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Electronic and vibrational spectroscopy studies of PffBT4T π -conjugated donor–acceptor copolymer

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Abstract. We used a variety of optical spectroscopies to investigate the charge excitations and correlated infrared (IR)-active and Raman-active vibrations in poly[(difluoro-benzothiadiazol-diyl)-alt-(di(2-octyldodecyl)-quaterthiophen-diyl)], PffBT4T, a π -conjugated donor–acceptor (DA) copolymer, which, when blended with fullerene PCBM molecules, serves as an active layer in high-performance photovoltaic solar cells. The applied optical spectroscopies in films of pristine PffBT4T and PffBT4T/PCBM blend include absorption, photoluminescence, electroabsorption, photoinduced absorption (PA), and resonant Raman scattering. We found that the PffBT4T copolymer chain contains 11 strongly coupled Raman-active vibrational modes, which are renormalized upon photogeneration of charge polarons onto the chain. As the lower energy polaron absorption band overlaps with the renormalized vibrational modes, they appear in the PA spectrum as antiresonance (AR) lines superposed onto the induced polaron absorption band. We show that the Raman scattering, doping induced, and photoinduced AR spectra in PffBT4T are well explained by the amplitude mode model (AMM), where a single vibrational propagator describes the renormalized Raman modes and their related photoinduced AR intensities in detail. Surprisingly, we found that two of the IR-active modes in the pristine copolymer must be included in the AMM propagator for explaining the complete photoinduced AR spectrum. This feature is unique to DA-copolymers and indicates that some intrachain C_{2v} symmetry breaking occurs because of the different electron affinities of the donor and acceptor moieties. © 2018 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: [10.1117/1.JPE.8.032203](https://doi.org/10.1117/1.JPE.8.032203)]

Keywords: π -conjugated copolymer; doping-induced absorption; photoinduced absorption; electroabsorption; resonant Raman scattering; infrared-absorption; polaron excitations, antiresonances; amplitude modes model.

Paper 18006SS received Jan. 11, 2018; accepted for publication Mar. 13, 2018; published online Mar. 28, 2018.

1 Introduction

The potential for low-cost solar energy harnessing drives the development of organic photovoltaic (OPV) solar cell technology,^{1–3} in particular, PV solar cell based on π -conjugated polymers because the devices may be fabricated using extremely high-throughput roll-to-roll printing methods. The active layer in polymer PV solar cells has been a blend of two components, namely the polymer chains as electron donors and fullerene molecules as electron acceptors.^{4–7} About 6 years ago the donor polymers consisted of homopolymers such as polythiophene that absorb in the visible range of the solar spectrum.⁸ Recently, however, the π -conjugated polymers have been replaced by π -conjugated block copolymers of which repeat units consist of alternating donor (*D*) and acceptor (*A*) moieties that are called donor–acceptor (DA) copolymers (Fig. 1 inset).^{2,9,10–15} This chain architecture substantially reduces the optical gap, so the DA-copolymers absorb more sunlight in the near-infrared (IR), where the largest fraction of

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Fig. 1 The PL and absorption spectra of pristine PffBT4T film at ambient conditions. Various bands and phonon replicas are assigned. The inset shows the backbone structure of PffBT4T DA-copolymer that contains two different moieties.

the photons emitted by the Sun lie. The power conversion efficiencies of organic solar cells based on DA-copolymers as donor materials and fullerene molecules as acceptors have exceeded 10%.¹⁴ In particular, OPV cell based on fullerene blend with the DA-copolymer PffBT4T, namely poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3'-bis(2-octyldodecyl)-5,5'-quaterthiophen-2,2',5,2'-diyl)] (Fig. 1 inset), has reached a power conversion efficiency of up to 10.8%.¹⁵ In addition to the lower energy bandgap, the main reason given for this high-yield solar cell is the improved film morphology, which has been measured to be highly crystalline. We focus our present optical studies on films of pristine PffBT4T and PffBT4T/PCBM blends.¹⁵

Despite the increasing interest in device applications, there is only limited understanding about the nature and properties of the charge excitations (polarons) in these materials.^{16–22} This requires deeper understanding of the vibrational modes associated with the polaron excitation in the DA-copolymer chains as the strongly coupled vibrations may enhance the polaron mass, thereby inhibiting its mobility. The polaron excitation in π -conjugated polymers distorts the chain dimerization pattern, and this renormalizes the strongly coupled vibration frequencies and IR-activity.^{23,24} Specifically, Raman active modes having even parity character (i.e., A_g symmetry modes) become IR active with very large oscillation strengths.²⁵ These modes, dubbed infrared active vibrations (IRAVs), appear upon doping or charge photogeneration and are thus a signature of charges added onto the polymer chain.^{26–28} An efficient method to describe the IRAVs in π -conjugated polymers has been the amplitude mode model (AMM) that was successfully advanced by Horovitz and collaborators for polyacetylene, $(\text{CH})_x$.^{24,25} The AMM has had enormous success in describing the strong dispersion of the Raman modes with the laser excitation frequency in $t\text{-(CH)}_x$ as measured by resonant Raman scattering (RRS) spectroscopy.^{24,27} Recently, the AMM has also been shown to describe the vibrational modes of PTB7, a prototype DA-copolymer.²⁹ If the absorption bands of the charge polaron in π -conjugated polymers do not overlap with the vibrational modes, then the IRAVs appear in the absorption spectrum as intense absorption lines.²⁴ However, when the charge polaron lower absorption band overlaps with the vibrational modes, then quantum interference between the two features may occur in the form of multiple Fano effect, where the IRAVs manifest themselves in the form of antiresonances (ARs) superimposed on the polaron lower absorption band.^{23,28} As the lower polaron absorption band in DA-copolymers may be in resonance with the IRAVs, it is thus expected that ARs would dominate the absorption spectrum when charges are added to the DA-copolymer chains. Indeed, ARs have been observed in the photoinduced absorption (PA) spectrum of PTB7/PCBM blend.²⁹ However, important information that could have been obtained from the photoinduced ARs spectrum about the loss of the C_{2v} symmetry in the copolymer chain²² has been ignored so far.

Due to the combined effects of strong electron correlations and loss of C_{2v} symmetry (“symmetry breaking”) caused by a different electron affinity, Δ_{af} , between the donor and acceptor moieties, theory predicts²² that there is considerable mixing between a charge-transfer exciton that defines the optical gap and an energetically proximate triplet–triplet (TT) state with overall spin singlet. The TT state, optically forbidden in homopolymers, is allowed in DA-copolymers due to the anticipated symmetry breaking. For intermediate Δ_{af} values, the TT state can have even stronger oscillator strength than the charge-transfer exciton.²² So far, however, this prediction has been elusive when linear optical spectroscopies have been studied in a number of DA-copolymers. It would be interesting to apply optical nonlinear spectroscopies such as electroabsorption (EA), PA, and vibrational spectroscopies such as RRS and IR-absorption to study the C_{2v} “symmetry breaking” in DA-copolymers.

In this work, we first present that the absorption, photoluminescence (PL), and EA spectra in PffBT4T do not show the anticipated “double-band” predicted by the theory.²² This is most likely because of a possible resonance between the energies of the TT state and charge-transfer exciton in this copolymer.³⁰ To characterize the strongly coupled vibrational modes of the copolymer that influence the polaronic excitations, we measured the RRS and PA spectra in films of pristine PffBT4T and PffBT4T/PCBM blends, respectively. We show that the main charge excitation in the PffBT4T chains is the polaron having two characteristic absorption bands below the gap.²¹ As the low-energy polaron absorption band entirely overlaps with the strongly coupled vibrational modes, these modes mostly appear in the PA spectrum as ARs superimposed on the polaron lowest energy absorption band. We also show that the AMM provides an excellent basis for understanding the various vibrational spectra as it describes the RRS and ARs spectra in detail. In addition to the well-resolved Raman-active modes that contribute to the AMM phonon propagator in PffBT4T, we conclude that, to describe the complete set of the ARs in the PA spectrum of the copolymer/fullerene blend, two IR-active modes must be included for the pristine copolymer. These modes contribute a pair of ARs that cannot be explained by renormalized RRS modes. This is unique to the class of the DA-copolymers and shows the influence of the C_{2v} symmetry breaking in the chains, which is induced by the different donor and acceptor moieties.

2 Experimental Section

The PffBT4T copolymer powder was purchased from Solarmer and used without further purification. Thin films of PffBT4T were spin cast or drop cast from PffBT4T solution in 1,2-dichlorobenzene (ODCB) and chlorobenzene (CB) [ODCB:CB (1:1)] at a concentration of 10 mg/ml onto sapphire or KBr substrates, depending on the spectral range of interest. For the PffBT4T/PCBM blend, we used a solution of PffBT4T and PC₇₀BM (1:1.4 in weight) with the same concentration in ODCB:CB solvent, which was stirred in nitrogen atmosphere overnight. The sample films were placed in a cryostat equipped with transparent windows in the visible to mid-IR, where the temperature could be regulated between 40 and 300 K.

The PL and absorption spectra of the pristine PffBT4T films were measured using a steady-state photomodulation pump–probe setup,³¹ where the pump was a CW laser diode at 486 nm and intensity of ~ 100 mW/cm². For the PA measurements, the probe beam was derived from an incandescent tungsten lamp (visible spectral range) or glow-bar (mid-IR range) and passed through a one-fourth met monochromator having a number of interchangeable gratings that are optimized for various wavelengths throughout the visible, near-IR, and mid-IR spectral ranges. A variety of semiconductor detectors such as Si, Ge, and InSb were used to monitor the transmission, T , through the sample film, and the changes, ΔT , induced by the pump beam. The PA spectrum was subsequently calculated as $-\Delta T/T$. To cover the spectral range of 500 to 4000 cm⁻¹, we used an FTIR spectrometer. To obtain the PA spectrum, we used a shutter to modulate the laser illumination on the film, and we signal-averaged the IR absorption spectrum for 6000 scans. The Raman scattering spectrum was measured using a micro-Raman spectrometer equipped with a CW laser at 486 nm, where the inelastic scattered light was detected with a filter and a photomultiplier tube.

To identify the lowest singlet exciton (SE) and/or TT energies in the absorption spectrum, we used EA spectroscopy as this type of modulation spectroscopy is able to more accurately

determine transition energies. The PffBT4T film in this case was deposited on interpenetrating gold electrodes, 30 μm apart, subjected to a 300-V voltage that was modulated at frequency $f = 500 \text{ Hz}$ ¹⁷, whereas the EA was measured at $2f$ using a phase-sensitive technique.

3 Results and Discussion

Figure 1 shows the PL and absorption spectra of pristine PffBT4T film. The inset shows the copolymer backbone repeat unit, which is composed of donor and acceptor moieties.¹⁵ It is seen that the absorption onset of the copolymer (band 1) occurs at 1.6 eV, whereas the absorption peaks at $\sim 1.8 \text{ eV}$ (0 to 0 transition in band 1) with the maximum slope at 1.7 eV; this is the mean exciton energy in PffBT4T. One of the reasons for the low optical gap here is the difference in electron affinity between the donor and acceptor moieties in the copolymer chain.^{20,22} The absorption spectrum shows a second pronounced band (0 to 1 transition within band 1) $\sim 180 \text{ meV}$ higher than the first band, which we consider to be “vibration replica.” We note that a second band #2 occurs in the absorption spectrum at $\sim 2.7 \text{ eV}$, which may be due to a second transition of the copolymer chain^{32,33} rather than being caused by phonon replicas.

The PL spectrum of the pristine PffBT4T film (Fig. 1) is composed of two pronounced bands that are in the form of “mirror image” of the absorption spectrum close to the band-edge of band 1 that are $\sim 180 \text{ meV}$ apart, namely 0 to 0 and 0 to 1 transitions. The PL main peak (0 to 0 transition) is at 1.55 eV having an apparent “Stokes shift” of $\sim 250 \text{ meV}$ from the main 0 to 0 absorption peak. However, this large energy difference may be caused by exciton diffusion to sites on the copolymer chain that have the lowest energy, rather than a natural, intrinsic Stokes shift. We note that the relatively low optical gap of PffBT4T makes it attractive for OPV applications.¹⁵

To identify the lowest SE energy, E_{SE} , in the absorption spectrum of PffBT4T, we used EA spectroscopy as this type of modulation spectroscopy is able to more accurately determine transition energies such as van-Hove singularities in the density of states.^{34,35} Figure 2(a) shows the EA spectrum of pristine PffBT4T film measured at 40 K. Four features dominate the EA spectrum: (i) the EA feature at lowest photon energy resembles the first derivative of the absorption spectrum at the band-edge [see Fig. 2(b)]; it is therefore caused by Stark shift of the lowest SE with a zero-crossing energy at 1.75 eV, which is therefore assigned to E_{SE} of the copolymer.^{30,36}

Fig. 2 (a) The EA spectrum of a pristine PffBT4T film measured at 40 K and a field of 100 kV/cm. Various bands and EA spectral features are assigned (see text). (b) The spectrum of the absorption derivative of PffBT4T calculated from Fig. 1 is shown for comparison with the EA spectrum.

(ii) The second EA feature is a derivative-like of the phonon replica³⁷ [0 to 1 transition in Fig. 2(b), ~ 180 meV higher than E_{SE}]. (iii) The third EA feature is an induced absorption band at 2.25 eV that does not have any relation with the derivative of the absorption spectrum in Fig. 2(b). We, therefore, assign it, due to the forbidden exciton, m^1A_g state in the singlet manifold that becomes partially allowed due to the symmetry breaking caused by the applied electric field in the PffBT4T film.^{30,37} The energy difference, $\Delta_{SE} = E_{mAg} - E_{SE} = 0.5$ eV, is traditionally taken to be the lower bound of the exciton binding energy, E_b , in π -conjugated polymers;³⁷ and we adopt this interpretation here for PffBT4T. We note that E_b of ~ 0.5 eV is much lower than E_b values in traditional polymers, such as MEH-PPV and P3HT (~ 0.9 eV).³⁷ The lower E_b value here helps in the exciton dissociation process, which facilitates charge photo-generation in this compound.¹⁵ (iv) The fourth EA feature is again a derivative-like of the second absorption in the PffBT4T absorption spectrum [Fig. 2(b)] with zero crossing at 2.5 eV, which we identify as the second dominant allowed exciton in the singlet manifold.²¹ We note that the EA spectrum does not contain any spectral features associated with an additional absorption band that has been predicted to occur in DA-copolymers due to the TT state.²²

This might originate from an interaction between the SE and TT band that is enhanced due to their mutual resonance; more theoretical analysis is needed to elucidate this effect.

The expected difference in electron affinity of the donor and acceptor moieties in PffBT4T raises the question of whether the C_{2v} symmetry is broken in the copolymer chains.²² This can be checked by comparing the Raman scattering and IR-absorption spectra.³¹ If the chain C_{2v} symmetry still holds, then the Raman active vibrations are not IR-active, and vice versa. Figure 3 shows the RRS spectrum compared with the IR-absorption spectrum in pristine PffBT4T film deposited on KBr substrate. The RRS spectrum contains 11 strongly coupled modes that are labeled 1 to 11 [Fig. 3(a)]. It is interesting to note that the C=C stretching mode in PffBT4T shows a group of Raman-active modes stretching from 1350 to 1600 cm^{-1} . This is probably caused by a distribution of the C=C frequency due to the different environments on the copolymer chain close to the donor, acceptor, and the “in between D–A” place.³⁸ In contrast to the RRS spectrum, the IR absorption spectrum shown in Fig. 3(b) contains many more IR-active modes;

Fig. 3 Comparison between the (a) RRS and (b) IR-absorption spectra of the pristine PffBT4T film measured at room temperature. The 11 Raman-active modes in the RRS spectrum are enumerated. The asterisks on the two IR-active modes emphasize that these modes might also be Raman active (see text).

and there is no clear resemblance of the two spectra. We, therefore, conclude that the copolymer chain approximately retains the C_{2v} symmetry group.

In our theoretical analysis, to be presented below, we found that two of the IR-active vibrations marked with asterisks in Fig. 3(b) also appear in the PA spectrum of the copolymer/PCBM blend and thus might have small oscillator strengths in the RRS spectrum [marked with asterisks in Fig. 3(a)].

We now turn to study the vibrational modes from another point of view. It has been shown that the addition of charge excitation onto the copolymer chain renormalizes the strongly coupled Raman-active mode frequencies and turns them to be IR-active (namely IR-active vibration or IRAV) having huge oscillator strength.²⁴ As the exciton binding energy is large in PffBT4T, it is common practice to add charges on the copolymer chains by photogeneration in a blend of the copolymer as an electron donor with a fullerene molecule acceptor. In this case, the photoexcited excitons may ionize at the copolymer/fullerene interface, thereby transferring an electron from the copolymer chain into the fullerene molecule, leaving behind a hole in the chain in the form of a positive polaron.³⁹

Figure 4(a) shows the doping-induced absorption (DIA) spectrum of the PffBT4T film doped with iodine. The spectrum contains two polaron bands P1 and P2. Figure 4(c) shows the doping induced IRAV of the doped copolymer emphasizing the AR features denoted with arrows. Figure 4(b) shows the PA spectrum of PffBT4T/PCBM blend film. The spectrum contains two polaron absorption bands P1 and P2, as predicted by the theory,³³ followed by strong absorption below the optical gap. Associated with the polaron electronic transition, there are several photoinduced IRAVs as shown in Fig. 4(d). It is clearly seen that there are at least nine large AR dips in the PA spectrum. These ARs replace the traditional IRAVs that are formed upon photogeneration in many blends of π -conjugated homopolymers with fullerene molecules.²³

Fig. 4 (a) The DIA spectrum of PffBT4T film doped with Iodine at 300 K. (b) The PA spectrum of PffBT4T/PCBM film measured at 40 K. (c) DIA spectrum in the mid-IR shows ARs, which are measured with the FTIR spectrometer. The PA spectrum in the mid-IR/visible spectral range was measured using the photo-modulation set-up. The polaron PA bands P1 and P2 are assigned. (d) The PA spectrum in the mid-IR that shows a more complete P1 band of polarons, superposed by a number of ARs.

This happens since the P1 band overlaps with the IRAV so that quantum interference occurs in the form of Fano-type ARs.²⁸ We checked that P1, P2, and ARs in the PA spectrum have the same dependence on the laser excitation intensity and temperature, and therefore they originate from the same photoexcitation species, which we identify as photogenerated hole polarons on the PffBT4T chains.⁴⁰ The interaction between the IRAVs and P1 that leads to ARs has been well described by the AMM of Österbacka et al.,²³ which we apply below to the vibrational modes of the PffBT4T chains.

3.1 Analysis of PffBT4T Strongly Coupled Vibrations Using the Amplitude Mode Model

We now introduce the AMM^{24,25} for analyzing the strongly coupled vibrations that are revealed as peaks in the copolymer RRS spectrum and ARs in the PA spectrum, respectively. In previous applications of the AMM, it has been explicitly assumed that the adiabatic approximation holds true.²⁴ This approximation however does not hold in our case since the vibrational frequencies are in resonance with the P1 polaron band. We thus need to use the modified AMM that includes nonadiabatic effects.²³ This was successfully applied to π -conjugated homopolymers²³ as well as copolymers.²⁹ We bring here the essence of the AMM to show that, through its correct analysis in the case of PffBT4T, we need to include two additional modes that are IR-active in the pristine copolymer film and form their own ARs.

An important ingredient of the AMM is that all IRAVs are interconnected by being coupled to the same phonon propagator. The bare phonon propagator in the copolymer chain is given by²⁵

$$D_0(\omega) = \sum_n \frac{\lambda_n}{\lambda} \frac{(\omega_n^0)^2}{\omega^2 - (\omega_n^0)^2 - i\omega\delta_n}, \quad (1)$$

where ω_n^0 , δ_n , and λ_n are the bare frequencies, their natural width, and electron–phonon (e–p) coupling constants and $\sum \lambda_n = \lambda$ is the total e–p coupling constant. The index, n varies from 1 to N , the number of coupled modes in the polymer chain; for example, $N = 11$ for the PffBT4T copolymer. The bare frequencies in the coupled e–p chain are renormalized since they interact with the electronic gap so that their modified propagator is given by a “Dyson-type” equation²⁵

$$D(\omega) = \frac{D_0(\omega)}{1 + (1 - 2\lambda^*)D_0(\omega)}, \quad (2)$$

where the renormalization parameter, $2\lambda^* = [1 - 2\lambda E''(2\Delta_0)]$, E'' is the second derivative of the total e–p system versus the dimerization amplitude, Δ , and $2\Delta_0$ is the dimerization gap at equilibrium. The poles of Eq. (2) are the renormalized Raman frequencies, ω_n^R , of the copolymer, given by the relation^{24,25}

$$D_0(\omega) = -(1 - 2\lambda^*)^{-1}. \quad (3)$$

In contrast, the renormalized AR frequencies ω_n^{AR} appear as zeroes in the conductivity response, $\sigma(\omega)$ ²³

$$\sigma(\omega) \sim \frac{1 + D_0(\omega)(1 - \alpha')}{1 + D_0(\omega)[1 + c_1 - \alpha]}, \quad (4)$$

which, from the Eq. (4) numerator, are given by the relation

$$D_0(\omega) = -(1 - \alpha')^{-1}, \quad (5)$$

where α' is a nonadiabatic renormalization parameter. In contrast, the IRAV frequencies appear in this case as poles in Eq. (4), given by the relation $D_0(\omega) = -[1 + c_1 - \alpha]^{-1}$ (where c_1 and α are the independent constants), which are practically suppressed by their proximity to the ARs in the conductivity spectrum.

When plotting the function $D_0(\omega)$ [Fig. 5(b)], we note that it has poles at the bare frequencies, ω_n^0 , and approaches the value (-1) as ω reaches zero. This is because at $\omega = 0$ the numerator and denominator in $D_0(\omega)$ [see Eq. (1)] cancel each other, and $\sum -\lambda_n/\lambda = -1$. Equations (3) and (4) are in fact polynomial of order N in ω^2 , and thus it is much easier to solve for the renormalized vibrational mode frequencies by drawing a horizontal line at different values that correspond to the parameters λ^* or α' [see Fig. 5(b)]. To fit the various renormalized frequencies using the AMM, we have to find $2N - 1$ parameters associated with $D_0(\omega)$ and two additional parameters, namely λ^* and α' for the RRS and AR frequencies, respectively. This has been a formidable task, but considering also the RRS intensities has made it much easier (see below).

The curve-fitting parameters of the vibrational propagator from the AMM were solved using routines developed by the Numerical Algorithms Group (NAG). These routines are found in the NAG Library and may be accessed using programming languages and traditional mathematical software suites. More specifically, routines designed to numerically solve optimization problems

Fig. 5 The measured spectrum (lines) and calculated vibrational mode frequencies (symbols) in PffBT4T film for (a) RRS, (c) DIA, and (d) photo-induced absorption spectrum in PffBT4T/PCBM blend. The “bare” AMM phonon propagator, $D_0(\omega)$, that is based on 13 vibrational modes is shown in (b), where the horizontal lines are obtained using $2\lambda^* = 0.47$ (RRS, up triangles), α' (PA) = 0.56 (ARs, down triangles), and α' (DIA) = 0.51 (ARs, circles). $D_0(\omega)$ parameters are given in Table 1. The (*) symbol in panel (d) denote modes that are also IR-active in the pristine copolymer dark state (see text).

were utilized for this case. To obtain realistic, physical, and unique solutions under the correct local, an initial point (first guess), constraints and conditions that are already stated under the AMM, and a bound of a finite set were declared for all equations and parameters of interest.

In analyzing the AR frequencies in PffBT4T, we found that 11 RRS modes are insufficient to describe the complete ARs spectrum. This is evident in Fig. 5(d) for two ARs at ~ 700 and ~ 745 cm^{-1} , respectively, each denoted by an asterisk. We thus conclude that we need two additional coupled vibrations to fit the entire photoinduced ARs spectrum, as seen in Figs. 5(b) and 5(c). These additional modes do not have substantial RRS intensities [Fig. 5(a)] and thus were not taken into account in the original $D_0(\omega)$ propagator. When including the extra mode in the modified $D_0(\omega)$ having weak e–p coupling strength (see Table 1), we could fit the entire photoinduced ARs spectrum as seen in Fig. 5(d). However, these extra modes have substantial oscillator strengths in the IR absorption of the pristine PffBT4T film, as seen by the two separate asterisks in Fig. 3(b). As these two modes are both IR-active and Raman-active, we conclude that the additional IR-active modes in $D_0(\omega)$ of PffBT4T originate from the C_{2v} intrachain symmetry breaking that occurs in the copolymer chain due to the different donor and acceptor moieties. This has been observed before in the PA spectrum of PTB7 copolymer²⁹ but has not been properly analyzed. We therefore conclude that both Raman and IR activities for few modes in the PffBT4T chain are unique to the class of π -conjugated copolymers.

The best fitting function $D_0(\omega)$ that describes the 13 most strongly coupled vibrations in PffBT4T is shown in Fig. 5(b), together with three horizontal lines that represent the cases of RRS, DIA, and photoinduced AR spectra [Eqs. (3) and (5)]. The fitting parameters for the best $D_0(\omega)$ are given in Table 1. The fit with the experimental frequencies is excellent. We therefore conclude that the AMM is a good basic model for describing the strongly coupled vibrations in PffBT4T. We found that, in general $2\lambda^* < \alpha'$; this contrasts with the case in homopolymers, where α' is in fact α (pinning) upon doping or photogeneration.²⁵ We therefore conclude that the polarons in copolymers have an additional pinning due to the D–A nature of the copolymer chain. In principle, we could use the AMM parameters and the DIA spectrum to estimate the polaronic mass in this copolymer.²⁹ However, we choose not to go this route at this stage since we lack the theoretical justification for this. We can only say from the large IRAV oscillator

Table 1 The best fitting parameters for the bare phonon propagator, $D_0(\omega)$, that describes the 13 most strongly coupled vibrational modes in PffBT4T. ω_n^0 are the bare frequencies, λ_n/λ are their relative e–p coupling, δ_n (RRS) are their natural widths used to fit the RRS spectrum [Fig. 6(b)], and δ_n (AR) are their widths used to fit the photoinduced AR spectrum [Fig. 7(b)].

Mode index	ω_n^0 (Bare frequency) cm^{-1}	λ_n/λ	δ_n (RRS) cm^{-1}	δ_n (AR) cm^{-1}
1	507	0.005	15	1
2	700	0.008	20	5
3	742	0.001	25	1
4	782	0.001	35	1
5	930	0.150	35	200
6	1010	0.015	10	15
7	1060	0.015	10	15
8	1185	0.005	10	15
9	1215	0.005	10	15
10	1290	0.001	10	10
11	1350	0.02	25	25
12	1500	0.03	30	30
13	1800	0.744	20	20

Fig. 6 The RRS spectrum of PffBT4T as measured (a) and calculated (b) using the AMM parameters given in Table 1. The (*) symbol denotes a mode that has both Raman- and IR-activity (see text).

Fig. 7 The PA spectrum of PffBT4T/PCBM blend in the mid-IR spectral range as measured (a) and calculated (b) using the AMM parameters given in Table 1. The (*) symbols denote modes that appear in both photoinduced ARs and IR-absorption spectra.

strength that the polaronic mass here is similar to that of other, more traditional conjugated polymers.

One of the benefits of using the AMM to describe the most strongly coupled vibrations of the copolymer chain is that it can predict the relative scattering intensities in the RRS spectrum²⁴ and

the AR strengths for the AR dips in the PA spectrum.²³ The reason behind this extraordinary ability is that all renormalized RRS modes and ARs are related to each other through the same phonon propagator, which is not the case in RRS spectra of most compounds. It turns out that the Raman scattering intensity, I_n , of each renormalized mode is inversely proportional to the slope of $D_0(\omega)$ at the renormalized frequencies;²⁴ namely $I_n \sim |dD_0(\omega)/d\omega|$ at $\omega = \omega_n^R$. As the function $D_0(\omega)$ is known for PffBT4T and we also found the proper parameter $2\lambda^* = 0.47$ that describes the RRS frequencies, it is straightforward to calculate the RRS spectrum based on the AMM. This is nicely shown in Fig. 6, where the calculated RRS spectrum is compared with the experimental spectrum. The fit is superb, and this validates the conclusion that the AMM is a reliable theoretical model for the vibrational frequencies in PffBT4T and probably for many other DA-copolymers.²⁹

Another benefit of the AMM is that the photoinduced AR spectrum (both frequencies and intensities) can also be calculated using the general model given in Eq. (4). We used the $D_0(\omega)$ function and the parameters $(C_1 - \alpha)$ and α' as given in Table 1 to calculate the photoinduced ARs spectrum of the PffBT4T/PCBM blend as shown in Fig. 7. For this calculation, we used a polaron band that is peaked at $\sim 700 \text{ cm}^{-1}$ as predicted by the theory.²³ The agreement between the experimental and calculated photoinduced AR spectra is fair. Importantly, the calculated ARs spectrum supports the use of the AMM with the two extra modes due to the C_{2v} symmetry breaking in the copolymer chain.

4 Summary

In summary, we studied the most important excited states of the DA-copolymer PffBT4T using a variety of optical spectroscopies. We determined the allowed SE transitions at 1.75 and 2.5 eV, respectively, and the strongly coupled dark exciton at 2.25 eV. We thus predict that a signature of photoexcited excitons in this material would be a PA band at 0.5 eV in the ps transient spectrum that is correlated with a PL band. The charge excitations of this copolymer are polarons with two PA bands at ~ 0.1 and 1.1 eV, respectively, that are correlated with superposed antiresonance dips. The most strongly coupled vibrations in the pristine copolymer were studied using RRS in the pristine copolymer, iodine doping of the copolymer and in PffBT4T/PCBM blend using the PA technique. The 11 Raman-active modes are renormalized when charge polarons are added to the copolymer chains upon photogeneration. They revealed themselves as antiresonance dips superposed on the lower polaron absorption band. We have shown that the AMM accurately describes the vibrational modes using a single phonon propagator in which all 11 modes are coupled together. However, to describe the complete photoinduced ARs spectrum, we needed to add to the phonon propagator two additional modes with weak e-p coupling that appear in the IR-absorption spectrum but are much weaker in the RRS spectrum. We conclude that the two modes that show both Raman scattering and IR-absorption expose the predicted C_{2v} symmetry breaking in the PffBT4T copolymer chain, which is caused by the different electron affinities of the intrachain donor and acceptor moieties.

Disclosures

The authors declare no competing financial interest.

Acknowledgments

The work at the University of Arizona was supported in part by funding from the Space Exploration and Optical Solutions Technology Research Initiative Fund (S.R.V). The work at the University of Utah was supported by the AFOSR under award number FA9550-16-1-0207 (E.L.; RRS and PA spectroscopy) and NSF-MRSEC program DMR 1121252 (SB; PA spectroscopy, and help with the acquisition of the FTIR spectrometer).

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