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Spectral Signatures of Polarons in Conjugated Co-polymers

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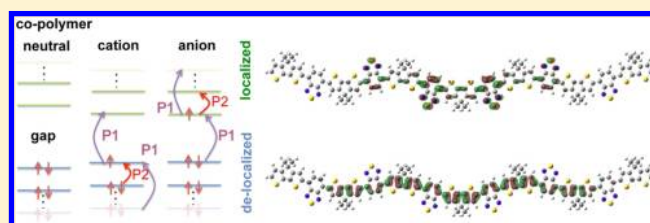
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Supporting Information

ABSTRACT: We study electronic and optical properties of the low-bandgap co-polymer PCPDT-BT (poly-cyclopentadithiophene-*co*-benzothiadiazole) and compare it with the corresponding homo-polymer PCPDT (poly-cyclopentadithiophene). We investigate the linear absorptivity in these systems for neutral molecules and for their singly charged ions based on quantum-chemical calculations and experiments. One of our main findings is that the ions of the homo-polymer show a polaron absorption that is symmetric between anion and cation, whereas for polaron excitations in the co-polymer this symmetry is strongly lifted. We demonstrate that this asymmetry can be attributed to the absence of symmetry between the high-lying occupied and low-lying unoccupied molecular orbitals in the co-polymer with type-II orbital alignment between the moieties constituting the chain. This notion is of importance for the qualitative and quantitative interpretation of spectroscopic polaron data and is not specific to the system studied here but similarly applies to other co-polymers.



1. INTRODUCTION

Semiconducting conjugated polymers are an emerging class of materials that bear great promise for various applications in optoelectronics,¹ photonics,² and photovoltaics.³ These molecular materials combine semiconductivity and desirable optical properties with attractive properties known from plastics such as mechanical flexibility, nontoxicity, affordability, and easiness to process. Through design of their molecular constituents, electronic and optical properties of these materials offer unprecedented flexibility. With more and more potential applications emerging, an increasing demand for the next generation of conjugated polymers has recently developed.

One promising route currently pursued in this field is the use of so-called co-polymers.^{4,5} In these materials, different molecular segments with desirable electronic properties are systematically combined into a single polymer with new properties.⁶ This way, novel low-band gap co-polymers have been designed, which are currently widely used and studied.⁷ Due to their specific chemical and electronic structure, they exhibit favorable behavior for charge separation in photovoltaics⁸—one of the big technological challenges in this area. This can be further enhanced by appropriate molecular doping.^{9,10} In nonlinear photonics, co-polymers can serve as

well-controlled guest–host systems in which exciton–exciton annihilation as one of the major loss mechanisms is reduced.¹¹

In the recent past, a large amount of research was dedicated to understanding the photophysics of these co-polymers.^{12–16} In many cases, in addition to the molecular species, also their ionic counterparts play an important role. In photovoltaics, molecules carrying a net charge inevitably emerge as a desired product after successful charge separation. In optoelectronics, they contribute directly through electrical pumping or indirectly as an unwanted byproduct at elevated excitation densities. Charge carriers in semiconducting polymers—known as polarons—and their photophysical properties have previously been investigated in homo-polymers.^{17–19} However, relatively little is known about the properties of charged species of co-polymers.²⁰ One way to obtain information about polaron properties is through spectroscopic studies.^{21,22} The interpretation of spectroscopic polaron data is typically based on the assumption that the anion and cation show the same optical properties.²³ However, upon closer inspection, this is expected

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to be true only in systems with a sufficient degree of symmetry between high-lying occupied and low-lying unoccupied molecular orbitals.

Here we shed light on this aspect and present a combined theoretical and experimental study of polaron spectra in co-polymers with a type-II orbital alignment (PCPDT-BT and PCPDT-2T-BT co-polymers, in which the alignment between different moieties leads to high-lying occupied and low-lying unoccupied molecular orbitals that are partly localized on different sections of the chain) and compare these with the corresponding homo-polymer (PCPDT). We demonstrate that the missing symmetry between occupied and unoccupied orbitals in the co-polymers destroys the symmetry between anion and cation polaron wave functions and spectra. In our calculations, polaron signatures can be exclusively studied and are not overshadowed by other effects, such as the regular absorption of the neutral species, excited state absorption, triplet absorption, etc. This way we obtain detailed insight into the nature of the polaron excitations. Differences in the anion and cation absorption are traced back to differences in the respective wave functions in the excited system (electron and hole wave function). In addition to detailed quantum-chemical calculations, we also develop a simple physical picture explaining our observations qualitatively.

Our study highlights a fundamental difference between polaron absorption of homo- and co-polymers not previously studied. Our conclusions are expected to play an important role for the interpretation of spectroscopic polaron signatures in co-polymers in the future and are not specific to the system investigated but have general applicability to other co-polymer systems with a type-II orbital alignment.

II. THEORETICAL METHODS

All calculations are based on density-functional theory (DFT) and linear response time-dependent DFT (TD-DFT). The Gaussian 09 program suite²⁴ was used, and all results presented were obtained with the Coulomb-attenuating method Becke three-parameter Lee–Yang–Parr hybrid functional (CAM-B3LYP) and 6-31G* basis set. Orbitals were visualized using GaussView 5.²⁵ In the donor–acceptor co-polymers studied, significant charge separation is expected to occur in the ground state and also electronic transitions show pronounced charge-transfer (CT) character. The long-range character in the electronic exchange interaction required to describe these phenomena can be captured using the long-range corrected CAM-B3LYP functional.^{14,19} For the charged species, all calculations were performed unrestricted. As successfully used in previous studies, calculations were done for long but finite-length oligomers to mimic properties of the corresponding polymers. To reduce the computational cost, alkyl side chains that are largely uninvolved in optical excitations were replaced by methyl groups. Furthermore, the spectra of smaller oligomers with and without symmetry constraints were compared and only small quantitative changes were observed. The dependence of the spectra on the length of the oligomers was studied, and no qualitative change is expected for longer chains than used in the present study. The total length of the different oligomers compared in this study is similar. The results for the longer PCPDT and PCPDT-BT oligomers reported in the present work were obtained using C_{2v} symmetry, and C_1 symmetry for PCPDT-2T-BT. Even without symmetry constraints in the calculations, we have observed only small changes in the overall molecular structures when charges

were removed from or added to the PCPDT and PCPDT-BT oligomers. For PCPDT-2T-BT, we have found a relaxation toward a slightly more planar structure, similarly for anion and cation. For each of the molecular species studied (including their ions), we have first optimized the molecular geometry in the electronic ground state (coordinates of each of the equilibrium geometries of the neutral and charged molecules are provided in the Supporting Information) and then calculated the lowest 20 electronic transitions. A homogeneous broadening of 100 meV was applied to all electronic spectra shown (this leads to a wavelength-dependent broadening in the spectra shown). We find good agreement of our CAM-B3LYP/6-31G* DFT based calculations for the charged molecules with the experimental data justifying the choice of the method. We do not include counterions (see the Experimental Methods section below) in our calculations following ref 19, where no significant change of polaron spectra in fluorene oligomers was found when counterions were explicitly included. To obtain a qualitative picture of electronic excitations in the systems studied, we inspect the different molecular-orbital contributions to each transition. Visualizations of the molecular orbitals are included in the Supporting Information. The main tool we use to analyze the character of electronic transitions also quantitatively is the introduction of natural transition orbitals (NTOs). The NTOs cast each electronic transition into a minimum number of pairs of effective single-particle orbitals. Ideally, a reduction to only one relevant pair of NTOs can be achieved for each transition; however, if correlations play a significant role, a larger number of NTOs remains to be analyzed.

III. EXPERIMENTAL METHODS

For the chemical ionization measurements, the materials were solved in 1,2-dichlorobenzene (Sigma-Aldrich) with a concentration of 15 $\mu\text{g/mL}$. Only for measuring the neutral absorption spectrum of PCPDT, toluene (Sigma-Aldrich) was used, because interaction with pure 1,2-dichlorobenzene led to a small fraction of ionized polymer chains already. Absorption measurements of these solutions filled in fused silica cells (Spectrocell) with a light pass of 10 mm were done with an absorption spectrometer (Cary 5000, Varian) covering the spectral range from 175 to 3300 nm. Infrared absorption of the solvent above 3000 nm, below 290 nm, and from 2560 to 2860 nm limited the measurement to the spectral range shown. After measuring the absorptivity of neat (co-)polymer solutions, small amounts of a dilute SbCl_5 solution (90 $\mu\text{g/mL}$ in 1,2-dichlorobenzene) in 1% wt steps (weight percent of dopant relative to polymer weight) were added. SbCl_5 is known to be a strong oxidizing agent and to generate a hole (positively charged) polaron in the ground state of most conjugated polymers.^{27,28} Up to a doping ratio of 5%, the observed growth of ground state bleaching and polaronic signal due to the ions has been linear and started to saturate at ratios above 5%. Subtraction of normalized ground state absorption measured in undoped solutions led to the chemically induced differential absorption spectra of the investigated materials, as shown in Figure 4 in the main manuscript. Due to the high reactivity of SbCl_5 with air and moisture, all preparation steps were done in a nitrogen atmosphere. The use of airtight cells prevented any kind of degradation during the spectroscopic measurements.

We have tried two different techniques to measure the absorption spectra of anions (electron polarons), both of which were not successful for the materials studied here. Chemical

doping with a NaK alloy, as it has been successfully applied to oligofluorenes recently,¹⁹ did not result in anionic absorption bands as expected. The observation of a pronounced ground state bleaching upon doping without formation of absorption bands below the optical bandgap points toward a sensitivity and instability of the polymer chains to chemical reduction. As an alternative approach, charge modulation spectroscopy has been tried. However, no anionic spectral features but only pronounced electro-absorption could be observed in the materials studied in the present work, indicating charge injection problems between the Ca electrode and the LUMO levels of the polymers. The electro-absorption method was successfully applied to a co-polymer with a significantly lower optical bandgap than the materials studied here. Technical details are reported in ref 8.

IV. RESULTS AND DISCUSSION

Our discussion will be focused on a comparison of the PCPDT-BT low-band gap co-polymer with the PCPDT homo-polymer. In particular, we focus our attention on the properties of their singly charged ions. Further below, we complete the series by comparing with PCPDT-2T-BT, in which additional connector units are systematically inserted to separate BT and PCPDT units and thus to reduce the low-bandgap character compared with PCPDT-BT. Figure 1 shows the calculated absorptivity of PCPDT and PCPDT-BT for neutral and singly charged molecules. In the spectra of the neutral molecules, the low-bandgap character of the co-polymer compared to the homo-

polymer is visible. The typical camelback structure we obtain for the absorptivity of the neutral co-polymer⁴ is not clearly visible on the wavelength scale used in Figure 1. As a feature known for polaron spectra, for both charged species, two well resolved polaron peaks P_2 and P_1 are visible at longer wavelengths. For the homo-polymer, we observe symmetry between the anion and cation polaron spectrum in the long-wavelength range which is absent for the co-polymer.

Before we turn our attention to details of the calculations, we provide a simple physical picture to explain the symmetry and asymmetry between anion and cation absorption spectra, respectively. For each of the polaron transitions in Figure 1, we have inspected the dominant molecular orbital contributions and energies. This leads us to the simple level scheme shown in Figure 2 for the interpretation of the different polaron

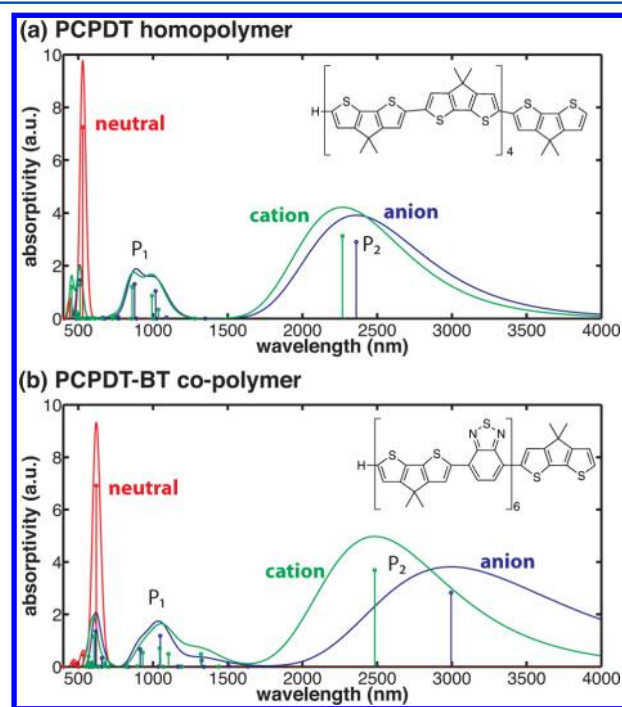


Figure 1. Calculated absorptivity of (a) PCPDT homo-polymer and (b) PCPDT-BT co-polymer. Results are for neutral species and singly charged ions; the insets show the structures used in the calculations. The sticks represent the wavelength and oscillator strength for each transition. While the absorptivity is almost symmetric between the anion and cation of the homo-polymer throughout the spectral range shown, for the co-polymer, this symmetry is lifted in the long-wavelength range due to asymmetry between the high-lying occupied and low-lying unoccupied molecular orbitals.

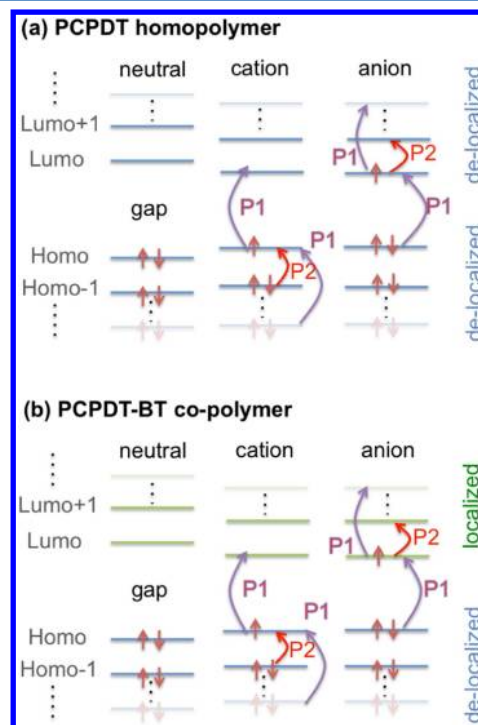


Figure 2. Schematic visualization of energy levels for (a) homo- and (b) co-polymer. Indicated by the arrows are the low-energy polaron transitions. For the co-polymer, these lowest polaron excitations have a different character for the anion and cation. For the anion, the lowest transition is between localized states on the BT unit and for the cation between states delocalized across the polymer. This difference is absent for the homo-polymer.

peaks P_1 and P_2 . Similar schemes have been discussed in previous studies on polarons in conjugated polymers.^{21,29,30} The arrows in Figure 2 indicate the dominant contributions to the low-energy polaron transitions. The first, P_2 , polaron peak can be interpreted as a transition between the lowest orbitals above the gap (anion) or a transition between the highest orbitals below the gap (cation), respectively. In the language of extended systems, the transitions are of “intraband” character. Although strictly speaking here we only study long oligomers, we will continue to use this language below as a convenient way to characterize transitions of different nature. The nature of the second peak, P_1 , is slightly more subtle, as it is not clearly dominated by only a single transition in the molecular orbital picture but has strong contributions from multiple and different

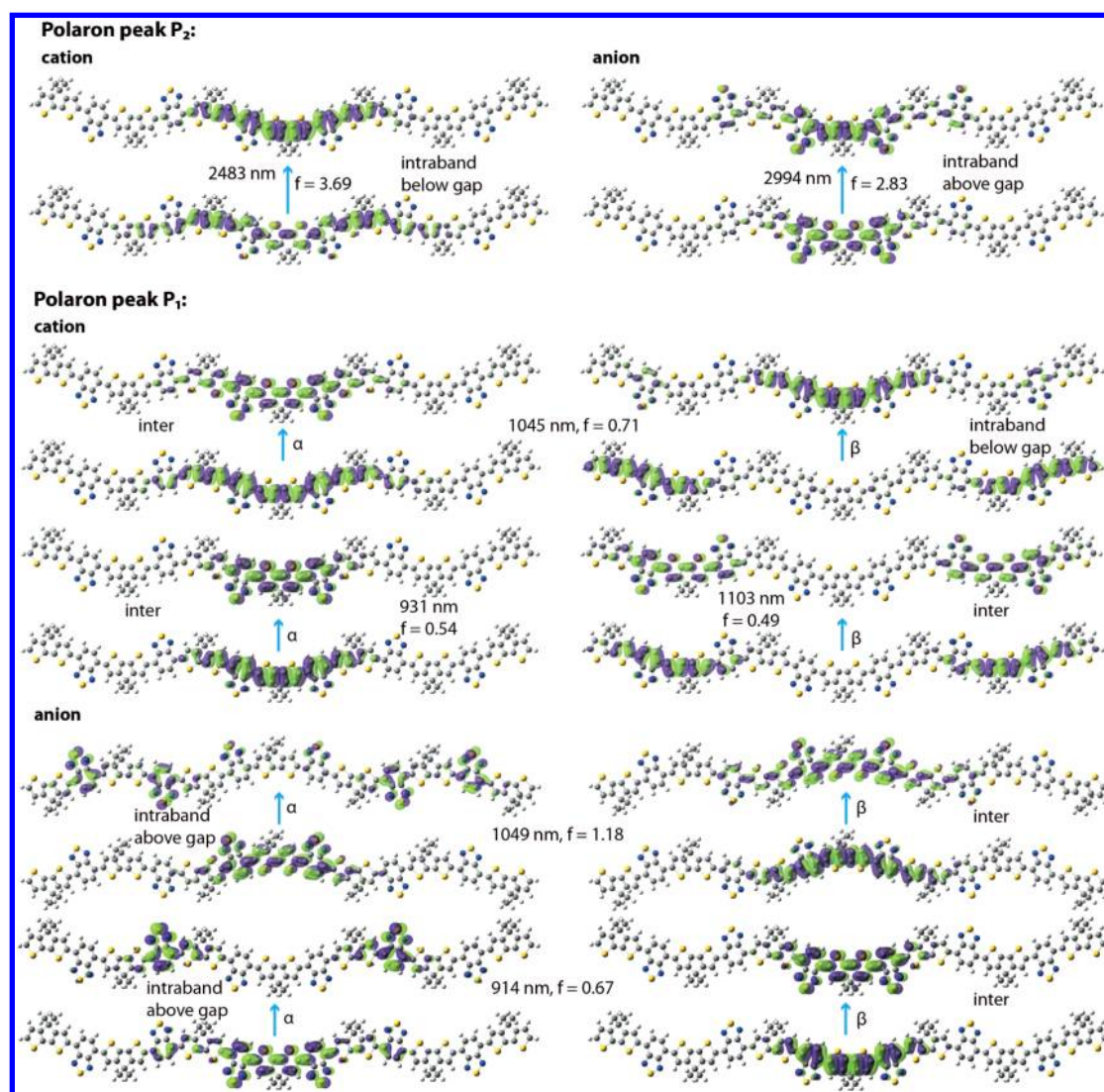


Figure 3. Analysis of long-wavelength polaron excitations in terms of natural transition orbitals for the PCPDT-BT co-polymer. Only one transition contributes to the P_2 polaron peak. Both for cation and anion, only one pair of NTOs significantly contributes to this P_2 transition. Clearly visible is the delocalized nature of the NTOs for the cation, whereas the NTOs for the anion are much more localized on the BT units. This result qualitatively coincides with the schematic interpretation in Figure 2. The NTO analysis of the polaron peak P_1 is more subtle. Multiple transitions significantly contribute to the P_1 peak; for the dominant transitions, the dominant NTOs are shown. The wavelength, oscillator strength f , spin character α or β , respectively, and dominant nature (inter- vs intraband) are noted for each pair of NTOs shown.

types of transitions. The first set of contributions stems from excitations across the gap involving several unoccupied and occupied orbitals (“interband” transitions). The second set of contributions stems from transitions between orbitals below or above the gap, respectively (“intraband” transitions), similar to P_2 but involving higher unoccupied or lower occupied molecular orbitals, respectively.

This interpretation is valid both for homo- and co-polymer. However, in the homo-polymer, states near the gap, both below and above the gap, show extended π -orbital character. In the co-polymer, states above the gap are well localized on the BT units,³¹ whereas states below the gap show a similarly extended π -orbital nature as in the homo-polymer (the orbital alignment between the moieties constituting the chain in this co-polymer is similar to a type-II heterostructure, where states slightly below and above the gap are (at least partly) localized on different parts of the chain). Accordingly, for the anion of the co-polymer, the P_2 peak stems mostly from transitions between states localized on the BT unit, whereas for the cation the P_2

peak is dominated by transitions between delocalized molecular states. In the latter case, the P_2 transition in the co-polymer is similar in nature to the P_2 transition in the corresponding homo-polymer. Consequently, the P_2 absorption of co-polymer cation and homo-polymer cation is similar and only slightly different in energy. In the case of symmetry between highest occupied and lowest unoccupied orbitals (“electron–hole” symmetry) as in the homo-polymer, the qualitative difference between anion and cation is largely absent. We find that the spectral signatures of the P_1 polaron peak are very similar in anion and cation, both for homo- and co-polymer. This indicates that the energy of the transitions contributing to the P_1 peak (though not necessarily the oscillator strength) is mostly determined by the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).²⁹ This energy difference is independent of the character and energy separation between states below and above the gap, and consequently similar for anion and cation also in the co-polymer.

Quantitative details of the different transitions will be further discussed below.

In the following, we solidify the reasoning presented above. In reality, when adding or taking away a charge to the molecular system, the molecular geometry changes according to the new electronic configuration, and the single-particle basis changes compared to the neutral species. Moreover, due to the doublet structure of the electronic ground state of the singly charged ions, the electronic spin-subsystems are not identical anymore and interpretation in terms of a single set of molecular orbitals only is not comprehensive. Excitations between states in different spin-subsystems have to be considered which contribute differently to the optical response of the system. These aspects have not been considered in the discussion of the previous paragraph; however, they are fully included in the quantum chemical calculations, and for a quantitative analysis, they need to be taken into account. One powerful method that allows us to analyze electronic excitations in the correlated electronic many-particle system more rigorously but still in relatively simple terms is the introduction of natural transition orbitals.²⁶

We have numerically calculated the NTOs for the dominant low-energy polaron transitions in PCPDT-BT. Results are shown in Figure 3. The wavelength and oscillator strength f of each transition are noted in the figure. Only the dominant NTO contributions for each transition are shown—NTO pairs with a relative weight of less than 50% are not shown. The polaron peak P_2 in both cation and anion is dominated by a single NTO pair only. In this case, the NTOs can be interpreted analogous to electron and hole wave functions involved in the respective transition. For the cation, both NTOs are delocalized over a larger number of aromatic units. For the anion, the localized nature of the transition on the BT unit is clearly visible. This is in good agreement with the reasoning of the previous paragraph based on Figure 2. This difference between anion and cation NTOs of the P_2 transition can be attributed to the “type-II” orbital alignment in the co-polymer which results in a broken symmetry of high-lying occupied and low-lying unoccupied orbitals. This asymmetry is largely absent for the homo-polymer PCPDT. The shorter-wavelength polaron peak P_1 visible at about 1000 nm in Figure 1 stays more complicated even in the NTO picture. First, more than one electronic transition significantly contributes to this peak, as can be seen in the stick spectra included in Figure 1. For each of the relevant sticks at about 1000 nm, the dominant NTO contributions are shown in Figure 3. For the cation, the dominant contributions are at 1045, 1103, and 931 nm, with oscillator strengths $f = 0.71$, $f = 0.49$, and $f = 0.54$, respectively. For the anion, the dominant transitions are at 1049 and 914 nm with oscillator strengths $f = 1.18$ and $f = 0.67$. Second, each electronic transition possesses a more subtle underlying structure, as already indicated qualitatively in Figure 2. For the P_1 polaron, NTOs belonging to the different spin subsystems are denoted as α and β . We find that those transitions that have significant contributions from more than one NTO pair show both strong inter- and intraband character. For the cation, we note interband contributions in both spin channels. For the transitions inspected for the anion, interband contributions are in the β channel only. The intraband contributions for the cation are between delocalized states below the gap, whereas for the anion they are between states mostly localized on the BT units. Considering this different nature of the transitions in the P_1 peak for anion and cation, it

is by no means safe to assume that there always exists symmetry for the higher-energy part of the spectrum of co-polymer anion and cation. The similarity of the anion and cation spectra we find for PCPDT-BT in the range of the P_1 peak in Figure 1 indicates that the energies of the transitions in this peak are mostly determined by the energy difference between the HOMO and LUMO.²⁹ This symmetry may be further lifted for other co-polymers, as is the case for anion and cation spectra for the three-component system PCPDT-2T-BT in Figure 4.

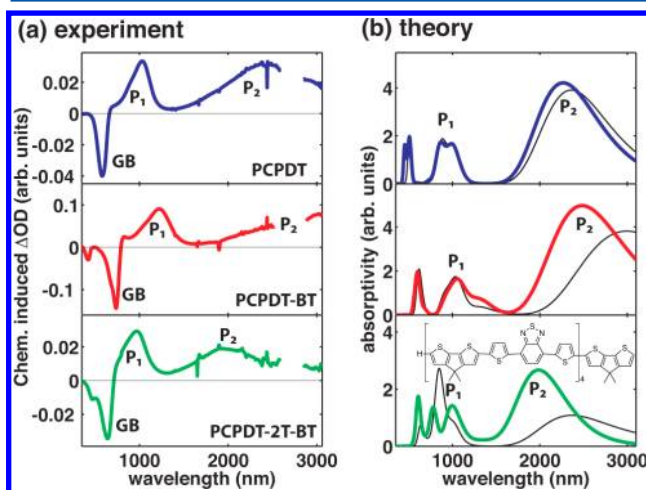


Figure 4. (a) Measured chemically induced change in optical density due to the presence of cations. (b) Calculated absorptivity for cations (colored) and anions (black).

We find that the intraband contributions to the P_1 peak have strong charge-transfer character; i.e., the NTOs within these pairs are localized at different regions of the molecule. We also note that in agreement with previous studies we find the low-energy polarons to be more localized than the extended π -orbitals of the corresponding neutral species (not shown). This is also true in the co-polymer; however, a difference in nature for the P_2 transitions in cation and anion (delocalized vs localized) remains clearly visible in Figure 3 and is reflected in the spectral properties in Figure 1.

We complete the discussion by comparing the theoretical data discussed so far with experiment. In this context, we extend the series studied by another co-polymer, PCPDT-2T-BT, resulting in a more representative series of homo- and co-polymers for this class of materials. In experiment, polaron absorption can be induced by chemically ionizing molecules (cf. the Experimental Methods section). For all three molecules in the series, in Figure 4, we show the measured chemically induced change in optical density due to the presence of cations. So far, we have not succeeded in measuring the corresponding anion spectra; details are given in the Experimental Methods section. In addition to the chemically induced polaron absorption features, the ground state bleach is visible as the negative change in optical density in the experiments. First, we turn our attention to the P_2 peak in the spectrum. Going from PCPDT to PCPDT-BT, the peak is slightly red-shifted. Moving on to PCPDT-2T-BT, the P_2 peak is significantly blue-shifted. These trends are similar but slightly less pronounced for the P_1 peak. We find good agreement between experiment in (a) and theory in (b). Comparing absolute numbers, we find that the calculated transition wavelengths are slightly blue-shifted with respect to the

experimental data. We find a similar trend for the calculated spectra of the neutral molecules (not shown). However, this is not unexpected for the methodology used. All calculations are for finite (albeit long) oligomers. Furthermore, a blue-shift in the calculated spectra was noted before for an extended one-dimensional conjugated system using the CAM-B3LYP functional (cf. the Theoretical Methods section).³² In addition to the P_1 and P_2 polaron peaks, in all three calculated spectra, an absorption feature can be identified close to the fundamental absorption line of the neutral molecules (see also spectra in Figure 1). This transition is also visible in the experimental data as a feature at the long-wavelength end of the ground state bleach for PCPDT-BT and PCPDT-2T-BT. The notion that there appears to remain some residual absorption of polarons at the fundamental resonance of the neutral molecule is not the main point of the present paper but could also be relevant for interpretation of spectral properties of charge carriers in these systems. Finally, we compare the calculated spectra for anion and cation for PCPDT-2T-BT. Here we note that the symmetry between anion and cation is further lifted. In this case, this is also true for the P_1 peak. Although the origin of the asymmetry is analogous to PCPDT-BT (missing symmetry between highest occupied and lowest unoccupied orbitals), due to the more complicated molecular structure, the inspection of the different transitions in PCPDT-2T-BT has not led us to a similarly clear physical picture as detailed above for PCPDT-BT.

V. CONCLUSIONS AND REMARKS

We have theoretically and experimentally studied optical properties of a series of co- (PCPDT-BT and PCPDT-2T-BT) and homo-polymers (PCPDT) and of their singly charged ions. These materials are currently widely used in organics-based photovoltaics and optoelectronics, and their ionic counterparts play a key role in the extraction and injection of charges. One of our main findings is that the ions of the homo-polymer show very similar polaron absorption (symmetric between anion and cation), whereas for polaron excitations in the co-polymer this symmetry between anion and cation is strongly lifted. On the basis of detailed quantum-chemical calculations, we trace the origin of this asymmetry back to differences in the orbitals contributing to the involved electronic transitions (caused by the absence of symmetry between occupied and unoccupied orbitals near the gap; missing “electron–hole” symmetry) in the co-polymer with type-II orbital alignment. This notion is of importance for future interpretation of spectroscopic polaron data and is expected to similarly apply to other homo- and co-polymer systems.

■ ASSOCIATED CONTENT

Supporting Information

Full author list of ref 24, comparison of the molecular orbitals of the homo- and co-polymer for the neutral species of PCPDT and PCPDT-BT, and equilibrium geometries of the neutral and charged oligomers of PCPDT, PCPDT-BT, and PCPDT-2T-BT. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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