

Driving Force and Optical Signatures of Bipolaron Formation in Chemically Doped Conjugated Polymers

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Molecular dopants are often added to semiconducting polymers to improve electrical conductivity. However, the use of such dopants does not always produce mobile charge carriers. In this work, ultrafast spectroscopy is used to explore the nature of the carriers created following doping of conjugated push–pull polymers with both F₄TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) and FeCl₃. It is shown that for one particular push–pull material, the charge carriers created by doping are entirely non-conductive bipolarons and not single polarons, and that transient absorption spectroscopy following excitation in the infrared can readily distinguish the two types of charge carriers. Based on density functional theory calculations and experiments on multiple push–pull conjugated polymers, it is argued that the size of the donor push units determines the relative stabilities of polarons and bipolarons, with larger donor units stabilizing the bipolarons by providing more area for two charges to co-reside.

aromatic to quinoid to stabilize the positive charge. The presence of the positive charge shifts the valence and conduction band positions relative to vacuum and creates new energy levels in the bandgap, leading to new optical transitions,^[9–12] as summarized at the left of Figure 1a. By further oxidation, it is also possible to create a radical dication, or bipolaron, removing the electron in the mid-gap level and causing the level to further rise into the gap, as shown at the left of Figure 1b.^[9] It is generally assumed that bipolarons can be created only at very high doping levels,^[9] but in this work, we show that for a particular push–pull conjugated polymer, bipolarons can be more stable than single polarons.

Like any semiconductors, conjugated polymers can be doped to create additional free charge carriers, expanding the potential uses for these materials in a variety of applications, including conductive layers,^[1,2] organic field effect transistors,^[1,3,4] and thermoelectric devices.^[5–8] Most conjugated polymers are *p*-type materials, so the charge carriers created by doping are holes.

For conjugated polymers, most dopants are strong oxidizing agents that remove an electron from the polymer's valence band, creating a polymer radical cation, also called a polaron. The doped polymer's backbone structure reorganizes from

Push–pull conjugated polymers, also called donor–acceptor polymers, are copolymers consisting of alternating electron-rich and electron-poor groups along the semiconducting polymer's backbone. This design provides the advantage that the polymer bandgap can be tuned by changing the offset between the donor and acceptor energy levels, which also furnishes the ability to create low-bandgap materials. Many studies have demonstrated successful chemical doping of push–pull polymers,^[8,13–18] and there is strong evidence that charge transfer only occurs when the dopant is located near one of the donor units on the copolymer backbone and not near one of the acceptor units.^[19]

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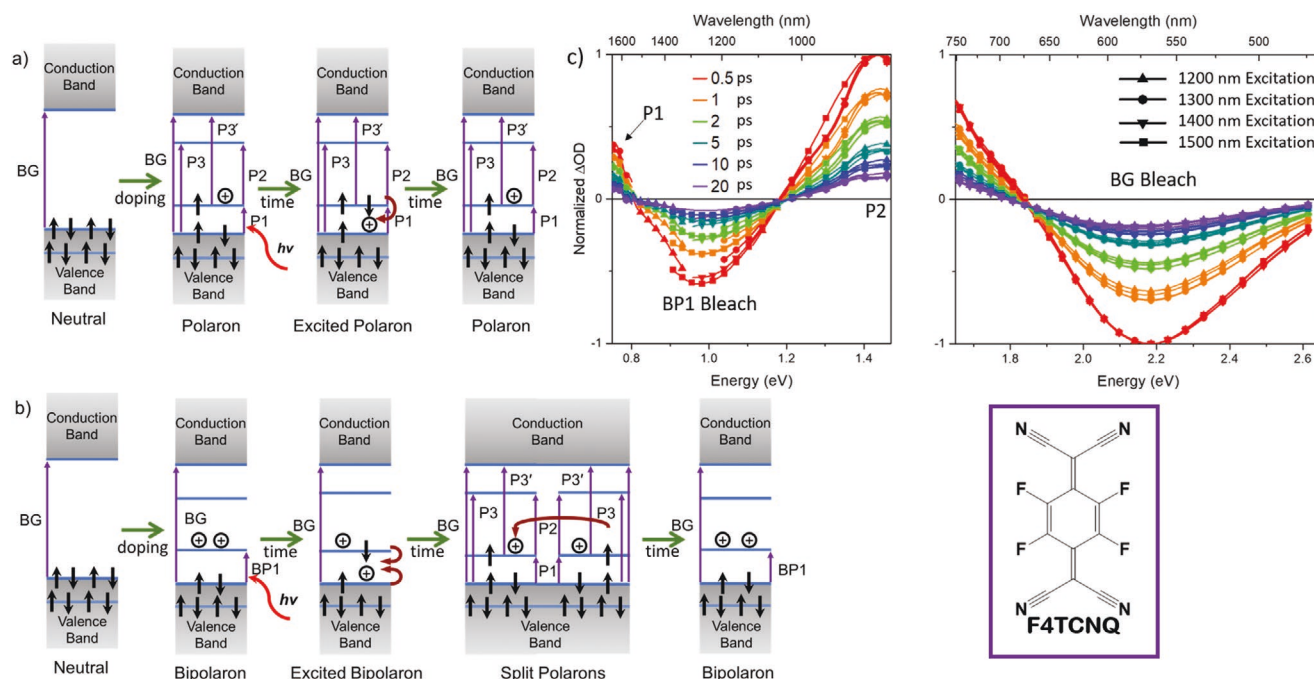


Figure 1. a,b) Energy level diagrams for conjugated polymer polarons (a) and bipolarons (b). The left-most diagrams in (a) and (b) show the neutral polymer before doping, with an empty conduction band and a full valence band with a continuum of electrons, a few of which are depicted as arrows. The next diagram shows the basic electronic structure of each kind of carrier, where BG represents the bandgap transition and the optical transitions created by doping are numbered in order of increasing energy; the Supporting Information contains a discussion of some of the theory underlying these energy level diagrams. The energies of the valence and conduction bands differ between the first two diagrams of (a) and (b) because doping shifts the fermi level and band energies. We note that transient absorption spectroscopy does not report on the magnitude of the energy level shifts, since only differences between energy levels are probed. The diagrams to the right in (a) and (b) show the expected dynamics following photoexcitation of the low-energy P1 or BP1 transition. c) Ultrafast transient absorption spectra of 1 mg mL⁻¹ F₄TCNQ-doped PBDTP films excited at ≈ 1.03 , ≈ 0.95 , ≈ 0.89 , and ≈ 0.83 eV (1200 nm (up-pointing triangles), 1300 nm (circles), 1400 nm, (down-pointing triangles), and 1500 nm (squares), respectively), at time delays of 0.5 (red), 1 (orange), 2 (green), 5 (light blue), 10 (dark blue), and 20 (purple) ps between the pump and the probe pulses. All excitation wavelengths (including the additional excitation wavelengths indicated in Figure 2 with the data in the Supporting Information) show similar transient spectral shapes and dynamics with clear isosbestic points, indicating that only a single excited electronic species is present. The gap in the data near 1.55 eV (800 nm) is due to scatter of laser fundamental and the fact that the NIR and visible portions of the data were collected separately. The transient absorption data from a similar experiment on doped PTB7 films are shown in the Supporting Information. The inset at bottom right shows the structure of the F₄TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) dopant.

In this paper, we focus on the nature of the charge carriers and their optical properties in a push–pull conjugated polymer oxidized with the commonly used molecular dopants FeCl₃ and F₄TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane),^[8,20–25] whose chemical structure is shown at the lower right of Figure 1. The push–pull copolymers we have chosen to study include (poly[(4-(2-hexyldecyl)-4H-dithieno[3,2-b:2',3'-d']pyrrole)-2,6-diyl-*alt*-(2,5-bis(3-dodecylthiophen-2-yl)benzo[1,2-d:4,5-[4d']bisthiazole)]), PBDTP, whose molecular structure is also shown in Figure 2a, and poly[{4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}], PTB7, whose molecular structure is given in the Supporting Information. PTB7 was purchased commercially, and PBDTP was synthesized as previously reported,^[26] with details provided in the Supporting Information. The gel permeation chromatography (GPC)-determined molecular weight (against polystyrene standards) in chlorobenzene at 60 °C for the PBDTP material used in this study was $M_w = 1476$ kDa, $M_w/M_n = 2.82$.

PBDTP has a relatively low ionization potential of 4.8 eV,^[26] making it easy to dope. It is worth noting that the donor group in PBDTP extends over 5 conjugated rings, which is larger

than other push–pull copolymers whose chemical doping has been studied,^[6,8,13–17,26,27] including PTB7.^[18,28] We will argue below that the large donor size and thus ability to delocalize the holes is what causes doping of PBDTP to directly create bipolarons without first creating single polarons, as seen with PTB7 and most other push–pull polymers.

We prepared samples of both F₄TCNQ-doped and FeCl₃-doped PBDTP via solution sequential processing,^[29] starting with polymer films cast from a hot 100 °C 1.5 mg mL⁻¹ orthodichlorobenzene solution at 2000 rpm for 60 s after which the films dried for an hour. Doping was accomplished by casting a solution of F₄TCNQ in dichloromethane at 0.01, 0.1, or 1 mg mL⁻¹ concentration on top of the pre-cast polymer film at 4000 rpm for 10 s (see the Supporting Information for more details on FeCl₃ doping and sample preparation). FeCl₃-doped films of PTB7 were prepared via sequential processing as described in the Supporting Information.

We characterized the structure of the doped PBDTP films using 2D grazing-incidence wide-angle X-ray scattering (GIWAXS, Figure 2c,d for F₄TCNQ- and FeCl₃-doped films, respectively). We find that doping increases the lamellar spacing and decreases the π -stack spacing of the polymer, indicating that

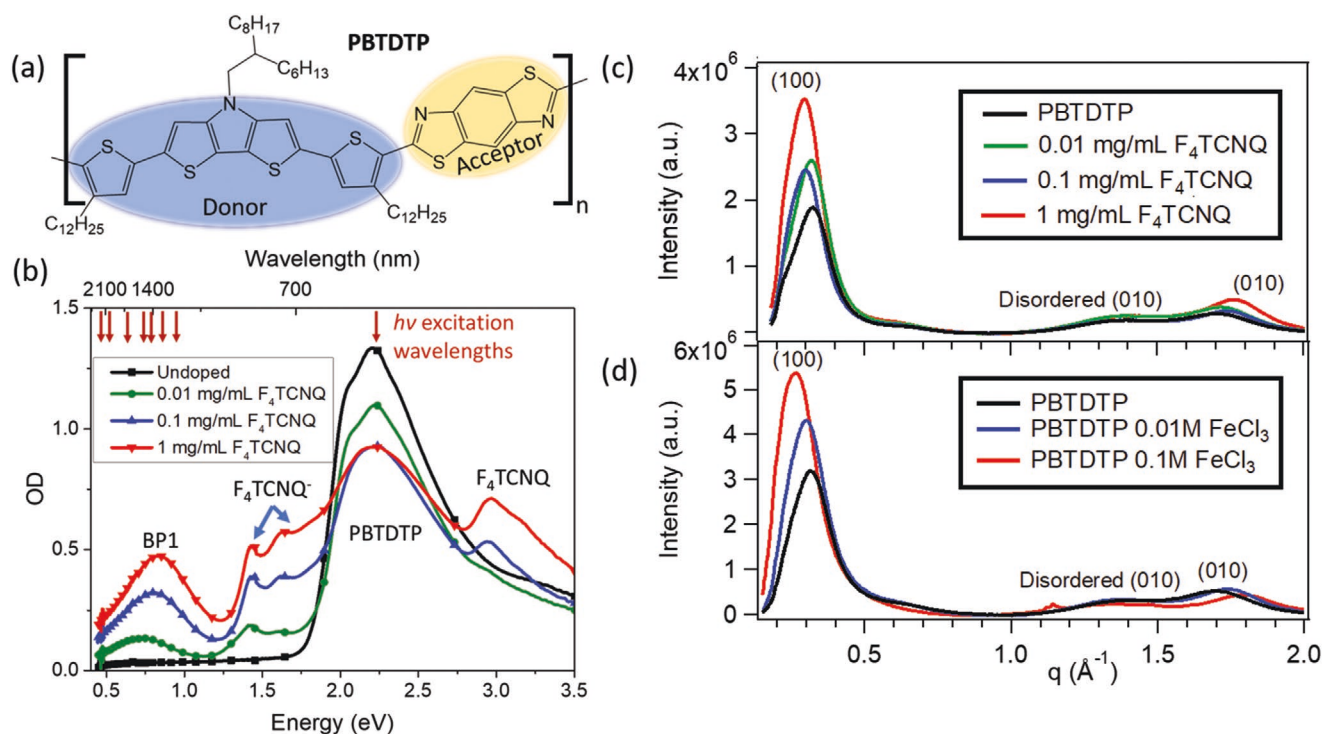


Figure 2. a) Chemical structure of the push–pull conjugated polymer PBTDTTP; the donor (push) and acceptor (pull) units are indicated with blue and yellow color, respectively. b) Steady-state optical spectrum of a film of PBTDTTP (black curve, squares) and films of PBTDTTP doped with F_4TCNQ by sequential processing, with the dopant supplied at concentrations of 0.01 (green curve, circles), 0.1 (blue curve, up-pointing triangles), and 1 (red curve, down-pointing triangle) mg mL^{-1} in dichloromethane solution. The red arrows at the top of (b) indicate the excitation wavelengths used for the transient absorption experiments shown in Figure 1c and the Supporting Information. c,d) GIWAXS measurements of PBTDTTP films doped with F_4TCNQ (c) or $FeCl_3$ (d) showing the (100) lamellar peak shifting monotonically to smaller q and the (010) crystalline π -stacking peak shifting smoothly to larger q upon doping for both dopants. Further details are given in the Supporting Information.

the dopant resides in the polymer side chain regions (see the Supporting Information for peak positions).^[25,30] Further discussion of texturing using in- and out-of-plane diffraction is also presented in the Supporting Information. The polymer structure changes smoothly with increasing dopant concentration, suggesting that only a single doped species is formed. The contraction of the π -stacking distance upon doping further indicates that any charge carriers created are likely delocalized across multiple chains.^[6]

Despite this evidence for delocalized charge carriers, when we investigated the electrical properties using standard 4-point probe methods,^[30] we found that 1 mg mL^{-1} F_4TCNQ -doped PBTDTTP films had barely measurable conductivities between $5 \times 10^{-4} \text{ S cm}^{-1}$ and $1 \times 10^{-3} \text{ S cm}^{-1}$, and films doped with lower amounts of F_4TCNQ had conductivities below our detection limit. This indicates that the chemical doping process did not create mobile charge carriers, even though field-effect transistors fabricated with PBTDTTP showed a hole mobility of $5.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, comparable to other conjugated polymers.^[26] We note that our doped PTB7 films had conductivities $\geq 1 \text{ S cm}^{-1}$, similar to that reported previously for both PTB7^[28] and other doped push–pull conjugated polymers.^[6,8,31]

Figure 2b shows the steady-state optical spectroscopy of F_4TCNQ -doped PBTDTTP films. As expected with the addition of increasing amounts of dopant, the neutral polymer bandgap absorption at $\approx 2.2 \text{ eV}$ (565 nm) decreases, and new peaks appear corresponding to absorption by the F_4TCNQ

anion at ≈ 3.54 , ≈ 1.80 , and $\approx 1.76 \text{ eV}$ (350, 690, and 705 nm, respectively).^[32] More importantly, we also see a single new peak characteristic of the absorption of charged species on the polymer at $\approx 0.83 \text{ eV}$ (1500 nm). Figure 2b shows that the position and shape of this polymer charge carrier absorption is independent of dopant concentration, and we show in the Supporting Information that the properties of this peak also do not depend on whether F_4TCNQ or $FeCl_3$ is used as the dopant.

In most chemically doped conjugated polymers, including PTB7 as shown in the Supporting Information, the new low-energy optical absorption that results from polarons, labeled P1 in Figure 1a, appears near 0.5 eV ($\approx 2480 \text{ nm}$).^[30] We^[33,34] and others^[35,36] have argued that when the dopant counterion resides close to the polaron on the polymer backbone the polaron can be trapped by the attractive Coulomb interaction, lowering its mobility and blueshifting the absorption of the P1 transition. As shown in Figure 1b, bipolarons are also expected to have an optical transition (BP1) that is higher in energy than that of single polarons.^[9] Given the blueshifted carrier absorption and the poor electrical conductivity of chemically doped PBTDTTP, this leads to the question of whether the immobile carriers in this material are Coulombically trapped polarons or bipolarons.

In previous work, we showed that we could distinguish free and Coulombically trapped polarons using ultrafast transient absorption spectroscopy.^[33] The idea behind the experiment is shown in Figure 1a. By exciting the polaron P1 transition,

an electron from the valence band is moved to the half-filled state in the bandgap (left energy level diagram); in essence, the excitation is a photoinduced charge transfer taking an electron from a neutral region of the polymer and filling the hole, thus moving the hole to a new location on the polymer backbone (center diagram). Once the backbone relaxes to accommodate the charge, the stable polaron now resides in a new physical location (right diagram). The optical signatures of this process are a bleach (loss) of the bandgap transition, a bleach of the P1 transition, and an increase in absorption of the P2 transition, all of which uniformly and smoothly recover on a time scale of a few ps.^[33] If the photoexcited carriers are Coulombically trapped polarons, then the photoinduced P2 transition is blueshifted, and the recovery time lengthens to tens of ps because the relocated carrier needs time to diffuse back to the place where it was Coulombically trapped. Thus, time-resolved spectroscopy is capable of separating the presence of free and trapped polaron species.^[33] We note that although many other groups have explored the time-resolved spectroscopy of charge carriers on conjugated polymers,^[37–41] none that we are aware of used photoexcitation directly into the P1 band, explaining why it previously had been difficult to interpret the results.^[37]

In our previous work, we saw exactly the transient absorption signatures expected for polarons based on Figure 1a when exciting doped poly(3-hexylthiophene) (P3HT).^[33] To see how our work on P3HT carries over to push–pull polymers, in this work we studied doped films of PTB7. PTB7 is a weakly crystalline polymer that tends to lie face-on to the substrate, very much like PBTDTTP. As mentioned above, the electrical conductivity of the doped PTB7 films was much more like P3HT than like PBTDTTP, and the position of the P1 band in the absorption spectrum also resembles P3HT more than PBTDTTP (see the Supporting Information). Perhaps more importantly, the shape and dynamics of the transient absorption signals from doped PTB7 (see the Supporting Information) all are very much like that of doped P3HT.^[33] Figure S10 in the Supporting Information shows the results of ultrafast transient absorption experiments on 0.025 M FeCl₃-doped PTB7 films excited at ≈ 0.69 eV (1800 nm). The results show a bleach of the P1 band, seen at the red edge of the detection window, an increase of the P2 peak, and the bleach of a small P3 peak seen at the blue side of the spectrum, all of which decay in a few ps, exactly as predicted from the simple diagram in Figure 1a. Thus, our experiments on PTB7 verify that transient absorption spectroscopy exciting the P1 band can identify the polaron charge carriers in push–pull donor–acceptor copolymers.

Figure 1c shows the results of similar ultrafast transient absorption experiments on F₄TCNQ-doped PBTDTTP films. The data show the same transient absorption spectral shape and dynamics following excitation at any wavelength under the carrier absorption band (the data for additional excitation wavelengths are shown in the Supporting Information). The spectral pattern, however, does not match the behavior expected for the transient absorption from either free or trapped polarons, and shows striking differences from what we saw previously with doped P3HT in ref. [33] and PTB7 in the Supporting Information. In particular, the transient spectra show a new induced absorption band appearing at energies lower than the steady-state near-IR absorption band, a peak that could not appear for either excited free or trapped polarons. Moreover, the recovery of the

transiently induced signals occurs on a time scale longer than that seen following the excitation of free or trapped polarons.

Remarkably, however, the transient absorption of PBTDTTP seen in Figure 1c makes perfect sense if the steady-state near-IR absorption is due entirely to the BP1 optical transition of bipolarons. Figure 1b shows that exciting the low-energy BP1 transition would move a charge from a neutral region of the polymer to fill one of the pair of holes, leading to two separate polarons in separate places on the polymer backbone. After rapid stabilization of the relocated holes, the bipolaron can only recover if the two newly created polarons diffuse to find each other and recombine, a process that should be slower than reorganization of the backbone to stabilize a single polaron. Figure 1b also shows that the expected optical signatures following bipolaron excitation are a bleach of the BP1 transition, a loss of the bandgap transition, and the appearance of new polaronic absorptions, specifically the P1 and P2 polaron transitions, which correspond perfectly with the data in Figure 1c.

The clear isosbestic points seen in Figure 1c indicate that only a single excited species was created, which based on the above arguments must be bipolarons. We verified that only bipolarons are present in our doped PBTDTTP samples by performing two additional sets of ultrafast transient absorption measurements, both of which are shown in the Supporting Information (Figures S7 and S8). First we excited the near-IR absorption as far red as ≈ 0.56 eV (2200 nm), a wavelength where any single polarons would be expected to absorb more intensely than bipolarons. The results are identical to the data in Figure 1c, indicating that there is no secondary electronic species (such as single polarons) hiding under the broad steady-state NIR absorption band. Second, we also excited the bandgap transition at ≈ 2.25 eV (550 nm). As shown in the Supporting Information, the optical signatures we observe for this experiment are exactly what is expected for bipolarons and not for single polarons. Thus, transient absorption spectroscopy can unambiguously identify the presence of bipolarons in doped conjugated polymer films.

In other words, what we have done by photoexciting bipolarons in doped PBTDTTP is to separate them into two single polarons, which take a relatively long time to recombine. We note that the transient appearance of new polaron P1 (and P2) peaks have also been seen in other ultrafast experiments where polarons were photogenerated in semiconducting polymers;^[13,14,40] here, we generate these peaks by photo-splitting of bipolarons, verifying that the single electronic species that is present in doped PBTDTTP must be the bipolaron.

Although the low electrical conductivity, steady-state and ultrafast spectroscopy experiments all point clearly to the fact that chemically doped PBTDTTP forms solely bipolarons and not single polarons as with PTB7 and other doped push–pull polymers, the question is: why do bipolarons form in this system? We are aware of no other conjugated polymer systems where only bipolarons are observed with no stable polarons, and in fact, there are very few reports of bipolarons on conjugated polymers achieved by chemical doping.^[42–44] The relatively high valence band of PBTDTTP means that strong oxidants such as FeCl₃ and F₄TCNQ likely have the electrochemical potential to oxidize polarons to bipolarons, but this does not explain why bipolarons form even at low doping concentrations.

To understand the reasons that doping PBTDTTP favors bipolarons instead of polarons, we modeled doped PBTDTTP, doped PTB7 and doped P3HT using density functional theory (DFT). Briefly, our calculations^[45] were performed using the PBE0 hybrid functional with the 6-31g** basis set on geometry-optimized oligomers; for PBTDTTP, this consisted of four polymer repeat units (32 rings along the backbone) with the side chains truncated to single methyl groups; similar-sized calculations were also performed for P3HT and PTB7, as described in the Supporting Information. We verified, also as described in the Supporting Information, that the trend of the results we obtained did not vary with either the choice of functional or basis set. We note that we do not expect DFT to give a quantitative description of the electronic structure of the doped polymers studied in this work; rather, we use DFT as the only affordable quantum chemistry theory available to provide a qualitative understanding of the relative stabilities of polarons and bipolarons in these systems.

To compare the energetic cost for polaron and bipolaron formation, we started by calculating the total energy of the neutral oligomer and subtracting that energy from the same calculation on the singly ionized oligomer. For PBTDTTP, we found the energy difference to be 4.94 eV, in excellent agreement with the experimentally measured 4.8 eV ionization energy of the material.^[26] When we then remove a second electron from PBTDTTP to create a singlet bipolaron, the calculated energetic cost was slightly higher at 5.49 eV; in other words, in the calculation, the singlet bipolaron is expected to be only 0.55 eV more unstable than making two separated polarons. We also calculated the properties of triplet bipolarons,^[46] but found that for this system they dissociated into two single polarons, as discussed in the Supporting Information.

Our calculations do not predict PBTDTTP bipolarons to be more stable than single polarons, in contrast to experiment; however, we can get a rough sense of what the 0.55 eV energetic cost means by comparing to calculations of bipolaron stability for P3HT and PTB7. For P3HT, metastable bipolarons have been observed experimentally following chemical doping with FeCl₃, but only at very high doping concentrations.^[42] Our calculations indicate that the P3HT polaron is 0.64 eV more stable than the bipolaron, as shown in the Supporting Information. Thus, our calculations predict that bipolarons are ≈ 100 meV more stable on PBTDTTP than P3HT, which is consistent with our experimental observations. We also find from similar calculations that bipolaron formation is less favored for PTB7 than for PBTDTTP, as also shown in the Supporting Information, which is again consistent with the observation that doping PTB7 forms polarons while doped PBTDTTP forms bipolarons.

This leads to the question of why bipolaron formation is favored for PBTDTTP. To investigate this, we compared the relative energies of the PBTDTTP neutral, polaron, and bipolaron species as we changed the physical size of the donor moieties by removing the thiophene units, as shown in Figure 3b and Table S4 in the Supporting Information. The trend in energies is quite clear: removing thiophenes from the donor moieties destabilizes the singlet bipolaron relative to the polaron. When the two thiophenes per donor unit are removed, the calculated singlet bipolaron energy is 0.70 eV less stable than the single polaron. This shows that the presence of the two thiophenes per repeat unit, i.e., the large size

of the donor units, is primarily what stabilizes the singlet bipolaron relative to two single polarons.

To understand why donor size is related to bipolaron stability, Figure 3 also shows the calculated bond length changes of the PBTDTTP bipolaron species relative to the neutral polymer. The aromatic-to-quinoid transition that helps to stabilize the positive charges produces a bond-order alternation that is a clear signature of where the charges reside. Figure 3c shows that the singlet bipolaron on PBTDTTP spreads over all four donor and three of the four acceptor units, but that the amount of charge that resides on the acceptor units is small. The DFT calculations also yield the NBO charges on each atomic site, and we find that the bipolaronic charges are ≈ 4.1 times more likely to reside on the donor rather than the acceptor units, as discussed in the Supporting Information. When the two thiophene rings are removed from the donor unit, Figure 3d) shows that the lack of room to hold the positive charges on the donor units forces the positive charges to spend more time on the high-energy acceptor units as the donor units, making the bipolaron less energetically stable. Indeed, the NBO charges show a $\approx 1.6:1$ donor charge:acceptor charge ratio for the bipolaron when the two thiophenes are absent. In fact, nearly every (but not all^[41]) other push-pull copolymer in the literature has four or fewer rings in the donor unit, and when doped, all of these polymers form only single polarons, consistent with the idea that the bipolaron is destabilized with smaller donor units; this is discussed in more detail in the Supporting Information.

In summary, we have found that in a push-pull conjugated polymer, PBTDTTP, with large donor units, bipolarons form stably even at low doping concentrations. Both steady-state absorption and structural measurements confirm that a single charge carrier species smoothly appears upon doping, with no secondary species or single polarons present at low doping levels. We were able to verify the identity of the bipolaronic charge carriers using ultrafast transient absorption spectroscopy, which shows clear optical signatures for bipolarons that are distinct from free and Coulombically bound single polarons seen in P3HT or other doped push-pull polymers like PTB7. Bipolarons have a poor mobility, explaining the lack of electrical conductivity in chemically doped PBTDTTP. The reason PBTDTTP favors bipolaron formation at all doping levels is due to the large donor units in its chemical structure: our DFT calculations indicate that making the donor units smaller destabilizes bipolarons by forcing them to delocalize more over the higher-energy acceptor units. All of these findings can be used to inform the rational design of new push-pull polymers for better charge mobility upon chemical doping.

Experimental Section

Details of the materials, characterization and experimental methods for sample preparation, electrical, structural, and spectroscopic measurements, as well as DFT calculations can be found in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

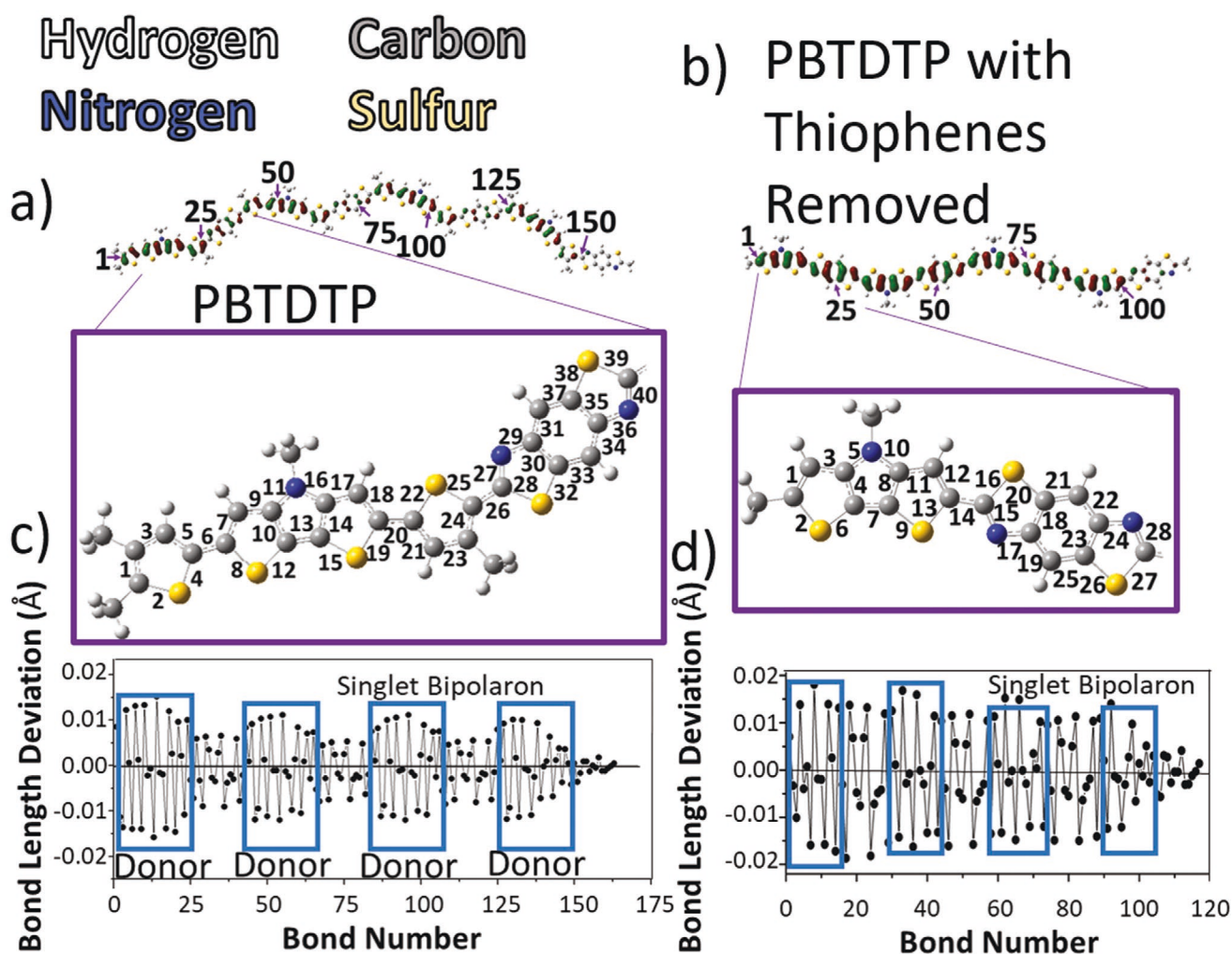


Figure 3. a) Singlet bipolaron LUMO orbital of the side-chain truncated PBTDTTP oligomer used for the DFT calculations, showing the definitions of the bond numbers and atom types for four repeat units of the polymer. b) Singlet bipolaron LUMO orbital of bond-number definitions for four repeat units of the PBTDTTP polymer with the two "extra" thiophene rings that were present in the donor unit removed throughout the oligomer. c) Bond length deviation (difference in bond length between the neutral and charged oligomers) of the singlet bipolaron for PBTDTTP using the PBE0 DFT functional; see the Supporting Information for calculation details. The bonds corresponding to the donor units are boxed in blue. The singlet bipolaron is delocalized across all four of the donor and three of the acceptor units, but there is significantly more bond alternation on the donor units, indicating that the bipolaron prefers to avoid the higher-energy acceptor units. d) Bond length deviation for the singlet bipolaron for PBTDTTP oligomers with the "extra" donor thiophenes removed. Without the thiophenes, the bipolaron resides nearly equally on the donor and acceptor units, explaining why larger donor units provide for more stable bipolarons.

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Conflict of Interest

The authors declare no conflict of interest.

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bipolarons, donor–acceptor copolymers, molecular dopants, semiconducting polymers, transient absorption spectroscopy

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