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Polaron delocalisation softens electronic and vibrational transitions in conjugated polymers

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Abstract

In this work we study the photoinduced signatures of polarons in conjugated polymers and the impact of charge carrier delocalisation on their spectra. The variation of film crystallinity for two prototypical systems – blends of the homopolymer P3HT or the donor-acceptor polymer PCPDTBT with PCBM – allows to probe changes of the polaron absorption in the mid infrared spectral region. Increased polaron delocalisation entails a shift of the electronic transition to lower energy in both cases. Also, infrared active vibrations soften for higher polymer chain order. Our findings help in the development of a more complete understanding of polaron properties in conjugated materials and bring the application of the polaron absorption spectrum as indicator for the environment on a more thoroughly studied foundation.

1 Introduction

Charge carriers in conjugated polymers affect the energetics of their environment and lead to the formation of strongly coupled polarons. Although recently contested,^[3] this mechanism is generally assumed to be governed by their strong electron-phonon coupling with the polymer backbone. Based on the Holstein model for molecular polarons,^[15] the relaxation is commonly assumed to shift the polaron energy levels into the fundamental band gap of the material – the magnitude of which is termed the relaxation energy. Although the details of level occupation and position is still debated,^[14] there is a general consensus that this process gives rise to two new optical transitions (classically termed P_1 and P_2) in the mid (MIR) and near infrared (NIR) spectral region (consider Figure 1 (a) for a sketch of a positive polaron).

Studies involving crystalline polymers furthermore revealed additional absorption bands to form when polarons delocalise not only along the polymer backbone (intrachain), but also over adjoining chains (interchain). These transitions are denoted DP^[20] (sometimes CT,^[25] consider Figure 2 for a scheme (a)). The polaron delocalisation has consequently been identified as a crucial factor for the shape, position and strength of the polaron absorption signature in the mid infrared spectral region.^[22] Whilst amorphous materials allow polarons to only reside localised on a short unit (depicted in Figure 2 (b) (top)), the planarisation of the polymer backbone allows for a delocalisation in intrachain direction (middle panel). The presence of aligned chains, finally, enables the necessary polaron delocalisation perpendicular to the backbone (bottom). Theoretical studies generally suggest a shift to lower energy of the absorption band for larger delocalisation.^[12] It was furthermore proposed that the concept of two independent transitions P_1 and DP₁, although descriptive, was oversimplified and the shape of the absorption band was formed by a complex interplay based on the extent of polaron delocalisation in intra- and

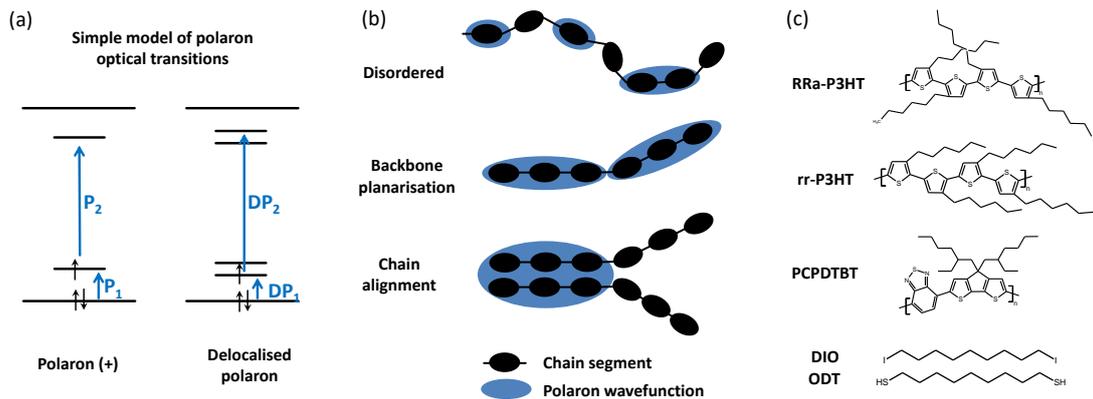


Figure 1: Classical schematic of polaron energy levels and allowed optical transitions (a) along with the mechanisms for wavefunction delocalisation in conjugated polymers with different degrees of disorder (b). The materials used in this study are depicted in (c), where RRa- and rr-P3HT denote the regiorandom and regioregular variants of poly-(3-hexylthiophene), DIO denotes 1,8-diiodooctane and ODT denotes 1,8-octanedithiol.

interchain direction.^[22]

Additional to the broad electronic absorption bands, polaron spectra also exhibit narrow and strong vibrational signals, commonly referred to as infrared active vibrations (IRAVs). These are traditionally explained through the infrared activation of Raman modes in the presence of the carrier's electric field – discussed in the frameworks of the effective conjugation coordinate (ECC)^[5] or the amplitude mode model (AM).^[16] These material specific vibrations can be used as a fingerprint for the environment of the charge carriers. Also this classical explanation has recently been contested and it was suggested that pronounced vibrational signals should be considered as related to polarons instead of the ground state of the polymer.^[1,26]

The low energy signatures of polymer polarons have lately moved back into the focus of research interest as a means to extract information about the chain conformation in the environment of the charge carrier. The groups of Schwartz^[24] and Salleo,^[7] *e.g.*,

studied the spectra of doped films of P3HT to investigate the location of doping induced charge carriers. Simultaneously, we studied the spectra of polymer wrapped single walled carbon nanotubes and assessed the location of carriers in these hybrid systems to find that wrapping polymers actually carry polarons despite nominally unfavourable energy levels.^[19]

Experimental studies evaluating the impact of the carrier delocalisation on the polaron signature so far either considered the two extreme cases of amorphous and highly crystalline materials – making it difficult to predict the effect of subtle changes in polaron delocalisation – or tested the impact of the molecular weight as a means to change the chain order – which requires using different batches of material.^[6,20,25] Missing still, is a proper assessment of incremental morphology changes of the same material as well as a consideration of state-of-the-art donor-acceptor type (DA) polymers.

Since dopants affect the delocalisation of polarons in polymer films and can also corrupt the morphology,^[7] we study the photoinduced absorption of films of two prototypical conjugated polymers under variation of their crystallinity. The homopolymer P3HT is employed in its regiorandom (RRa) and regioregular (rr) variant and the degree of chain order of the latter is varied through thermal annealing. Additionally, the DA polymer PCPDTBT is investigated when cast in presence of solvent additives to enhance the polymer crystallinity. Using these two well-studied systems, we are able to carefully vary the polymer chain order and observe the effect on the polaron signatures.

For both polymers, we find a significant red-shift of the electronic absorption bands in the MIR with increasing crystallinity. In accordance with theoretical propositions, we ascribe this effect to the extended delocalisation of polarons in more ordered films. A close consideration of the position of polaron IRAVs furthermore reveals that also these features undergo a softening, *i.e.* a reduction in energy, for more extended polarons.

2 Experimental

RRa-P3HT was purchased from Rieke Specialty Polymer, rr-P3HT from Sigma Aldrich, PCPDTBT from 1-material and PC₆₀BM from Solenne. All materials were used as received. P3HT-related materials were dissolved in chloroform at 60 °C and PCPDTBT-related materials in chlorobenzene at 80 °C. Solutions were prepared at 20 mg/mL concentration and stirred overnight. Blends with PCBM were mixed at a ratio of 1:1 (polymer:PCBM) in case of P3HT and of 1:2 for PCPDTBT. Additives were used with 3 vol-% concentration. Films were spin-cast at 1200 rpm on quartz or ZnSe substrates.

Absorption spectra of films on quartz slips were recorded with a Shimadzu 3600 UV-vis-NIR spectrometer.

For PIA measurements at low energy, the samples were mounted into a cryostat without being exposed to air and brought into the beam path of a Bruker Vertex 70 FTIR spectrometer. As discussed in detail in our previous work,^[18] We carried out at least 1024 measurement cycles of "light on"/"light off".

Quasi-steady-state PIA studies in the NIR were performed by exciting the sample with a 2.3 eV laser, chopped at 141 Hz, and probing with the continuous spectrum of a Xe lamp. The transmitted light is dispersed by a 1200 lines mm⁻¹ grating monochromator (iHR320, Horiba) and detected by a silicon photodetector. Additional measurements with a blocked Xe lamp account for the sample PL.

3 Results and Discussion

Figure 1 (c) displays the materials studied in this investigation. The polythiophene derivative P3HT was used with a random (RRa) and highly regular (rr) head-to-tail con-

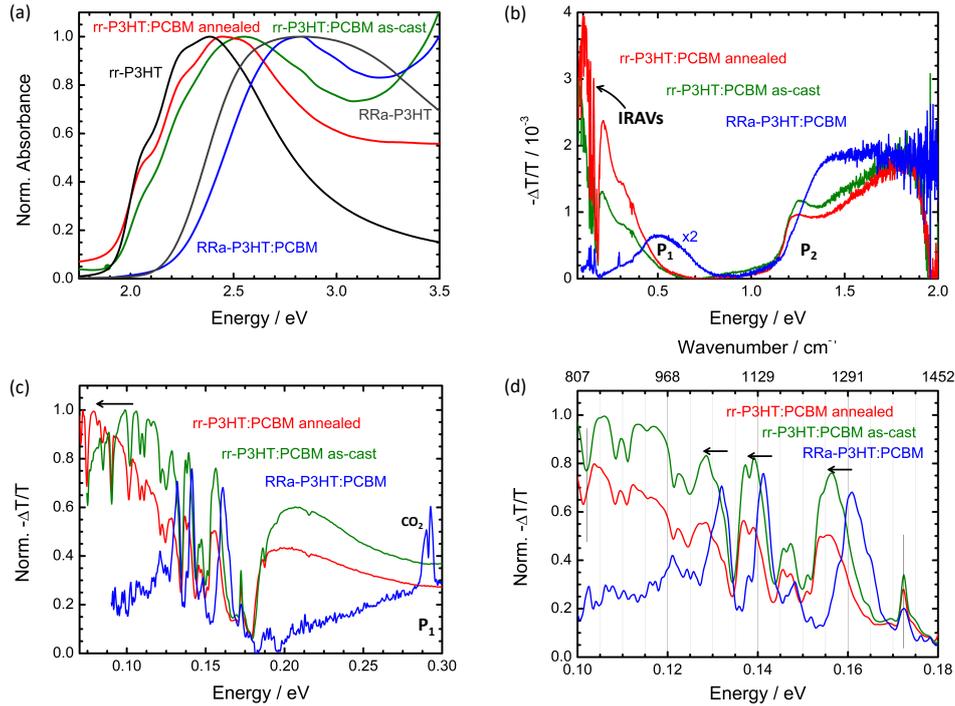


Figure 2: The normalised direct absorbance spectra of P3HT containing films display a broad and unstructured band peaking around 2.3 eV in case of an amorphous film and an increasingly pronounced vibrational substructure as well as a red-shifted peak for more crystalline samples (a). The photoinduced absorption spectra of selected films include two pronounced regions of absorption in the NIR and MIR respectively (b). Amorphous P3HT exhibits an absorption band around 0.5 eV, whilst more crystalline films peak at lower energy. A close-up of the low energy region (c) reveals a red-shift upon increasing the polymer crystallinity – a similar softening can also be observed for the narrow vibrations (d).

figuration. The former is known to generate highly disordered, *i.e.* amorphous, films and the latter generally forms films, which exhibit both crystalline and amorphous regions. The crystallinity can be increased through post-deposition exposure to elevated temperatures – thermal annealing.^[10] We here use the well-established connection between the degree of P3HT film crystallinity and its absorption spectrum to assess the chain order in films.^[8,21] Ascertaining the degree of crystallinity is especially important, as previous studies on the effect of chain order unfortunately lacked such information.^[17]

The absorbance spectra of corresponding films are given in Figure 2 (a). The amorphous RRa-variant exhibits a broad and unstructured absorption band around 2.8 eV. When casting a mixture with the electron acceptor PCBM, this band becomes narrower and the absorption increases at high energy due to the contribution of PCBM. As expected, thermal annealing does not affect this material (neither neat or when blended, Figure S1), as the steric hindrance of the side chains is too large for a proper alignment. For neat films of the rr-variant, we find the absorption band to peak at 2.4 eV. Additionally, the broad band exhibits a strong substructure, which is due to the vibrational levels participating in the transitions. Surprisingly, despite casting from volatile CF at 60 °C, we could not achieve further improvement in chain order of the neat polymer through thermal annealing (Figure S2 (a)).

For the blend of rr-P3HT with PCBM, finally, the polymer absorption peaks around 2.5 eV and the degree of chain order lies between the two aforementioned cases. Importantly, the disorder due to the presence of PCBM can be reduced through thermal annealing, as shown by the enhanced vibrational substructure in Figure 2 (a). Spectroscopy of photoconductors fabricated under the same conditions (Figure S2 (b)) and IR transmission spectra (Figure S4) furthermore support this assessment.

Turning to the photoinduced absorption spectra, we only consider the results for blends with the as-cast RRa-variant and the two cases of rr-P3HT in the main text. Additional data can be found in the ESI. We note, that in contrast to earlier reports,^[20] it was not possible for us to detect a PIA signal for neat RRa-P3HT. We assume this to be due to a higher purity of our material, since defects are considered to be sites of exciton dissociation.

Figure 2 (b) depicts the three relevant spectra over the entire in-gap energy range. As introduced above, two distinct regions of absorption can be identified in the NIR and MIR spectral region. The amorphous RRa-P3HT:PCBM (Figure 1 (b) top) displays a

broad and featureless absorption peaking at 1.5 eV in the NIR (the signal magnitude in (b) was doubled to allow for a better comparison). In the low energy region, a PIA band forms around 0.5 eV, which is generally attributed to the intrachain polaron transition P_1 .^[20,25]

The two spectra involving rr-P3HT, on the other hand, display a more structured absorption in the NIR with one peak between 1.2 and 1.3 eV and another at 1.85 eV. Whilst $PCBM^-$ gives rise to an absorption at 1.23 eV, this signal is generally weak and eclipsed in blend with P3HT. The observed absorption band at this energy can thus safely be attributed to the P_2 transition of P3HT. In the MIR spectral region, no band forms around 0.5 eV for either sample, but both spectra display a broad and structured absorption at lower energy superimposed with aforementioned IRAVs.

A closer look at the respective normalised spectra, as given in Figure 2 (c), reveals that the maximum of the electronic transition shifts from approximately 0.1 to 0.08 eV upon annealing of the rr-variant. This trend agrees well with the propositions by the Spano group that predicted a red-shift in the MIR upon larger polaron delocalisation.^[22] A similar trend has also been observed upon increasing the molecular weight of P3HT chains.^[6] The simple polaron model introduced above assigns the strong absorption peaking around 0.1 eV to the delocalised interchain transition, whereas Figure 2 (b) shows the intrachain transition in this case to form as a shoulder between 0.3-0.4 eV (red-shifted due to a larger delocalisation along the backbone compared to RRa-P3HT, Figure 1 (b)). Whilst these assignments are in agreement with the emergence of the second polaron absorption peak at 1.85 eV – consequently identified as DP_2 transition^[20] – this discussion is oversimplified and the interplay of intra- and interchain polaron delocalisation contribute in a complex way to the shape of the electronic absorption band.^[22]

The close-up in (c) furthermore shows a finite, albeit weak, absorption band of the RRa variant between 0.1 and 0.2 eV underneath the strong IRAVs. This weak contribution is unexpected from the classical description and has recently been connected to a third

Table 1: Position of most relevant IRaVs for P3HT:PCBM as discussed in the main text

RRa		rr as-cast		rr annealed	
meV	cm ⁻¹	meV	cm ⁻¹	meV	cm ⁻¹
131.2	(1058)	129.6	(1045)	128.6	(1037)
138.0	(1113)	137.2	(1107)	136.7	(1103)
141.3	(1140)	139.1	(1122)	138.9	(1120)
		145.6	(1174)	145.6	(1174)
148.3	(1196)	147.3	(1188)	147.3	(1188)
158.1	(1275)	154.0	(1242)	153.7	(1240)
160.9	(1298)	156.4	(1261)	156.1	(1259)
172.0	(1387)	172.0	(1387)	172.0	(1387)

type of polaron transition termed P_0 .^[22]

In contrast to the extreme comparison between RRa- and rr-P3HT, considering the latter upon annealing allows to observe that the red-shift of the PIA spectra in the MIR is also accompanied by a blue shift of the NIR contribution for the annealed film (also consider Figure S3 for additional spectra in the NIR). As discussed above, the P_1 transition energy is considered to scale with the polaron reorganisation energy – a lower reorganisation energy in more crystalline samples leads to the observed trend and thereby underlines the descriptive power of the classical model.

As a side note, we also investigated the MIR signature of rr-P3HT when blended with the non-fullerene electron acceptor o-IDTBR. This material has recently attracted considerable attention since it outperforms the fullerenes in solar cells.^[2] The data is shown in Figure S3 for an as-cast film and compared with neat rr-P3HT as well as annealed rr-P3HT:PCBM (in p-type polymers, negative charges do not contribute to the photoinduced signature^[9]). The spectrum exhibits a maximum at low energy indicating highly ordered polymer chains and thereby proving the favourable morphology to be one reason for the attractive performance of this blend.

Finally, we consider the infrared active vibrations at low energy, as depicted in Figure 2

(d). Molecular vibrations give rise to a plethora of narrow features superimposed on the electronic contributions. Due to the interplay with the electronic background, these can manifest as peaks or as dips. Whilst some of them can be traced back to ground state modes, the distinct assignment to polaron related modes has recently been invoked for the most prominent features.^[1,18,26] Of the smaller features, some shift to lower energy (*e.g.* at 0.102 eV). This mode was previously identified as the =C-H out of plane bending mode in IR transmission and to be a strong indicator for the polymer conformation.^[4] In crystalline phases, this mode leads to an absorption at 101.7 meV (820 cm⁻¹) and in disordered phases the peak shifts to 103-104 meV (830-840 cm⁻¹). This trend is similarly observed in the transmission data given in Figure S4. The red-shift is thus attributed to the changes in the groundstate energetics of the polymer (values are given in Table 1). Notably, other modes remain unaffected by the polaron chain order, *e.g.* the indicated peak at 0.173 eV, which corresponds to another IR active mode of the ground state, whose position remains constant also in direct transmission. More importantly, all three depicted spectra include prominent peaks between 0.13 and 0.16 eV – the region predicted to contain the most prominent vibrational modes of P3HT polarons.^[26] All peaks of this class undergo a softening upon increasing the polaron delocalisation.

Concluding the data obtained for P3HT, we find a red-shift of the low energy absorption of the polaron upon slightly increasing the chain order. This observation is accompanied by a blue-shift in the NIR spectral region underlining the viability of the concept of the polaron reorganisation energy. IRAVs in the MIR can be divided according to their origin. Those related to the ground state behave according to the impact of chain conformation on the ground state mode, but a general softening is observed for modes attributed to the polaron for extended carrier delocalisation.

The neat DA polymer PCPDTBT (Figure 1 (c)) can form a partially crystalline film. In

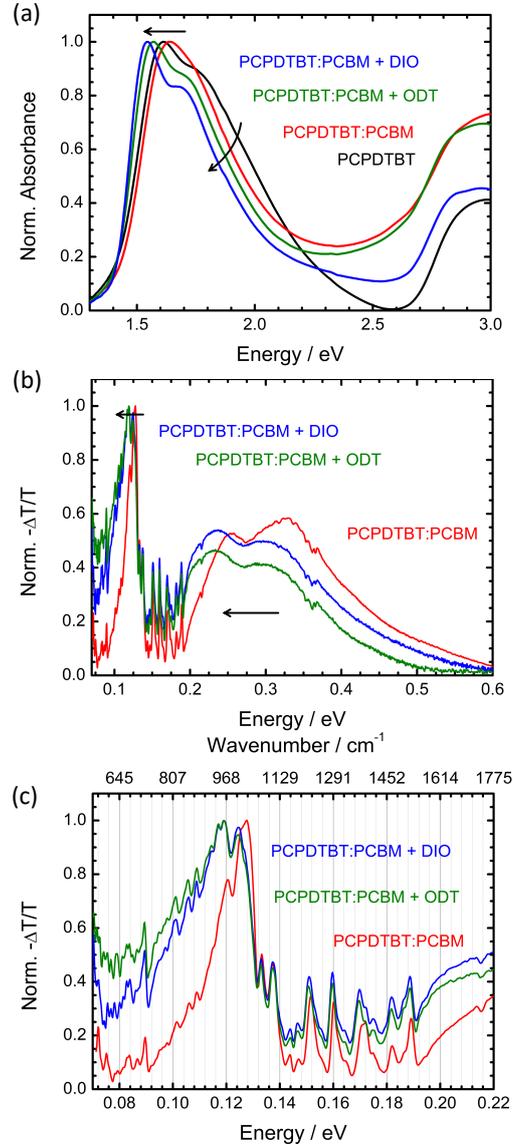


Figure 3: Crystalline films of PCPDTBT produce a red-shift of the low energy absorption band as well as a more pronounced vibrational substructure (a). The corresponding PIA spectra show similar polaron signatures for all samples (b), which shift to lower energy for more ordered films. A close-up of the low energy region indicates a softening also of the vibrational modes and a broad signal around 0.1 eV, associated with the DP_1 electronic transition (c).

presence of PCBM, however, the chains are highly disordered and films are considered amorphous.^[13] In contrast to P3HT, the degree of chain order can be affected through the addition of small amounts of solvents with a high boiling point, which selectively dissolve PCBM (most commonly 1,8-octanedithiol or 1,8-diiodooctane), instead of thermal annealing. Doing so leads to a high degree of chain conformation with a pronounced π -stacking of approximately 3.8 Å separation between the chains.^[13,23]

This alignment again manifests as a pronounced substructure in the absorption spectra.^[11] The relevant curves are plotted in Figure 3 (a), showing the two absorption bands typical for DA polymers around 1.6 and 3 eV. The low energy band is virtually unstructured for the amorphous PCPDTBT:PCBM film, but exhibits two subpeaks at 1.61 and 1.76 eV in the neat case. Film deposition with either additive also gives rise to this vibrational structure and shifts the subpeaks towards lower energy – thereby indicating an even higher degree of order than found for the neat film.

Figure 3 (b) displays an overview of the photoinduced spectra in the MIR region. As discussed before,^[18] the electronic P_1 transition of PCPDTBT:PCBM consists of a substructure already in the disordered film – illustrating the limits of applicability of the polaron scheme in Figure 1 (a). In absence of solvent additives, two broader peaks are found at 0.33 and 0.25 eV and a sharp peak forms around 0.12 eV in the region of IRAVs. The spectra obtained for films with either additive display a red-shift of the broader peaks to approximately 0.31 and 0.23 eV – the emergence of an identical signature for both additives also rules out the possible observation of signals from these molecules. Also the neat polymer exhibits the same energies (Figure S5).

Again, as for P3HT, the larger delocalisation, enabled by the greater crystallinity, leads to a reduction of what is commonly described as P_1 transition energy. It is striking, though, that the change in electronic signature is distinctly small – the shape remains largely unaffected and only shifts by approximately 0.02 eV. Given the formed extended

crystals in presence of additives, these results thus show that the polaron delocalisation is rather limited in this system and their spectral signature is mostly governed by partial alignment already found in the amorphous case.^[18] Nonetheless, the results confirm delocalisation to reduce the electronic transition energies of polaron's in the MIR.

Figure 3 (c) gives a close-up of the region below 0.2 eV containing the pronounced vibrational structure. In all cases, a strong absorption around 0.12 eV dominates the spectra. From our previous work, using DFT calculations, we know that polarons give rise to strong vibrational modes in this region.^[18] Importantly, also these vibrations shift to lower energy for more delocalised polarons in films processed with additives. This is in agreement with above observations for P3HT and calculations by Anderson *et al.*^[1] Notably, the extended polymer order also leads to an increased and broad absorption below 0.12 eV, which cannot be accounted for by a narrow vibrational mode. This effect is indicated by an arrow and supports our previous claim of an additional electronic contribution (DP₁) at this energy.^[18] Extended crystallinity leads to a larger signal at lower energy, which again proves the red-shift of this electronic transition.

Similar to P3HT above, many of the minor vibrational features manifesting as dips are not affected by the polaron delocalisation. The three peaks between 0.15 and 0.18 eV, however, exhibit a measurable red-shift as well (consider Table 2). Again, these modes have been attributed to polaron modes before.^[18]

Table 2: Position of relevant PCPDTBT:PCBM IRAVs affected by the polaron delocalisation. The energy is reduced for more crystalline films

no additive meV	cm ⁻¹	ODT meV	cm ⁻¹	DIO meV	cm ⁻¹
120.5	(972)	119.1	(961)	119.1	(961)
127.7	(1030)	124.5	(1004)	124.6	(1005)
151.6	(1223)	150.6	(1215)	150.9	(1217)
160.2	(1292)	159.7	(1288)	159.7	(1288)
171.7	(1385)	169.5	(1367)	169.8	(1370)

4 Conclusions

We investigated the photoinduced absorption spectra of two different conjugated polymers whilst varying the degree of chain order. We chose the greatly studied homopolymer P3HT and the prototypical donor-acceptor polymer PCPDTBT and their blends with the electron acceptor PCBM, for which the film morphology can be adjusted through post-deposition thermal annealing or through the use of solvent additives. A more crystalline morphology enables a larger delocalisation of the polaron leading to a significant red-shift of the electronic transition energy in the mid infrared spectral region (P_1 & DP_1). Simultaneously, polaron induced vibrational modes (IRAVs) furthermore undergo a softening for more delocalised charge carriers.

These investigations show the great power of using the low energy polaron signatures to identify and study the materials carrying the electric charge, as well as to study their local environment. MIR PIA spectra can thus not only be used as a fingerprint for specific polymers, but also offer information about the chain alignment in the vicinity of charge carriers.

The careful changes in chain conformation investigated here help to prospectively enable a more thorough understanding of the involved energy states that give rise to the observed transitions.

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