Optical studies of native defects in π -conjugated donor–acceptor copolymers

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We used multiple spectroscopies such as photoinduced absorption (PIA), magneto photoinduced absorption, and doping induced absorption for studying native defects in π -conjugated donor–acceptor copolymer chains of benzodithio-phenylene fluorinated benzotriazole. The PIA spectrum contains characteristic photoinduced absorption bands that are due to polarons and triplet exciton species, whose strengths have different dependencies on the modulation frequency, temperature, and laser excitation, as well as magnetic field response. We found that the native defects in the copolymer chains serve as efficient traps that ionize the photoexcited excitons, thereby generating charge carriers whose characteristic optical properties are similar, but not equal to those of intra-chain polarons formed by doping. The native defects density is of the order of 10^{17} cm^{-3} indicating that most of the copolymer chains contain native defects upon synthesis; however, this does not preclude their use for photovoltaic applications. *Published by AIP Publishing.*

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INTRODUCTION

Low band gap π -conjugated polymers have attracted substantial interest, especially in the field of organic photovoltaic (OPVs) applications because of their extended sunlight absorption, lightweight, and ease of fabrication.^{1–5} In traditional OPV cells, the donor π -conjugated polymers have been homopolymers such as polythiophene that absorb in the visible spectral range of the solar spectrum.⁶ Recently, the homopolymers have been replaced by copolymers as electron donors whose repeat units consist of alternating donor (D) and acceptor (A) moieties.^{7–16} This chain architecture substantially reduces the optical gap, and thus, the D-A copolymers absorb in the near infrared, and this increases the power conversion efficiency (PCE) of OPV based on copolymer/fullerene blends above 10%.^{16,17} However, the open circuit voltage, V_{oc} of cells based on D-A copolymers, is relatively low due to the inherent low band gap.^{17–19} Thus, intermediate band gap ($\sim 2.0 \text{ eV}$) copolymers are still relevant for use in OPV cells, since they are designed to achieve high V_{oc} , which is especially important for tandem geometry.^{19–21} We also note that despite the increasing interest in device applications, there is only limited understanding of the molecular doping of D-A π -conjugated copolymers,²² or the nature and properties of the charge excitations (polarons) in these materials, which prevent further improvements in OPV applications.^{23–31}

For our present research investigation, we have chosen the π -conjugated D-A copolymer benzodithio-phenylene (BnDT) fluorinated benzotriazole (FTAZ); see structure in Fig. 1(a).^{19–21} PBnDT-FTAZ is a copolymer having intermediate band-gap with an optical gap in the visible spectral range, namely at $\sim 600 \text{ nm}$ [Fig. 1(b)].^{19,20} OPV cells based on PBnDT-FTAZ/([6,6]-phenyl-C61-butyric acid methyl ester) (PCBM) blend

have achieved PCE of up to 7% in an optimized device architecture.^{19,20} Here, we have studied native defects in pristine PBnDT-FTAZ using photoinduced absorption (PIA) spectroscopy compared with doping induced absorption (DIA). We found that the pristine films contain $\sim 10^{17} \text{ cm}^{-3}$ defects density that are formed during the synthesis process, which efficiently dissociate the photoexcited excitons and trap positive

FIG. 1. (a) The backbone structure of the PBnDT-FTAZ D-A copolymer that contains two different moieties. (b) The photoluminescence (PL) and absorption (O.D.) spectra of the copolymer film at ambient conditions.

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charges. We have identified the charges as polarons having two characteristic absorption bands below the gap²⁹ that also show associated IR-active vibration (IRAV) with a huge oscillator strength. To characterize the various photoexcitation species, we have also used the magnetic field effect to discriminate between the triplet excitons and polaron excitations.

EXPERIMENTAL

The PBnDT-FTAZ copolymer powder was synthesized in Wei You group at North Carolina University. Thin copolymer films were spin cast or drop cast from solution in trichlorobenzene at a concentration of 12 mg/ml onto sapphire or KBr substrates, depending on the spectral range of interest. The sample films were placed in a cryostat equipped with transparent windows in the visible to mid-IR, where the temperature could be regulated from 50 K to 300 K.

The photoluminescence (PL) and absorption spectra of the pristine films were measured using a steady-state photo-modulation pump-probe set-up,³² where the pump was a diode laser at 486 nm and an intensity of ~ 100 mW/cm². For PIA, the probe beam was derived from an incandescent Tungsten lamp (visible spectral range) or glow-bar (mid-IR range) and passed through a $\frac{1}{4}$ met monochromator optimized at 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 PIA spectrum was subsequently calculated as $-\Delta T/T$. To cover the spectral range of 500–4000 cm⁻¹, we used an FTIR spectrometer. In this case, the PIA spectrum was obtained using a shutter to modulate the laser illumination on the film, and we signal-averaged the IR absorption spectrum for 5000 scans^{33,34}. For the DIA spectrum, we doped the film p-type by exposing it to iodine vapor for various time durations ranging from a few seconds to 1 h.

The magneto-PIA (MPA) measurements were performed using the same cw PIA set-up described above upon the application of an external magnetic field provided by an electromagnet that produced field, B up to 1800 Gauss applied parallel to the film surface. The MPA(B) response is defined by the relation $\text{MPA}(B) = [\text{PIA}(B) - \text{PIA}(0)]/\text{PIA}(0)$, where $\text{PIA}(B)$ is the PIA at field strength B , and $\text{PIA}(0)$ is the PIA at $B = 0$.³⁵ We measured the MPA response at several wavelengths in order to study the existence of correlation among various bands in the PIA spectrum.

RESULTS AND DISCUSSION

Figure 1 shows the absorption and PL spectra of pristine PBnDT-FTAZ film. Figure 1(a) shows the copolymer backbone repeat unit; it is composed of both donor and acceptor moieties.^{19–21} In Fig. 1(b), it is seen that the absorption onset of the copolymer is at 2 eV, whereas the absorption peaks at ~ 2.15 with maximum slope at 2.1 eV, which set the mean exciton energy in PBnDT-FTAZ at ~ 2.1 eV. The absorption spectrum also shows a second pronounced band ~ 180 meV higher than the first band, which we consider to be a

“vibration replica.” We also note that a third band occurs in the absorption spectrum at ~ 3.0 eV, which may be due to a second transition of the copolymer chain.^{36,37}

The PL spectrum shown in Fig. 1(b) is composed of two pronounced bands that are in the form of a “mirror image” of the absorption spectrum close to the band-edge, that are ~ 180 meV apart. The PL main peak is at 1.86 eV having an apparent “Stokes shift” of ~ 250 meV from the first absorption peak. However, this large energy difference may be caused by exciton diffusion to sites on the chain that have the lowest energy, rather than a natural, intrinsic Stokes shift.

In order to better study the excited states of the copolymer, we used the electro-absorption (EA) spectroscopy, which is capable of more accurately determining the transition energies such as van-Hove singularities in the density of states.³⁸ Figure 2 shows the EA spectrum of pristine PBnDT-FTAZ film measured at 50 K; the inset shows quadratic EA voltage dependence that is traditionally obtained in π -conjugated polymers. The EA feature at the lower photon energy resembles the first derivative of the absorption spectrum at the band-edge; it is therefore caused by Stark shift of the lowest SE. In this case, the first zero crossing energy at 2.08 eV is therefore assigned to the average singlet exciton energy, E_{SE} of the copolymer.^{39,40} The second EA feature is a derivative-like of the phonon replica⁴¹ (0–1 transition) ~ 180 meV higher than E_{SE} . The third EA feature is an induced absorption band at 2.64 eV, which does not have any relation with the absorption derivative spectrum. We therefore assign it as 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 PBnDT-FTAZ film.^{39,41} The energy difference, $\Delta E_{SE} = E_{mAg} - E_{SE} = 0.56$ eV, is traditionally taken to be the lower bound of the exciton binding energy, E_b in π -conjugated polymers;⁴¹ and we adopt this interpretation here for PBnDT-FTAZ. We note that E_b of ~ 0.56 eV is substantially lower than E_b values in traditional π -conjugated polymers such as Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]

FIG. 2. The electroabsorption (EA) spectrum of pristine PBnDT-FTAZ film measured at 50 K and field strength of 100 kV/cm. The inset shows a quadratic dependence of the EA on the applied voltage.

FIG. 3. (a) The photoinduced absorption (PIA) spectrum of pristine PBnDT-FTAZ film. The triplet (T) and polaron ($P1$) PA bands are assigned. (b) The detailed PIA spectrum in the vibrational spectral range emphasizing the polaron $P1$ band and associated vibrational modes. Various anti-resonances (AR) are shown by the arrows.

(MEH-PPV) and Poly(3-hexylthiophene-2,5-diyl) (P3HT) (~ 0.9 eV).⁴¹ The lower E_b value here may help the exciton dissociation process, which facilitates charge photogeneration in this compound.¹⁶

Figure 3(a) shows the steady-state PIA spectrum of pristine PBnDT-FTAZ copolymer which contains several PA bands. The PA band $P1$ at 0.4 eV is superposed by several anti-resonances (AR), and therefore we tentatively identify it as due to photogenerated polarons.³⁴ The second PA, namely band T at ~ 1.1 eV, is long-lived and neutral (since it is not correlated with photoinduced IRAVs) and therefore, we identify it as due to triplet excitons.^{35,42} A more detailed PIA spectrum in the frequency range of the vibrational modes is shown in Fig. 3(b), where some AR dips are marked with arrows. These features can be well described by the amplitude mode model,^{33,34} which is beyond the scope of the present work.

To prove that the two PA bands in the PIA spectrum are not correlated to each other, and therefore they belong to different photoexcitation species, we compare the frequency, temperature, and excitation intensity dependencies of the two PA bands. Figures 4(a) and 4(b) show the frequency

dependent PA strength at 50 K from 30 Hz to 100 kHz for the T and $P1$ bands, respectively. It is seen that the PA lifetime, determined by the angular frequency $\omega_{\max}$ at which the PA at quadrature gets maximum, is very different for the two bands. Whereas $\omega_{\max} \approx 5$ kHz for the T band, it is ~ 30 Hz for the $P1$ band. To estimate the photoexcitations lifetime, we use the relation $\omega_{\max} = 2\pi/t_0$ where t_0 is the mean lifetime. Whereas we estimate the polarons lifetime to be ~ 300 ms at 50 K, the triplet lifetime is about 1 ms. We note that is not possible to fit the frequency dependence with a single lifetime, since the disorder in the copolymer gives rise to a distribution of lifetimes (dispersive recombination); and this justifies our method to determine the mean lifetime. More accurate models for the lifetime determination are outside the scope of this contribution.

Figures 4(c) and 4(d) show the temperature dependence of the T and $P1$ band, respectively. The T band decreases with the temperature rather monotonically from 50 to 300 K, whereas the polaron band $P1$ does not decay with the temperature in the range of 50 – 250 K; however, it vanishes at 300 K. Based on these observations, we conclude that the PA bands $P1$ and T are due to different photoexcitation species.

FIG. 4. (a) and (b) PIA frequency dependence and (c) and (d) temperature dependence of the PA bands T and $P1$, respectively.

FIG. 5. (a) and (b) The PIA spectrum of band *T* and P1 measured at different pump intensities. The absolute-PA intensity dependence of bands *T* and P1, plotted in (c) and (d), respectively, in log-log form.

Based on these observations, we conclude that the PA bands P1 and *T* are due to different photoexcitation species.

Moreover, we compare the pump intensity (I_L) dependent of the two PA bands shown in Figs. 5(a) and 5(b), respectively. Both PA bands increase with I_L . To determine the recombination kinetics, we plot the PA intensity dependence in a log-log format, as seen in Figs. 5(c) and 5(d). Both intensity dependencies are in the form of a power law $PA \sim (I_L)^p$, whereas the exponent $p = 1/2$ for the triplet band *T* [Fig. 5(c)]; $p = 1$ for the polaron band P1. We therefore conclude that the recombination kinetics of the triplet excitons is bimolecular, probably caused by triplet-triplet annihilation (TTA) process, whereas the polaron species represented by band P1 is monomolecular. This is odd, since the polarons should recombine in pairs: $(P^+) + (P^-) \rightarrow GS$, where (P^+) is a positive polaron, (P^-) is a negative polaron, and GS is the ground state. We therefore conclude that the polarons are generated at a charge defect on the chain, which may be considered as a deep trap in a Shockley-Reed type recombination. This recombination process is known to be monomolecular.

Figure 6 shows the magneto photoinduced absorption (MPA) response of the copolymer at 50 K. The $MPA(B)$ response, where B is the field strength, is very different for bands *T* and P1. Whereas MPA is positive (increases with B) for the band *T*, it decreases for the band P1. Furthermore, the two MPA responses are not correlated to each other, since they show different characteristic widths. Whereas the $MPA(B)$ full width at half maximum due to triplets is ~ 345 G, it is only ~ 180 G for the polaron band. In general, the MPA originates from the field induced change in the photoexcitation recombination dynamics that originates from induced changes in the spin-mixing processes. The different MPA response thus shows that the two photoexcitations have very different recombination kinetics, in agreement with the conclusion from the PA intensity dependent. The $MPA(B)$ response for the *T* band is in agreement with TTA process, where its width is related to the zero-field splitting parameters of the triplet excitons. In contrast, the $MPA(B)$ width of the polaron band is related to the difference, Δg between the g -factors of the hole-polaron and the traps in the copolymer.

FIG. 6. Magneto photoinduced absorption [$MPA(B)$] response of (a) triplet and (b) polaron PA bands in the PIA spectrum, measured at 50 K.

Next, we identify the P1 band as due to polarons from the similarity with the lower energy of the doping induced absorption (DIA) band. Figure 7(a) shows the complete DIA spectrum of the PBnDT-FTAZ copolymer upon doping with iodine. It is seen that, in fact, the DIA spectrum of the charge excitations contains two bands, namely P1 peaked at ~ 0.4 eV and P2 with a peak at ~ 1.3 eV (Refs. 33 and 42) where $2E(P1) + E(P2) \approx E_g$, the copolymer optical gap. We therefore identify the charges on the copolymer chains as *polarons* since these excitation species have two allowed absorption bands, as seen in many DIA and PIA spectra of homopolymers,³⁴ and calculated for the copolymers.²⁹ From the photon energy of the P1 band maximum, we estimate the polaron relaxation energy in PBnDT-FTAZ copolymer upon doping to be ~ 0.3 eV. Importantly, we note that apart from the photon energy of the maximum absorption of the P1 band in the PIA and DIA spectra, they are quite similar to each other. This validates our interpretation that the P1 band in the PIA spectrum is due to photogenerated polarons. The red-shift of P1 upon photogeneration relative to that formed upon doping can be readily explained as due to smaller charge pinning for the photogenerated polarons.

FIG. 7. (a) The doping induced absorption (DIA) spectrum of PBnDT-FTAZ film. The polaron bands P1 and P2, and the IRAV are assigned. (b) The evolution of the PIA spectrum upon exposure to iodine vapor measured at various time durations, as given. P1 polaron band and related IRAVs are assigned.

It is known that in π -conjugated polymers, the optical cross section, σ for polarons, is estimated to be $\sigma \sim 10^{-16}$ cm². Thus, the photogenerated polaron density, N , can be obtained from the PA strength using the relation: $-\frac{\Delta T}{T} = \Delta\alpha d = N\sigma d$.⁴³ Here, d is the film thickness, and $-\frac{\Delta T}{T}$ is the PA strength. Using this relation, σ for polarons, and $d \approx 100$ nm, we estimate the photoinduced steady-state polaron density, N , in the pristine film to be $N = 10^{17}$ cm⁻³. Direct photogeneration of polarons in DA-copolymers is not a viable process because, as we determined above, the exciton binding energy in these compounds is ~ 0.56 eV, much larger than $k_B T$ at room temperature. We thus conclude that there are native defects in the copolymer chains that aid exciton dissociation; in this case, the photogenerated polaron density is a lower limit for the defects density on the copolymer chains. These native defects may efficiently ionize the photo-excited excitons into electron-hole pair, while trapping the holes in the form of positive polarons.

Figure 7(b) shows the evolution of the IR-absorption spectrum in PBnDT-FTAZ upon iodine doping for various time durations. We note that doping of PBnDT-FTAZ occurs relatively easy here, similar to doping of many homopolymers, and in contrast to other copolymers discussed in the literature.²² We can divide the DIA spectrum in PBnDT-FTAZ into two regions, namely the vibrational spectral range up to ~ 1500 cm⁻¹ and the electronic spectral range at higher photon energy. The absorption strength in both spectral ranges intensifies similarly with the iodine exposure time, showing that they are correlated. We identify the strong vibrations as IR-active vibrations (IRAVs) related to the added charges onto the copolymer chains, which form an extra IR absorption activity to the otherwise inactive Raman modes.⁴⁴ It is interesting that the IRAVs oscillator strengths are similar (but weaker overall) to that of the electronic absorption band associated with the charge excitation. The immense oscillator strength of the polaron related vibrations indicates that the added charges are “easy to move,” pointing to a relatively small effective kinetic mass^{33,44} despite the relaxation energy associated with the added charges on the chain, namely the “polaronic effect.”

SUMMARY

In summary, we identified the native defects in PBnDT-FTAZ copolymer chains with a density of $\sim 10^{17}$ cm⁻³ using the photoinduced absorption technique. This is possible since direct polaron photogeneration is not a viable process in these copolymers, and therefore, the existence of polaron bands in the PIA spectrum of the pristine copolymer indicates that defects are responsible for the photogeneration of these photoexcitation species. Magneto photoinduced absorption, frequency dependent temperature, and excitation intensity dependence of photoinduced absorption allow us to identify the two PA bands in the PIA spectrum as due to triplet excitons and polarons, respectively.

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