abstract

The conjugated polymer poly(3-hexylthiophene) (P3HT) p-doped with the strong acceptor tetrafluorotetracyanoquinodimethane (F4TCNQ) is known to undergo ion-pair (IPA) formation, i.e. integer-charge transfer, and, as only recently reported, can form ground state charge-transfer complexes (CPXs) as a competing process, yielding fractional charge transfer. As these fundamental charge-transfer phenomena differently affect doping efficiency and, thus, organic-semiconductor device performance, possible factors governing their occurrence have been under investigation ever since. Here, we focus on the role of a critical dopant concentration deciding over IPA- or CPX-dominated regimes. Employing a broad, multi-technique approach, we compare the doping of P3HT by F4TCNQ and its weaker derivatives F2TCNQ, FTCNQ, and TCNQ, combining experiments with semi-classical modeling. IPA, CPX, and neutral-dopant ratios (estimated from vibrational absorption spectroscopy) together with electron affinity and ionization energy values (deduced from cyclic voltammetry) allow calculating the width of a Gaussian density of states (DOS) relating to the highest occupied molecular orbital in P3HT. While a broader DOS indicates energetic disorder, we use grazing-incidence x-ray diffraction to assess spatial order. Our findings consider the proposal of nucleation driving IPA formation and we hypothesize a certain host-dopant stoichiometry to be key for the formation of a crystalline CPX phase.

1. Introduction

Organic semiconductors (OSCs) are commercially highly successful in organic light-emitting diodes (OLEDs) [1–3] and have shown significant recent progress in areas as diverse as photovoltaics [4], flexible electronics [5], and thermoelectric energy harvesting [6, 7]. As for their inorganic counterparts, electrical doping as a method to generate mobile charge-carriers (electrons and holes) and spatially control their density is key for organic and hybrid devices, as it allows engineering efficient electron/hole injection, transport, and blocking layers. For the fundamental process of doping, that is, electron transfer between the OSC host and its molecular dopant, two complementary phenomena have been identified to occur, namely, the formation of spatially separated ion-pairs (IPAs) via integer charge transfer, and the formation of ground state charge-transfer complexes (CPXs) with only fractional charge transfer [8–10]. On the one hand, IPA
formation is energetically favorable for the system if, in first approximation, the electron affinity $EA$ of the p-dopant, typically a strong electron acceptor, matches or exceeds the ionization energy $IE$ of the donor, that is, the conjugated molecule/polymer forming the OSC host; n-doping proceeds in analogy (with an electron donor) but is not the focus of this present work. On the other hand, CPX formation is based on the spatial overlap and rehybridization between the frontier molecular orbitals, i.e. the lowest unoccupied molecular orbital in the ground state (LUMO) of the acceptor and the highest occupied molecular orbital in the ground state (HOMO) of the donor. Figure 1(a) shows a simple energy-level diagram for IPA and CPX formation. Notably, the two complementary processes do not exclude each other for a given system but can prevail in certain ratios governed by parameters yet to be fully identified. To maximize the mobile charge carrier density in an OSC, in most cases, suppressing CPX and promoting IPA formation is desired [9–11]. However, some examples exist where a moderate CPX fraction optimizes hole-transport in polymer-OLEDs [12] or maintains the performance of thermoelectric devices over time [13]. As such, achieving an in-depth understanding of the charge transfer processes upon doping and resilient knowledge of the parameters favoring one phenomenon over the other is of high application-related relevance for organic and hybrid electronics. The system of the conjugated polymer poly(3-hexylthiophene) (P3HT) p-doped with the strong molecular acceptor tetrafluorotetracyanoquinodimethane (F4TCNQ), seems to be ideal to address this issue, as it has long been assumed to form only IPAs, while recent studies have also reported CPX formation under certain conditions [13–18]. In the following, we first provide a comprehensive overview of the vast literature addressing the doping behavior of this prototypical system and then suggest a model to rationalize charge transfer by differently strong dopants.

Figure 1(b) shows the possible spatial arrangements of P3HT and F4TCNQ as agreed upon by numerous studies. To begin with, Neelamraju et al [15] reported increased CPX-prevalence in regio-random (rra) versus regio-regular (rr) P3HT, as well as with increasing dopant molar ratio $\chi$, creating an essentially pure CPX system with rra-P3HT at $\chi = 17\%$. In this study, the investigation of rra-P3HT suggests the importance of amorphous P3HT regions—and their effectively higher $IE$ (5.42 versus 5.13 eV in rr-P3HT [21]); values from redox potentials, see section 2 for conversion)—to promote CPX over IPA formation. In contrast, Jacobs et al [14] created a crystalline, essentially CPX-only precedence in low-molecular weight rr-P3HT for $\chi = 13\%$ and 17%, which was possible by keeping the blend dissolved throughout the deposition via spin-coating and holding solution, pipette tips, and substrates constantly at 80 °C. While this system turned out to be unstable as it reverts to IPA-prevalence under ambient conditions in $< 1 \text{ h}$ (and in 1 d under $N_2$), Watts et al [16] observed in IPA-dominated samples the CPX fraction to increase over the course of weeks. Most recently, Stanfield et al [22] largely reconciled these discrepancies by studying the thermal annealing of F4TCNQ-doped rr-P3HT with different degrees of crystallinity. They concluded that there exists, indeed, a kinetically unstable, crystalline CPX polymorph, as found by Jacobs et al in addition to a stable CPX phase in the amorphous regions. These findings were followed up by Wu et al [23] employing all-atom molecular
dynamics simulations which demonstrated that the IPA and CPX crystalline phases in this system are respectively entropy- and enthalpy-driven. There, however, the key mechanism favoring IPA formation was suggested to be a nucleation process starting with as few as 2–3 dopant radical anions as critical nucleus among the simulated 1728 P3HT monomer units while, in contrast, no critical nucleus was found for the crystalline CPX phase up to the maximum dopant loading that was investigated (144 CPX-forming dopants).

In an own previous study [24] we doped rr-P3HT with $\chi = 2\%$ F4TCNQ in comparison with FTCNQ and TCNQ—two derivatives with lower degree of fluorination and, hence, lower EA. Besides the full ionization of the F4TCNQ content, we observed that 88% of the FTCNQ and none of the TCNQ dopant molecules underwent IPA formation (the remainder forming CPXs). The stark contrast in ionization percentage between the latter two dopants, while their EA values differ disproportionately little, led us to assume a self-amplifying effect: an initially small percentage of ionized dopants drives a structural disorder (e.g. polarization energy) and conformational disorder (local conjugation length-dependent $IE$) induced broadening of the host-HOMO density of states (DOS). This, in turn, provides more states at lower $IE$, hence, allowing to ionize a greater content portion of weak-EA dopants such as FTCNQ.

Here, we now aim to determine the extent to which the nucleation process put forward by Wu et al [23] can be consistent with a process of initial ionization that triggers further IPA formation. For $\chi > 8\%$, that is for dopant loadings higher than those investigated by Wu et al [23], we study whether crystalline CPX-phase nucleation-sites may occur. This possibility has been suggested by the authors and appears likely because CPX-formation in rr-P3HT-F4TCNQ is typically found for high $\chi$ values [14–16]. To this end, we build upon our previous study [24] by adding F2TCNQ as an intermediate $EA$-case between F4TCNQ and FTCNQ, extending the $\chi$ range to values of 1%, 2%, 5%, 9%, 17%, and performing all relevant analysis on that multitude of systems at a time, which we regard as inevitable in order to establish a consistent picture of the parameters governing the charge transfer processes at work. We first employ optical absorption spectroscopy in the ultraviolet to near-infrared range (UV–vis/NIR; section 3.1) supported by Fourier-transform infrared spectroscopy (FTIR; section 3.2) to quantify IPA and CPX occurrence. Then, we use grazing-incidence x-ray diffraction (GIXRD; section 3.3) to assess structural aspects and, subsequently, the influence of IPA and CPX formation on thin film conductivity (section 3.4). Finally, we use our FTIR data to determine the percentage of ionized dopants, perform cyclic voltammetry (CV) to estimate the $IE$ and $EA$ of P3HT and the dopant series, respectively (from the redox potentials [25], see section 3.5), and finally pursue semi-classical modeling of the DOS (section 3.6). The latter is motivated by recent publications using energy resolved–electrochemical impedance spectroscopy (ER-EIS) [26, 27] and an improved analysis of time-of-flight photocurrent transients [28], which found a very narrow distribution of the P3HT HOMO-DOS of only 0.06–0.07 eV (Gaussian standard deviation $\sigma$)—a value at least four times smaller than that inferred from ultraviolet photoelectron spectroscopy (UPS) [26, 29]. This finding was explained by the UPS deduced DOS being convoluted with the electron escape function while the ER-EIS DOS is the result of direct electron transfer with electrolyte molecules [26]. Assuming $IE$ and $EA$ as the onsets of the Gaussian HOMO- and LUMO-DOS, respectively, and calculating $\sigma$ such that theoretical IPA occurrence agrees with our experimental data (see section 2 for details), we interpret larger $\sigma$ to result from greater disorder in the sample. With our calculations showing that the percentage of IPA-forming dopants concomitantly increases with $\sigma$, we can then find the initial $\sigma$ required to start the aforementioned nucleation effect. Our comprehensive data from multiple experimental techniques allows us, further, to assess the validity of using shifts of the F4TCNQ $C\equiv N$ stretching-modes in FTIR (see section 3.2) for deriving the degree of charge transfer, which is a common practice in the field but subject of debate [17, 30–33]. Thereby, we heed the initial advice from the seminal 1986 paper by Meneghetti and Pecile [34] that the ring $C\equiv C$ stretching mode would better serve that purpose—albeit often being masked by host-related peaks—as the $C\equiv N$ modes are particularly sensitive to the molecular environment. We show that reliable conclusions about the degree of charge transfer can only be drawn if these data are interpreted very cautiously.

2. Methods

2.1. Sample preparation

All samples were prepared and, if not specified otherwise, measured under inert $N_2$ atmosphere in a glovebox ($H_2O < 2$ ppm, $O_2 < 6$ ppm). Anhydrous chloroform (Sigma-Aldrich, anlyenes as stabilizer, purity $\geq 99\%$) was used as the common solvent. Tetrafluorotetracyanoquinodimethane (F4TCNQ), 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane (F2TCNQ), 2-fluoro-7,7,8,8-tetracyanoquinodimethane (FTCNQ), and 7,7,8,8-tetracyanoquinodimethane (TCNQ) were used as purchased from Tokyo Chemical Industry Co., Ltd (TCI) (all: purity $\geq 98.0\%$) and dissolved at a concentration of 1.2 mM through stirring on a heater at 60 °C for 1 h and left to cool at room temperature for at least 1 h before further use. Poly(3-hexylthiophene-2,5-diy) (P3HT; $M_W > 45$ kDa; 93% regio-regularity) was used as purchased from
Luminescence Technology Inc. (Lumtec) and dissolved at 60 mM immediately prior to use. Doped blends were made immediately before film deposition from pure-compound solutions, aiming at molar ratios of 100, 50, 20, 10, and 5 P3HT repeat units per dopant molecule, achieving dopant molar ratios $\chi$ of $(0.99 \pm 0.06)$%, $(2.0 \pm 0.2)$%, $(4.8 \pm 0.3)$%, $(9.1 \pm 0.6)$%, and $(17 \pm 1)$%, being referred to as 1%, 2%, 5%, 9%, and 17%, respectively. For UV–vis/NIR, 50 $\mu$L solution were drop-cast onto 1 cm × 1 cm quartz slides. For FTIR and GIXRD, 50 $\mu$L solution were drop-cast onto 1 cm × 1 cm double-side polished undoped Si wafer pieces. For CV on P3HT, 150 $\mu$L solution were spin-coated (static dispense, 30 s at 1000 rpm) onto 1 cm × 2 cm ITO coated glass. For conductivity measurements, 150 $\mu$L solution were spin-coated (static dispense, 30 s at 1000 rpm) onto 1.5 cm × 1 cm pre-patterned ITO electrodes on glass substrates. The latter were manufactured by Ossila and have a 3 cm electrode width and 5 electrode pairs with different channel lengths of $(40.4 \pm 0.6)$, $(64.7 \pm 0.6)$, $(90.7 \pm 0.6)$, $(140.5 \pm 0.6)$, and $(189.8 \pm 0.6) \mu$m (measured as explained further below). Drop-casting was chosen to improve the signal-to-noise ratio where required, otherwise, spin-coating was performed to assure homogeneous coverage. Prior to use, substrates were cleaned in chloroform, acetone, deionized water, and isopropyl alcohol (in that order) each 10 min in an ultrasonic bath and left to dry for a few seconds on a precision wipe.

2.2. Optical and vibrational absorption spectroscopy
UV–vis/NIR absorbance spectra were recorded on an Agilent (ex. Varian) Cary 5000 while keeping the samples under inert N$_2$ atmosphere in custom-built sealed boxes with quartz windows. Likewise, FTIR absorbance spectra were recorded on a Thermo Scientific Nicolet 6700 using a liquid-nitrogen cooled mercury cadmium telluride detector with the samples under inert N$_2$ atmosphere in sealed boxes with KBr windows. To assess the impact of ambient conditions in situations where the inert atmosphere could not be maintained, that is, atomic force microscopy (AFM) and GIXRD, FTIR was done once in the sealed spectroscopy box and then again after storing the samples in simple plastic boxes which were exposed to ambient conditions for one week (Parafilm-sealed under inert N$_2$ atmosphere), and fully exposing the samples to air 1 h prior to measurement. The observed changes do not significantly influence our results (see figure 3).

2.3. Grazing-incidence x-ray diffraction (GIXRD)
Grazing-incidence x-ray diffraction (GIXRD) data was collected at Canadian Light Source Saskatoon, SK, Canada on beamline BXDS-IVU employing a Rayonix MX300 detector, 0.92 Å primary beam wavelength, an incidence angle of 0.15°, and beam dimensions of 100 $\mu$m vertical, 2 mm horizontal.

Preliminary data were collected at Elettra Sincrotrone Trieste, Italy on beamline XRD1 employing a stationary Dectris Pilatus 2 M detector, 1.4 Å primary beam wavelength, an incidence angle of 0.2°, and 400 $\mu$m$^2$ beam diameter. In that setup, the samples have been rotated by 360° during acquisition to achieve radially homogeneous powder patterns; data analysis however did not reveal relevant texture.

With $q_{xy}$ and $q_z$ being the out-of-plane and in-plane components of the scattering vector $q$, intensities in figure 4(a) and b have been obtained through cake slice-integration along constant $q = |q| = (q_{xy}^2 + q_z^2)^{1/2}$ within $3–13^\circ$ of the $q_{xy}$ and $q_z$ axis, respectively, of the reciprocal space maps depicted in supplementary material figure S6 (only Canadian Light Source data). The error margin on the calculated lattice spacing $d = 2 \pi / q$ was estimated from half of the largest full width at half maximum (FWHM) that we observed among the associated $q$ peaks, i.e. $\pm 1.9 \AA$ for $d_{100}$ and $\pm 0.13 \AA$ for $d_{020}$.

2.4. Conductivity
$I$–$V$ measurements were done employing a Keithley 2400 source measure unit connected to an Ossila OFET test board to collect conductance data. For conductivity calculation, film thicknesses were determined by AFM on a Bruker Dimension Icon with a silicon nitride tip in its proprietary PeakForce QNM mode under ambient conditions. The channel length between electrodes and the electrode width were acquired using the optical microscope that is part of the same AFM. Trends in conductivity were reproduced three times, however, only the last series was fully analyzed in the present study as it was prepared with much improved experimental accuracy in $\chi$.

2.5. Cyclic voltammetry (CV)
Cyclic voltammetry (CV) measurements were recorded employing a CH Instruments CHI604d potentiostat, Ag/AgCl$^+$ reference electrode, Pt-wire counter-electrode, glassy carbon working electrode (where applicable), and a scan rate of 0.05 V s$^{-1}$. The glassy carbon working electrode was consecutively polished using 1.0, 0.3, 0.05 $\mu$m alumina powder before each measurement. Likewise, the counter electrode was polished using 0.05 $\mu$m alumina powder, only. Before running CV, a blank voltammogram without analyte has been recorded to confirm the absence of contamination. Solution CV experiments on the dopants were done in
0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) in acetonitrile (ACN). Reduction potentials were recorded as half-wave potentials between corresponding anodic and cathodic peak potentials, representing the electron affinity \( EA \) of the dopants. Further, CV was done with a spin-cast P3HT film on ITO as the working electrode using an electrolyte solution of 0.1 M TBAHFP in ACN and a scan rate of 0.02 V s \(^{-1} \). Because of the great overlap between peaks, the half-wave potential could not be determined for the P3HT film and the oxidation onset in the anodic sweep was taken to represent the ionization energy \( IE \) of P3HT. All redox potentials were measured against Fe/Fe\(^{2+} \) internal standard which, for broader comparability with literature values, was estimated as the commonly used \(-5.1\) V versus vacuum energy [25]. This number was chosen for best agreement of our value for the \( IE \) of P3HT with its HOMO-DOS onset as determined by Bässler \textit{et al} through ER-EIS (the publication provided the Gaussian distribution center \( E_0 = -5.21 \) eV and standard deviation \( \sigma = 0.06 \) eV while applying the onset definition of \( E_0 + 2\sigma = -5.09 \) eV) [26]. Note that \( EA \) and \( IE \) values in our work are given as positive numbers for the sake of clarity by associating higher \( EA \) with higher dopant strength.

### 2.6. Density of states (DOS) calculations

For the modeling of the occupation of the DOS in mixed host-dopant systems, we closely followed the method introduced in [36] and also detailed in [9, 11, 24, 37]. The molecular volume densities were taken from single-crystal structures: 4.0, 3.9, and \( 3.7 \times 10^{21} \) cm\(^{-3} \) for TCNQ [38], FTCNQ [39], F2TCNQ [40], and F4TCNQ [41], respectively, as well as \( 4.1 \times 10^{21} \) cm\(^{-3} \) for P3HT [42]. The energy distribution of the HOMO and LUMO levels of each compound were assumed to follow a Gaussian distribution [26, 27, 36, 43] described by the position of its center and of \( \sigma \), the standard deviation, equal to half the FWHM. Our experimental \( IE \) and \( EA \) values, as determined by CV, served as the distribution onsets of the host HOMO and the dopant LUMO, respectively, in the pristine materials, i.e. \( IE \) (\( EA \) lie higher (lower) than the center by twice the standard deviation \( \sigma \).

For pristine P3HT, \( \sigma \) values between 0.06 and 0.07 eV have been reported [26–28], notably, with the most recent study placing \( \sigma \) to the lowest value of \( \sigma_{\text{pristine}} = 0.06 \) eV [26]. No such study exists for the other materials in our study, however, the same work by Bässler \textit{et al} which yields \( \sigma_{\text{pristine}} \) for P3HT, provides \( \sigma \) values for other OSCs as well. They report the smallest value for the polyphenylene MeLPPP with 0.05 eV and the largest one for the fullerene derivative PC\(_{60}\)BM with 0.10 eV [26]. While MeLPPP is a polymer, it yields the lowest value reported by the authors; we therefore assume 0.05 eV as well for the FxTCNQ series since it can be expected that small molecules incur only limited geometrical disorder due to their rigid structure as compared to a polymer such as P3HT, which can undergo a plethora of conformational changes [44] and where geometrical disorder is a leading cause of DOS broadening; note that a greater diversity of conformations also affects the supramolecular structure, which presumably leads to a greater diversity of local polarization energies as well, broadening the DOS. This is also the very reason for keeping \( \sigma \) fixed for the dopants in our calculations and for exclusively investigating the broadening of the host HOMO-DOS. We stress that this approach is different to related works where charge separation was studied between both small-molecule dopants and hosts [45, 46].

While we eventually find the occupancy of the dopant HOMO-DOS and host LUMO-DOS to be negligibly small (see supplementary material figure S8), these levels were still taken into account in our modeling, again, assuming \( \sigma = 0.05 \) eV except for P3HT. We used \( IE = 9.50 \) and 8.30 eV for TCNQ [47] and F4TCNQ [48], respectively. The values for FTCNQ and F2TCNQ were estimated by subtracting from our CV-derived \( EA \) of FTNCNQ and F2TCNQ the average energy gap between our recorded \( EA \) and the reported \( IE \) of TCNQ and F4TCNQ. For the P3HT LUMO-DOS we followed the findings of [26] which already provided \( \sigma \) for the HOMO-DOS, i.e. \( EA = 2.50 \) eV with \( \sigma = 0.17 \) eV.

Having the Gaussian DOS defined, it was then imposed that the system be neutral. The occupancy of each energy level as well as the Fermi level were found self-consistently. States were filled up to the Fermi level as initialized at the midpoint between the host and dopant frontier energy levels; then the calculated charge density was used to solve the Poisson equation. The latter was done using a finite difference method (variable grid; second order, central-difference scheme; mixed Dirichlet and von-Neumann boundary conditions). The calculated potential was used to shift the Fermi level; a new charge density was generated from the updated Fermi level and then used for a new solution of the Poisson equation. These iterations were repeated until the change between iterations was less than one elementary charge per layer and meter squared. To explore the role of the host DOS broadening as a function of the dopant and its concentration \( \chi \), these calculations were repeated for all systems using \( \sigma \) values for the host ranging from 0.05 to 0.50 eV while keeping the center of the distribution fixed. For the dopant, the width of the DOS was held constant at a value of 0.05 eV, thus, essentially assuming all the broadening to occur in the host DOS. For all systems, calculations were done for \( \chi \) from 0.001% to 50%. 

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2.7. Molecular dipole and quadrupole moments DFT calculation

Molecular structures for the TCNQs in their neutral form and in their radical anionic form were optimized using the ωB97X-D functional [49] with 6–31+g(d,p) as the basis set. The ground state nature of the optimized molecules was verified via the absence of negative vibrational frequencies. These calculations were carried out in the Gaussian computational package (version 09 revision E.01) [50]. The wave functions were exported to calculate the molecular dipole and quadrupole moments analytically using the software Multiwfn [51].

2.8. Free open-source software (FOSS)

For experimental data analysis and general figure creation, the following free/libre open source software released under the GNU General Public License (GPL) and other free-software licenses was employed.

GIDvis (GPL v3.0; https://www.if.tugraz.at/amd/GIDVis/) was used for general GIXRD data analysis [52].

GIXRD cake slice-integrated intensity and FTIR fitting was done in Fityk (GPL v2.0; https://fityk.nieto.pl) [53]. Further data analysis and plotting was done in SciDAVis (GPL v2.0; http://scidavis.sourceforge.net/index.html) and Matplotlib for Python (under various BSD-compatible licenses; https://matplotlib.org) [54]. Figures were fine-tuned for publication using Inkscape (GPL v2.0; https://inkscape.org) and the Gnu Image Manipulation Program (GIMP; GPL v3.0; https://gimp.org).

3. Results

3.1. Optical absorption spectroscopy

A first idea of the host-dopant interactions at work can be inferred from optical absorption features in figure 2 which shows pristine and doped P3HT-FxTCNQ film absorbance spectra from UV–vis/NIR merged with the respective FTIR data. The fundamental absorption of pure P3HT has its onset at 1.95 eV which defines the optical gap. In the sub-gap region, distinct IPA features emerge in the spectrum for 1% F4TCNQ-doping, namely, two broad absorption bands around 0.5 and 1.6 eV stemming from the P3HT positive polaron (yellow shaded areas in figure 2) [11, 55–57], and two prominent features from the F4TCNQ radical anion at 1.45 and 1.63 eV [9, 11, 14, 56, 58, 59]. Another peak at 3.0 eV also is due to the F4TCNQ radical anion [11, 58], but cannot be regarded as a strong IPA indicator for its overlap with the fundamental transition of neutral F4TCNQ. These radical anion related features gain in magnitude with increasing F4TCNQ concentration, however, decrease again for 17%. Analogue IPA indicators similar to those in P3HT-F4TCNQ are also seen for F2TCNQ and FTCNQ, however, reduced to a small radical anion peak at 1.44 eV for χ = 9% and absent for 17%. In the range of 1%–5% where they appear prominently, these features show a trend of being weaker for dopants of lower EA [11]. Further, they are completely absent for doping with TCNQ, where the radical anion related absorption would be expected at 1.45 eV [59].

On the one hand, our 17% F4TCNQ spectrum is similar to that of P3HT sequentially doped with F4TCNQ in chloroform as investigated by Stanfield et al [22] who confirmed the presence of IPA formation alongside CPX in their sample. The pure-CPX P3HT-F4TCNQ system isolated by Jacobs et al [14] shows a red-shifted main P3HT absorption, which we also observe along a decrease in IPA features, as well as two broad CPX-assigned peaks at 0.66 & 1.15 eV, which are likely masked by the prominent polaron peaks in our data. For both F2TCNQ and FTCNQ, however, these CPX indicators are dominant at χ = 9% and make up the only sub-gap transitions for the 17% films. Likewise, they are the only sub-gap bands observed for all TCNQ concentrations, clearly rising in intensity with the dopant loading. These CPX peaks are observed at very similar energies for the different dopants (centered at 0.82 and 1.31 eV for F2TCNQ, 0.86 and 1.31 eV for FTCNQ, 0.87 and 1.28 eV for TCNQ; see vertical dashed lines in figure 2). The blue-shift of the lower energy peak with decreasing dopant EA is in line with previous work on quarterthiophene (4 T) for the same dopant series (4 T-FxTCNQ: 0.8, 1.0, 1.1, 1.2 eV for x = 4, 2, 1, 0, respectively) and stems from the larger energy offset between the hybridizing orbitals, i.e. the HOMO of 4 T and the LUMO of the weaker dopants [11]. Then, the overall higher energies with 4 T versus P3HT are explained as these transitions occur at lower energy for oligothiophenes of larger conjugation length (F4TCNQ-doped hexylated oligothiophenes: 0.9, 0.7, 0.6 eV for 4, 6, 8, 10 repeat units, respectively [60]) as their IE scales inversely with the number of the thiophene repeat units [61].

On the other hand, our 17% F4TCNQ spectrum also compares to that reported by Tsokkou et al [62] by drop-casting from common solution (but using chlorobenzene as solvent). They used an advanced deconvolution technique in combination with spectra of electrochemically doped P3HT to ascribe a broad peak at 0.92 eV to the formation of bipolarons. We do not observe any such indication of bipolaron formation for F2TCNQ, FTCNQ, or TCNQ, which is not surprising as even F4TCNQ has been long viewed as incapable of producing (measurable) amounts of bipolarons, restricting this phenomenon rather to stronger dopants or electrochemical doping [62–65]. For our 17% F4TCNQ spectra we find that the
Figure 2. UV–vis/NIR data merged with FTIR thin-film absorbance spectra of P3HT doped with FxTCNQ ($x = 0, 1, 2, 4$) at increasing dopant molar ratios $\chi$ as well as those of the corresponding pure compounds. The gray box shows the four times magnified NIR region of the 1% TCNQ spectrum, highlighting the CPX peaks; sharp peaks below 0.5 eV are due to vibrational transitions in the mid infrared. All P3HT-containing spectra are normalized to the P3HT main absorption maximum centered around 2.4 eV; spectra of the pure dopants are scaled for the sake of clarity.

Figure 3 shows the FTIR spectra in the region of the C≡N modes for the pristine materials alongside F4TCNQ-, F2TCNQ-, FTCNQ-, and TCNQ-doped P3HT (ring C=C stretching modes in supplementary material figure S3); it further includes spectra of the same samples after one week of aging (see section 2 for...
values to be similarly shifted from ν_2202 = 1 for ν = 17% which are in good agreement with literature. The pure-P3HT spectra (0%) are magnified by the same factor as the spectrum of the 1% doped film; the raw data are given in supplementary material figure S2.

The pure-P3HT spectra (0%) are magnified by the same factor as the spectrum of the 1% doped film; the raw data are given in supplementary material figure S2.

In good agreement with the ν_0 values, we find the neutral dopant peaks (dotted vertical lines in figure 3) at 2226, 2231, 2223, and 2225 cm⁻¹ in the 100% spectra of F₄TCNQ, F₂TCNQ, FTCNQ, and TCNQ, respectively. Notably, these peaks are also present in 17% F₂TCNQ and FTCNQ which indicates overdoping. Such a weak appearance, again, is quite astonishing for F₄TCNQ since both optical absorption and the ring modes (1530 and 1500 cm⁻¹) are not observed.

Regarding the indicators for IPA (marked by vertical solid lines in figure 3), no ν₁ peak is seen with TCNQ-doping. In contrast, 1% F₄TCNQ-, F₂TCNQ-, and FTCNQ-doped films show ν₁ at 2192 (ν₁A), 2184, and 2181 cm⁻¹, respectively, which shift to 2185 (ν₁B), 2178, and 2179 cm⁻¹ for ν = 9%; ν₁A and ν₁B are labeled for a later discussion (vide infra). The ν₁ position for 17% is not considered in the analysis for F₂TCNQ and FTCNQ, respectively [11]; as the F₄TCNQ and TCNQ ν₀-positions coincide and show a comparable shift upon ionization, we assume the ν₁ values to be similarly shifted from ν₀ for both FTCNQ and F₂TCNQ.

In good agreement with the ν₀ values, we find the neutral dopant peaks (dotted vertical lines in figure 3) at 2226, 2231, 2223, and 2225 cm⁻¹ in the 100% spectra of F₄TCNQ, F₂TCNQ, FTCNQ, and TCNQ, respectively. Notably, these peaks are also present in 17% F₂TCNQ and FTCNQ which indicates overdoping. i.e. the limit of how many dopants can undergo charge-transfer interactions with P3HT is exceeded; the same is potentially true for 17% TCNQ as well, however, the peak cannot be resolved unambiguously as it is masked by the neighboring CPX peak (see supplementary material figure S4). While the ring C=C modes are not as easily interpreted as the C≡N modes due to the presence of P3HT features in the spectral vicinity, our data is exceptionally clear on the 17% F₄TCNQ sample. Most remarkably, although taken from the very same FTIR spectrum, the ring C≡C stretching in 17% F₄TCNQ provides a clear peak for the neutral dopant (1597 cm⁻¹ in supplementary material figure S3; see [34, 71, 74]) while the charge neutral C≡N modes are not observed.

Regarding the indicators for IPA (marked by vertical solid lines in figure 3), no ν₁ peak is seen with TCNQ-doping. In contrast, 1% F₄TCNQ-, F₂TCNQ-, and FTCNQ-doped films show ν₁ at 2192 (ν₁A), 2184, and 2181 cm⁻¹, respectively, which shift to 2185 (ν₁B), 2178, and 2179 cm⁻¹ for ν = 9%; ν₁A and ν₁B are labeled for a later discussion (vide infra). The ν₁ position for 17% is not considered in the analysis for ν₁B because it only appears as a shoulder to other peaks. Such a weak appearance, again, is quite astonishing for F₄TCNQ since both optical absorption and the ring modes (1530 and 1500 cm⁻¹ in supplementary material figure S3) speak for a stronger presence of the radical anion at that dopant loading.

Additional peaks ν_{CPX} (dashed vertical lines) can be observed in-between our so-far assigned ν₀ and ν₁ values. F₂TCNQ-, FTCNQ-, and TCNQ-doping yield ν_{CPX} at 2208, 2209, and 2216 cm⁻¹ for ν = 17% which shift with increasing dopant loading towards 2214, 2215, and 2219 cm⁻¹ for 17%, respectively. For F₄TCNQ we find ν_{CPX} = 2202 cm⁻¹ for 9% and 2207 cm⁻¹ for 17% which are in good agreement with literature values on CPX formation in P3HT-F₄TCNQ [14–18, 22, 33], most importantly, with the work by Jacobs et al [14] where optical absorption data showed virtually no IPA features. The correlation of ν_{CPX} with the
CPX features of our optical absorption spectra is trivial for TCNQ. It is also safe to assume all our other $\nu_{\text{CPX}}$ values to stem from CPX formation since their presence rises with $\chi$ like the CPX optical absorption features, and because their position in-between the $\nu_0$ and $\nu_1$ values suggests fractional charge transfer [69, 70]. Nevertheless, we would like to highlight the nontriviality of the latter assessment as, e.g. $\nu_1$ for F4TCNQ had also been found at higher wavenumbers, mostly depending on its cationic partner species [30, 34].

Overall, our combined optical and vibrational data are generally in line with previous reports indicating that higher F4TCNQ content in P3HT films favors the formation of CPX over IPA beyond a threshold in dopant concentration [14, 15] and shows the same to be true for F2TCNQ and FTCNQ.

3.3. Grazing-incidence x-ray diffraction (GIXRD)

To gain insight into the differences in crystal structure between IPA, CPX, and mixed IPA/CPX systems we collected GIXRD data on both doped and pure P3HT films. Considering the semi-crystalline nature of P3HT, it must be kept in mind that while the spectroscopic methods above probe the whole sample, both amorphous and crystalline regions, GIXRD provides information exclusively on the latter. We find the pure P3HT films to be in a preferential edge-on orientation where the out-of-plane features represent the (000) lattice planes (reciprocal space maps in supplementary material figures S6 and S7), which is a common finding for such films [76]. This feature corresponds to the lamellar stacking direction and translates into a lattice spacing of $d_{100} = 16.5$ Å. The present in-plane feature is assigned to the (020) $\pi - \pi$ interchain stacking with $d_{020} = 3.83$ Å (with two P3HT chains in the unit cell [42], ‘$d_{020}$’ effectively describes half the unit cell in [010] direction, here). This is also in line with similarly processed P3HT films in literature [11, 14, 15, 18, 22, 31, 77, 78] and representative of the so-called type-I structure with the stacked polymer backbones tilted by approximately 26° toward the crystallographic b-axis, notably, without side-chain intercalation [42, 79].

For enhanced comparability between the doping cases, a select range of cake slice-integrated intensities in the vicinity of the $q_x$ (out-of-plane) and $q_y$ (in-plane) axis in figure S6 are depicted in figures 4(a) and b, respectively. Upon doping with F4TCNQ we observe $d_{100}$ to increase gradually with $\chi$ to a value of 18.5 Å for 5%. From there it again decreases to 17.0 Å at 17% where the corresponding peak is joined by a very strong shoulder yielding 14.2 Å. In turn, $d_{020}$ gradually decreases with $\chi$ to 3.43 Å for 17%. The smaller $d$ values for $\chi = 17\%$, i.e. $d_{100} = 14.2$ Å paired with $d_{020} = 3.43$ Å, can be assigned to a crystalline CPX phase and are well in line with the 17% F4TCNQ-doped P3HT sample reported by Jacobs et al. [14] which exclusively showed CPX, as well as the prominent presence of $\nu_{\text{CPX}}$ in our FTIR data at this dopant loading. The according (020) peak for 17% F4TCNQ and that of pure P3HT are remarkably sharper, with a FWHM smaller by about 30% than that of the 1%–9% cases. It is therefore likely that the decrease in $d_{020}$ from 9% to 17% is not a continuous trend but the leap to another polymorph of higher crystalline quality. Indeed, a smaller $d_{020}$ is also expected resulting from a reduced backbone tilt in a non-mixed $\pi - \pi$ stack of P3HT backbones as a consequence of dopant radical anions residing in the hexyl chain region; the latter being commonly indicated by the increased $d_{100}$ [11, 18–20, 31, 33, 78, 80, 81] which we also observe for $\chi = 1\%$–9%, again in line with our spectroscopic data showing dominant IPA representation.

For 5%–17% F4TCNQ an additional peak appears corresponding to a lattice spacing of 3.88 Å. This peak is small and consistent for all three $\chi$ values, but it showed increased relative intensity for higher dopant content in recent studies [15, 77]. As discussed in detail in section 4.1, we assign this peak to $d_{020}$ of P3HT regions that did not include any dopant molecules during their growth.

As with F4TCNQ, also in our F2TCNQ- and FTCNQ-doped samples we see a gradual increase in $d_{100}$ with $\chi$, now, to 17.8 and 17.5 Å for 5% where its peak is joined by a shoulder indicating 14.1 and 15.3 Å, respectively. This shoulder then becomes the only observed peak for 9 and 17% FTCNQ as well as 9% F2TCNQ; for 17% F2TCNQ it is again accompanied by a small shoulder corresponding to 17.8 Å. The $d_{020}$ values are found to decrease with increasing $\chi$ from 3.83 Å (pristine P3HT) to 3.65 Å (5% F2TCNQ) and 3.68 Å (5% FTCNQ), where a prominent shoulder appears for 3.46 and 3.47 Å, respectively. For 9% and 17% F2TCNQ this shoulder turns into the only peak, but for FTCNQ it is still accompanied by a feature corresponding to a spacing of 3.59 Å. In general, we can assign the (100) features yielding 17.5 to 17.8 Å to IPA formation as they mirror rather IPA than CPX occurrence according to the FTIR results (C=N stretching modes), especially, the disappearance and return of the IPA peak at 9% and 17% F2TCNQ, respectively; complementarily, the features yielding 14.1 to 15.3 Å can be associated with CPX formation. The gradual increase in $d_{020}$ with $\chi$ toward a value of $\approx 3.7$ Å versus the sudden appearance of a shoulder at $\approx 3.5$ Å reminds of the association with crystalline IPA versus CPX phases, respectively, suggested for our F4TCNQ-doped samples (vide supra). With these assignments and considering their similarity in $d$ values, it is sensible to assume that the assignments of the IPA and CPX crystalline phases in F4TCNQ-doped P3HT are equally applicable to the F2TCNQ and FTCNQ cases.

In our CPX-only system of P3HT-TCNQ, $d_{100}$ and $d_{020}$ gradually decrease up to 9% to values of 15.1 and 3.60 Å, respectively, but then abruptly recover the values of pure P3HT for 17%, where the (020) peak is
found largely attenuated for $\geq 9\%$. The trend up to 9% TCNQ matches that observed with the fluorinated dopants interpreted as the emergence of a crystalline CPX phase, but with $d$ values dependent on the dopant loading and peak widths consistently larger than those of the pristine film, thus indicating less order. We note that, in general, all our dopants show Bragg reflections of pure-dopant crystals at 17% (best seen in the 2D reciprocal space maps, supplementary material figures S6 and S7) which is clear evidence for pure dopant precipitation.

3.4. Conductivity
In order to understand how the occurrence of IPA and CPX formation impacts the charge transport in P3HT, we recorded the thin-film conductivity (figure 5(a), supplementary material table S1). For increasing $\chi$, a maximal rise in conductivity by over five orders of magnitude from pure P3HT to $\chi = 9\%$ F4TCNQ is observed. For the weaker dopants we observe maximal increases of four and two orders of magnitude for 5% F2TCNQ and FTCNQ, respectively. Notably, conductivity saturates for higher F4TCNQ content. Recalling the discussion of our UV–vis/IR data (figure 2, supplementary figure S1) this can both be due to unfavorably high bipolaron-to-polaron ratios [63, 82] and the increased CPX occurrence which reduces the doping efficiency. For the other dopants, the trends are not so clear at higher $\chi$ since their values decrease when

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**Figure 4.** GIXRD intensities from integrated cake slices in the vicinity of the (a) $q_z$ and (b) $q_{xy}$ axis from reciprocal-space maps in supplementary material figure S6 on films of pure P3HT as well as doped with FxTCNQ ($x = 0, 1, 2, 4$) at increasing dopant molar ratios $\chi$: focused on the (a) (100) and (b) (020) peaks; dashed vertical lines serve as a guide to the eye, indicating the pure-P3HT peak; pure FTCNQ and TCNQ features are indicated according to [39, 75], respectively.
increasing the dopant loading towards 9% F2TCNQ and 17% FTCNQ. For TCNQ, the conductivity only decreases with increased dopant concentration until 9% where it reaches an even one-order-of-magnitude lower value than that of pure P3HT.

At 17%, F2TCNQ and TCNQ show significant conductivity increases over their 9% data point. However, since the presence of neutral dopants is indicated by the 17% FTIR spectra and the signature of pure dopant precipitation in the respective GIXRD data, the corresponding conductivity values should be taken with caution because pure-dopant domains can also contribute to the conduction in that low range of conductivity [38]; those films are, in fact, at the threshold between FxTCNQ-doped P3HT and 'P3HT-doped FxTCNQ' and using the term 'doping' does not appear entirely justified anymore. Note that, while highly reproducible up to 9% dopant loading, at 17% we found conductivity values to become less reliable for nominally identical preparation parameters, e.g. we once observed a further, though slight, decrease for 17% TCNQ over its 9% data point, which points to a subtle dependency of the film morphology on parameters beyond the control of our experimental setup in highly doped systems.

With this in mind, in terms of both dopant strength and concentration, stronger IPA signals in our spectroscopic data clearly correlate with an increase in conductivity while more prevalent CPX formation is detrimental to it, yielding a saturation in conductivity with F4TCNQ and even (relative) decreases with the weaker dopants.

3.5. Cyclic voltammetry (CV)
To further investigate the IPA and CPX occurrence in P3HT for the TCNQ derivatives, we investigated their EA values in relation to the host IE. To this end, we employed CV-derived redox potentials $V_{\text{HOMO}}^{\text{redox}}$ and $V_{\text{LUMO}}^{\text{redox}}$ of host and dopant as a proxy for IE and EA, respectively (see section 2 for conversion between $V_{\text{redox}}$ versus ferrocene/ferrocenium (Fc/Fc$^+$) and EA/IE values versus vacuum energy). A recent publication by Wegner et al. [83] found the $V_{\text{redox}}$ values derived from CV to be more reliable for predicting IPA formation than IE and EA obtained from UPS and inverse photoelectron spectroscopy (IPES), respectively. They saw the greatest agreement in solution and argued that, while UPS and IPES are subject to the collective electrostatic properties of the sample, the charge transfer between analyte and electrode/electrolyte in CV occurs on the molecular level, similar to the doping process. For the solid state, the authors observed that the percentage of ionized dopants was systematically larger than in solution and, thus, deviated from the
prediction based on CV data, but it remained still superior to UPS/IPES derived values. This might seem counter-intuitive as the latter are solid-state techniques, in contrast to CV done in solution, however, their pronounced surface-sensitivity and the orientation dependence of these values [84] together with final-state effects [85] can provide a large spread in these values. In contrast, Sweetnam et al [21] argued that, if the analyte is deposited as a thin film on the working electrode, solid-state influences are effectively probed by the migration of electrolyte into the film; more recently, electrolyte-anion intercalation into the P3HT side-chain region had been shown [86], which once more highlights the value of CV. For the present study, we performed CV on the dissolved dopants thus obtaining EA values largely based on a molecular level, combined with CV performed on a P3HT thin film providing an IE value which does include solid-state effects. Clearly, also this approach is only an approximation to the actual effects experienced by each individual dopant molecule but, in our view, probably the most justified one.

We recently published the present data obtained for F4TCNQ, FTNCNQ, TCNQ, and P3HT in [24] and provide them for the reader’s convenience together with data on F2TCNQ (corresponding voltammograms in supplementary material figure S9). On that basis, F4TCNQ, F2TCNQ, FTNCNQ, and TCNQ exhibit an EA (V\text{\textregistered}_{\text{HOMO}} versus Fc/Fc\textsuperscript{+}) of 5.31 eV (0.21 V), 5.01 eV (−0.09 V), 4.97 eV (−0.13 V), and 4.91 eV (−0.19 V), respectively; our pristine P3HT film on ITO shows an IE (V\text{\textregistered}_{\text{LUMO}}) of 5.21 eV (0.11 V). Within the error margin expected for energy levels derived from CV (±0.1V) [25], our data is in very good agreement with literature values of both the dopants [83] and P3HT [21], where Fc/Fc\textsuperscript{+} was employed as a reference standard as well. The corresponding IPES derived EA values of TCNQ, FTNCNQ, F2TCNQ, and F4TCNQ in literature are 4.23, 4.55, 4.59, and 5.08 eV, respectively [87], while UPS yields 4.8 eV for the IE of P3HT [88]. We note that all CV-derived values hinge on the IE of Fe and because there is no conclusive consensus on the potential of the Fc/Fc\textsuperscript{+} redox pair versus vacuum [25]; using 4.8 instead of 5.1 eV for the IE of Fe would bring above IPES values into good agreement with our CV-derived ones. For P3HT good agreement is also maintained by employing the linear correlation between \(\chi\) from CV and IE from UPS as formulated by D’Andrade et al [89]. Notably, while the fact that FTNCNQ and F2TCNQ are very close in EA in our data set is well reflected in the IPES data of [87], the EA of TCNQ is significantly lower in the latter, which might result from orientation effects common to UPS/IPES relevant for ordered molecular assemblies [84, 90, 91].

3.6. Density of states (DOS) calculations

Based on our CV data, only the EA of F4TCNQ would exceed the IE of P3HT and, thus, allow for IPA formation. However, there is no doubt from our spectroscopic data that integer charge transfer occurs with F2TCNQ and FTNCNQ as well. In a recent study [24], we followed the idea that this is due to a broadening of the host HOMO-DOS as a result of doping-induced disorder [92] and performed semi-classical modeling to assess how IPA formation can be triggered by disorder, leading to greater variance in polarization energy and polymer conjugation length [43]. Our calculations were based on the common assumption that both the HOMO and LUMO DOS are well-represented by Gaussian distributions [87] and maintained by employing the linear correlation between \(\chi\) from CV and IE from UPS as formulated by D’Andrade et al [89]. Notably, while the fact that FTNCNQ and F2TCNQ are very close in EA in our data set is well reflected in the IPES data of [87], the EA of TCNQ is significantly lower in the latter, which might result from orientation effects common to UPS/IPES relevant for ordered molecular assemblies [84, 90, 91].

All calculated percentages of ionized dopants \(p_{\text{calc}}\) resulting from our modeling are visualized in figure 6; colors represent \(p_{\text{calc}}\). Within the range of our experimental data, our modeling clearly highlights three trends that lead to higher \(p_{\text{calc}}\): (i) increased host HOMO-DOS \(\sigma\) (less order), (ii) lower \(\chi\) (fewer dopants) for (iii) higher dopant EA (stronger dopants).

We then investigate \(p_{\text{CN}}\), the ionized dopant percentage estimated from FTIR deduced from the area of the main C≡N stretching mode peak of the dopant anion relative to that of the CPX and/or neutral main peaks (if present). Table 1 lists the \(\sigma\) values for which \(p_{\text{calc}} \approx p_{\text{CN}} ; \sigma = 0.06\) eV is the value for pristine P3HT, as recently determined experimentally [26] (dashed line in figure 6). The highest value, \(\sigma = 0.23\) eV, is obtained for 2% FTNCNQ which is comparable to the 0.26 eV suggested in previous studies on molecular doping [45, 46]. Note that, while the high-\(p_{\text{CN}}\) samples of 1%–2% F2TCNQ and FTNCQ content yield about twice the \(\sigma\) value of the respective F4TCNQ samples, one must keep in mind that \(p_{\text{calc}}\) is calculated with the minimum \(\sigma\) required, thus, all three fluorinated dopants might well induce similar amounts of DOS broadening. Generally, we can say that \(\sigma\) must increase significantly over its pristine-P3HT value to explain the experimentally found \(p_{\text{CN}}\) for F4TCNQ-, F2TCNQ-, and FTNCQ-doped P3HT, with only few exceptions (17% F4TCNQ, 9% F2TCNQ). Thus, broadening of the P3HT HOMO-DOS up to a factor of three upon
Table 1. Dopant ionization percentage \( p_{\text{CN}} \) as estimated from the relative fitted area of the radical anion main \( \text{C}≡\text{N} \) stretching mode peak versus CPX and neutral peaks in figure 3, and P3HT HOMO-DOS Gaussian standard deviation \( \sigma \) as calculated to yield \( p_{\text{CN}} \); 0.06 eV is the experimentally obtained value for pristine P3HT [26].

| \( \chi \) (%) | \( p_{\text{CN}} \) (%) | \( \sigma \) (eV) | \( p_{\text{CN}} \) (%) | \( \sigma \) (eV) | \( p_{\text{CN}} \) (%) | \( \sigma \) (eV) | \( p_{\text{CN}} \) (%) | \( \sigma \) (eV) |
|----------------|-----------------|----------------|-----------------|----------------|-----------------|----------------|-----------------|----------------|
| 1              | 100             | 0.10           | 90              | 0.19           | 80              | 0.19           | 0               | \( \leq 0.06 \) |
| 2              | 100             | 0.11           | 80              | 0.20           | 88              | 0.23           | 0               | \( \leq 0.06 \) |
| 5              | 100             | 0.14           | 53              | 0.20           | 32              | 0.18           | 0               | \( \leq 0.06 \) |
| 9              | 88              | 0.11           | <0.06           |                | 14              | 0.15           | 0               | \( \leq 0.06 \) |
| 17             | 32              | <0.06          | 2               | 0.08           | 9               | 0.15           | 0               | \( \leq 0.06 \) |

Figure 6. Ionized dopant percentage \( p_{\text{calc}} \) as calculated for increasing P3HT Gaussian HOMO-DOS width (standard deviation) \( \sigma \) for doping with \( \text{FxTCNQ} \) \( (x = 0,1,2,4) \) with increasing dopant molar ratios \( \chi \). Vertical dashed lines mark \( \sigma = 0.06 \) eV, the experimentally obtained value for pristine P3HT [26].

Doping emerges as a natural explanation for this finding in order to rationalize the observed \( p_{\text{CN}} \) values (see section 4 below).

In our previous study [24] we hypothesized that an initially small percentage of IPA content causes \( \sigma \) broadening and, subsequently, ionization of further dopants. In the same vein, we also consider the nucleation effect for IPA formation at its threshold-concentration \( \chi_{\text{IPA}} \approx 0.1\% \) (excluding non-ionized dopants from the total dopant molar ratio \( \chi \)), as postulated in the aforementioned study by Wu et al [23]. As \( \chi_{\text{IPA}} \) regards only ionized dopants versus P3HT, it best corresponds to our data when we only consider the ionized portion at the dopant molar ratio \( \chi \), which we can calculate since the respective \( p_{\text{calc}} \) values provide us with the fraction of ionized dopants:

\[
\chi_{\text{IPA}} = p_{\text{calc}} \left( \frac{p_{\text{calc}}}{100\%} + \frac{100\%}{\chi} - 1 \right)^{-1}.
\]

\( \sigma \) data points where the \( \chi_{\text{IPA}} \approx 0.1\% \) threshold is reached, are listed in table 2. Most remarkably, less broadening is needed for higher dopant loading, suggesting a higher probability for the crystalline IPA phase—a trend opposite to our experimental data which shows increased CPX formation, instead.
was shown to exclusively result in CPX formation forcing the dopant into backbone stacking by using a P3HT derivative with branched-out hexyl substitutions.

IPA/CPX indicators and, in particular, their use for quantifying the relative population of IPA versus CPX in comparison to the ring C modes despite the convolusion of these various influences, correlations with other experimental data such as optical absorption features must be taken into account.

However, our present data shows no such correlation because of its weak, consistent appearance independent from the dopant loading, which is in contrast to the concomitant reduction we observe in the effective dopant from the dopant crystallite occurrence in our GIXRD data. This suggests that the oscillator strengths are a change in polaron coherence but also be due to bipolaron formation. Therefore, it is conceivable that the partially on the shift of the low-energy polaron peak which, as discussed above, can not only be interpreted as changing the electric field causing the Stark effect. However, we note that Stanfield et al based their view on the shift of the low-energy polaron peak which, as discussed above, can not only be interpreted as a change in polaron coherence but also be due to bipolaron formation. Therefore, it is conceivable that the latter is the basis for this electric-field change and that \( \nu_{1B} \) is another hint of bipolaron formation.

We also want to highlight here the discrepancy between the C=C (figure 3) and the ring C=C modes (figure S3) in 17% F4TCNQ found in our data. The C=C modes exhibit only a small peak of the radical anion (\( \nu_1 \)) and no peak of the neutral dopant (\( \nu_0 \)), in marked contrast to the ring C=C vibrations providing clear indication of the dominance of IPA and of neutral dopants being present—the latter being supported by the pure-dopant crystallite occurrence in our GIXRD data. This suggests that the oscillator strengths are incomparable, likely, as different molecular environments impact the vibrational modes [30]; this makes the magnitude of the CPX peak (\( \nu_{CPX} \)) in the C=C modes potentially overestimate the CPX population in comparison to the ring C=C modes. This discrepancy once more reminds us that the assignment of these IPA/CPX indicators and, in particular, their use for quantifying the relative population of IPA versus CPX in a given system must be handled with great prudence.

### 4.2. The scope of our DOS calculations

The potential over-representation of the CPX population by the C=C stretching modes (\textit{vide supra}) entails that the derived percentages of ionized dopants \( p_{CN} \) and, subsequently, the P3HT HOMO-DOS widths \( \sigma \) associated with them through our modeling, must both be regarded as lower limits; e.g. we cannot exclude that TCNQ does induce \( \sigma \) broadening as this cannot be captured by our data. For 9% F2TCNQ and 17% F4TCNQ, \( p_{CN} \) would be associated with a \( \sigma \) value well below the 0.06 eV that had been determined experimentally for pristine P3HT [26]. Such an obvious underestimation of \( \sigma \) for these cases of high CPX occurrence is likely due to the fact that no explicit driving force that is intrinsic to CPX formation and

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**Table 2.** P3HT HOMO-DOS Gaussian standard deviation \( \sigma \) calculated for the threshold to IPA nucleation as recently modeled [23], here, represented by the ionized dopant molar ratio \( \chi_{IPA} \approx 0.1\% \), excluding non-ionized dopants, of the total dopant molar ratio \( \chi \); 0.06 eV is the experimentally obtained value for pristine P3HT [26].

| \( \chi \) (%) | F4TCNQ | F2TCNQ | FTCNQ | TCNQ |
|----------------|--------|--------|-------|------|
| 1              | <0.06  | 0.08   | 0.10  | 0.12 |
| 2              | <0.06  | 0.07   | 0.09  | 0.11 |
| 5              | <0.06  | 0.06   | 0.08  | 0.10 |
| 9              | <0.06  | <0.06  | 0.07  | 0.09 |
| 17             | <0.06  | <0.06  | 0.06  | 0.09 |
counters IPA formation, is modeled in our approach. Therefore, the host HOMO-DOS broadening as a driving force behind IPA formation will be underestimated. An additional CPX driving force would be required to be modeled such as the aforementioned work by Wu et al [23], where they suggest the formation of crystalline IPA and CPX phases being subject to nucleation effects and the overall change in free energy, which however goes beyond the scope of our work. Consequently, in our discussion of the drivers behind IPA and CPX formation, we essentially employ the results of our DOS modeling only in IPA-rich cases and lean more firmly on our experimental findings when significant CPX formation occurs.

On a different note, while our σ values in IPA-dominated cases align well with recent studies focusing on charge transport [45, 46], we acknowledge that our approach focusing on DOS modeling is agnostic of shifts in the effective IE/EA not directly related to the DOS per se. On the one hand, Li et al [95] had recently calculated that the EA of F4TCNQ is effectively reduced by up to 0.7 eV when placed into an electron-donor host-matrix, exemplified by pentacene and N,N′-di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (known as NPB or NPD). On the other hand, a more recent publication by Comin et al [94] showed that F4TCNQ residing in the hexyl side-chain region of poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (known as PBTTT) effectively gains >0.5 eV in its EA as compared to a mixed π − π stack of F4TCNQ with the polymer backbone. Therefore, as our GIXRD data indicates the dopant radial anion residing in the hexyl-chain region, it is plausible to assume the latter effect on the IPA occurrence between FTCNQ and TCNQ, all while demanding the highest initial DOS broadening. While

\[ \chi_{IPA} \approx 0.1\% \] of ionized dopants for each total dopant molar ratio \( \chi \), we observe less broadening for higher \( \chi \), suggesting a higher probability for the occurrence of the crystalline IPA phase, all while our experimental data shows increased CPX formation. This apparent discrepancy speaks, again, for an independent, competing CPX-formation mechanism. With this in mind, we turn our focus to the \( \chi = 2\% \) cases as they yield the strongest contrast in IPA occurrence between FTCNQ and TCNQ, all while demanding the highest initial DOS broadening. While

\[ \chi_{IPA} > 0.1\% \] is readily obtained for all F4TCNQ data points with the pristine-P3HT σ = 0.06 eV, the threshold would only be reached with σ ≥ 0.07, 0.09, and 0.11 eV for F2TCNQ, FTCNQ, and TCNQ, respectively. Again, observing virtually the same, high ionization percentage \( p_{CN} \) for F2TCNQ and FTCNQ while TCNQ only shows CPX formation, the nucleation effect does not seem to demand too different conditions in the three cases. It can therefore not be considered as the reason why IPA formation is possible with the EA of FTCNQ but not with that of TCNQ, unless crystalline IPA-phase nucleation in P3HT substantially differs between the TCNQ derivatives.

In the following, we discuss the nucleation effect for IPA formation, postulated by Wu et al [23], as a potential way to explain the differences between the doping phenomenology of FTCNQ and TCNQ. When assigning a host HOMO-DOS width σ to the nucleation threshold-concentration \( \chi_{IPA} \approx 0.1\% \) of ionized dopants for each total dopant molar ratio \( \chi \), we observe less broadening for higher \( \chi \), suggesting a higher probability for the occurrence of the crystalline IPA phase, all while our experimental data shows increased CPX formation. This apparent discrepancy speaks, again, for an independent, competing CPX-formation mechanism. With this in mind, we turn our focus to the \( \chi = 2\% \) cases as they yield the strongest contrast in IPA occurrence between FTCNQ and TCNQ, all while demanding the highest initial DOS broadening. While

\[ \chi_{IPA} > 0.1\% \] is readily obtained for all F4TCNQ data points with the pristine-P3HT σ = 0.06 eV, the threshold would only be reached with σ ≥ 0.07, 0.09, and 0.11 eV for F2TCNQ, FTCNQ, and TCNQ, respectively. Again, observing virtually the same, high ionization percentage \( p_{CN} \) for F2TCNQ and FTCNQ while TCNQ only shows CPX formation, the nucleation effect does not seem to demand too different conditions in the three cases. It can therefore not be considered as the reason why IPA formation is possible with the EA of FTCNQ but not with that of TCNQ, unless crystalline IPA-phase nucleation in P3HT substantially differs between the TCNQ derivatives.

Subsequently, we resort to the other reasoning which we had put forward in our previous study [24], considering a self-amplifying effect where only a small difference in initially ionized content with FTCNQ or F2TCNQ versus TCNQ would suffice to cross a threshold toward causing effective host HOMO-DOS broadening, thus, enabling more ionization and even further broadening. We note that this loop of broadening stops when further disorder is associated with a sufficiently high energetic cost such that CPX formation becomes more favorable than IPA formation following disorder.

4.4. Drivers of CPX formation

Clearly, CPX formation cannot be handled as a mere fall-back mechanism when IPA formation is energetically not viable but requires drivers of its own that compete with IPA-favoring factors.
To begin with, the idea of preferential CPX formation in the amorphous phase of P3HT due to its effectively higher $IE$ detrimental to IPA formation [15] is supported by the lack of GIXRD features related to the crystalline CPX phase at lower $\chi$, while our spectroscopic data clearly show CPX indicators. Note that, beyond the higher $IE$ in amorphous phases, the intermolecular binding energies upon CPX formation are substantial and represent an appreciable driving force for the preferential formation of such complexes [97].

Regarding crystalline CPX phases, we again return to the computational study by Wu et al [23] which showed that, while crystalline IPA and CPX phases yield similar changes in free energy, the IPA scenario profits from a nucleation threshold as low as 2-3 dopant radical anions among the simulated 1728 P3HT monomer units, i.e. $\chi_{IPA} \approx 0.1-0.2\%$. In turn, no CPX nucleation sites where seen even for the highest dopant loading they investigated, which was 144 CPX-forming dopants, i.e. $\chi_{CPX} \approx 8\%$. (Wu et al studied pure IPA and pure CPX systems, hence, $\chi$ in our mixed system is the convolution of $\chi_{IPA}$, $\chi_{CPX}$, and neutral dopant content.) Where the dopant $EA$ is sufficiently high for IPA formation, as it is the case for F4TCNQ, F2TCNQ, and FTCNQ, we can therefore speculate that a nucleation effect for the crystalline CPX phase does still occur at high ratios, because we observe a crystalline CPX portion for $\chi = 9$ and 17%. Alternatively, we can hypothesize that, in terms of enthalpy, a well-defined CPX polymorph only prevails over the IPA phase for a certain stoichiometry, e.g. $\chi = 14.2\%$ as reported by Jacobs et al [14]; hence, we are to see the GIXRD CPX feature for the fluorinated FxTCNQs only at certain well-defined values instead of the gradual shift in the TCNQ case. For F2TCNQ, the loss of IPA related features in spectroscopy for 9% would then indicate this ratio to be close to such a stoichiometry, and any additional dopant loading to then form IPAs (or stay neutral) as we increase $\chi$ to 17%. For TCNQ, in contrast, its low $EA$ readily inhibits competition with IPA formation and, thus, makes CPX formation favorable even if no specific stoichiometry is met, which allows observing intermediate crystalline phases with changing $d$ values between pure P3HT and a fully mixed crystal.

Finally, we take a look at the potential response of conductivity to these different scenarios of CPX occurrence. In contrast to the absolute conductivity decrease we observe for our CPX-only system of P3HT-TCNQ, the conductivity was reported to increase significantly for other CPX-only systems such as quarteterthiophene (4 T)-F4TCNQ [11], which can probably be understood by the fact that conductivity is a convolution of carrier density and their mobility. For 4 T-F4TCNQ, CPX crystallites (growing in co-crystal structure with 4 T) were found embedded into an equally crystalline 4 T matrix, which is potentially less detrimental to mobility as it is for the semi-crystalline P3HT system. Further, the broader peaks in x-ray diffraction for the P3HT case, their gradual shift with the TCNQ loading, and a loss of diffraction features at high $\chi$ (cf figure 4(b), all together indicate less order in the CPX phases themselves, in contrast to the 4 T-F4TCNQ case. In further contrast, although CPX-rich, F2TCNQ thin film conductivity is still three orders of magnitude higher for 9% dopant loading than for pure P3HT; this could be accounted to the CPX polymorph that is subject to a certain host-dopant stoichiometry, as we hypothesize.

5. Conclusion

To better understand conditions and mechanisms underlying IPA versus CPX formation in molecularly doped OSCs, we analyzed the doping of P3HT with F4TCNQ, F2TCNQ, FTCNQ, and TCNQ using optical and vibrational spectroscopy, x-ray diffraction, and conductivity data to serve as the basis for semi-classical modeling of the DOS. Our study shows that the ratio between IPA and CPX formation in P3HT yields higher IPA content by using TCNQ derivatives of higher degree of fluorination and for lower dopant concentrations. As a result from our combined analysis we can state that beyond a certain host-dopant stoichiometry, $\chi \geq 9\%$ for P3HT-FxTCNQ, crystalline CPX formation undergoing partial charge transfer can compete with integer charge transfer forming IPAs.

Juxtaposing the vast body of knowledge in literature to our own comprehensive data obtained from various experimental techniques all applied to the same systems in one study, we highlight challenges in providing consistent information on the occurrence of the different dopant scenarios, that is, CPX or IPA formation. Our data suggests that this is due to differences in oscillator strength between these scenarios and the respective spectral regions studied, as well as the fact that amorphous and crystalline phases are not equally probed by diffraction and spectroscopy. Especially FTIR stands out in that regard since the C=N stretching modes of the TCNQ derivatives—commonly utilized to quantify the degree of charge transfer—appear to largely over-represent CPX formation, while the ring C=C stretching modes—mostly neglected in pertinent literature—provide conclusions that are more in line with the neutral and ionized dopant occurrence deduced from optical spectroscopy and diffraction data. Thereby, our work strongly supports a number of studies, recent and as far back as the 1980 s, which highlight that interpretations of the C=N stretching modes are complex as the origins of their shift can go far beyond the sole impact of charge transferred to the dopant.
We ultimately aimed to explore the energetics behind IPA formation in our experimental data as competing mechanism to CPX formation, starting with a comparison of host $IE$ with dopant $EA$ values as deduced from own CV results. We confirmed that the pure materials’ $EA$ and $IE$ are no sufficient predictors for IPA formation alone, because it is well observed also for $EA < IE$. Going beyond our previous study assuming doping-induced broadening of a Gaussian DOS for the P3HT host material in the low doping regime [24] we applied semi-classical modeling that mimics the experimentally found trends of increased IPA content with lower dopant loading and higher dopant $EA$. Despite our caution in deducing the doping scenario via the $C≡N$ stretching modes in FTIR, we could estimate the IPA content such that conclusive results for the DOS width emerged from our modeling. We found that for the $EA < IE$ cases of P3HT doped with F2TCNQ and FTCNQ, the host HOMO-DOS must broaden by about three to four times the width recently reported for pristine P3HT [26].

Still, our approach could not conclusively explain why TCNQ forms a CPX-only system with P3HT while FTCNQ can yield high percentages of ionization despite not having a significantly stronger $EA$. On the one hand, we hypothesize that this is due to a self-amplifying effect where low initial ionization causes DOS broadening which supports further ionization. Its activation threshold would need to lie between the $EA$ values of TCNQ and FTCNQ, explaining their stark difference regarding IPA formation. Alternatively, the current lack of explicit CPX modeling in our approach neglects potential driving forces towards CPX formation that could suppress IPA formation for TCNQ, but less so for FTCNQ. To explicitly include CPX formation, the spatial arrangement of host and dopant as well as effects of the surrounding bulk must be included into the modeling, which requires information that cannot be deduced for intrinsically semi-crystalline P3HT and goes beyond the scope of our current study [23, 94, 96, 98, 99].

The direction of future work naturally emerges from our present data. While the crystalline IPA phase shows a variable lattice-spacing in the stacking direction which decreases with increased dopant loading, the crystalline CPX phase has an even smaller spacing that appears to be impossible to be gradually reached, but is fixed and independent of dopant concentration. Furthermore, that phase shows a significantly sharper peak than the corresponding IPA feature, which indicates higher order. Identifying host systems, polymeric and small molecular, where the mutual arrangement with the dopant can be precisely resolved for both scenarios of IPA and CPX formation is therefore part of our current dedication to this field.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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