

## Transient Magnetophotoinduced Absorption Studies of Photoexcitations in $\pi$ -Conjugated Donor-Acceptor Copolymers

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We have utilized a plethora of transient and steady state optical and magneto-optical spectroscopies in a broad spectral range (0.25–2.5 eV) for elucidating the primary and long-lived photoexcitations in a low band-gap  $\pi$ -conjugated donor-acceptor (DA) copolymer used for efficient photovoltaic solar cells. We show that both singlet excitons (SE) and intrachain triplet-triplet (TT) pairs are photogenerated in the DA-copolymer chains. From the picosecond transient magnetic field response of these species we conclude that the SE and TT spin states are coupled. The TT decomposition into two intrachain geminate triplet excitons maintains spin coherence and thus their spin entanglement lasts into the microsecond time domain.

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The field of “photoexcitations in  $\pi$ -conjugated polymers” has been debated since as early as 1980 with trans polyacetylene [1]. The debate heated up when the nature of the primary photoexcitations, namely, free carriers vs excitons was considered [2]. This debate took a new twist when the exciton dissociation in polymer-fullerene blends was discussed [3,4], since this process has bearing on potential applications in organic photovoltaic solar cells [5]. Recently the organic solar cell quantum efficiency has dramatically increased when the low band-gap ( $E_g \sim 1.4$  eV)  $\pi$ -conjugated donor-acceptor (DA) copolymers were introduced [6,7]. However, the nature of the primary photoexcitations in these materials has not been well characterized, probably because of limited available ultrafast spectroscopies in the mid-IR spectral range [8].

The DA-copolymer chains contain, by definition, two different organic moieties with different electron affinities [see Fig. 1(a) inset] that play the role of electron donor ( $D$ ) and electron acceptor ( $A$ ) [6–10]. This intrachain DA character leads to lower  $E_g$  than that in more traditional polymers [11], and therefore can absorb more photons from the solar spectrum, which consequently increases the solar cell efficiency [9–12]. However, the small  $E_g$  (1.4–1.6 eV) in the most efficient DA copolymers may lead to another phenomenon that has not been explored yet. It is known that the energy difference  $\Delta_{ST}$  between the singlet exciton (SE) and triplet exciton (TE) energies in polymers [13] is about 0.7 eV. If this is true also in DA copolymers, then the TE energy,  $E_T (=E_g - \Delta_{ST} = 1.4$  to  $1.6 - 0.7)$  is  $\sim 0.7$ – $0.9$  eV. This would lead to a “resonant condition” between the lowest SE (at  $E_S = E_g \approx 1.4$ – $1.6$  eV) and the intrachain triplet-triplet (TT)-pair state at energy  $2E_T \approx 1.4$ – $1.8$  eV. This may have strong influence on the photophysics of the DA

copolymers, since SE-TT coupling may occur. For investigating a possible SE-TT resonant interaction in DA copolymers having  $E_S \approx 2E_T$ , we have used, for the first time, the transient magnetophotoinduced absorption (t-MPA) technique in the time domain from 0.2 ps to milliseconds, which is the magnetic field effect ( $M$ ) of the transient photoinduced absorption (t-PA) spectrum. We indeed measured spin-entanglement between the SE and TT states in the copolymer chains resulting in a unique magnetic field response. Furthermore, the spin coherence is conserved upon TT decomposition into two geminate intrachain TE's, and, consequently, their spin entanglement is maintained up to microseconds, the copolymer spin-lattice relaxation time.

We have focused our studies on the  $\pi$ -conjugated DA-copolymer PDTP-DFBT [Fig. 1(a) inset] [16], but other DA copolymers with different  $D$ - $A$  moieties have similar photoexcitations [12,17]. As is clearly seen in Fig. 1(a) the PDTP-DFBT backbone structure does not possess inversion symmetry in contrast to the more traditional  $\pi$ -conjugated polymers; this has important implications on the photoexcitation species in these materials. For example, the SE is not strictly an odd-parity state, whereas the TT is not strictly a covalent state; this effect may provide the basis of a possible interaction between these two states.

For our studies, we have used standard cw spectroscopies such as photoluminescence (PL), photoinduced absorption (PA) [18] and its magnetic field version, namely, MPA [14]. We have also used the optically detected magnetic resonance of the PL [19] to identify the spin state of the long-lived photoexcitations, as well as electroabsorption (EA) [20] to discern the excited states of this DA copolymer. Our *unique* transient ps experimental setup in the mid-IR is described in detail elsewhere [18]. The pump excitation beam was delivered by pulsed Ti:sapphire laser; it provides pulses of

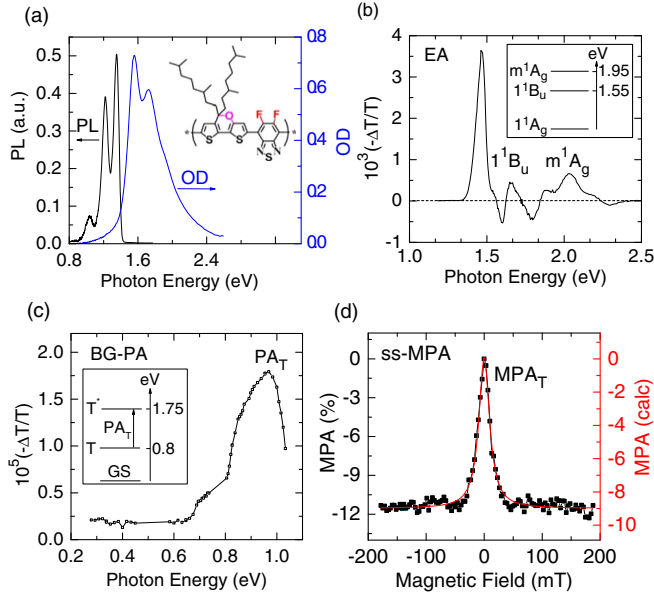


FIG. 1. Steady state (ss) spectroscopies of pristine PDTP-DFBT  $\pi$ -conjugated DA copolymer; the repeat unit is shown in panel (a) inset. (a) The photoluminescence and absorption spectra of the DA-copolymer film. (b) The copolymer electroabsorption spectrum, where the two important excited states (namely, the lowest odd parity,  $1^1B_u$  and most strongly coupled even parity,  $m^1A_g$ ) and their energy levels are assigned (inset). (c) The steady state photoinduced absorption (ss-PA) spectrum measured via the background PA (BG-PA) in the ps pump-probe correlation, modulated at 1 kHz (see the Supplemental Material [15]). The triplet PA band ( $PA_T$ ) is assigned. The inset shows the energy levels of the lowest TE state ( $T = 1^1B_u$ ) and its most strongly coupled excited state ( $T^* = m^3A_g$ ). (d) The steady state magneto-PA [ss-MPA( $B$ )] response of  $PA_T$  (namely,  $MPA_T$ ) measured at 40 K. The line through the data points is a fit based on TE having zero-field splitting parameters,  $D = 38$  and  $E = 15$  mT [14] (see model in the Supplemental Material [15]).

150 fs duration, energy 0.1 nJ/pulse, 80 MHz repetition rate at 1.55 eV photon energy. The probe spectral range could be varied between 0.25–1.1 eV. The transient photoexcitation density ( $\sim 2 \times 10^{16}$  cm $^{-3}$  at  $t = 0$ ) was monitored by the changes  $\Delta T$  of the probe transmission  $T$  induced by the modulated pump, and measured by an InSb detector (Judson IR) using a phase-locked technique with a lock-in amplifier (SR830) [18].

The PDTP-DFBT absorption and PL spectra are shown in Fig. 1(a). The Stokes shifted 0-0 PL band peaks at 1.38 eV, considerably lower than in any traditional  $\pi$ -conjugated polymers [21]. To more precisely determine the energies  $E_s = E(1^1B_u)$ , and  $E(m^1A_g)$  of the most strongly coupled even-parity state, we measured the EA spectrum of pristine PDTP-DFBT film deposited on an interdigitated electrode substrate, subjected to a modulated applied voltage at frequency  $f$ , where the EA was monitored at  $2f$ . In general, the EA spectrum in  $\pi$ -conjugated polymers shows two dominant optical features: a derivativelike Stark shift feature

at  $E(1^1B_u)$ , and a field-induced absorption at  $E(m^1A_g)$  due to the partial symmetry breaking associated with the applied field [20,22]. The EA spectrum of PDTP-DFBT [Fig. 1(b)] indeed exhibits such spectral signatures: a derivativelike feature with zero crossing at  $\sim 1.55$  eV, which we identify as  $E(1^1B_u)$ , and a positive band with 0-0 vibronic transition at  $\sim 1.95$  eV, which we assign as  $E(m^1A_g)$  [see Fig. 1(b) inset]. The energy difference,  $\Delta E = E(m^1A_g) - E(1^1B_u)$  has been traditionally used to estimate the exciton binding energy [18,22]. Thus, in PDTP-DFBT we get  $\Delta E \approx 0.4$  eV, which is also expected to be the transition energy of the PA band from the photogenerated  $1^1B_u$  exciton into the  $m^1A_g$  ( $1^1B_u \rightarrow m^1A_g$ ), namely,  $PA_{SE}$  [18,21].

Figure 1(c) depicts the steady state PA (ss-PA) spectrum in a film of solid state solution, in which *isolated* pristine PDTP-DFBT chains are embedded in polystyrene matrix. The spectrum is dominated by a single PA band ( $PA_T$ ) that peaks at  $\sim 0.95$  eV, which we assign to the strongest transition in the TE manifold, namely,  $1^3B_u \rightarrow m^3A_g$  [Fig. 1(c)] [18]. From the PL-detected magnetic resonance powder pattern shown in the Supplemental Material (Fig. S.1) [15] we conclude that the long-lived photoexcitations are TE's, with zero-field splitting parameters,  $D/2\mu_B = 38$  and  $|E|/2\mu_B = 15$  mT. We also performed steady-state magneto-PA [ss-MPA( $B$ )], where  $MPA = [PA(B) - PA(0)]/PA(0)$  and  $B$  is the magnetic field, at the  $PA_T$  band [Fig. 1(d)], which shows a typical TE response [14]. Since we determined  $E(m^1A_g) \approx 1.95$  eV from the EA spectrum, we can now estimate its triplet counterpart, namely,  $E(m^3A_g) \approx 1.75$  eV, which is lower by  $\sim 0.2$  eV [23]. Consequently, from  $E(m^3A_g)$  and  $PA_T$  transition energy in the triplet manifold, we can determine the energy of the lowest TE  $E_T = E(1^3B_u) = E(m^3A_g) - E(PA_T) \approx 1.75 - 0.95 \approx 0.8$  eV [see Fig. 1(c)]. It is thus clear that the lowest SE in PDTP-DFBT ( $= 1.55$  eV) is in resonance with twice the lowest triplet ( $2 \times 0.8 = 1.6$  eV), i.e.,  $E(1^1B_u) \approx 2E_T$ , which calls for a possible interaction between the lowest SE and TT states in this copolymer [12]. This interaction may lead to the occurrence of a direct optical transition from the copolymer ground state into the TT manifold, as predicted theoretically [12]. This may be identified via the formation of *two PA bands* in the t-PA spectrum: a lower energy band,  $PA_1$  close to  $PA_{SE}$  in the singlet SE manifold, and a higher energy band,  $PA_2$  that is related to TT pair excitations at energy slightly lower than  $PA_T$ .

We discuss the ps transient spectroscopy of PDTP-DFBT by first examining the mid-IR ps t-PA spectrum of a traditional  $\pi$ -conjugated polymer, which is a soluble derivative of the polymer poly-(*p*-phenylene-vinylene), namely, DOO-PPV [Fig. 2(a)]. The t-PA spectrum of DOO-PPV film contains a *single* PA band ( $PA_{SE}$ ) due to the photogenerated SE that peaks at 0.95 eV [23]. This PA band is correlated with the stimulated emission band of

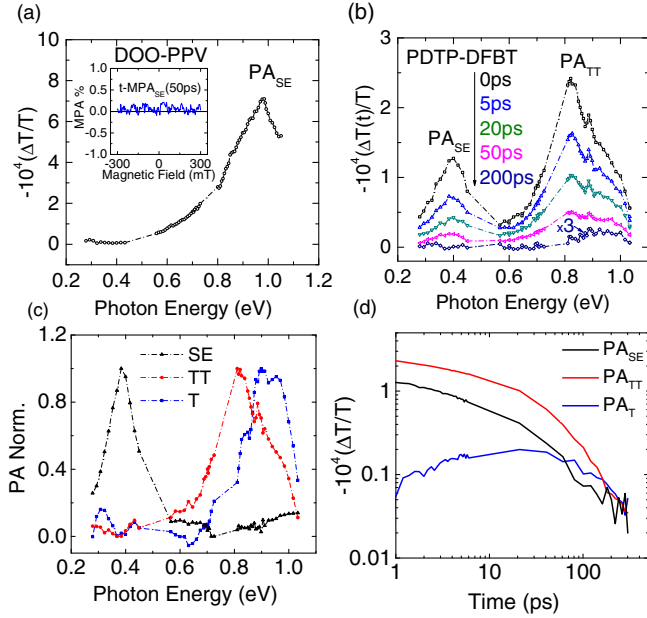


FIG. 2. Room-temperature ps transient PA spectroscopy of pristine PDTP-DFBT embedded in a polystyrene matrix, where the copolymer chains are isolated. (a) The transient PA (t-PA) spectrum of DOO-PPV polymer film in the midinfrared measured at  $t = 0$  excited at 3.1 eV that is shown here for comparison with the transient PA in PDTP-DFBT. The inset shows the lack of t-MPA(B) response at 100 ps. (b) The time evolution of the t-PA spectrum in isolated chains of PDTP-DFBT measured at several delay times  $t$  following the pump excitation at 1.55 eV.  $PA_1$  and  $PA_2$  bands are assigned. (c) The normalized SE (black), TT (red), and TE (blue) PA bands extracted from the t-PA spectrum in (b) using the GA method (see Supplemental Material [15]). (d) The PA band dynamics as calculated by the GA method plotted in logarithmical scale for  $t$ , which shows that early decay of the  $PA_{SE}$  and  $PA_{TT}$  leads to buildup of  $PA_{TE}$  within  $\sim 50$  ps.

DOO-PPV and decays with a time constant  $\tau$  of  $\sim 200$  ps, in agreement with the PL quantum efficiency of this polymer ( $\tau/1(\text{ns}) \sim 20\%$ ) [24].

In contrast, the t-PA spectrum of the PDTP-DFBT copolymer film of 1% weight solid state solution in polystyrene, where the chains are *isolated* from each other exhibits *two* PA bands [Fig. 2(b)]: namely,  $PA_1$  at 0.4 and  $PA_2$  at 0.82 eV, which are formed within our experimental pump-probe time resolution ( $\sim 300$  fs). The two PA bands decay together, with time constant  $\tau \approx 30$  ps showing the same dynamics [Fig. S.2(a)]. This PA lifetime agrees with the PL quantum efficiency of  $\tau/1(\text{ns}) \sim 3\%$  that we measured in neat PDTP-DFBT films. Furthermore,  $PA_1$  peaks at 0.4 eV where  $PA_{SE}$  should be. Based on these two findings, we identify  $PA_1$  as due to photogenerated SE in this copolymer (namely,  $PA_{SE}$ ), similarly as in the t-PA spectrum of DOO-PPV [Fig. 2(a)]. We also observed transient photoinduced dichroism  $P(t)$  for the two t-PA bands [Fig. S.2(b)], and found that it decays similarly for the two PA bands, namely, within  $\sim 50$  ps. From the same

PA decay dynamics and  $P(t)$  kinetics we infer that the two PA bands are correlated. Since  $PA_2$  is close in energy to that of ss- $PA_T$  [Fig. 1(c)] but not at the same photon energy we identify it as due to transition within the TT manifold (namely,  $PA_{TT}$ ). From their similar decay dynamics we consequently conclude that the SE and TT states are *correlated* in this copolymer.

As seen in Fig. 2(b) the two PA bands completely decay within 300 ps; at that time the t-PA spectrum is dominated by a different PA band that peaks at 0.94 eV; its spectrum is enlarged in Fig. 2(c). This PA band is exactly the same as  $PA_T$  in the ss-PA spectrum [Fig. 1(c)] that we have identified as TE, and therefore it is due to triplet excitons ( $PA_T$ ) that are photogenerated in the ps time domain. Since the spin-orbit coupling of this copolymer is relatively weak due to lack of heavy atoms, the intersystem crossing rate should be small and cannot explain the fast TE generation. We therefore conclude that the fast TE's are generated via decomposition of the TT excitations, namely, singlet fission.

It is important to know whether the fast  $PA_T$  is photo-generated immediately, or is a by-product of the  $PA_{SE}$  and  $PA_{TT}$  decays. To study the  $PA_T$  fast dynamics, we have employed a generic algorithm (GA) as a numerical method to decompose the overlapping PA bands in the t-PA spectrum [25,26]. Figure 2(c) shows three decomposed bands for SE, TT, and TE and their associated dynamics is shown in Fig. 2(d). We see that SE and TT are instantaneously photogenerated within 300 fs resolution and decay together. Importantly, some of  $PA_T$  is also generated within 300 fs; however, the decay of SE and TT continues to generate TE. We thus conclude that  $PA_T$  is in fact a by-product of  $PA_{TT}$ , which is correlated with  $PA_{SE}$ . The following t-MPA studies further characterize the curious interrelation of these primary photoexcitation species.

Figure 3(a) shows the transient magnetic field response, t-MPA(B) of  $PA_{SE}$  and  $PA_{TT}$  bands at a fixed time,  $t = 200$  ps, whereas Fig. 3(b) depicts the t-MPA time evolution at a fixed field of  $B = 300$  mT. It is clearly seen that  $PA_{TT}$  increases with  $B$ ; whereas  $PA_{SE}$  decreases with  $B$ , having the same t-MPA(B) response. Also the two t-MPA responses have the same dynamics; namely, t-MPA $_{TT}$  increases with time the same way that t-MPA $_{SE}$  decreases with time. The t-MPA experiment was also attempted on the  $PA_{SE}$  band in the DOO-PPV polymer; however, we found *null* response at any delay time [see Fig. 2(a) inset]; this “control experiment” shows that  $PA_{SE}$  in DOO-PPV is due to pure SE and thus is not susceptible to relatively small magnetic fields. We thus conclude that the t-MPA obtained in PDTP-DFBT is a unique feature of the primary photoexcitations of this compound. Although the SE species in the copolymer have a predominantly spin singlet character (since they are instantaneously photogenerated) they nevertheless possess a unique spin character whose different components may have spin  $\neq 0$ .



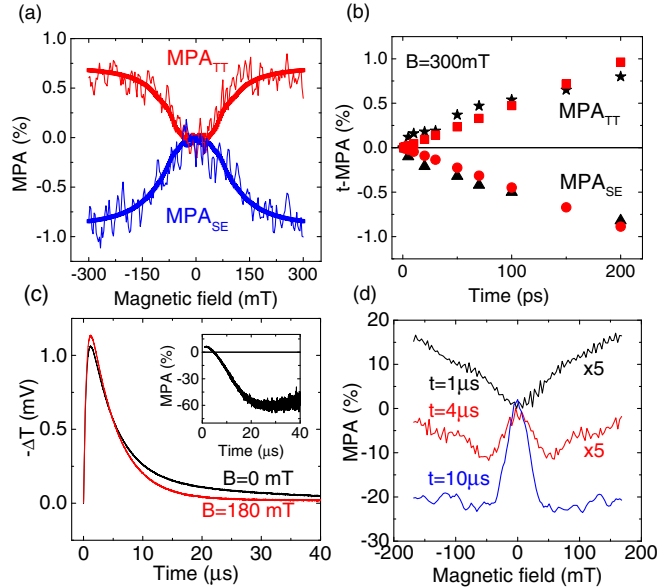


FIG. 3. Transient magneto-PA (t-MPA) response of pristine PDTP-DFBT film in the ps to microsecond time domains. (a) The t-MPA( $B$ ) response of  $PA_{SE}$  (blue line) and  $PA_{TT}$  (red line) measured at  $t = 200$  ps up to  $B = 300$  mT. The lines through the data are fits using a  $10 \times 10$  model Hamiltonian (see text). (b) The evolution of the t-MPA at  $B = 300$  mT for  $PA_{SE}$  (black triangle) and  $PA_{TT}$  (black star) up to  $t = 200$  ps. The red symbols are calculated based on the  $10 \times 10$  model Hamiltonian (see text). (c) The PA decays in the  $\mu$ sec time domain measured at 0.9 eV and 40 K, at magnetic field  $B = 0$  (black line) and  $B = 180$  mT (red line), respectively up to  $t = 40$   $\mu$ sec. The inset shows the t-MPA at  $B = 180$  mT up to 40  $\mu$ sec calculated from the PA decays dependence on  $B$ . (d) The t-MPA( $B$ ) response up to  $B = 180$  mT measured at different times,  $t$  as indicated.

Importantly, the t-MPA( $B$ ) response seen in Fig. 3(a) cannot be understood using the “Merrifield model” spin Hamiltonian of the TT pair [27], which describes well the *intermolecular* singlet fission and triplet-triplet annihilation processes in various organic compounds [28], because this model does not fit the experimental t-MPA( $B$ ) response here (see Fig. S.3 [15]). Also the t-MPA( $B$ ) response does not originate from an isolated TE with larger zero field splitting parameters either [see Fig. 1(d)], since such a species would not show *two* PA bands [18,23]. We thus conclude that the obtained t-MPA originates from photoexcitations that have more elaborate properties compared to simple SE or TT, and thus the magnetic field response needs to be described by a spin-Hamiltonian that has not been used before in the field of “organic magnetic field effect” [14,27–30].

To explain the correlated opposite t-MPA( $B$ ) response for  $PA_{SE}$  and  $PA_{TT}$  bands and its transient dynamics we have to consider that SE and TT are nearly in resonance. We therefore propose that there exists resonant spin coupling among the lowest SE and the various spin states of the lowest TT state [i.e., TT singlet ( $S$ ), triplet ( $T$ ), and quintet ( $Q$ )],

which may be responsible for the obtained correlated t-MPA( $B$ ) response. To describe the t-MPA we employed an appropriate spin-Hamiltonian in  $10 \times 10$  Hilbert space (namely SE and 9 TT spin substates). The  $10 \times 10$  Hamiltonian matrix is comprised of a  $9 \times 9$  TT pair block, a  $1 \times 1$  block of the SE state, and coupling terms between the various TT states and SE (see the Supplemental Material [15]).

A key ingredient for the MPA generation is spin-dependent decay rates for the four spin configurations (SE,  $S$ ,  $T$ , and  $Q$ ); this leads to field-dependent level population and decay rates. Because PA is proportional to the specific excited state population, namely, SE or TT, and these populations are field dependent, it generates MPA( $B$ ). Using the density matrix approach we have calculated the time and field dependencies of each spin configuration density in each of the 10 levels (see the Supplemental Material [15]). Identifying  $PA_{SE}$  with optical transition from the lowest SE and  $PA_{TT}$  with transitions from the triplet spin configuration, we show in Fig. 3(a) the calculated response overlaid on the measured t-MPA( $B$ ) response of these two PA bands. For our calculation we have used a powder pattern angular average over the  $\mathbf{B}$  direction with respect to the TE axes in the TT pair. The following best fitting parameters were used to obtain the fit shown in Fig. 3(a): The zero field splitting parameters of the two parallel TE in the TT state are  $D/2\mu_B = 50$  mT,  $E/2\mu_B = -18$  mT; the exchange interaction,  $X$  between the two TE’s is  $X/2\mu_B = 7$  mT; the resonance coupling parameters between the SE and the TT pair spin states are  $SE-S$ ,  $SE-T$ ,  $SE-Q = 31, 32, 0$  mT, respectively; the average system decay time is  $\sim 1$  ns; and the spin-dependent decay rate ratios are  $SE:S:T:Q = 1.07:1:0.8:1$ . The good agreement between the experimental and calculated t-MPA( $B$ ) response validates our approach.

Obviously, at  $t = 0^+$  (i.e., immediately following pulse photoexcitation), no decay has occurred yet and thus  $t\text{-MPA}(t = 0^+, B) = 0$  for both  $PA_{SE}$  and  $PA_{TT}$ . As time progresses, the imbalance of spin densities increases leading to growing t-MPA( $t, B$ ) response, as observed experimentally. Figure 3(b) shows the calculated transient response of t-MPA( $t, B = 300$  mT) for  $PA_{TT}$  (positive) and  $PA_{SE}$  (negative) along with the respective experimental responses. Our model nicely reproduces the increasing t-MPA value with the delay time for both PA bands.

It is interesting to study the t-MPA response at longer times using transient nanoseconds to milliseconds PA spectroscopy. The optical setup for these measurements was the same as the cw PA apparatus, except that the pump excitation was a pulsed laser (Quanta-ray) having 10 ns pulse duration at 10 Hz repetition rate, operated at 680 nm. For monitoring  $\Delta T(t)$  we used a probe beam from a laser diode at 1300 nm [see details in the Supplemental Material [15], Sec. S2(ii)].

Figures 3(c) and 3(d) show the t-PA decay and t-MPA evolution of  $PA_T$  in the microsecond ( $\mu$  sec) time domain at 40 K. Figure 3(c) shows that  $PA_T$  decay measured at 0.9 eV is strongly magnetic field dependent. From the change,  $\Delta PA(t)$  in t-PA with  $B$  we obtain the t-MPA( $B, t$ ) response and study its time evolution. Figure 3(c) inset shows that the t-MPA at  $B = 180$  mT changes polarity at  $t \sim 4 \mu$  sec. This is reflected in the t-MPA( $B$ ) response [Fig. 3(d)], which dramatically changes in the interval  $1 < t < 10 \mu$  sec. In fact, the t-MPA( $B$ ) response changes from an early time response that is similar to that obtained for  $PA_{TT}$  in the ps time domain [Fig. 3(a)], to a longer time response similar to that of individual, uncorrelated TE in the ss-MPA [Fig. 1(d)]. We therefore interpret this interesting t-MPA( $B$ ) evolution as spin *decoherence*, when the spins of the two geminate TE's that were born from the same TT photoexcitation, lose their initial spin *entanglement*. This experimental result is strong evidence for the existence of initially photogenerated intrachain TT pairs, which subsequently decompose into two geminate TE's at  $t < 200$  ps. The surprising finding here is that even though TT decays into geminate TE's in the ps time domain, their spin entanglement is still preserved into the  $\mu$  sec time domain.

In summary, we introduced here a new technique, namely, the magnetic field effect of the transient photo-induced absorption, t-MPA for studying the primary and long-lived photoexcitations in pristine DA-copolymer films of PDTP-DFBT. Using t-PA spectroscopy in the mid-IR spectral range we found two distinct PA bands that originate from two primary photoexcitations in the DA copolymer: namely, the SE and TT pair. This result may be robust, unique to the class of  $\pi$ -conjugated copolymers. Using t-MPA( $B$ ) magnetospectroscopy we found that the SE and TT spin states in PDTP-DFBT strongly interact. We also discovered that the TT decomposition into two intrachain geminate TE's still maintains spin coherence, which lasts into the  $\mu$  sec time domain. The implication of the obtained SE-TT correlation on carrier photogeneration in copolymer or fullerene blends is studied and promised to be quite interesting.

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