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Impact of Molecular Order on Polaron Formation in Conjugated Polymers

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ABSTRACT

The nature of polaron formation has profound implications on the transport of charge carriers in conjugated polymers, but still remains poorly understood. Here we develop in situ electrochemical resonant Raman spectroscopy, a powerful structural probe that allows direct observation of polaron formation. We report that polaron formation in ordered poly(3-hexyl)thiophene (P3HT) polymer domains (crystalline phase) results in less pronounced changes in molecular conformation, indicating smaller lattice relaxation, compared to polarons generated in disordered polymer domains (amorphous phase) for which we observe large molecular conformational changes. These conformational changes are directly related to the effective conjugation length of the polymer. Furthermore, we elucidate how blending the P3HT polymer with phenyl C-61 butyric acid methyl ester (PCBM) affects polaron formation in the polymer. We find that blending disturbs polymer crystallinity, reducing the density of polarons that can form upon charge injection at the same potential, whilst the lost capacity is partly restored during post-deposition thermal annealing. Our study provides direct spectroscopic evidence for a lower degree of lattice reorganisation in crystalline (and therefore more planarised) polymers than in conformationally disordered polymers. This observation is
consistent with higher charge carrier mobility and better device performance commonly found in crystalline polymer materials.
INTRODUCTION

Organic semiconducting materials attract intense research interest partially owing to their intriguing fundamental chemistry and physics. Due to the strong electron-phonon coupling in conjugated polymers and small molecules, any changes in the electronic structure, by charge generation or photo-excitation, will cause a distortion of the local molecular environment resulting in changes to the molecular vibrations.\textsuperscript{1,2} Different kinds of charge carriers can be formed and defined by their number of charges, spin and electronic states. A single charge coupled to the lattice distortion is known as a polaron, whilst two charges form a bipolaron. These different types of excitations in conjugated polymers are characterised by their different sub-gap electronic transitions in the UV/Vis and N-IR spectral region.\textsuperscript{3} Both types of polaron are self-localised within a polymer chain, usually over several units, and are transported by “hopping” from one localised state to another. Some overlap of the initial and final state electronic wavefunctions (coupling) is required for effective hopping to occur, and can be greatly enhanced by the delocalisation of the polaron wavefunction and reduced lattice reorganisation energy. These two parameters are dependent on the intra-molecular order (polymer conformation) and it is commonly found that ordered (crystalline) phases exhibit higher charge carrier transport,\textsuperscript{4,5,6} although this is not ubiquitous among all conjugated polymers.\textsuperscript{7,8}

Conjugated polymers can be used in electronic devices, such as organic photovoltaics (OPVs). A model material for OPV applications is the conjugated polymer poly(3-hexyl)thiophene (P3HT), which absorbs photons resulting in a bound electron and hole pair, known as an exciton.\textsuperscript{9,10,11} Typically, the polymer serves as an electron donor when blended with an electron acceptor (often a fullerene, e.g. PCBM) creating an energy level offset required for efficient exciton dissociation.\textsuperscript{12} This dissociation process generates mobile electron and hole polarons in the acceptor and donor material, respectively. The performance of OPV devices is dependent...
on the formation and transport of the polarons through the photoactive layer to collecting electrodes.\textsuperscript{13} Thus it is important to understand the effects of polymer order and blending on polaron formation.

Here, we elucidate the relationship between molecular order and polaron formation in P3HT by considering two isomers: \textit{regioregular (RR-P3HT) and regiorandom (RRan-P3HT) P3HT}. These analogues produce different degrees of molecular order: RR-P3HT is semi-crystalline, containing crystalline and amorphous phases, while RRan-P3HT is predominantly amorphous (see Materials section for details).\textsuperscript{14} We also investigate the effect of blending RR-P3HT with PCBM; such blending is known to disrupt the molecular order of P3HT, whilst thermal annealing reverses the disruption by driving phase separation.\textsuperscript{15}

Polarons can be formed by charge injection, chemical doping or electrochemical doping, as well as by charge generation via photoexcitation.\textsuperscript{16,17,18} Regardless of how they are formed, polarons in P3HT are similar in nature and exhibit similar spectroscopic signatures.\textsuperscript{19,20} Photoexcitation can lead to the formation of other types of charge carriers, such as polaron pairs, whose spectral signatures are difficult to distinguish from those of polarons.\textsuperscript{20,21} Compared to photo-generation and chemical doping, electrochemical doping of P3HT allows precise control of polaron formation in terms of its density.\textsuperscript{22} Here, a P3HT film is deposited on conductive glass, immersed in an inert electrolyte, and the polaron density is controlled via an electrochemical potential to the film in a three electrode cell configuration, whilst Raman spectroscopic measurements are performed simultaneously (see Figure S1 for experimental set-up) under resonant excitation conditions in order to perform \textit{in situ} electrochemical resonant Raman spectroscopy (ERRS).

Raman spectroscopy is a vibrational spectroscopy and it is particularly sensitive to $\pi$-electrons, which are highly polarizable under photoexcitation, and thus gives information on polymer conformation and structure.\textsuperscript{23,24,25} In this work, we demonstrate the capability of ERRS in
experimentally probing the structural reorganisation of P3HT conjugated polymer. We identify the vibrational modes associated with the formation of polaron in P3HT and correlate the changes of these modes to the molecular order of the polymer. We use this alongside \textit{in situ} spectroelectrochemical measurements to provide a comprehensive understanding of the electronic and vibrational structure of the polymer chain. We combine experimental ERRS with quantum chemical calculations (density functional theory (DFT)) to allow us to evaluate the extent of polaron delocalisation, which relates to the effective conjugation length of the polymer.

Our results indicate that the polaron formed in P3HT polymer does not possess the extreme quinoidal structure proposed by previous studies,\textsuperscript{20,26,27} and that polaron structure depends on the conformation of the hosting polymer, i.e. the planarity of the P3HT conjugated backbone. We show that polaron formation in ordered polymers (crystalline phase) causes less pronounced changes to the molecular conformation, indicating smaller lattice relaxation, than polarons generated in disordered polymers (amorphous phase) for which we observe large conformational changes. Our DFT calculations reveal that this is caused by the effective conjugation length of the polymer that either delocalises or confines the polaron wavefunction in ordered or disordered polymers, respectively. Our study provides direct spectroscopic evidence for a lower degree of lattice reorganisation in more ordered polymers compared to disordered polymers. This is consistent with higher charge carrier mobility and better device performance, as commonly found in crystalline polymer materials. In addition, we elucidate the impact of blending P3HT with PCBM and the impact of thermal annealing on the nature of polaron formation in the polymer, showing in particular how polymer crystallinity is disturbed by blending with PCBM and is partially restored by post-deposition thermal annealing. This changes the polaron structure in the polymer and the density of polarons that can be formed at a given applied potential.
EXPERIMENTAL SECTION

Materials

The p-type conjugated polymer considered in this study is a homopolymer composed of thiophene units substituted with hexyl side chains at the 3’ position. Coupling the thiophene monomers in the 2, 5’ position is known as head-to-tail coupling and yields regioregular poly(3-hexylthiophene) referred to as RR-P3HT. Coupling in the 2, 2’ or 5, 5’ position is known as head-to-head or tail-to-tail coupling respectively. Allowing the coupling to occur in head-to-tail or head-to-head arrangements at random yields regiorandom P3HT, referred to as RRan-P3HT. RR-P3HT is a semicrystalline material and can exhibit a high degree of molecular order whilst RRan-P3HT is totally amorphous.28 Details of the polymers used in this work are as follows: RRan-P3HT (regioregularity = 1:1 (head-to-head):(head-to-tail) linkages of regioisomers) was bought from Sigma Aldrich, with weight-average molecular weight (M_w) ~87 kg/mol; RR-P3HT (95.2 % regioregularity) was bought from Merck, with weight-average molecular weight (M_w) ~36.6 kg/mol and polydispersity index of 2. PCBM was purchased from Solenne.

Methods

The oxidation potential of P3HT depends on polymer conformation, which is characterised using cyclic voltammetry.29 In order to inject holes into the material and control the charge density, we use chronoamperometry to apply a square wave potential and simultaneously measure the temporal current response. Characterisation techniques, such as UV-Vis and resonant Raman spectroscopy can be performed in situ, and provide information about changes to the optical and structural properties of the oxidised material.22.

Film Preparation

Polymer and polymer/fullerene blends were dissolved in chlorobenzene at a concentration of 20 mg/ml and left stirring at 80 °C overnight. Fluorine-doped tin oxide (FTO) coated glass
substrates were cleaned in a sonicator for 10 minutes at a time in soap solution, followed by acetone and finally IPA before plasma ashing. The solution was deposited on the clean FTO glass substrates and spun at 1000 rpm for 60 seconds. Films were then dried under vacuum overnight.

Electrochemical measurements

All electrochemical measurements were made using an Autolab potentiostat (PGSTAT) and the custom-made three electrode electrochemical cell (shown in Figure S1). The cell components are as follows: thin film deposited on FTO coated glass (working electrode), platinum dispersed on FTO coated glass (counter electrode), silver (Ag) wire (pseudo reference electrode), and 0.1 M TBA PF₆ (tetrabutylammonium hexafluorophosphate) in acetonitrile (inert electrolyte). Cyclic voltammetry was measured by applying an oxidising potential to the working electrode and scanning the potential from –0.5 V to 1.2 V vs. Ag at a scan rate of 20 mVs⁻¹, followed by reversing the direction. The current response waveform was measured simultaneously. Chronoamperometry was used to oxidise the polymer film during in situ spectroscopy measurements. It was performed by applying an excitation square-wave potential to the working electrode in the following configuration: 0 V for 20 seconds (neutral state), an oxidising potential (Vox) for 40 seconds (oxidised state), and 0 V for 20 seconds (back to neutral state). In situ Raman and UV-Vis measurements were taken during the application of an oxidising potential when the current response reached steady state (usually after 5-10 seconds).

In-situ Electrochemical Resonant Raman Spectroscopy

Raman spectra were measured with a Renishaw inVia microscope in back scattering configuration. Two excitation wavelengths were used; 488 nm and 785 nm, with 130 mW and 9.0 mW power respectively. 10 % power and 25 % defocus was applied to avoid photodegradation of the film. The frequency of the lines were first calibrated using a silicon reference.
The spectro-electrochemical cell was integrated with the Raman spectroscope to perform in situ resonant electrochemical Raman measurements. The working electrode lies perpendicular to the incident laser beam to allow precise focusing of the laser on the organic thin film and movement of the laser spot on the thin film in the x, y plane.

**DFT calculations**

Raman spectra of neutral and cationic thiophene heptamers were calculated using the Gaussian 09 package. DFT calculations were performed at the B3LYP/6-31 G (d) level of theory.\textsuperscript{14} Oligomer ground-state geometry was first optimised in the gas phase. The optimised geometry was then used for the frequency calculation (see Figure S2 c). The hexyl side chains were replaced by methyl groups to reduce computation time, this was found to give a reasonable representation of the alkylthiophene polymers.\textsuperscript{14}
RESULTS AND DISCUSSION

We monitor the formation of hole polarons in P3HT polymer during oxidation (hole injection), where its molecular order (conjugated backbone planarity) is altered by: polymer regioregularity, blending with PCBM small molecules, and post deposition thermal annealing of blended films.

Polaron formation in P3HT

Figure 1a shows the spectro-electrochemical absorption spectra of RR-P3HT in its neutral state and during oxidation with increasing oxidising potentials. In its neutral state (0V), RR-P3HT exhibits a ground state absorption transition between 400 nm and 650 nm. There are distinguishable peaks at 520 nm, 550 nm and 600 nm whose origins have been reported to involve both intrachain through bond (J-aggregate) interactions and interchain Coulombic (H-aggregate) interactions.\textsuperscript{30-31} In the oxidised state (0.8 – 1.0 V), the ground state absorption features are bleached, concurrently a new absorption peak becomes visible (from 650 nm to 950 nm with a peak at around 800 nm) due to the formation of polarons.\textsuperscript{10} The isosbestic point (~630 nm) is characteristic for the conversion of neutral polymer to cationic radicals (polarons).\textsuperscript{3,29} The polaron band is red-shifted and much broader with respect to the ground state absorption band. Hole polarons induce electronic energy levels that lie within the optical band gap of the neutral polymer producing a smaller optical band gap. This gives rise to the red-shifted polaronic absorption band in the (near)-IR.\textsuperscript{32} The intensity of this polaron absorption band increases with increasing oxidising potential as more holes are injected into the polymer at higher voltages.

The absorbance spectra are used to select an excitation wavelength for resonant Raman spectroscopy measurements, i.e. to resonantly excite the ground state neutral polymer (using 488 nm excitation) or the polarons in the charged polymer (using 785 nm excitation).
Figure 1. (a) Spectroelectrochemical absorbance spectra of RR-P3HT as a function of increasing oxidising voltages. The band appearing at 400-650 nm is assigned to the ground state absorption and the broad band with a peak at 800 nm is due to the polaron absorption generated under the oxidation potential above 0.6V. The spectra at 0 V and 0.4 V are hidden behind 0.6 V (oxidation onset for RR-P3HT) above which oxidation starts. Arrows indicate bleaching of the ground state absorption band and rising of the polaron absorption band during oxidation. 2 b) Cyclic voltammograms of RR-P3HT and RRan-P3HT. RR-P3HT is cycled three times and shows good electrochemical stability. RR-P3HT shows two oxidation peaks; an oxidation onset (0.6 V) measured with a sharp peak at lower voltage (0.7 V) and a broader peak at higher voltage (1.1 V) which coincides with the RRan-P3HT oxidation peak (onset = 1.05 V). Arrows indicate oxidising potentials selected for in-situ electrochemical Raman spectroscopy.

We first examine the oxidation potentials of semi-crystalline RR-P3HT, between -0.5 and 1.2 V (vs. Ag), using cyclic voltammetry (Figure 1b). All oxidising potentials are given with reference to silver throughout. The cyclic voltammetry sweep was cycled three times with little variation in peak position and shape between each cycle, indicating reasonable electrochemical stability of P3HT to repeated charging (hole injection) and discharging (hole extraction). The oxidation onset at 0.6 V corresponds to oxidation of the highest occupied molecular orbital (HOMO) energy level. Beyond the onset a sharp peak rises (0.7 V) and as the voltage increases...
further, a second peak appears at around 1.05 V. We confirm the nature of these two peaks by comparing semi-crystalline RR-P3HT to amorphous RRan-P3HT shown as the dashed line in Figure 1b. The oxidation onset for RRan-P3HT is shifted to higher potential (1.05 V) compared to RR-P3HT, suggesting its HOMO energy level is deeper by up to 0.45 eV. This suggests that the two peaks observed for semi-crystalline RR-P3HT correspond to oxidation of the crystalline (0.7 V) and amorphous phases (1.05 V). The shape of the cyclic voltammogram for RR-P3HT that we show here is consistent with others previously reported, although the oxidation onset varies depending on the reference electrode used.\textsuperscript{3,29,33} The different oxidation peaks of P3HT have previously been ascribed to oxidation of the polymer zones of different morphology and thus different average conjugation length.\textsuperscript{34} Skompska et al. show that oxidation of the ordered polymers corresponds to the oxidation peak at lower potential and the disordered polymers correspond to the peak at higher potential.\textsuperscript{29} Enengl et al. also provide evidence for the formation of bipolarons at higher potentials.\textsuperscript{3} Thus, the oxidation peak corresponding to oxidation of amorphous phases likely coincides with the formation of bipolarons.

A final observation is made on the tail of the peak of the reverse reduction sweep that extends from 0.6 V to 0.0 V. This is likely de-trapping of polarons formed in localised electronic states that lie above the HOMO level, and require lower potentials to extract holes.

Having identified the oxidation potentials of different polymer conformations, we can investigate changes to molecular structure upon hole polaron formation in RR and RRan-P3HT using electrochemical resonant Raman spectroscopy. At 488 nm excitation we expect a selective increase in Raman scattering from the neutral polymer compared to the oxidised polymer due to its absorption transition being resonant with the Raman excitation energy, whilst the 785 nm excitation is resonant with the absorption of the charged species (see Figure S2. for Raman spectra).
We monitor the molecular structure changes of neutral RR-P3HT polymer during hole polaron formation by applying a series of potentials from 0 - 1.2 V (Figure 2a).

Figure 2. Resonant electrochemical Raman spectra of RR-P3HT (C=C and C-C modes) under 488 nm excitation subject to increasing oxidising potentials, a) raw and b) normalised. Raman spectra obtained c) at 0.4 V (before oxidation onset) and d) at 1 V (after oxidation). The C=C mode of RR-P3HT was fitted with three Gaussian peaks representing different phases of the polymer; neutral disordered phase,
neutral (disordered) (1462 cm\(^{-1}\)); neutral ordered phase, neutral (ordered) (1446 cm\(^{-1}\)); charged polymer, charged (1419 cm\(^{-1}\)). e) Compares integrated peak areas under C-C and C=C modes calculated from experimental spectra in a), and f) compares the relative peak areas of three phases of RR-P3HT as a function of applied oxidation voltage, calculated from fitting Gaussian peaks to normalised Raman spectra in b).

The peak at 1448 cm\(^{-1}\) corresponds to the intra-ring C=C vibrational mode whilst the peak at 1383 cm\(^{-1}\) corresponds to the intra-ring C-C vibrational mode.\(^{27}\) There are no changes in peak position or shape as we increase the oxidising potential from 0 V to the oxidation onset (0.6 V). Immediately after the oxidising potential exceeds the oxidation onset (\(\geq 0.7\) V), we observe changes in the Raman spectrum: the intensity of the C=C mode decreases with increasing oxidising potential as the amount of neutral polymer decreases. Normalising the spectra (Figure 2b) reveals this broad peak is a convolution of high and low energy regions. Figure 2c and 2d are representative Raman spectra before (0.4 V) and after (1.0 V) polaron formation respectively. We have fitted three Gaussian peaks to illustrate the three different vibrational frequencies of the C=C mode corresponding to different phases of the neutral polymer and the oxidised species: charged (1419 cm\(^{-1}\)) due to the formation of polarons, neutral-ordered (1446 cm\(^{-1}\)) and neutral-disordered (1462 cm\(^{-1}\)). Our assignment is consistent with those previously reported for ordered and disordered P3HT,\(^{14,15,23}\) and the assignment to neutral or charged species is confirmed by DFT calculations of the optimised geometry and Raman spectra (Figure S 2c and Figure S 3a respectively) which reveal that polaron formation increases the length of the C=C bond (1.38 Å to 1.40 Å) and shifts the C=C Raman peak to lower energy by 21 cm\(^{-1}\).

This can be understood as follows, the C=C bond becomes weaker as \(\pi\)-electron density is lost from \(\pi\)-bonding molecular orbitals during hole polaron formation. These electronic states are strongly coupled to the nuclear vibrational modes of the molecule: loss of \(\pi\)-electron density
causes the bond to lengthen and the force constant to decrease, shifting its vibrational frequency to lower energy. Such changes in localised modes (C=C and C-C) due to polaron formation, reveals that the P3HT polymer backbone has become more planar – the π-electrons are now more delocalised along the polymer backbone. This can be understood by the effective conjugation coordinate model (ECCM) which states that as the conjugation length increases, the force constant associated with the collective oscillation of nuclei that move from the ground state geometry to the minimum geometry of the first electronic excited state weakens, resulting in a shift of the Raman band to lower frequencies.\textsuperscript{35}

Enhanced planarity of the polaron molecular structure is also demonstrated by a rise in the relative peak intensity ratio between the C-C (1383 cm\(^{-1}\)) and C=C mode (1415 cm\(^{-1}\)) (Figure 2e). The \(I_{\text{C-C}}/I_{\text{C=C}}\) ratio has been used to monitor molecular order in neutral P3HT,\textsuperscript{14} where greater π-electron density delocalisation over the C-C bond in planar, ordered P3HT causes the Raman scattering cross-section of this mode to increase. Our DFT calculations (Figure S 3b) reveal a reduction in the dihedral angle from 17-25° in the neutral oligomer to 0° in the oxidised oligomer, which support our interpretation of polymer backbone planarisation upon polaron formation. At \(V \geq 0.7\) V, both the C-C and C=C modes of the neutral polymer are quenched (Figure 2e).

The fitted Gaussian peaks provide more detailed information on how hole polarons are formed in the semi-crystalline phase of the P3HT polymer (Figure 2f). The relative intensity of the neutral-ordered phase decreases dramatically above 0.7 V, indicating selective initial oxidation of this phase. This is accompanied by a rise in relative intensity of charged phase starting at the same voltage (0.7 V). During the oxidation of the ordered phase (0.7 V - 1.0 V), the relative fraction of neutral-disordered phase increases, which causes the C=C peak to broaden. At \(V > 1.0\) V the neutral-disordered phase now starts to oxidise, implying that even disordered
segments of the polymer chain contribute to hole polaron formation at higher voltages. The high voltage (1.1 V) corresponds to the oxidation onset for amorphous RRan-P3HT.

It is interesting to notice that before oxidation (Figure 2e, 0.4V < V < 0.7 V) both the intra-ring C=C and C-C peaks increase in intensity without changing shape or position. The lack of peak shift or shape change eliminates the possibility of π-electron density changes within the molecule. Raman scattering intensity is dependent upon the orientation of π-electrons with respect to the electric field vector of the incident light. This may imply that the application of potential before oxidation (0.4V < V < 0.7 V) causes the polymer chains to become more aligned with the plane of the electric field, similar to the electric-field induced structural changes previously observed in pentacene.36

Using a 488 nm excitation we have successfully observed the spectral signature of the charged C=C mode, which is at lower wavenumbers to the neutral-ordered and neutral-disordered. Using a 785 nm excitation, we can now directly monitor the nature of the polaronic species in much greater detail.
Effects of polymer regioregularity on polaron formation in P3HT

Figure 3. Electrochemical Raman spectra of RR-P3HT (C=C and C-C modes) under 785 nm excitation (resonant with the polaron absorption band) subject to increasing oxidising potentials, a) raw, and b) normalised. c) Integrated total peak area (C=C, C-C intra-ring and C-C inter-ring modes) measured from peak deconvolutions (see figure 4 for fitted spectra), d) Peak position (C=C and C-C modes) as a function of applied voltage, measured from experimental data.

Figure 3a shows the spectral changes of RR-P3HT during oxidation when the excitation wavelength is resonant with the polaronic absorption (785 nm). It is evident from Figure 3c, that all peaks increase in intensity during oxidation (starting at 0.6 V) due to the rise in polaron density. The peak intensity increases until 0.9 V and at more positive potentials, the intensity starts to decrease. This is likely due to the formation of bipolarons, which absorb in the mid-
IR range and hence, are not resonant at 785 nm. Figure 3b allows us to understand the mechanism of oxidation: the neutral polymer is oxidised at 0.6 V, after which the C=C peak position shifts from ~1446 cm<sup>-1</sup> to ~1415 cm<sup>-1</sup>, then to ~1403 cm<sup>-1</sup> at 1.2 V (discussed further below). There is greater sensitivity to polaron formation at 785 nm excitation, compared to 488 nm, which required 0.8 V of oxidising potential for apparent polaron signatures. The increased sensitivity is achieved by resonance with the polaronic absorption band allowing us to distinguish that changes to molecular conformation during polaron formation involve not only the C=C bond, but all bonds along the conjugated backbone, including intra-ring and inter-ring C=C bonds. The inter-ring C=C mode (1207 cm<sup>-1</sup>) increases in intensity and shifts to higher frequency (1207-1213 cm<sup>-1</sup>) (Figure 3c and 3d respectively), indicating it becomes more ‘double-bond’ like in nature. Whilst the intra-ring C=C mode broadens and peak shifts to lower frequency (1380-1379 cm<sup>-1</sup>) which signals a slight weakening of this bond (for residual C=C mode without C=C modes see figure S4).

Most importantly, we observe that after the oxidation onset (0.6 V), the C=C peak position shifts to lower frequency linearly with increasing voltage. Comparison of the spectra of RR-P3HT and RRan-P3HT at V > V<sub>ox</sub> (dotted line peak in Figure 3b and Figure S5) indicates that there are more substantial conformational changes when polarons are formed in more disordered segments of the P3HT chain. Oxidising RR-P3HT at 0.7 V injects holes into the ordered phase of P3HT, whilst for RRan-P3HT holes are only injected into disordered P3HT at 1.2 V. Whilst the shift of the C=C mode to lower frequency is gradual for RR-P3HT, it is very abrupt for RRan-P3HT (1464 cm<sup>-1</sup> to 1406 cm<sup>-1</sup>). RRan-P3HT, being amorphous, can only form polarons in short segments of disordered chains. The disordered nature of RRan-P3HT causes a broad distribution of different polymer conformations and hence a large FWHM of the C=C mode of polarons formed.
The main C=C mode consists of both neutral and charged phases: two neutral phases (ordered and disordered); and two charged phases (one from the initially ordered neutral phase and the other from the initially disordered neutral phase). We name these charged phases as charged-ordered and charge-disordered phases respectively (Figure 4a-4e). All of the information about peak fitting is provided in Figure S6.

**Figure 4.** Representative Raman spectrum of RR-P3HT under 785 nm excitation during 0 V (a), 0.7 V (b) and 1.2 V (c) applied with Gaussian fits illustrating the different polymer phases contributing to the main C=C mode: neutral disordered phase, neutral (disordered) (1462 cm⁻¹); neutral ordered phase, neutral (ordered) (1446 cm⁻¹); charged from ordered phase, charged (ordered) (1425 cm⁻¹); charged from disordered phase, charged (disordered) (1405 cm⁻¹). The residual resembles the C-C modes which have not been deconvoluted (see Figure S 4 Supporting Information for plots). All fitting parameters are shown in Figure S 6 (Supporting Information). d) Relative integrated peak areas of C=C mode (%) for the deconvoluted C=C modes as a function of voltage. The charged phase has been further separated in to charged ordered and charged disordered phase. e) Peak position of deconvoluted C=C modes as a function of voltage.
Interestingly the charged phase (~14 %) is present even between 0 and 0.4 V, which is likely to be due to unintentional p-doping of P3HT in air. At 0.7 V, the neutral-ordered phase is diminished producing the charged-ordered phase. At higher oxidising potentials (1.0 V and 1.2 V), hole polarons are now formed in more disordered segments of the polymer chain, which increases the relative intensity of the charged-disordered phase. The signal for charged polymer from ordered phase shifts to lower frequency (1424 – 1417 cm\(^{-1}\)) as voltage increases (Figure 4e). At 0.7 V, the mode corresponding to the charged from ordered phase remains constant until 1.2 V, and another mode corresponding to the charged from disordered phase is introduced to represent hole polarons with greater modification of C=C bond length.

The difference between the polaron structure in ordered and disordered phases is explained by their difference in effective conjugation length. To illustrate this, we perform DFT calculations (Figure 5) of a series of oligomers increasing in length from 3 – 11 units to simulate the different conjugation lengths existing in semi-crystalline P3HT. As oligomer length (effective conjugation length) decreases, the C=C bond becomes longer in the polaron (Figure 5a). The ordered polymer has a long effective conjugation length, which permits the polaron wavefunction to delocalise over several repeat units, whereas in disordered polymers the large intramolecular torsion between each unit shortens the effective conjugation length, similar to shorter oligomers confining the polaron wavefunction and localising it to a certain chain length.\(^2\) Hole polarons in the amorphous polymer therefore impact fewer bonds, and result in a larger change in bond length to minimise the overall potential energy. This manifests as a more extreme change in the C=C bond length compared to the polaron in crystalline, planar polymers.
Figure 5. DFT calculations of neutral and +1 charged RR-P3HT oligomers. Calculated C=C bond length a) for a series of oligomers both neutral and charged. Calculated bond length is taken from the C=C bond on the central unit to avoid end group effects. Series of oligomers increase in length from 3 – 11 units as representations of different conjugation lengths existing in semicrystalline P3HT. As oligomer length (conjugation length) decreases, C=C bond becomes increasingly modified to a longer bond in the charged oligomer, as illustrated on the right hand side. Measured torsion angles b) between each unit for both neutral and charged RR-P3HT heptamers. Side view of corresponding oligomers to the right hand side of the plot.
Our findings provide the first experimental evidence that longer effective conjugation length expected in RR-P3HT due to its planar backbone permits more effective delocalisation of hole polarons, reducing lattice distortion (less bond length and angle change). This greater delocalisation is expected to lead to a smaller associated reorganisation energy compared to the more disordered case. Charge transport in conjugated polymers is usually described as a hopping process from one localised state to another,\textsuperscript{38,39} the overlap of the initial and final state electronic wavefunctions is required for effective hopping to occur, which can be greatly enhanced by the delocalisation of the polaron wavefunction and reduced reorganisation energy observed in RR-P3HT.

Since P3HT is a commonly used donor material in OPV devices, we now draw our attention to how polaron formation in the polymer is affected by blending with the acceptor molecule PCBM and post-deposition thermal annealing.
Effect of blending and thermal annealing on polaron formation in P3HT

To investigate the impact of PCBM on P3HT molecular order and associated polaron formation, we compare cyclic voltammograms of neat RR-P3HT, RR-P3HT:PCBM (as-cast), RR-P3HT:PCBM (annealed) and RRan-P3HT (Figure 6a).

Figure 6. a) Cyclic voltammograms of RR-P3HT, RR-P3HT:PC60BM (1:1 wt.) blend as-cast and annealed and RRan-P3HT. b) Spectroelectrochemical absorption spectra for as-cast and annealed RR-P3HT:PCBM (1:1 wt.) blend films. Voff = 0 V and Von = 0.8 V vs. Ag. Normalised series of in situ electrochemical Raman spectra (785 nm ext.) during oxidation (0 – 1.2 V vs. Ag) for c) as-cast blend and d) annealed blend.
The oxidation onset for the neat RR-P3HT and the as-cast/annealed blends is approximately the same (0.6 V vs. Ag), which indicates that the HOMO level of the crystalline polymer phase is not influenced by PCBM.

There are clear changes to the intensity of the first oxidation peak, which we previously attributed to polymers with a high degree of molecular order (crystalline phase). We fit peaks to each cyclic voltammogram and integrate the area to estimate the total charge density generated in each phase (Figure S 7). On blending with PCBM, the peak associated with oxidation of highly ordered polymer is reduced to 28 % of the value of neat RR-P3HT. This indicates the PCBM mixes well with the P3HT, which forms regions of amorphous polymer and reduces the fraction of the crystalline domains. On annealing the ordered peak is partly restored to 88 % of the original value; the PCBM phase separates and the polymer recrystallises. Disturbing P3HT polymer molecular order by blending with PCBM correlates well with a reduction in polaron density formed in the blend thin films (Figure S 8).

We further investigate the nature of polarons formed in the blends using electrochemical Raman spectroscopy of the annealed and as-cast blends under 785 nm excitation (resonant with polaron absorption) (Figure 6c and 6d). The spectra of both as-cast and annealed blends show a very similar trend in downshift of the C=C peak position during oxidation (0 – 1.2 V) as in neat RR-P3HT. We present comparisons of the in situ electrochemical Raman spectra, in particular the C-C and C=C peaks of P3HT, for as-cast and annealed blends before oxidation (0 V), during oxidation of ordered phase (0.7 V), and during oxidation of disordered phase (1.2 V) (figure 7a).
Figure 7. a) Normalised Raman spectra of C-C and C=C modes of RR-P3HT:PCBM (1:1) blends as-cast (blue) and annealed (red) under 785 nm excitation line for 0 V (before charge formation), 0.7 V (during charge formation of ordered phase) and 1.2 V (during charge formation of disordered phase). The difference between as-cast and annealed blend C=C mode is highlighted in blue to illustrate more neutral-disordered phase (0 V and 0.7 V) and the less modified C=C bond length of polarons in the as-cast blend (0.7 V and 1.2 V). Arrows also indicate the difference in C=C mode and changes in (C-C/C=C) relative intensity. b) Relative integrated peak areas of C=C mode (%) for the deconvoluted C=C modes (785 nm ext. spectra) as a function of voltage for neat RR-P3HT, as-cast and annealed blends. For both blends spectra with deconvolutions see Figure S 10 in Supporting Information. Peak fitting data and parameters shown in Figure S 11.

At each voltage the FWHM of the C=C peak is greater for the as-cast blend compared to the annealed blend which is manifested as a shoulder to higher wavenumber. Before oxidation (0 V) the width of this shoulder is explained by a higher degree of polymer disorder in the as-cast
blend which also generates a lower C-C/C=C intensity ratio. This is shown in the relative integrated peak areas of deconvoluted C=C modes corresponding to different polymer phases (Figure 7b) (Figures S10 and 11 for spectra and fitting parameters). This clearly shows the as-cast blend film has a higher fraction of neutral disordered phase compared to the annealed blend and neat RR-P3HT (0 V and 0.4 V). When oxidising the ordered phase (0.7 V), the shoulder is still due to a higher fraction of neutral disordered phase (figure 7 b) requiring higher voltage to oxidise. When oxidising ordered and disordered phases (1.2 V), the shoulder is well below the frequency of the peak corresponding to neutral-disordered phase (1462 cm\(^{-1}\)) and therefore originates entirely from broadening of the C=C mode of the polaronic polymer.

There are two potential explanations for this observation. One is simply that the broader distribution of polymer conformation in the as-cast blend produces a large FWHM of the C=C mode of polarons formed, similar to what we observed with RRan-P3HT vs. RR-P3HT. Alternatively, the shoulder at higher frequency can be interpreted as a smaller change in C=C bond length upon polaron formation in the as-cast blend compared to the annealed blend. We previously showed that less change in C=C bond length of the polarons is associated with extended polaron delocalisation. It is therefore slightly surprising that the as-cast blend, which should contain more disordered polymer, shows signs of greater polaron delocalization. However, delocalisation also correlates to a higher \(\frac{I_{C-C}}{I_{C=C}}\) ratio, which we observe for the as-cast blend (Figure S 12c). This delocalisation stabilises the charge, resulting in smaller structural changes upon polaron formation (section B. Regioregularity). Stabilisation of charges can also be achieved by modifying the dielectric constant of the immediate environment surrounding the charged polymer chain. Increasing the dielectric permittivity of the environment has been shown to reduce the polarisation energy of the hole polaron by increasing the electronic polarisability of the surrounding environment.\(^{40}\) PCBM has a higher dielectric constant (3.9 -4.0)\(^{41,42,43}\) than P3HT (3.0),\(^{44,45}\) and therefore the extent of mixing...
between these components could affect the stabilisation of the hole polarons formed in the polymer.\textsuperscript{40} The as-cast blend has finer mixing of the P3HT donor polymer and PCBM acceptor molecules, which increases the interfacial area between the two components, whilst the annealed blend has undergone phase separation, decreasing the interfacial area.\textsuperscript{15} We therefore speculate that despite the overall negative effect of well-dispersed PCBM on polymer crystallinity and thus solar cell performance, the as-cast blend may provide a stronger dielectric environment immediately surrounding the hole polaron in the polymer, resulting in less changes to C=C bond length upon polaron formation. We note that the dielectric constant of PCBM depends on the density and arrangement of molecules,\textsuperscript{41} and thus dispersed single fullerene molecules exhibit lower dielectric constants than aggregates, but we do expect the greater polarisability of PCBM to provide a change in the dielectric constant of the surrounding medium. This is similar to other studies, which have reported that a higher PCBM concentration in finely mixed films increases the dielectric constant and stabilises the bound charge transfer (CT) state, resulting in a red-shift of the CT photoluminescence emission.\textsuperscript{46} Our results may represent experimental evidence for this effect on the charged polaron state.
CONCLUSION

Using *in situ* electrochemical resonant Raman spectroscopy (ERRS), we identify the conformational changes (vibrational modes) associated with the formation of hole polarons in P3HT. We demonstrate that the polaron formed upon oxidation does not possess the quinoidal structure and its characteristics strongly depend on the conformation and crystallinity of the hosting polymer. We show that ordered P3HT forms polarons with smaller changes to the molecular conformation indicating less lattice distortion, compared to large conformational changes associated with polarons in disordered P3HT. We correlate the difference in lattice distortion to the effective conjugation length of the polymer, which determines polaron delocalisation; well-ordered polymer segments have long effective conjugation lengths allowing delocalisation of the polaron wavefunction, which induce less changes in bond length. Whereas, disordered polymers localise polarons and cause more severe changes in bond lengths. Our study provides direct spectroscopic evidence for a lower degree of lattice reorganisation in planar polymers compared to disordered polymers, which is expected to lead to a smaller associated reorganisation energy in the former. This is consistent with higher charge carrier mobility and better device performance commonly found in crystalline polymer materials.

In addition, we elucidate the impact of blending P3HT with PCBM on polaron formation in the polymer, by comparing well mixed (as-cast) and phase separated (thermally annealed) blends. Polymer crystallinity is disturbed in the blends resulting in the formation of lower charge density at the same oxidising potential, than in neat RR-P3HT. When the Raman modes of the charged as-cast and annealed blends are compared, there is a broadening of the C=C mode peak to higher energy. This may correlate to the larger distribution of different polymer conformations in the as-cast blend, as well as the higher dielectric environment induced by PCBM, which can stabilise polarons in P3HT.
ASSOCIATED CONTENT

Supporting Information

Diagram of experimental set-up for in situ electrochemical resonant Raman spectroscopy (Figure S 1); normalised and raw electrochemical resonant Raman spectra of RR-P3HT (Figure S 2); DFT calculations of neutral and +1 charged P3HT oligomers (Figure S 3); residual C-C mode plots for electrochemical Raman spectra (785 nm ext.) (Figure S 4); electrochemical resonant Raman spectra with voltage just above the oxidation onset for RR-P3HT and RRan-P3HT (Figure S 5); Gaussian peak fit data for C=C mode deconvolution (Figure S 6); Gaussian peak fitting to the cyclic voltammogram scans (Figure S 7); polaron density as a function of oxidising potential (Figure S 8); chronoamperogram scans of RR-P3HT (Figure S 9); representative as-cast and annealed blend spectra with C=C mode deconvolutions using Gaussian fits (Figure S 10); Gaussian peak fit data for C=C mode deconvolutions (Figure S 11); normalised Raman spectra of C-C and C=C modes of RR-P3HT:PCBM blends under 785 nm excitation (Figure S12).

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Notes

The authors declare no competing financial interest.

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**Integrated Total Peak Area** (10^5)

- **RR-P3HT** (785 nm ext.)
  - C=C (intra-ring)
  - C=C (intra-ring)

**Raman Intensity (counts)** (10^4)
- **Wavenumber (cm\(^{-1}\))**
  - 0.0
  - 0.5
  - 1.0
  - 1.5
  - 2.0
  - 2.5
  - 3.0
  - 3.5

**Normalised Raman Intensity**
- **RR-an-P3HT** 1.2 V
  - 0 V
  - 0.4 V
  - 0.5 V
  - 0.6 V
  - 0.7 V
  - 0.8 V
  - 0.9 V
  - 1.0 V
  - 1.1 V
  - 1.2 V

**Peak Position (cm\(^{-1}\))**
- **Δ 42 cm\(^{-1}\)**
- **Δ 2 cm\(^{-1}\)**
- **Δ 6 cm\(^{-1}\)**

**Oxidising Potential (V) vs. Ag**

- **Integrated Total Peak Area**
  - C=C intra-ring
  - C-C intra-ring
  - C-C inter-ring

**Voltage (V) vs. Ag**

- **Δ 42 cm\(^{-1}\)**
- **Δ 2 cm\(^{-1}\)**
- **Δ 6 cm\(^{-1}\)**
Wave number (cm$^{-1}$)

Normalized Raman Intensity

Normalized Raman Intensity

Normalized Raman Intensity

Relative Integrated Peak Areas of C=C Mode (%)

Voltage (V) vs. Ag

Neat P3HT

Blended (Cast)

Blended (Annealed)

N: Neat P3HT

B_c: Blend (Cast)

B_a: Blend (Annealed)

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