4 Monitoring Polarons in Narrow Band Gap Polymers

In this chapter, the photoinduced absorption (PIA) spectra of the prototypical donor-acceptor polymers C-/Si-PCPDTBT are investigated over a spectral range from 0.07 to 1.5 eV. Comparison of time dependent density functional theory (TD)DFT simulations of the electronic and vibrational transitions with the experimental results prove the observed features to be due to positive polarons delocalised on the polymer chains.

By computing the properties of charged molecular aggregates, it is furthermore shown that polarons not only delocalise in intra- but also inter-chain direction, leading to inter-molecular transitions, which correspond well to experimental absorption features at lowest energy.

4.1 Introduction

Photons absorbed by organic materials are commonly considered to generate bound Frenkel-excitons. Nonetheless, as discussed in section 2.2.5, charge carriers can be formed even in neat polymers. Given the low permittivity of organics, charge carriers undergo self-localisation, structural relaxations and polarisation mechanisms generally described in the framework of polaron theory. Similarly to the initially formed singlet excitons and further species, including e.g. triplets and charge transfer states, these polarons can be probed via optical experiments (consider section 2.2.3).

Doping- and steady-state photoinduced absorption spectra of conjugated polymers in the mid infrared spectral region were initially rationalised in the framework of the Hückel and Su-Schrieffer-Heeger (SSH) models, assigning observed transitions to long lived species, such as polarons or bipolarons. According to these models, charge carriers occupy states within the band-gap of the polymer and thereby give rise to additional transitions – two polaron absorptions (namely \( P_1 \) & \( P_2 \)) in the MIR and near-infrared (\( \approx 0.5-1.6 \) eV) spectral region, or one bipolaron.

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Calculations were carried out by Daniele Fazzi.

Bipolarons are defined as two interacting and spatially confined polarons with antiparallel spin.
4.2 Results and discussion

The two prototypical D-A polymers C-PCPDTBT and Si-PCPDTBT (or PSBTBT) were investigated here. The corresponding structure for the former is displayed in Figure 4.1 (b). Their only difference lies in the bridging atom of the two thiophene rings linked to the alkyl side-chains. For Si-PCPDTBT, a silicon atom is substituted for the carbon found in C-PCPDTBT. This substitution has a profound impact on the morphology. Even in blends with the electron acceptor PCBM, the Si-bridged polymer was shown to readily form crystalline aggregates, which the C-bridged variant does not, unless cast in presence of additives with a high boiling point. Both materials exhibit two absorption bands (vide Figure 4.2 (a)), one at high energy (HE) in the blue spectral region (peaking at 2.9 eV) and another at lower energy (LE) in the red spectral region (from 1.5 to 2 eV).

Figure 4.2 (b) depicts an overview from 0.07 to 1.5 eV of the photoinduced absorption for neat
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Figure 4.2: Absorbance spectra of neat C-/Si-PCPDTBT and their blends with PCBM (a). The vertical bars denote the energy used for the pump light. Overview of the PIA spectra for the investigated samples from 0.07 to 1.5 eV (b), displaying two distinct regions of photoinduced absorption and narrow infrared active vibrations.

Films of both polymers and when blended with PC$_{60}$BM upon excitation at 2.3 eV. All samples exhibit two distinct spectral regions of absorption: below 0.5 eV and above 0.8 eV. It is apparent that for both materials, the signals are stronger for the blends (black & blue curve) than for the respective neat polymer films (green & red). As these PIA bands will in the following be identified as being due to polaron absorption, this trend is consistent with the expected higher yield of charge carrier generation in presence of an electron acceptor. Nonetheless, the magnitude of generated charge carriers is already remarkably high for the neat polymers, given that it is commonly considered to be an inefficient process. Notably, the only spectral contribution due to addition of PCBM, is a weak absorption feature at 1.21 eV, assigned to its polaron absorption.

The two absorption regions for the Si-variant are farther separated than for the C-bridged variant, which can be associated with a higher reorganisation energy $\lambda$ in the latter, shifting the polaron energy level deeper into the optical band gap (consider Figure 2.10). This difference results from the presence of crystalline areas in the former.

For a comprehensive understanding of the photogenerated species, the electronic states possibly involved in the light induced processes were investigated through simulation at the density functional theory (DFT) and time dependent DFT ((TD)DFT) level. These species include neutral ($S_0$), polaron ($P$), bipolaron ($B$), triplet ($T$) and singlet excited ($S_n$) states. Since the employed steady-state measurements are mostly sensitive to long-lived species, only $S_0$, $P$ and $B$ will be discussed here. For a more thorough discussion on additional excitonic contributions, the reader is referred to the original publication.

The computed (TD)DFT Frank-Condon energies and absorption spectra of the different species for both polymers are depicted in Figure 4.3. As documented in literature, the transition energies are overestimated in the neutral case (compare with Figure 4.2), because of the finite
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The two main absorption bands of the neutral polymer chains (red), LE and HE, are assigned to the dipole active $S_1$ and $S_8$ states. Analysis of the electron-hole density difference between excited and ground state (Fig. 4.4 left) reveals $S_1$ having a Frenkel-like exciton character, while $S_8$ is more delocalised, thus giving rise to a lower electron-hole binding energy. In particular, the HE state of Si-PCPDTBT has a more pronounced spatial separation of the electron-hole density distribution than that of C-PCPDTBT, presumably leading to a more efficient charge generation upon direct photoexcitation, as will be discussed below.

Polarons and bipolarons are here simulated as charged species. Both positive (hole) and negative (electron) were considered. Nonetheless, given the strong similarities of the experimental PIA spectra in presence and absence of PCBM, only the positive cases will be discussed here. For both C- and Si-PCPDTBT, polarons and bipolarons are predicted to show similar absorption spectra in the region below the fundamental gap, with intense transitions around 0.5-0.9 eV and 1.3-1.5 eV. This observation is in agreement with in-situ spectroelectrochemistry investigations that reported a broad region of absorption of PCPDTBT radicals in the NIR. These transitions are consequently assigned to the two absorption regions observed in the experimental results reported in Figure 4.2 (b). An important difference can be seen in the region from 1.3 to 1.5 eV. Calculated polarons exhibit two transitions in this spectral range, leading to an asymmetric absorption band, as seen in the experimental spectra of neat C- and Si-PCPDTBT. Contrarily, bipolarons present only one electronic transition in that energy region. At this point it is worth noting that bipolarons are classically considered to allow only one transition below the optical-gap ($B_1$ in Figure 4.1), but the computations reveal at least two active optical transitions (at 0.9 eV and 1.5 eV).

The experimental absorption bands at 0.9 and 1.3-1.5 eV for neat polymers are assigned to polaron transitions, which is in accordance with results from ESR studies on blends of these polymers.

Figure 4.3: Calculated (TD)DFT vertical transition energies and absorption spectra for neutral, polaron- as well as bipolaron- C-PCPDTBT (a) and Si-PCPDTBT (b).
with PCBM.\[20\] Further evidence for the presence of polarons instead of bipolarons is presented below. The experimentally observed and theoretically calculated splitting of this higher transition is not predicted by the traditional models for polaron absorption (as shown in Figure 4.1) and further PIA investigations on D-A-polymers are required to show whether this is a general feature or specific to the PCPDTBT structure.

In a next step, the effects of aggregation and inter-molecular interactions were investigated by DFT and (TD)DFT calculations on model-dimer aggregates. Aggregates with oligomers of different size were fully optimised for three different cases: 1) neutral, 2) singly charged, i.e. one polaron over the aggregate, and 3) doubly charged, i.e. two polarons over the aggregate.

Within the limits of the models and the computations (e.g. finite size, no medium effects, choice of the DFT functional), the low-energy transition ($P_1$) is assigned to the band experimentally observed around 0.3 eV (Figure 4.2 (b) or 4.5 (a)). This energy is overestimated in the calculations, but an increase in the system size (number of repetition units per chain) shifts the predicted energy of the $P_1$ transition to lower values, around 0.6 eV (consider Table A1).

Similar values were found before in other reports on C-PCPDTBT,\[19,21\] but the apparent difference in energy to the experimental data has hitherto not been discussed. For a comparison, calculations using standard hybrid GGA DFT functionals (e.g. B3LYP) were furthermore performed. They predict the $P_1$ transition at lower energy (ranging from 0.3 to 0.5 eV, depending on the oligomer size) than the one obtained with the ωB97X-D functional (0.6 eV). This better agreement of the hybrid GGA predictions is, however, considered to be fortuitous in view of the well-known general problems of hybrid GGA functionals in describing the excited and charged states of extended, narrow band gap, π-conjugated systems.\[17\] In contrast, range-separated XC functionals offer a reasonably balanced description of all these excitations at the DFT level, though they tend to overestimate the transition energies.\[22\] This latter deficiency can in part also be related to the important polarisation and outer-sphere reorganisation effects which are not accounted for in the calculations.

A close look at the low-energy region (\textit{vide} Fig. 4.5 left) reveals the broad absorption band at 0.3 eV to have an inflection point and to consist of two subbands at 0.3 and 0.22 eV (especially visible for C-PCPDTBT). Bipolarons can again be excluded to contribute significantly to the experimental spectra, since their predicted first electronic transition ($B_1$, in Fig. 4.3) lies at even higher energies than the polaron $P_1$ transition. Negative polarons, with their lower lying $P_1$ transition, could be responsible, but, as stated above, this is improbable in presence of PCBM. In contrast, the broad band is considered to be due to positive polarons only and the shoulders to be caused by an interplay of delocalisation, structural disorder and interactions of the polarons with their environment as previously discussed by Pochas and Spano in case of P3HT.\[23,24\]

Figure 4.4 (b) reports the low-energy transitions for singly charged C-PCPDTBT model dimers (\textit{i.e.} two chains, each comprising four monomers). For such molecular model aggregates, a
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Figure 4.4: Electron-hole density difference between excited and ground state for the $S_1$ and $S_8$ singlets, the first polaron- ($P_1$) and bipolaron ($B_1$) transition, corresponding to Figure 4.3 (a). The $S_8$ wavefunctions are spread over the entire oligomers with two side lobes for Si-PCPDTBT, whereas the $S_1$ transitions lead to a more confined wavefunction (indicated by the dashed line). Computed vertical transitions for a singly charged model-dimer of C-PCPDTBT (b). The $P_1$ transition is polarised along the chain axis (X). The $DP_1$ transition is polarised along the packing axis (Z). The spin density distribution is reported in grey.

splitting of the low-energy transition is computed, leading, additionally to the $P_1$ band (intra-molecular transition, localised on a single chain), to a so-called $DP_1$ band (delocalised inter-molecular transition). $DP_1$, predicted at 0.62 eV, is delocalised over the aggregate and polarised in the stacking direction (Z), while $P_1$ (at 0.72 eV) is localised on a single chain and polarised along the intra-molecular axis (X). The polaron spin density distribution is also reported in Figure 4.4 (b), displaying a delocalisation over the entire aggregate. The computed oscillator strength of the low-lying $DP_1$ transition in this model is rather low ($f=0.05$), but believed to be due to the reduced size of the molecular cluster limiting spin delocalisation. Nevertheless, this minimal model-dimer suffices to show that the local molecular packing and aggregation give rise to a splitting of the low-lying polaron transitions with an additional inter-chain component.

The comparisons between experimental and theoretical results thus allow for assigning all photoinduced absorption bands to polaron electronic transitions, which are either inter-molecularly delocalised (0.1 eV, namely $DP_1$) or intra-molecularly localised (0.3 ($P_1$) and 0.9-1.5 eV ($P_2$)). It is noteworthy that earlier works on P3HT, always related the inter-chain species to crystallites, whereas, as shown here (with the amorphous C-PCPDTBT), locally aligned chains seem to suffice to generate inter-chain polarons.

Turning to a closer look at the narrow features in the MIR, Figure 4.5 (a) depicts the transmission and PIA spectrum of C-PCPDTBT up to 0.4 eV. The former displays two main regions of vibrations, namely around 0.36 eV, evoked by CH$_x$ stretch vibrations, mostly of the side chains, and from 0.14 to 0.2 eV, due to stretch vibrations involving heavier atoms, as well as due to bending modes. None of the narrow features in the PIA spectrum are due to noise of the measurement, but instead so-called infrared active vibrations (IRAVs). These IRAVs are also found in both aforementioned energy regions, thus underlining their origin as being due to molecular vibrati-
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Figure 4.5: Transmission and MIR PIA of neat PCPDTBT (a) and the comparison for both variants with the calculated vibrational spectra of polarons (b). The IRAVs, especially in the region below 0.12 eV, are due to the infrared activation of previously silent modes when in proximity of an electric charge carrier.

 ons. While charge-induced shifts in resonant frequency of the modes observable in transmission could explain some of the minor features, the high oscillator strength, especially for energy lower than 0.2 eV, is explained by a different mechanism. Namely, IRAVs can be rationalised in the framework of the amplitude mode (AM) or the effective-conjugation-coordinate (ECC) theory. In these frameworks, movements of charge carriers along the polymer backbone generate a changing electric field and thereby affect the polarisability of bonds therein. This can lead previously IR silent modes to become strongly IR active.

Additionally, Fano resonances can occur when the narrow molecular vibrations energetically coincide with the broad electronic $P_1$ band (also consider Chapter [8]).

For both polymers, the vibrational spectra of the positive and negative polaron and the bipolaron species were calculated. In accordance with the analysis above, good agreement with the experiments was again obtained for positive polarons (vide Figure 4.5 (b)). For energy lower than 0.16 eV, vibrational features are predominantly explainable by IR active modes of the polarons. The strong peaks at 0.12 eV are related to the C=C/C-C stretching/shrinking oscillations along the polymer chain. In the framework of the AM and ECC theories, these oscillations become IR active and feature a high intensity for charged species.

For energy larger than 0.16 eV, the calculated, unlike the experimental, features become weaker. It is worthwhile to note that the simulations do not take possible Fano resonances or aggregation effects into account. Fano resonance seems responsible especially for the 0.18 eV (1500 cm$^{-1}$) feature, which, for both polymers, coincides with the onset of the $P_1$ absorption band.

In the following, the generation of free charge carriers in these polymers will be addressed. Most considerations for charge carrier generation in neat polymers published so far dealt with homopolymers, but the dominant generation mechanisms in D-A-polymers might be significantly different (vide e.g. Ref. [30] and references therein). As hinted by Tautz et al., the D-A groups might
lead to excitons with inhomogeneous distributions of their electron and hole wavefunction (i.e. with partial charge-transfer character, similar as shown in Figure 4.4 (a)) that could facilitate exciton dissociation. The impact of different excitation energy, namely 2.75, 2.3 and 1.95 eV (as indicated in Figure 4.2 (a)), is shown in Figure 4.6. There are pronounced differences between the spectra of blended and neat C-PCPDTBT in (a). While the signal is independent of the excitation energy for the blend (corresponding to the flat IQE seen in most solar cells), there is a big dependence for the neat polymer. Using 1.95 eV, only a vanishingly small signal is observed. This behaviour can be traced back to the calculated $S_1$ and $S_8$ electron-hole density differences reported in Figure 4.4 (corresponding to the LE and HE absorption). The HE state shows a more delocalised (consider the unoccupied benzothiadiazole end-groups for both oligomers in $S_1$), hence less strongly bound, exciton which can more easily dissociate into polarons. These results thus provide evidence that the generation of free charges in neat D-A-polymers can be enhanced by the formation of delocalised excitons with inhomogeneous spatial distribution as a precursor state. For Si-PCPDTBT in (b), excitation at lower energy generates a larger signal than found for C-PCPDTBT. Interestingly, the signal magnitude is not as similar in the blend as observed for the C-variant. It has to be noted, though, that this might be due to changes in pump-intensity, since the set-up did not allow to fully control the overlap of pump and probe beam.

4.3 Conclusion

In conclusion, the photoinduced absorption spectra of C- and Si-PCPDTBT in neat films and blends with PCBM were investigated, and experimental results were compared with DFT and (TD)DFT simulations. In the NIR, both polymers exhibit a split band stemming from the higher transitions of positively charged intra-chain polarons – an observation not accounted for

![Figure 4.6: Comparison of MIR PIA spectra of neat (top) PCPDTBT (a) and Si-PCPDTBT (b) and their respective blends with PCBM (bottom). Low energy excitation of PCPDTBT gives rise to a significantly lower polaron yield.](image-url)
in standard discussion of polarons in homopolymers. Crucially, positive inter- and intra-chain polarons are generally responsible for observed signals, already in neat polymers without the addition of an electron acceptor. The presence of inter-chain delocalised polarons in amorphous samples of C-PCPDTBT furthermore extends previous reports claiming that a high crystallinity was necessary for these to form. The computations reproduce a transition polarised perpendicularly to the chain backbone for oligomer aggregates as opposed to single chains. Electronic absorption bands for the Si-bridged variant in the MIR are found shifted to lower energy, which is attributed to the reduced reorganisation energy in presence of a more crystalline morphology. For blends with PCBM, the spectral features remain unaffected in position, but become significantly stronger, especially in the MIR. In contrast to neat C-PCPDTBT, the signal strength is virtually independent of the excitation energy, which is rationalised with a farther delocalised singlet exciton formed upon high-energy excitation facilitating the subsequent electron-hole dissociation.

Compared with homopolymers, concepts such as the delocalisation in intra- and inter-chain direction seem still applicable, but for D-A polymers especially the NIR signals in PCPDTBT-variants are more complex than reported for previously studied systems.
4.4 Methods

**Sample preparation:** Thin films were drop- or spin-cast (CB for C-PCPDTBT and oDCB for Si-PCPDTBT, both at 20 mg/mL) on ZnSe platelets in a glove box. The spinning speed was around 1200 rpm, which led to thicknesses of approximately 150 nm.

**MIR PIA:** The samples were then mounted into a cryostat without being exposed to air and positioned in the beam path of a Bruker Vertex 70 FTIR spectrometer. The beam passes two ZnSe windows and is detected using a liquid nitrogen cooled MCT detector. For the MIR, a KBr beamsplitter was employed and exchanged with quartz for the NIR. The samples were cooled down to 77 K and positioned under 45° to allow for the pump light to be sent through an additional quartz window. To avoid perturbations by the pump light, a filter was furthermore placed (Ge for the MIR and an appropriate long pass quartz filter in the NIR) in front of the detector. Spectra were acquired with a resolution of 5 cm\(^{-1}\) in the MIR (10 cm\(^{-1}\) in the NIR) and the following cycle was run at least 512 times: first, the pump was switched on followed by a delay of 1.5 s to establish equilibrium, which was then followed by a 16-fold averaging of the "light on" spectrum. Next, the light was switched off, followed by another 1.5 s delay and 16 co-additions for the "light off" spectrum were carried out. The "light off" spectrum was also used as transmission measurement.

**Calculations:** DFT and (TD)DFT calculations were performed using the range-separated \(\omega\)B97X-D functional, with inclusion of Grimme's dispersion corrections, with double and triple split Pople basis set with diffusion functions (6-31G* and 6-311G*). Restricted and unrestricted DFT calculations were carried out for the neutral ground state (\(S_0\)), singlet excited states (\(S_1\) and \(S_8\)), the lowest triplet state (\(T_1\)) and charged electronic states (\(\pm 1, \pm 2\)) respectively. Geometries were optimised without constraints in each electronic state considered. Equilibrium geometries were characterised by evaluating the Hessian matrix. For charged species (\(\pm 1, \pm 2\)), whenever an instability in the wavefunction was encountered, the geometries were fully relaxed for the lowest UDFT-BS solution. IR vibrational spectra and optical transitions were evaluated for each species at the optimised equilibrium geometry. Intra-molecular properties were evaluated for C- and Si-PCPDTBT oligomers with four and eight repeat units (\(n=4, 8\)), with their alkyl chains replaced by methyl groups. Inter-molecular properties were evaluated for model dimers built from \(\pi\)-stacked oligomers. Different dimer models were considered, namely: pairs of two-, three-, and four-unit oligomers. For each aggregate, neutral and charged (\(\pm 1, \pm 2\)) electronic states were considered at the DFT, UDFT, and UDFT-BS levels. Electronic transitions were evaluated at the (TD)DFT and/or (TD)UDFT-BS level.
Bibliography


