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Long-lived-correlated triplet-pair state in an imide substituted poly-thienylene vinylene-based π-conjugated polymer

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Abstract. We report on the photophysical properties of a soluble thienylene-vinylene π-conjugated polymer, namely imide poly-thienylene vinylene. Ultrafast pump probe spectroscopy reveals that a broad photoinduced absorption (PA) band is immediately photogenerated along with a narrower PA from the photoinduced singlet excitons. The broad PA is susceptible to magnetic field and thus is assigned to a correlated triple pair state. This feature shows a long lifetime persisting into the μs time domain, in contrast to the singlet exciton PA, which quickly decays on a 10-ps timescale. The steady-state PA spectrum is identical to the transient PA spectrum of the triplet pair state but shows a magnetic field response that is typical to isolated triplet excitons. © *2018 Society of Photo-Optical Instrumentation Engineers (SPIE)* [DOI: 10.1117/1.JPE.8.032217]

Keywords: conjugated polymer; photoinduced absorption; singlet excitons; triplet excitons; triplet–triplet pairs.

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1 Introduction

Organic semiconductors (OSCs) are described by localized excitonic states with large exchange coupling that pushes the lowest triplet exciton energies deep below the optically allowed lowest singlet state.[1] The properties of singlet and triplet excitons in OSCs have been well characterized and analyzed.[2–4] Typically, C_{2h} symmetry prevails, leading to a description of excitonic states with either A_g or B_u character. These symmetry representations have profound influence on optoelectronic device performance such as in light-emitting diode (LED) and solar cells. As an example, as the ground state is of A_g character, the ordering of the lowest excited A_g and B_u states determine whether the material will be a strong light emitter or be "dark."[5] More recently, interest has risen in more complex π-conjugated polymers for which C_{2h} symmetry is relaxed, or altogether absent. Particularly, donor–acceptor (D–A) low-band gap copolymers, where the intrachain interaction between the two building block moieties reduces the optical band gap, have been responsible for a notable increase in power conversion efficiency of organic photovoltaic cells.[6,7] It is less clear what kind of optical selection rules and internal conversion dynamics governs these kinds of polymers.

The conversion between singlet and triplet exciton states in OSCs has been intensely investigated in the context of thermally activated delayed fluorescence materials for higher yield LEDs. In this case, charge-injected polaron pairs that recombine into exciton states yield both singlet and triplet excitons. The triplet excitons are dark and represent a loss channel. However, by molecular and intramolecular design, the ability to convert triplet excitons to

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the "bright" singlet state increases the emission efficiency of devices significantly.[8,9] Meanwhile, the conversion of singlet and triplet multiexciton states has been actively interrogated in the context of singlet-fission in OSCs.[10,11] Similar to LEDs, triplet excitons may be considered a loss channel in solar cell operation as their ionization energies are generally too large to allow for efficient charge-separation in donor–acceptor bulk-heterojunctions. In certain materials, the ability for a high-energy singlet to spontaneously dissociate into low-energy triplets provides a basis for improving conversion efficiency in the high-energy portion of the solar spectrum.[12]

Poly-thienylene vinylene (PTV)-based polymers have demonstrated quite emblematically the concepts discussed above. Similar to poylthiophenes, PTVs could clearly be distinguished by their striking lack of photoluminescence.[13–15] As detailed experimentally[16] and consistent with theory,[5] this results from the ordering of A_g and B_u excited states leaving the optically dark A_g state as the lowest energy excited state. The PTVs have also shown evidence of singlet fission,[17] a result that hints at the possible relation between the A_g excited state and the triplet–triplet pair state, that is the precursor to the two independent triplet states formed via fission.

The modified PTV polymer studied here, referred to as imidePTV, is similar to donor–acceptor copolymers via the presence of electron-deficient imide moiety alternating with electron-rich thiophenes [see backbone structure in Fig. 1(a) inset], although in this case the interaction is not strong enough to influence the optical band gap. Characterization of this polymer showed that PL is still very weak.[18] However, the modification of excited state dynamical properties relative to the pristine PTV polymer has yet to be investigated.

Here, we study the excited state properties of imidePTV polymer films. Using electroabsorption (EA) spectroscopy we determine the energetic positions of the strongest dipole coupled exciton states, and probe population dynamics of these excitonic states using ultrafast pump-probe spectroscopy across a broad spectral range, ranging from 0.25 to 2.5 eV. We also

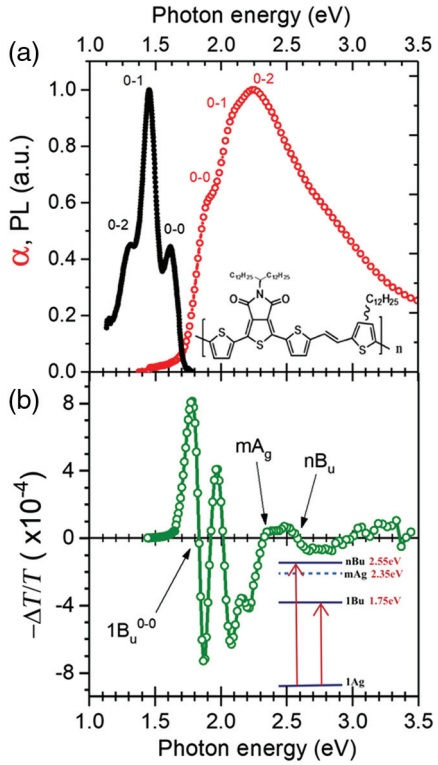

Fig. 1 (a) Absorption, α (red, open circles; measured at 300 K) and PL (black, solid circles; measured at 10 K) spectra of imidePTV film. The PL spectrum was corrected for the detector and grating responses. The vibronic replicas of each spectrum are assigned as 0–0, 0–1, and 0–2. (b) Electroabsorption spectrum of imidePTV measured at 10 K. Inset shows the energy-level diagram of exciton levels.

characterize the steady-state photoinduced absorption (PA) and its sensitivity to perturbative external magnetic field. We find a broad PA band composed of a quickly decaying optically allowed singlet exciton at low energy and broader PA band that persists beyond the nanosecond (ns) time domain. The broadband PA shows a magnetic field dependence on sub-ns timescale. Furthermore, the magnetic field effect observed for the broad PA in the steady state confirms conversion between singlet and triplet excitons in the photoexcited recombination kinematics and shows similarities to recent observations of spin-entanglement and time evolution of decoherence in D–A copolymers.[19]

2 Experimental Methods

Solutions of imidePTV were made by dissolving the powder in *o*-Dichlorobenzene at a concentration of 20 mg/mL. ImidePTV films were cast onto glass or sapphire substrates from such solutions by drop-casting or spin-coating.

Absorption, cw-PL, and cw-PA measurements were performed using a standard optical setup. An Ar^+ laser beam at $\hbar\omega = 2.5$ eV modulated at various frequencies, f (10 to 5 kHz) was used as a pump, and the emission from a tungsten lamp was used as the probe. The induced change in absorption, PA was measured using a lock-in amplifier referenced at f, a monochromator, and various combinations of filters, gratings, and solid-state photodetectors spanning the spectral range $0.3 < \hbar\omega(\text{probe}) < 2.7$ eV. Measurements were performed with the sample mounted inside a Janis cold finger cryostat to provide temperature control down to 10 K. The PA signal is calculated as $\Delta T/T = (T - T_{\text{pump}})/T$, where T_{pump} is the transmission measured whereas the pump excitation is incident on the sample, and T is the transmission without the pump. Magnetic field effects were studied by application of a magnetic field provided by an electromagnet during the measurement.[20]

Electroabsorption[21] was measured using the same setup but with the sample cast on a glass substrate with lithographically patterned, interdigitated aluminum electrodes of 20 μm, which were spaced by 20-μm gaps. A function generator in combination with a step-up transformer applied an electric field of 4×10^4 V/cm at a frequency of 400 Hz. The modulated transmission was collected at the second harmonic of the field frequency and calculated as $\Delta T/T = (T - T_{\text{E-field}})/T$, where $T_{\text{E-field}}$ is the transmission measured whereas the electric field is applied across the sample, and T is the transmission without the field.

Ultrafast pump-probe spectroscopy was carried out over a broad spectral range using two experimental setups. In the midinfrared (MIR), the two-color pump-probe correlation technique was used.[22] Ti:sapphire laser (80 MHz, ~0.1 nJ/pulse) output at 1.55 eV was frequency-doubled to 3.1 eV and served as pump, whereas an optical parametric oscillator was used to convert the fundamental into a probe beam spanning from 0.24 to 1.1 eV. In the near-infrared/visible range, a high-energy (10 μJ/pulse) low-repetition rate (1 kHz) laser system with frequency-doubled pump at 3.1 eV was used to excite the sample and to generate white light continuum to serve as probe, spanning the spectral range from 1.3 to 2.5 eV. The PA spectrum was dispersed by a monochromator.[16] For both systems, the temporal resolution was ~150 fs. The transient PA was measured as the change in transmission at a time t after photoexcitation, normalized by the transmission, namely $\Delta T(t)/T$.

3 Results and Discussion

In Fig. 1(a), we show the absorption and PL spectra of an imidePTV thin film. The absorption and PL onset determine the optical band gap energy $E_G = 1.75$ eV. In both the absorption and PL spectra, multiple peaks (labeled as 0 to 0, 0 to 1, and 0 to 2) due to the vibrational progression within the electronic manifold are resolved. The peaks are equally spaced by ~0.17 eV, which corresponds to the strongest coupled vibrational mode, generally assigned to the C=C stretching mode.[23] The PL quantum yield and solvent dependence of the PL in solution were previously reported.[18] In that work, we found that the PL is weakly allowed, with PLQE on the order of 1%. This value is intermediate between completely nonemissive PTV parent polymer and more strongly luminescent polymers such as derivatives of polyphenylene vinylenes.

In Fig. 1(b), we show the electroabsorption (EA) of imidePTV film. The EA spectrum is consistent with other spectra previously measured for numerous π-conjugated polymers;[21,24] hence, although the chemical structure suggests that C_{2h} symmetry is not strictly maintained here, we still reference these features using the conventional nomenclature. The zero-crossing of the lowest energy first EA derivative-like feature occurs at 1.8 eV consistent with the value of E_G obtained from the absorption and PL spectra assigned to the 0–0 level of the $1B_u$ singlet exciton. At higher energies, riding on top of the photobleaching, we find a series of vibronic replicas consistent with those found in the absorption and PL spectra discussed above. In addition, above 2.35 eV there is an EA band (marked mA_g) where there is no corresponding feature in the linear absorption spectrum. This is evidence of a dark exciton state that becomes partially allowed due to the breaking of symmetry imposed by the electric field that has been assigned as the mA_g exciton in previous studies.[21,24] This state is strongly coupled to the allowed singlet ($1B_u$) and therefore contribute to the $\mathrm{Im}[\chi^{(3)}]$ response that dictates the EA response. At even higher energies, we see another derivative-like feature that occurs in the vicinity of a kink in the linear absorption [Fig. 1(a)], suggesting a weakly optically allowed state such as nB_u exciton.

Generation and relaxation dynamics of the photoexcitations were probed in the picosecond (ps) timescale using the pump-probe spectroscopy with 3.1 eV excitation and the MIR probe energy range. The PA spectra at different times after pump pulse excitation are displayed in Fig. 2(a). A PA band peaked near 1.0 eV is observed at $t = 0$, with an extended tail down to 0.3 eV. With increasing delay time, the PA decreases and appears more flat, broad, and featureless. On the high-energy side of the spectrum, the PA is long-lived, extending well beyond the ~12 ns period between successive pump pulses. This results in a "background" signal, obtained by measuring the PA spectrum a few ps before the arrival of the pump pulse. The resultant PA background is shown in Fig. 2(b) (green triangles). As the background signal might be generated instantaneously right after photoexcitation due to ultrafast singlet fission phenomenon, its contribution to the transient t-PA spectra [Fig. 2(a)] needs to be eliminated to see other t-PA features of short lived photoexcitations. Figure 2(b) shows the corrected spectrum decomposed from the raw spectra shown in Fig. 2(a) upon removal of the background. We can see the temporal evolution of the spectrum more clearly; it contains a PA band peaked near 0.9 eV. This pronounced PA band vanishes on a 10-ps timescale leaving behind the long-lived broad, featureless PA band that resembles the background PA. The PA decay dynamics at 0.6 and 0.9 eV are shown in Fig. 2(c). After the rapid decay of ~10 ps, a quasiexponential decay with a lifetime of ~150 ps is observed followed by a plateau, or long tail. If we use the equation $\mathrm{PLQE} = \tau/\tau_R$, where PLQE is the PL quantum efficiency or PL yield, τ is the exciton lifetime obtained from the PA dynamics, and τ_R is the exciton radiative lifetime (~1 ns in π-conjugated polymers), the fast decay time of ~10 ps is in agreement with the previously reported PL yield of ~1%. We, therefore, identify the fast decay to emissive singlet excitons.[25] This suggests that the limiting factor for the PL yield in imidePTV is the $1B_u$ conversion of into a low-energy "dark" exciton such as the $2A_g$.[18] In support of this assignment, we consider the EA spectrum in Fig. 1(b), where the $1B_u$ exciton was found at 1.75 eV and the onset of the mA_g exciton was observed at 2.35 eV. The difference between these levels corresponds roughly to the onset of the single exciton PA onset (~0.6 eV). The indirectly formed $2A_g$ band successively decays with a lifetime of 150 ps. Finally, the long tail seen in the 0.9 eV kinetics suggests the contribution of background signal to the early t-PA spectra.

The change of the PA strength with the application of magnetic field (t-MPA) at $t = 200$ ps is shown in Fig. 2(d). This delay time was chosen to ensure that the $1B_u$ component of the PA spectrum is absent. The t-MPA response thus corresponds to the broad, long-lived component in the t-PA spectrum. It is evident from the observation of the MPA response that the broader PA cannot be a pure singlet state, because such a state is not susceptible to small fields. As the broad and unsaturated t-MPA response in imidePTV is similar to the response of the triplet-triplet pair state (TT) state reported previously,[19] we can assign the broad PA feature to the TT state. In the context of singlet fission, TT state having overall singlet character could be formed immediately after photoexcitation in resonance with the singlet, or subsequently populated via singlet.[26,27] It has previously been suggested that the $2A_g$ state is similarly a state composed of two triplets with overall spin singlet character.[28] The TT state contains spin sublevels of which population may be

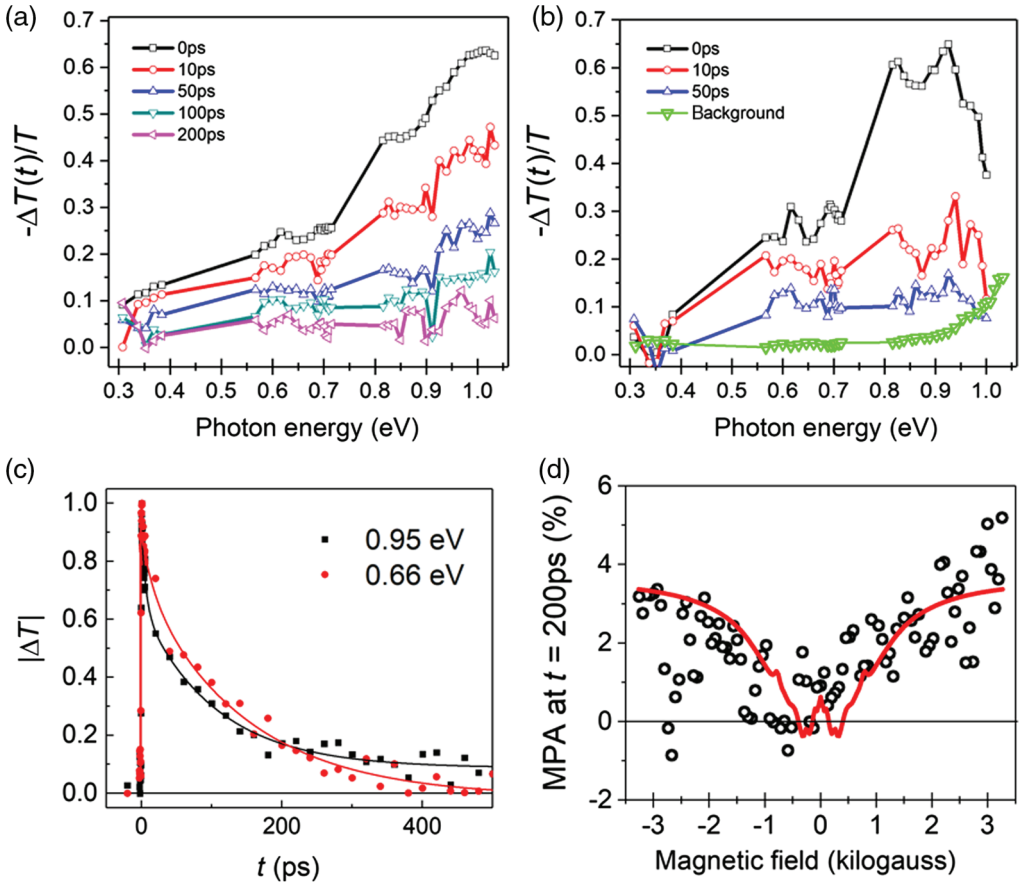

Fig. 2 (a) PA spectra at different delay times after pump pulse excitation, as denoted. (b) Same as in (a) but corrected for the PA background signal as shown (green triangles) that were obtained by measuring the long-lived PA response before the arrival of the pump pulse, namely $t < 0$. The background originates from the long lived photoexcitations such as triplets or charged polarons whose lifetime is longer than the inverse of the pump laser's repetition rate of 80 MHz, equivalent to ~12 ns. (c) PA dynamics at the probe energies as indicated. (d) Magnetic field response of PA (MPA) at $t = 200$ ps measured at 0.9 eV. The red line is a fit to the data (circles) using the spin Hamiltonian described in Ref. 19. A good fitting can be obtained with the zero field splitting parameters: $D/2\mu_B = 50$ mT, $E/2\mu_B = -2$ mT, and the exchange coupling constant between two triplets of the TT pair: $X/2\mu_B = 5.5$ mT.

influenced by a magnetic field.[29] Recently, using the transient MPA (t-MPA) technique we have recently shown that the resonant singlet and TT states display spin entanglement.[19] The t-MPA response of the broad PA band of imidePTV is similar to that of the TT state reported therein. Using the spin Hamiltonian,[19] a good fitting can be obtained with the zero field splitting parameters, $D/2\mu_B = 50$ mT and $E/2\mu_B = -2$ mT, and the exchange coupling constant between the two triplets of the TT pair is $X/2\mu_B = 5.5$ mT. However, in this case the rapid decay of the singlet band signals such anticorrelation behavior is not possible in imidePTV. The key for the observation of a long-lasting, anticorrelation response on the hundreds of picoseconds timescale is the resonant coupling between the singlet exciton and TT state, which are the two primary photoexcitations in this class of material. However, for the ImidePTV, such a resonant condition is absent as the energy of singlet exciton is above that of the 2Ag/TT state, leading to fast decay of singlet exciton into the TT state within 10 ps.

We further extend the ultrafast pump-probe investigation to include the visible/near-infrared spectral range, as shown in Fig. 3(a). Immediately after photoexcitation, a broadband is formed extending from the optical gap, E_G, to the low-energy spectral limit of the high-energy low repetition rate laser system. At early times, the PA spectrum is weighted toward higher energy near E_G, and also toward lower energy in the NIR, suggesting that there are two PA bands peaked

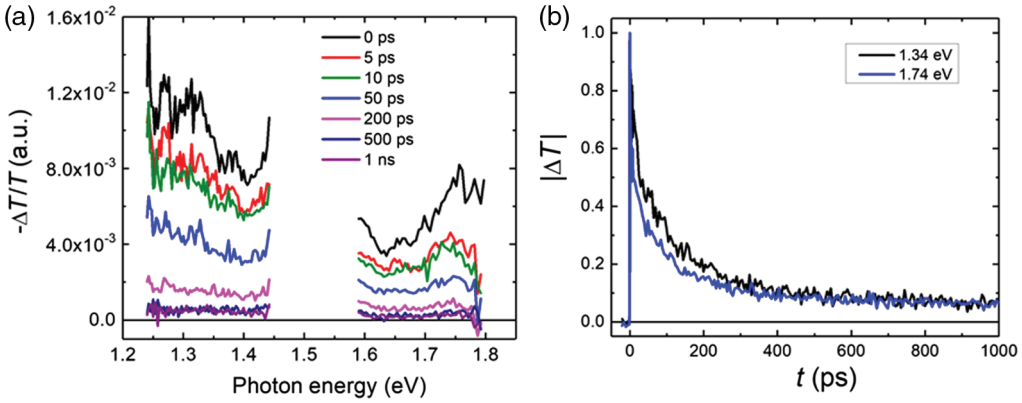

Fig. 3 (a) Photoinduced absorption at different times after photoexcitation and (b) photoexcitation dynamics at the probe energies indicated.

at 1.7 and 1.3 eV, respectively. These features decay leaving a broad PA spectrum at timescales on the order of 100 ps. These two features show similar dynamics, as shown in Fig. 3(b). A rapid decay at early times gives way to a quasiexponential decay with a lifetime of ~150 ps. Beyond this, a long tail is observed, extending into the ns regime, consistent with that obtained in the MIR part of the PA spectrum. Considering these observations, the lower energy band at near 1.2 eV is most likely an extension of the singlet exciton PA observed in the MIR; specifically, a fast decay band on top of a broad, featureless, long-lived PA. However, the higher energy feature near E_G is most likely the signature of indirect index modulation via thermal or strain effects resulting from the aforementioned excitations, and the energy dissipation occurring through their recombination. Recalling the low PL yield of this polymer, most of the recombination is in fact nonradiative, lading to heat that increases the film temperature. In turn the temperature increase broadens the absorption tail toward lower energy, resulting in excess PA at the low-energy part of the exciton absorption.

The cw-PA spectrum of an imidePTV film at 10 K [Fig. 4(a)] displays a broadband centered at 1.2 eV with an onset near 0.8 eV. At energies higher than the optical gap at 1.8 eV, the spectrum shows a pronounced photobleaching (PB) of the ground-state absorption. The PB feature rides on top of the broad PA that extends above the band edge. The broad PA band is striking similar to the PA spectrum obtained in the ultrafast regime. The pump intensity, I_p dependence of the PA shown in Fig. 4(b) is linear at all probe energies in the range $10\ \mathrm{mW/cm^2} < I_p < 300\ \mathrm{mW/cm^2}$; similar to the PL emission intensity versus I_p (not shown here), which indicates a monomolecular recombination kinetics. This allows us to rule out exciton–exciton annihilation effects that are known to occur at large I_p, as this process

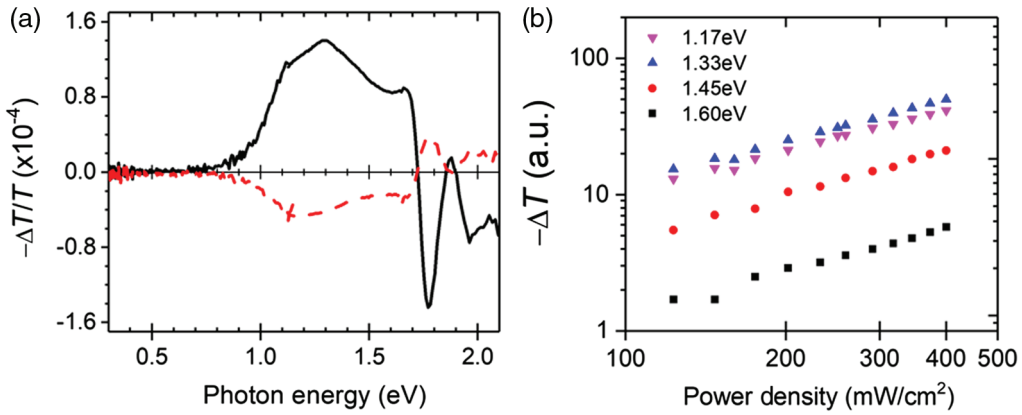

Fig. 4 (a) In-phase (black) and quadrature (red) cw-PA spectrum of a film of imidePTV at 10 K, using a 2.54-eV excitation modulated at 3 kHz. (b) cw-PA versus the pump intensity at several different probe energies as indicated.

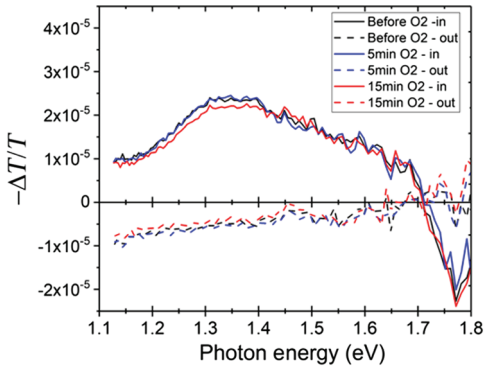

Fig. 5 CW PA of imidePTV during oxygen exposure, achieved by purging the chamber with gas having high percentage of oxygen. The time of exposure is indicated. The measurements were performed with the sample held at 100 K before exposure to O_2.

is bimolecular, having an $(I_p)^{1/2}$ at steady-state conditions. Furthermore, measurements at different pump frequencies and different sample temperatures (not shown here) also display no spectral variation, confirming that the broad PA band is due to a single photogenerated species, having monomolecular recombination kinetics. At the modulation frequency of 3 kHz in Fig. 4(a), the PA is almost entirely obtained in-phase with the pump modulation, and the frequency dependence is unable to determine the lifetime as it is shorter than the resolution of the setup of $\sim$15 μs. We note that the PA spectrum does not contain contribution from other photoexcitation species such as charged polarons, for example.

As oxygen is an effective quenching agent for triplet states having energy of $\sim$1 eV above the ground state, exposure of the sample during the optical measurements may be used to identify the excited state species. In Fig. 5, we show the PA spectrum in the presence of oxygen exposure. The sample is held at 100 K to maintain a quality signal-to-noise ratio while avoiding condensation of oxygen vapor in the cryostat. As can be seen, the signal is unaffected after 5 min of immersion in atmospheric pressure oxygen gas. The PA strength remains unchanged until the sample temperature begins to rise. We thus conclude that if the PA results from isolated triplet excitons, then the energy of this state must be below 1 eV (the triplet oxygen level). If indeed this is the case here, it places the lowest triplet energy close to half the lowest optically allowed singlet exciton, possibly allowing for energetically favorable singlet fission. However, we explain below how this is not likely the case.

Figure 6(a) shows the magnetic field dependence of the cw-PA (MPA) measured at 1.2 eV. The application of the field decreases the PA intensity. This field susceptibility cannot come from a pure singlet excitation. Lacking any evidence of charged polarons, this points to evidence of

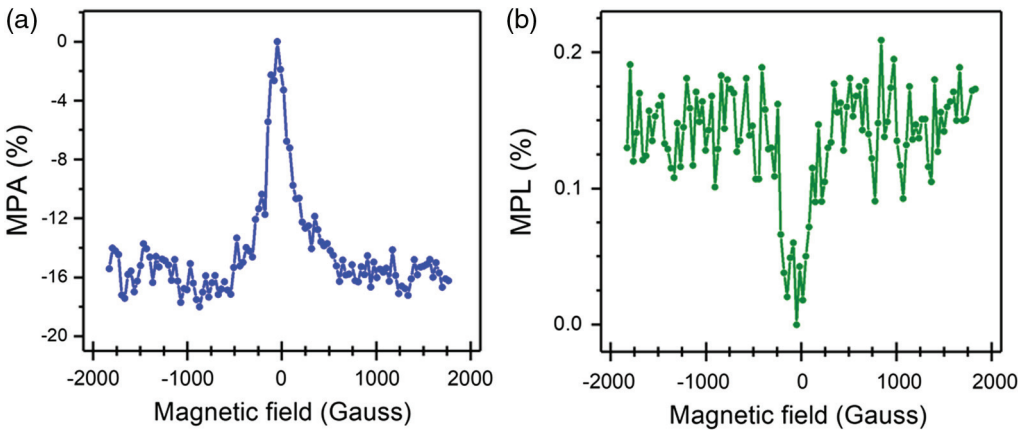

Fig. 6 Magnetic field dependence (MPA) at 10 K of (a) cw-PA at a probe energy of 1.20 eV and (b) PL at an emission energy of 1.48 eV.

a triplet excitations. This is further supported by the magnetic field dependence of PL shown in Fig. 6(b), where the PL increases, albeit weakly, with increasing field. Comparison of the steady-state response in Fig. 6(a) along with the ultrafast response shown in Fig. 2(d), to the temporal evolution of the MPA response observed in donor–acceptor copolymers,[19] we see a similar evolution for the broad PA band in imidePTV. This was interpreted[19] as displaying the loss of coherence between the initially photogenerated geminate TT pair, and two distinct noninteracting triplets. We note, however, that the cw-PA spectrum is identical to the transient spectrum at long times, and quite different from the typical profile for isolated triples. This suggests that the TT state persists into the μs regime and is persistent under steady-state illumination. The magnetic-field response of isolated triplets is much larger, and thus washes out the TT response of opposite sign and smaller magnitude. Therefore, although isolated triplets dominate the steady-state MPA response, they may exist at low densities compared with the long-lived TT state. In the other words, even if the TT-state dissociates into isolated triplets, it must have been a very inefficient process.

4 Conclusions

We have investigated the excited state energies, dynamics, and magnetic field response of a new version of the π-conjugated polymer imidePTV, through a series of ps transient and cw spectroscopic characterizations. We found a singlet exciton PA band that decays rapidly within 10 ps, leaving a broadband with magnetic field sensitivity attributed to a correlated triplet pair state that is a precursor to singlet fission. Coherence between the singlet exciton and the TT-state is thus rapidly lost in this material. In the steady-state regime, the triplet band still dominates the PA spectrum but shows a magnetic field response of individual triplets. These findings are useful in deepen our understanding of the way electronic modifications through chemical substitution may be used to further tailor the spin-dependent optoelectronic properties of OSCs. In particular, the role of interchain coupling in facilitating TT state dissociation is an interesting topic for further investigation.

Disclosures

The authors declare no conflict of interest.

Acknowledgments

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Biographies for the authors are not available.