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Polarons in Narrow Band Gap Polymers Probed over the Entire Infrared Range: A Joint Experimental and Theoretical Investigation

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S Supporting Information

ABSTRACT: We investigate the photoinduced absorption (PIA) spectra of the prototypical donor–acceptor polymer [2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (C-PCPDTBT) and its silicon bridged variant Si-PCPDTBT over a spectral range from 0.07 to 1.5 eV. Comparison between time-dependent density functional theory simulations of the electronic and vibrational transitions of singlet excitons, triplet excitons, polarons, and bipolarons with the experimental results proves that the observed features are due to positive polarons delocalized on the polymer chains. We find that the more crystalline Si-bridged variant gives rise to a red-shift in the transition energies, especially in the mid-infrared (MIR) spectral range and furthermore observe that the pristine polymers' responses depend on the excitation energy. Blending with PCBM, on the other hand, leads to excitation-independent PIA spectra. By computing the response properties of molecular aggregates, we show that polarons are delocalized in not only the intra- but also the interchain direction, leading to intermolecular transitions which correspond well to experimental absorption features at the lowest energies.

Photons absorbed by organic materials commonly generate bound excitations which, in order to dissociate (e.g., in organic solar cells), require an energy offset that facilitates the splitting into free electrons and holes. Whereas in the simplest picture this involves a diffusion toward an interface (often between polymer and fullerene phases),^{1,2} it has also been shown that long-range electron transfer, i.e., not involving diffusion processes, can lead to the formation of free carriers.² Given the low permittivity of organic materials (typically in the range of 2–4) the presence of charges leads to self-localization, structural relaxations, and polarization mechanisms generally described in the framework of the polaron theory.³ Similarly to the initially formed singlet excitons and further species (including e.g. triplets and charge transfer states), polarons may be probed via optical experiments.^{4,5}

Investigations of the photoinduced mid-infrared (MIR, ≈ 400 – 4000 cm^{-1}) response of semiconducting polymers date back to the 1980s.^{6–9} The MIR spectra were rationalized in the framework of the Hückel and Su–Schrieffer–Heeger (SSH) models,^{7,10} 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 P1 and P2) in the MIR and near-

infrared (NIR, ≈ 4000 – $12\,500\text{ cm}^{-1}$) spectral region, or one bipolaron transition (named BP1 or B1) in the NIR as depicted in Figure 1a. Despite several approximations, these schemes remained the picture of choice for analyzing photoinduced absorption (PIA) spectra in the MIR region for a long time. Only recently, an alternative scheme for the states occupied by charged species was proposed first for molecular semiconductors¹¹ and subsequently for conjugated polymers (Figure 1).¹²

All aforementioned models, however, account for only single-chain processes (i.e., intrachain), thus neglecting the possibility of interchain mechanisms. Around the year 2000, the effect of interchain delocalization on the PIA spectra of poly-3-hexylthiophene (P3HT) aggregates and crystallites was investigated.^{4,13,14} It was reported that upon increasing the head-to-tail ratio in the polymer chains, i.e., from regiorandom (RRa-) to regioregular (RR-) P3HT, signals at lower energies emerged, which were attributed to interchain delocalized polarons (or “charge-transfer like” transitions). Still, P3HT is a homopolymer, whereas state-of-the-art polymers in organic

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Figure 1. Traditional scheme for energy levels of a neutral state, positive polaron, bipolaron, and delocalized polaron (refs 4 and 7,) with optically allowed transitions (a). For polarons, the recently proposed scheme (ref 12) offers different states and occupations but leads to similar transitions below the S_1 energy (b).

Figure 2. Normalized absorption spectra of pristine C/Si-PCPDTBT and of blends with PCBM (left). The vertical bars denote the wavelengths used for the pump light. Overview of the PIA spectra for the investigated samples from 0.07 to 1.5 eV (right). The molecular structure of the polymers is depicted in the inset.

electronics, photovoltaics in particular, commonly include electron donor and acceptor (D–A) functional units. Such D–A polymers (also called “push–pull polymers”) might thus lead to different photophysical and polaron properties.

We deem it important to stress that to our knowledge no reports to date considered photoinduced signals of D–A polymers at energies lower than ~ 0.4 eV; this region is expected to contain the lower polaron transition as well as the molecular vibrations, hence also offering useful insights into the structural properties of the materials.

In this work, we examine the spectral region below ~ 0.4 eV and monitor the more easily accessible NIR of the prototypical narrow band gap polymer [2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (C-PCPDTBT),^{15–18} its silicon bridged variant Si-PCPDTBT (also named PSBTBT), and their blends with the fullerene derivative PC₆₀BM by using a Fourier transform infrared spectrometer. Density functional theory (DFT) and time-dependent DFT ((TD)DFT) computations, in their restricted (R) and unrestricted (U) broken symmetry (BS) formulations, were performed to obtain insights into the photoinduced electronic states generated in pristine polymers and to identify fingerprints of polaronic species via electronically and vibrationally induced transitions.

We find that positive polarons are largely responsible for our spectroscopic findings in pristine polymer films as well as in

blends. We rule out possible further species (bipolarons, triplet excitons, negative polarons) by comparison with the vibrational and electronic DFT/(TD)DFT computed transitions. We furthermore reveal that the concomitant lower reorganization energy shifts the polaron MIR absorption to smaller energies for the more crystalline Si-PCPDTBT and show that polymer:PCBM blend spectra are independent of the excitation energy, which is contrary to pristine C-PCPDTBT in particular.

By predicting and observing two photoinduced absorption bands in the NIR, we also show that the traditional framework used to explain polaron transitions does not fully cover phenomena in the hitherto not considered class of D–A polymers. Investigating the structural- and response properties of charged (i.e., polaron and bipolaron) polymer aggregates, we furthermore observe that the unrestricted DFT broken-symmetry scheme is necessary to reasonably describe the electronic and vibrational transitions, an issue to our knowledge not raised before in the literature.

Both investigated polymers exhibit two absorption bands (Figure 2, left), one at high energy (HE) in the blue spectral region (peaking at 415 nm) and another at lower energy (LE) in the red spectral region (from 600 to 800 nm). The Si-bridged polymer has been shown to form crystalline aggregates, which the C-bridged polymer does not,^{19–21} unless it is cast in the presence of additives.^{22,23} In our PIA experiments we

Figure 3. Computed (TD)DFT vertical transition energies and absorption spectra for neutral (red, DFT), polaron (blue, UDFT), and bipolaron (green, UDFT-BS) on C-PCPDTBT (left) and Si-PCPDTBT (right) (DFT, ω B97X-D/6-311G*).

Figure 4. Electron–hole density difference between excited and ground state for the S_1 and S_8 singlet states; the first polaron (P1) and bipolaron (B1) transition corresponding to Figure 3. The S_8 wave functions are spread over the entire oligomers with two side lobes for Si-PCPDTBT, whereas the S_1 transitions lead to a more confined wave function (indicated by the dashed line). Computed ((TD)-UDFT-BS, (ω B97X-D/6-311G*)) vertical transitions for a singly charged model-dimer (right). The P1 transition is polarized along the polymer axis (x). The DP1 transition is polarized along the packing axis (z). The spin density distribution is reported in gray.

selectively excite either the HE or LE band, as indicated in Figure 2.

The right-hand panel of Figure 2 depicts an overview from 0.07 to 1.5 eV of our measurements of the different samples using a 532 nm pump wavelength. All samples exhibit two distinct spectral regions with pronounced signals: below 0.5 eV and above 0.8 eV. Comparing the spectra of the C- and Si-PCPDTBT polymers blended with PCBM (black and blue lines, respectively), we observe that the signals for the blends are stronger than those for the respective pristine polymers (green and red line). Because we show below that the observed features are predominantly due to polaron absorption, this is consistent with the expected higher charge generation yield in the presence of an electron acceptor. Nonetheless, the magnitude of charge generation in the pristine polymer is already remarkably high. In the blends, the weak absorption feature at 1.21 eV is assigned to the electronic transitions of the PCBM polaron, which we will not further discuss in this work.²⁴

The two absorption regions for the Si-bridged variant are more separated than those for the C-bridged variant, which can be associated with a higher reorganization energy, λ , in the latter shifting the polaron energy level farther into the optical gap. We attribute this difference to the absence of crystalline areas in C-PCPDTBT.

For a comprehensive understanding of the photogenerated species, we investigated the electronic states possibly involved in the light-induced processes, namely, neutral (S_0), polaron (P), bipolaron (B), triplet (T), and singlet excited (S_n) states at the DFT and (TD)DFT level. Herein, only the S_0 , P, and B

species are discussed, while a full comparison among all electronic states for each polymer is reported in the Supporting Information (e.g., Figures S5–S7). Figure 3 displays the comparison between the computed (TD)DFT vertical transition energies and absorption spectra of the different species for both polymers. As documented in the literature,^{25,26} the transition energies are expected to be overestimated in the neutral case because of the finite size of the oligomer examined (i.e., four repeat units) and the choice of the exchange–correlation DFT functional (i.e., the range-separated ω B97X-D).²⁷ The use of a range-separated functional here is motivated and justified by the need for a balanced description of localized, delocalized, charge transfer, and charged excitations in extended organic π -conjugated materials.^{28,29}

The two main absorption bands of the neutral polymer chains (red line, Figure 3), 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 (Figure 4, left) reveals that S_1 has a Frenkel-like exciton character, while S_8 is more delocalized (i.e., lower electron–hole binding energy).³⁰ In particular, the HE state of Si-PCPDTBT has a spatial separation of the electron–hole density distribution that is more pronounced than that of C-PCPDTBT, presumably leading to a more efficient charge generation upon direct photoexcitation (vide infra). Polarons and bipolarons are here simulated as charged species. Both positive (hole) and negative (electron) cases were considered, and for a full comparison of their properties we refer the reader to the Supporting Information. In the text of this Letter, we report the results only for positively charged species. The polarons are well-

Figure 5. MIR PIA of the pristine polymers displaying the red-shift of the electronic bands for the Si-bridged polymer (left). The IRAs are largely identical, as can be seen from the comparisons with the experimental curves (middle and right). The polaron species (blue curves) are described at the UDFT level (ω B97X-D/6-311G*).).

described by an unrestricted UDFT treatment, leading to $\langle S^2 \rangle$ values of 0.8 (small spin contamination). In the bipolarons, however, we found the UDFT solution to be unstable, because the unrestricted broken-symmetry (UDFT-BS) solution has a lower energy leading to a stabilization energy ($\Delta E = E(\text{UDFT-BS}) - E(\text{UDFT})$) of about -0.7 eV (i.e., -16 kcal/mol). In UDFT-BS, α ($\uparrow$) and β ($\downarrow$) spin densities are allowed to separately relax and localize over different atomic centers leading to the physical representation of a bipolaron, i.e., two interacting and spatially confined polarons with antiparallel spin.³ The longer the oligomer, the more stable the UDFT-BS solution (Table S4). This is a fundamental point, to our knowledge never raised before in the literature of D–A polymers but crucial to reasonably predict the spectroscopic properties of polarons and bipolarons in extended π -conjugated systems at the DFT level. UDFT-BS solutions are common for systems featuring an inherently multiconfigurational character, for example, biradicals or low-lying energy triplet states.^{31–34} In such cases, multiconfigurational wave function-based methods would be more appropriate to describe the electronic structure; however, they are too computationally expensive to be applied here, while UDFT-BS represents a good compromise between accuracy and feasibility.

For both C- and Si-PCPDTBT, polarons and bipolarons are predicted to show similar absorption spectra in the low-energy region, with intense transitions around 0.5 – 0.9 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.³⁵ These transitions can be assigned to the absorption bands observed in the experimental results reported in Figure 2. An important difference can be seen in the spectral region from 1.3 to 1.5 eV. In fact, polarons exhibit two transitions in this spectral range, leading to an asymmetric absorption band, as seen in the experimental spectra of pristine C- and Si-PCPDTBT. In contrast, bipolarons present only one electronic transition in that energy window (Figures S4 and S5). At this point it is worth noting that bipolarons are thought to allow only one transition below the optical-gap (B_1 in Figure 1), but computations reveal at least two optically active transitions (at 0.9 and 1.5 eV). On the basis of (TD)UDFT-BS calculations, these transitions mainly involve frontier single occupied/unoccupied orbitals. Further insights into the nature of bipolaron transitions in the frame of donor–acceptor polymers will be the subject of future in-depth studies.

We assign the experimental absorption bands at 0.9 and 1.3 – 1.5 eV for pristine polymers to polaron transitions, which is in accordance with results from ESR studies on blends of these polymers with PCBM.³⁶ Further evidence for the presence of polarons instead of bipolarons is presented below. At this point we stress that the observed splitting of this higher transition is not predicted by the traditional models for polaron absorption (vide supra), and further PIA investigations on D–A polymers are required to show whether this is a general feature or specific to the PCPDTBT structure.

The effects of aggregation and intermolecular interactions were investigated by DFT and (TD)DFT calculations on model-dimer aggregates. Aggregates with oligomers of different sizes (Table S4) were fully optimized 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. UDFT-BS solutions were checked for each case.

Within the limits of the models and the computations (e.g., finite size, no medium effects, choice of the DFT functional), we believe that the low-energy transition (P1) can be assigned to the band experimentally observed around 0.3 eV (Figure 2). This energy is overestimated in our calculations; however, as shown in Table S2, an increase in the system size (number of repetition units per chain) shifts the predicted energy of the P1 transition to lower values, around 0.6 eV. We note that similar values were found before by other authors for C-PCPDTBT,^{35,37} but the apparent difference in energy compared to the experimental data has hitherto not been discussed.

We furthermore performed calculations using standard hybrid GGA DFT functionals (e.g., B3LYP, Figure S10), which predict the P1 transition at lower energies (ranging from 0.3 to 0.5 eV, depending on the oligomer size) than the one obtained with the ω B97X-D functional (0.6 eV). We consider the better agreement of the hybrid GGA predictions 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.²⁷ 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.²⁸ This latter deficiency might also be related to polarization and outer-sphere reorganization effects which are so far not accounted for. We sought to take the dielectric relaxations into account by employing a polarizable continuum model (PCM), but we did not find a significant energy shift. Possible strategies for a

quantitative investigation may involve the use of quantum mechanics–molecular mechanics approaches³⁸ which are currently under investigation in our group.

A close look at the low-energy region (Figure 5, left) reveals that the broad absorption band at 0.3 eV has an inflection point and consists of two subbands at 0.3 and 0.22 eV (especially visible for C-PCPDTBT). We can exclude bipolarons from contributing significantly to our experimental spectra because their predicted first electronic transition (named B1, in Figure 3) lies at energies even higher than the polaron P1 transition. Negative polarons, with their lower-lying P1 transition, could be responsible (Figure S7), but this seems improbable in the presence of PCBM. In contrast, we believe, in accordance with Pochas and Spano,^{39,40} that the broad band is due to positive polarons only and the shoulders are caused by an interplay of delocalization, structural disorder, and interactions of the polarons with their environment.

The right-hand panel of Figure 4 reports the low-energy transitions for singly charged C-PCPDTBT model dimers (i.e., two chains each comprising four monomers; see Tables S2 and S3 for further model dimers and a comparison between singly and doubly charged dimers). For such molecular model aggregates, a splitting of the low-energy transition is computed leading, in addition to the P1 band (intramolecular transition, localized on a single chain), to a so-called DP1 band (delocalized intermolecular transition). DP1, predicted at 0.62 eV, is delocalized over the aggregate and polarized in the stacking direction (*z*), while P1 (at 0.72 eV) is localized on a single chain and polarized along the intramolecular axis (*x*). The polaron spin density distribution is also reported in Figure 4, displaying a delocalization over the entire aggregate. The computed oscillator strength of the low-lying DP1 transition in our model is rather low ($f = 0.05$); we believe that this can be traced back to the reduced size of the molecular cluster, which limits spin delocalization. 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.

The comparisons between experimental and theoretical results allow us to assign all the absorption bands observed around 0.1, 0.3, 0.9, and 1.3–1.5 eV to polaronic transitions, which are intermolecularly delocalized (0.1 eV, namely DP1) or intramolecularly localized (0.3 (P1) and 0.9–1.5 eV). We note that earlier works, e.g., on P3HT, always related these interchain species to crystallites, whereas we show (with the amorphous C-PCPDTBT) that in contrast to extended crystallinity, locally aligned chains seem to suffice to generate interchain polarons.

We now turn to a closer look at the MIR signals and the differences between C- and Si-PCPDTBT. The left-hand panel of Figure 5 depicts the PIA spectra of both pristine films up to 0.5 eV. There are two possible origins for the narrow IRAVs: either IR activation of Raman modes or Fano resonance effects (none of the narrow lines below 0.2 eV are due to noise, as can be seen from the signal-to-noise ratio for 0.2–0.5 eV).⁴¹ Most IRAVs can be explained in the framework of the amplitude mode (AM) or the effective conjugation coordinate (ECC) theory: movements of charges along the polymer backbone affect the bond length, the polarizability of bonds changes due to the electric field, which in turn can lead to previously IR-silent modes becoming IR active.^{42–45} For Fano resonance to occur, two absorption processes need to energetically coincide: a broad background (in this case the electronic transition) and

a narrow line superimposed. As reported previously, the narrow vibrations of the polymers can lead to strong Fano resonance peaks.⁴⁴ Comparing the two polymers, we find that their vibrational features are largely identical (Figure 5, left), which is in accordance with their similar molecular structure. Minor differences around 0.17 eV probably arise due the substitution of C by Si. For both polymers, we computed the IR spectra of the positive and negative polaron (UDFT) and the bipolaron (UDFT-BS) species. Details are reported in Figures S11–S13. Good agreement between calculations and experiments is obtained for the case of the positive polaron for both polymers (Figure 5, right; 0.12 eV region). For energies 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 and 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.

Notably, the detected IRAV signals (0.07–0.18 eV) can be reproduced neither by UDFT-BS calculations representative of bipolarons nor by UDFT and (TD)DFT calculations on the triplet (T_1) and the singlet (S_1) excited state (Figures S11 and S12). This point further strengthens the conclusion that polaronic species are probed. As mentioned above, we also calculated the spectrum of the anion (as displayed in Figure S14) but found no agreement with the experimental data. This might be rationalized by the negative charges being localized on molecular defects rather than moving along the polymer chains. At energies higher 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 mechanisms or aggregation effects into account. Fano resonance could be responsible especially for the 0.18 eV ($\approx 1500\text{ cm}^{-1}$) feature, which for both polymers coincides with the onset of the P1 absorption band (Figure S4).

In the following, we address the generation of free charges in these polymers. Most considerations for charge generation in pristine polymers so far dealt with homopolymers,⁴⁶ but the dominant generation mechanisms in D–A polymers might be significantly different (e.g., see ref 42 and references therein). As indicated by Tautz et al., the D–A groups might lead to excitons with inhomogeneous distributions of their electron and hole wave function (i.e., with partial charge-transfer character) that could facilitate exciton dissociation.^{37,47} We investigated the PIA spectra using different excitation wavelengths, namely 450, 532, and 635 nm as indicated in Figure 2. As shown in Figure S14, there are pronounced differences between the spectra of blended and pristine C-PCPDTBT. Whereas the signal is independent of the wavelength for the blend (corresponding to the flat IQE seen in most solar cells),⁴⁸ there is a big dependence for the pristine polymer. We find a significantly higher signal when exciting with blue light than with green light, and at 635 nm we observe a vanishingly small signal. A similar trend may be observed for Si-PCPDTBT in Figure S15, where excitation in the red leads to a signal that is slightly higher than that for C-PCPDTBT, but it remains significantly lower than for 450 or 532 nm. This behavior can be traced back to the calculated S_1 and S_8 electron–hole density differences reported in Figure 4 (corresponding to the LE and HE absorption). The HE state shows a more delocalized, hence less bound, exciton which can more easily dissociate into polarons. In particular, the HE state of Si-PCPDTBT shows a more pronounced spatial separation (i.e., two lobes) than C-

PCPDTBT, which should favor polaron generation, as experimentally detected. Our results thus provide evidence that the generation of free charges in pristine D–A polymers can be enhanced by the formation of delocalized excitons with inhomogeneous spatial distribution as a precursor state.

In conclusion, we investigated the photoinduced absorption spectra of C- and Si-PCPDTBT in pristine films and blends with PCBM and compared experimental results with DFT/(TD)DFT simulations. In the NIR, both polymers exhibit a split band stemming from the higher transitions of positively charged intrachain polarons. We are able to identify positive inter- and intrachain polarons to be generally responsible for observed signals already in pristine polymers. The presence of interchain delocalized polarons in amorphous samples of C-PCPDTBT extends previous reports claiming a high crystallinity was necessary for these to form. Our computations reproduce a transition polarized perpendicular 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 we attribute to the reduced reorganization energy in the 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 pristine C-PCPDTBT, the signal strength is virtually independent of the excitation energy, which we rationalize with a farther delocalized singlet exciton formed upon high-energy excitation facilitating the subsequent electron–hole dissociation.

We believe that our investigations can help to better understand the photophysical properties of D–A polymers and their behavior upon optical excitation. Compared to homopolymers, we find that concepts such as the delocalization in intra- and interchain direction are still applicable, but we also note that especially the NIR signals in PCPDTBT derivatives are more complex than reported for previous systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpclett.6b02083](https://doi.org/10.1021/acs.jpclett.6b02083).

Additional comparisons of the experimental MIR spectra, calculated electronic transition energies of further species, electron–hole density maps corresponding to different models and transitions, calculated energy values, comparison of different DFT functionals, calculated PIA spectra in the MIR, and the experimental spectra upon different excitation energy (PDF)

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Notes

The authors declare no competing financial interest.

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