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Heavy-atom effects on intramolecular singlet fission in a conjugated polymer

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ABSTRACT

A chief aim in singlet fission research is to develop new materials concepts for more efficient singlet fission. The typical approaches such as tuning π -overlap and charge-transfer interactions, enhancing delocalization, altering diradical character, or extending the conjugation length have profound effects simultaneously on the singlet and triplet energetics and the couplings between them. While these strategies have resulted in a handful of high-efficiency materials, the complex interplay of these factors makes systematic materials development challenging, and it would be useful to be able to selectively manipulate the properties and dynamics of just part of the singlet fission pathway. Here, we investigate the potential of heteroatom substitution as just such a selective tool. We explore the influence of heavy atoms within the main backbone of polythiophenevinylene and its selenophene and tellurophene derivatives. We find no significant effects on the prompt <300 fs intramolecular singlet fission dynamics but a clear heavy-atom effect on longer time scales.

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INTRODUCTION

The field of singlet fission has seen remarkable progress in the last decade, with an increasingly sophisticated understanding of the underlying mechanism^{1–5} and spin physics.^{6–8} However, despite many attempts at systematic study in a range of materials systems,^{9–12} a detailed picture of the structure-property relationships that define the intermolecular singlet fission dynamics relevant to devices remains elusive. This is not only due to the complexity of the fission mechanism itself—intrinsically tied to molecular vibrations,^{13–16} charge-transfer interactions,^{17–19} coherence^{13,16,20,21} and delocalization,²² often proceeding on experimentally challenging time scales^{13,14,16,21}—but also reflects on broader challenges in characterizing organics in the solid state. Not least is the challenge of determining what is the “structure” that is actually relevant to the experiment in the presence of disorder. In several instances,

polycrystalline films of singlet fission materials have been reported to exhibit significantly different properties from single crystals,^{9,13,22–26} yet the general fission properties of (polycrystalline) acene films can be well predicted based on single-crystal packing geometries.⁹ One of the most important recent advances to help circumvent this difficulty was the discovery of efficient intramolecular singlet fission in covalent dimers.^{27–29} This technique allows for decoupling of the critical interactions for singlet fission from harder-to-control solid-state packing and means that intersite couplings can be carefully tailored through molecular design.³⁰ In principle, such structures could then be incorporated into the solid state with fission properties intact, although there remain few examples where this is explored.^{31–33}

In considering intramolecular fission, it is useful to distinguish between dimeric/multichromophoric systems, where the main focus is engineering the coupling between two or more

base chromophores already known to be capable of singlet fission (e.g., acenes,^{19,34–43} rylenes,^{18,44} and diphenylisbenzofurans^{45,46}) and polymeric materials.^{31,47–55} In the latter, the distinction between individual chromophores is lost and the fission event represents a localization of the singlet wavefunction into triplets on particular chain segments. Polymeric singlet fission materials are often described in terms of polyene photophysics.^{56–60} In polyenes, the lowest singlet excited state S_1 shares the same A_g symmetry as the ground state and is thus optically forbidden.^{56,57,61} Excitation is instead into the higher S_2 state, of B_u symmetry, and is typically followed by ultrafast relaxation into $2A_g$.^{62,63} The wavefunction of this “dark” $2A_g$ state can be described as carrying significant triplet-pair (TT) character, and it was originally proposed that singlet fission can be achieved from this state through a slight distortion or energetic push to “liberate” the triplets.⁵⁶ Singlet fission has indeed been reported in numerous polyenes,^{31,47–50} and the careful balance of polyene and charge-transfer character resulted in the first high-efficiency polymer singlet fission system.⁵¹ Despite the evident importance of polyene character in enabling singlet fission, our own work has suggested that the $2A_g$ state is not directly involved in the process,³¹ which may be in accord with predictions of triplet-pair states distinct from $2A_g$ that can form when polyene segments interact through space, for instance through chain folding.⁵⁸ Using sub-20-fs transient absorption spectroscopy, we observed parallel population of the $2A_g/S_1$ state and triplet pairs formed through singlet fission, both directly from the initial $1B_u/S_2$ state. The fission channel was favored under excitation with excess photon energy. This interpretation has recently sparked controversy,⁶⁴ which we address in detail in the section titled “Discussion,” but it is in accord with measurements on other polyene systems.^{10,65} It is clear that much more work is needed to understand the electronic structure and singlet fission properties of these materials.

As a step in this direction, in this work, we explore if and how the intrachain singlet fission properties of polyenes can be modified through the introduction of heavy atoms. The chief aim is to use the increase in spin-orbit coupling as a tool to selectively manipulate the product states of singlet fission without substantially perturbing the

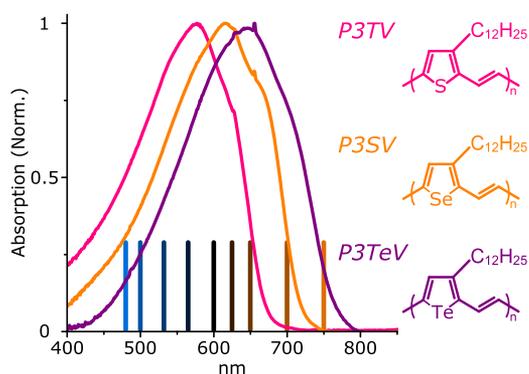


FIG. 1. Visible absorption spectra in dilute ($<50 \mu\text{g/ml}$) *ortho*-dichlorobenzene solution and chemical structures of P3TV, P3SV, and P3TeV. Vertical bars indicate laser excitation wavelengths used in transient absorption measurements.

initial dynamics. To this end, we have applied the detailed pump-wavelength dependent transient absorption analysis developed for P3TV³¹ to P3SV and P3TeV (Fig. 1), in which the heteroatom is substituted with selenium or tellurium. Our results show that the fundamental photophysics of the polymers are essentially unchanged: they still exhibit rapid intrachain singlet fission from a vibrationally “hot” $1B_u$ state, in parallel with relaxation into a “dark” $2A_g$ state. Once formed, the triplets show clear sensitivity to the identity of the heteroatom, opening a route to selectively tune the later stages of the fission pathway.

RESULTS

The synthesis, purification, and basic physical and chemical characterization of P3TV, P3SV, and P3TeV are presented in a previous report.⁶⁶ Here, we reiterate that the solubility of the polymers decreases with heteroatom as $S > \text{Se} > \text{Te}$, but at low concentration and with prolonged heating in dichlorobenzene, we were able to obtain stable solutions of all materials over the time scales of our measurements. The visible absorption spectra in dilute *ortho*-dichlorobenzene solution ($<50 \mu\text{g/ml}$) are presented in Fig. 1. All measurements were performed at this concentration unless otherwise noted. Following our previous analysis, we consider this preparation to result in well-dissolved, isolated polymer chains.³¹ We observe the same basic lineshapes for all three, with comparable linewidths $\sim 0.5 \text{ eV}$ and similar weakly resolved vibronic structure. In our previous study of the photophysics of P3TV,³¹ we found that singlet fission could be best identified from the excitation wavelength dependence in transient absorption, and indeed that the photophysics could not be fully understood without consideration of the excitation wavelength dependence. Accordingly, in this work, we have also scanned the excitation wavelength across the entire absorption band, from 480 nm to 750 nm, using the previously reported apparatus³¹ (see Methods, [supplementary material](#)).

Heteroatom controls triplet lifetime

We first explore the behavior of these polymers on long time scales, where the effects of the heteroatom can be more clearly distinguished. Figure 2 shows nanosecond transient absorption data for P3TV, P3SV, and P3TeV solutions. The primary dynamics in these polymers are complete within $<20 \text{ ps}$ (see below), and on the ns time scale, the only species expected to be present are trace triplet excitons. The long-lived species in P3TV exhibits photoinduced absorption toward the near-infrared, consistent with the earlier assignment to triplet excitons.³¹ P3SV and P3TeV reveal similar spectral features, with spectral shifts similar to those observed in the ground-state absorption (Fig. 1). The decay lifetime of the state probed here directly depends on the heteroatom, yielding faster decays as the atomic weight increases [Fig. 2(d)]. This direct heavy atom effect, with no sign of population of other electronic states (the singlet population is depleted on substantially earlier time scales, see below), confirms the assignment of this red-absorbing species to triplet excitons and validates the approach of using heteroatoms to manipulate them. In order to better understand the formation dynamics of these species, we turn to sub-picosecond transient absorption.

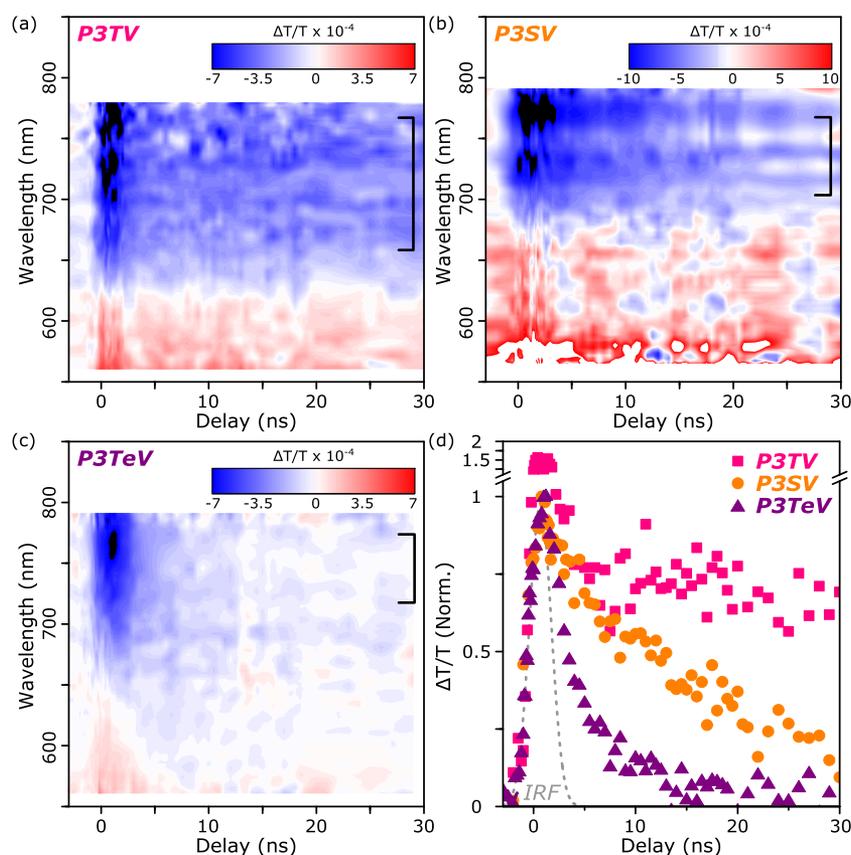


FIG. 2. False-color transient absorption maps of (a) P3TV, (b) P3SV, and (c) P3TeV solutions excited at 532 nm with a Q-switched Nd:YAG laser (pulse duration ~ 1 ns). The photoinduced absorption (blue) on these time scales can be attributed to triplet excitons as the primary singlet decay is orders of magnitude faster (see below). Because of low signal levels, the P3TV and P3SV solution concentration was increased to $100 \mu\text{g/ml}$. Previous work on P3TV found no evidence of aggregation at this concentration.³¹ (d) Decay kinetics integrated over the probe wavelength ranges indicated with black brackets in (a)–(c). The dashed line approximates the instrument response (IRF), with a FWHM of ~ 2.5 ns due to jitter of the excitation pulse.

Optically activated singlet fission

In agreement with previous work by ourselves and others,^{31,67–69} we find that band-edge excitation of P3TV results in extremely rapid excited-state decay, with no signal detectable beyond ~ 20 ps. In addition to the prominent ground-state bleach signal ($\Delta T/T > 0$) in the region of the steady-state absorption, we identify four regions of the transient absorption signal which can be distinguished based on their different kinetics and/or pump-wavelength dependence. On the earliest time scales, we observe a photoinduced absorption (PIA, $\Delta T/T < 0$) band peaked beyond 1550 nm (PIA1). At the same time, we observe a stimulated emission (SE, $\Delta T/T > 0$) band to the red edge of the ground-state bleaching (650–800 nm, gray dashed), which we previously showed closely matches the weak photoluminescence peaks reported for this polymer.^{31,67} The presence of SE enables assignment of the features on this time scale, chiefly PIA1, to the “bright” initial photoexcited state, S_2 . Our earlier work revealed the internal conversion time scale to be ~ 50 fs,³¹ well within the instrument response of the present system.

Following the disappearance of PIA1 and SE, we observe a prominent excited-state absorption band peaked ~ 1000 nm which can be attributed to the lower-lying “dark” state $S_1/2A_g$ reported elsewhere.^{31,67–69} Its distinct spectral features ensure that it must be a different electronic state from the initial excitation. We denote

the low-energy edge of this band as PIA2. This is the primary excited-state absorption signature of P3TV, and it decays with very short lifetime (~ 1 ps). This rapid nonradiative decay process deposits significant vibrational energy into the ground electronic state,^{31,67} resulting in a vibrationally “hot” ground state with slightly red-shifted absorption as manifested in the spectrum at 6 ps (PIA4). This terminal species decays with a lifetime of ~ 3 ps.

Upon excitation with excess photon energy [500 nm, Fig. 3(b)], we detect the same initial S_2 state (e.g., PIA1), and the low-energy edge of the S_1 excited-state absorption is also unchanged (PIA2). We also observe additional excited-state absorption intensity 700–1000 nm (PIA3), present at all time delays and formed in parallel with the S_1 feature. This extra intensity corresponds with the signature of triplet excitons in P3TV identified in previous work³¹ and in Fig. 2. Based on the extremely fast time scales for triplet formation and subsequent decay, this feature was previously assigned to pairs of triplet excitons “TT” formed through intrachain singlet fission from a vibrationally hot S_2 state, known as optically activated singlet fission.³¹ More recently, the field has recognized that the strength of interactions within triplet pairs can vary widely,^{5,24,70–73} with “strongly coupled” triplet pairs behaving more similarly to singlet than triplet states, in terms of lifetime and the ability to emit photons.⁵ Translating this

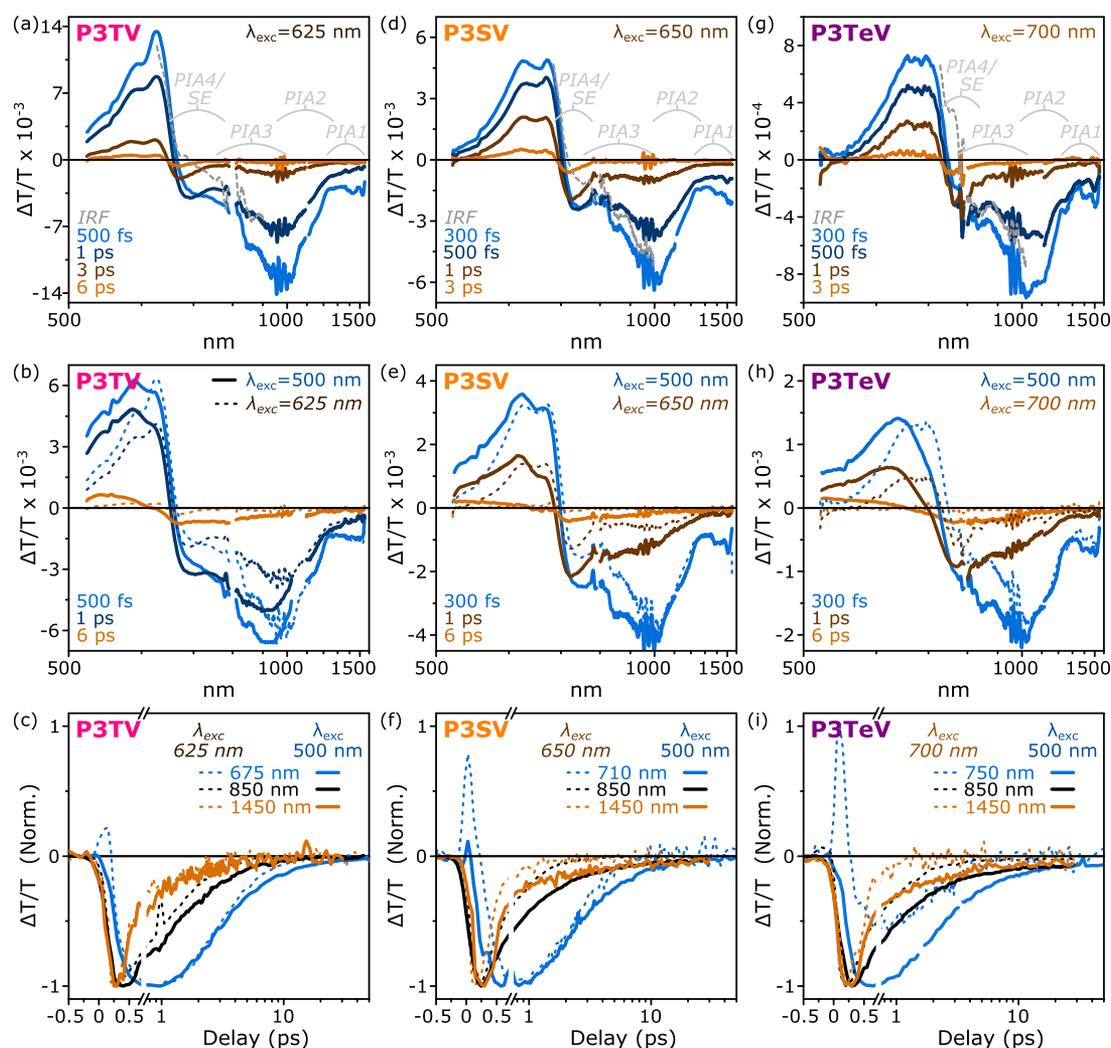


FIG. 3. (a) Transient absorption spectra of P3TV solutions following band-edge excitation at selected pump-probe delays. Within the instrument response, we detect additional features from stimulated emission (gray dashed). Gray brackets indicate distinct spectral regions identified from the kinetics and/or pump-wavelength dependence; see main text for details. (b) Excitation well above the band edge (500 nm, solid lines) results in similar excited-state absorption >1000 nm but distinct additional absorption in the 650–1000 nm range, relative to band-edge excitation (dashed line). This additional feature is observed through the entire decay lifetime. (c) Normalized transient absorption decay kinetics, integrated over 20-nm spectral windows centered at the indicated wavelengths, for band-edge (dashed) and excess-energy (solid) excitation. The enhancement in lifetime is evident throughout the spectrum. Qualitatively similar behavior is observed for P3SV (d)–(f) and P3TeV (g)–(i). The fundamental fast photophysics for these polymers are equivalent.

phenomenology to polyenes such as P3TV, we suggest that the $2A_g/S_1$ state is most closely equivalent to a strongly coupled triplet pair,^{56,57,73} while the previously reported TT state in P3TV would be a more weakly coupled pair. These weakly coupled triplets are the longest-lived electronic state in the system [Fig. 3(c)] but, nonetheless, exhibit very rapid decay, with lifetime ~ 5 ps. Fast TT decay is common in intramolecular singlet fission materials and can be attributed to both nonradiative decay following a standard gap-law dependence⁵ and a high probability of pair recombination due to their low-dimensional confinement.^{27–29,51–53} TT lifetimes are

especially short in polyene systems,^{47–50} but such materials are well documented to exhibit higher rates of nonradiative decay in general.⁵ This is at least in part due to the strong coupling of polyene electronic states to the vibrational manifold and the similarity of the ground ($1A_g$) and lowest excited ($2A_g$) states.⁷⁴ As such, even the extremely short TT lifetimes in polyenes are consistent with gap-law behavior.

We have performed similar measurements on solutions of P3SV and P3TeV [Figs. 3(d)–3(i)]. The spectral evolution under band-edge excitation is equivalent for both polymers to P3TV,

including detection of faint instrument-limited features suggestive of stimulated emission (see the [supplementary material](#), Figs. 5–6). Likewise, excitation with excess pump photon energy results in additional excited-state absorption intensity at ~ 700 – 1000 nm (the region in which triplets absorb, [Fig. 2](#)) and slightly longer lifetime [Figs. 3(f) and 3(i)]. We thus consider all three polymers to undergo the same fundamental processes, suggesting that to first order increasing the heteroatom atomic mass has no impact on the polymer's fast photophysics. Likewise, we consider these results to suggest that the heteroatom substitution does not substantially alter the polymer electronic structure. In P3TV, our earlier observation³¹ of optically activated singlet fission requires that $E(\text{TT}) > E(\text{S}_2) = 1.85$ eV, with a likely TT energy of ~ 2 eV. This is substantially above the energy of S_1 , reported to be ~ 1 eV.⁶⁷ We expect similar relative state energies in P3SV and P3TeV although the S_1 energies are currently undefined. From the absorption spectra above and the pump-wavelength-dependent data presented below, we estimate the S_2/TT energies of P3SV as 1.72 eV/ ~ 1.9 eV and of P3TeV as 1.63 eV/ ~ 1.75 eV.

A detailed comparison of the integrated decay kinetics in [Fig. 4](#) reveals very slight systematic differences between the polymers. When no triplets are formed, following band-edge excitation

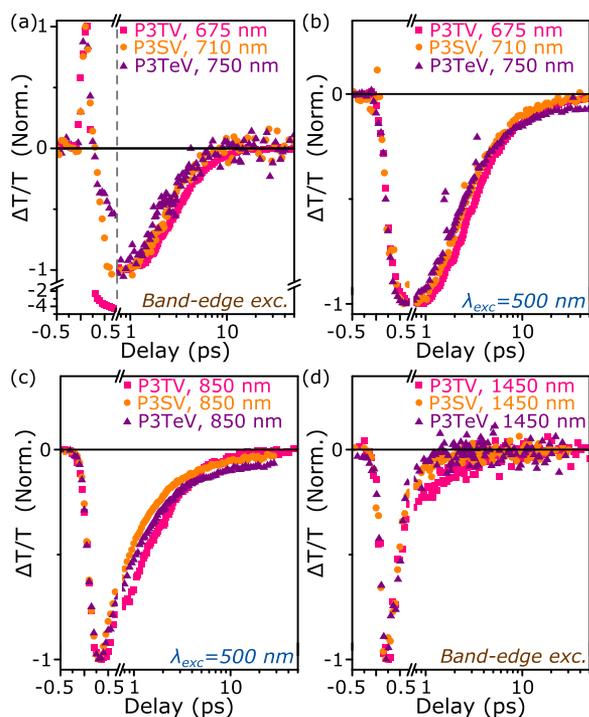


FIG. 4. Transient absorption kinetics for all polymers, following near-band-edge excitation (P3TV: 625 nm, P3SV: 650 nm, and P3TeV: 700 nm) or excitation with excess pump photon energy (500 nm), as noted. Kinetics are integrated over a 20-nm window centered on the indicated wavelength, to capture (a), (b) SE and PIA4, (c) PIA3 and (d) PIA1 dynamics. In (a), the data before 750 fs (vertical dashed) are normalized to the SE peak ($\Delta T/T > 0$) and after 750 fs are normalized to the peak PIA ($\Delta T/T < 0$) signal.

[Figs. 4(a) and 4(d)], the lifetime of the final signal varies as $\text{S} > \text{Se} > \text{Te}$. This can be primarily attributed to higher nonradiative decay rates in the heavier-atom polymers, consistent with their electronic states being slightly lower in energy than in P3TV (observed directly in [Fig. 1](#)) and the gap-law behavior mentioned above. However, following excess-energy excitation, we observe longer-lived signals in the Se and Te polymers, indicating a higher yield of triplets > 10 ps, suggesting a relative yield ordering of $\text{Te} > \text{Se} > \text{S}$. Given that the degree of enhanced excited-state absorption following 500-nm vs band-edge excitation is similar for all polymers [Figs. 3(b), 3(e), and 3(h)], we further posit that this difference in yield is not related to the initial TT formation process (this appears to be at most slightly affected). Rather, it reflects the ability of triplets to survive the initial fast recombination phase 1–10 ps, which we suggest below is related to enhanced spin evolution out of the purely singlet $^1(\text{TT})$ state. We additionally note that there is no detectable difference between polymers in the initial decay of SE [[Fig. 4\(a\)](#)] or PIA1 [[Fig. 4\(d\)](#)], which reports on the conversion from the initial photoexcited state to 2A_g or TT. In all cases, this process is instrument limited.

In order to develop a more complete picture of the optically activated singlet fission process suggested by the results in [Figs. 3](#) and [4](#), we have measured the detailed pump-wavelength dependence for P3SV and P3TeV. Summary results for P3SV are presented in [Fig. 5](#) and for P3TeV in [Fig. 6](#). For direct comparison of the spectra obtained under different excitation conditions, we took advantage of the fact that the dynamics of these isolated polymer chains in solutions are fully independent of excitation laser power over the range used ([supplementary material](#), Figs. 1–2). We can thus scale each transient absorption dataset such that the initial signal beyond 1100 nm immediately after the instrument response (300 fs) matches. We highlight that the very close agreement in spectral shape in this range, regardless of excitation wavelength, suggests that our measurements are not sampling polymer chain segments of vastly different conjugation length. A systematic oligomer study by Apperloo *et al.* found very substantial shifts in excited-state absorption spectral position as a function of chain length,⁷⁵ inconsistent with the small changes we observe here. Moreover, the constant spectral shape in this PIA2 region provides an important metric to distinguish it from the PIA3 feature, with which it partially overlaps and shares similar dynamics. Following our scaling procedure, we find that in both polymers, increasing pump photon energy systematically increases the relative weight of PIA3 even on the earliest detected time scales [Figs. 5(a) and 6(a)]. The effect appears to saturate by ~ 480 – 500 nm excitation. This enhanced excited-state absorption remains apparent throughout the decay lifetime [Figs. 5(b) and 6(b)] and manifests as a systematic increase in the decay lifetime across the spectrum [Figs. 5(c)–5(e) and 6(c)–6(e)] with the most prominent effects where the band is peaked. It is thus clear that PIA2 and PIA3 report on different electronic species. In our earlier work on P3TV, we found close agreement between this “additional” PIA3 intensity and the triplet absorption,³¹ allowing assignment to TT, and by analogy and comparison with [Fig. 2](#), we make the same assignment to TT in P3SV and P3TeV. As in P3TV, the yield of longer-lived triplets increases monotonically with pump photon energy although the primary decay is always very rapid in these polyenes.

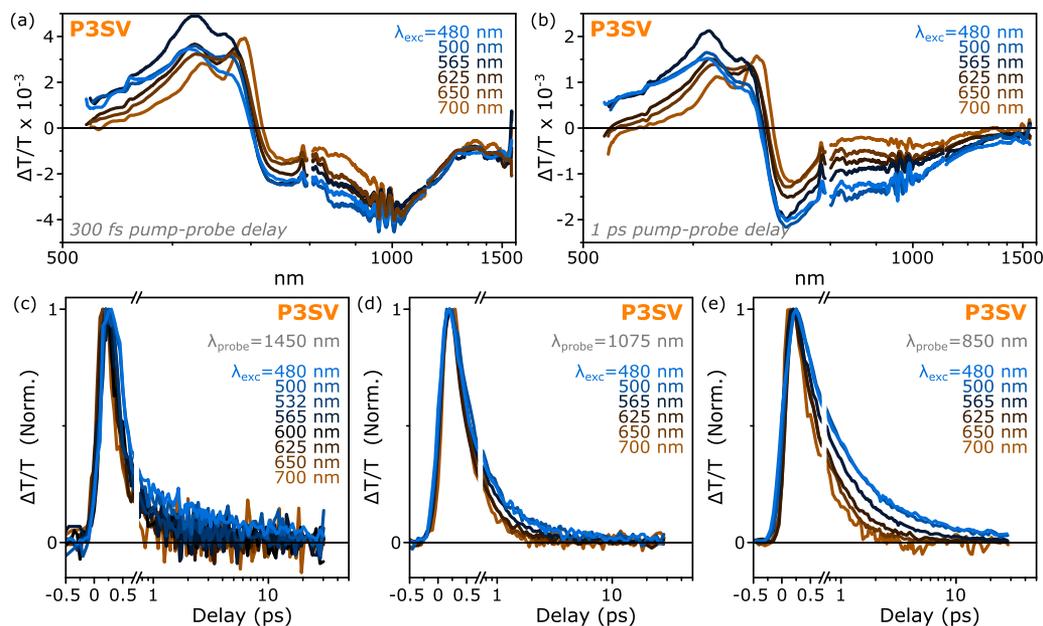


FIG. 5. Excitation-wavelength dependence of P3SV transient absorption. (a) Spectra immediately after the instrument response (300 fs) were scaled to match intensity in the region >1100 nm, revealing systematic increase in intensity 700–1000 nm with an increase in pump photon energy. (b) The increase in intensity remains evident on longer time scales (1 ps). (c)–(e) Decay kinetics integrated over a 20-nm window centered on the indicated wavelength reveal a systematic increase in lifetime with increasing pump photon energy. The enhancement is most pronounced in the central region of TT absorption, 850 nm. Corresponding spectra are presented in the [supplementary material](#), Fig. 3.

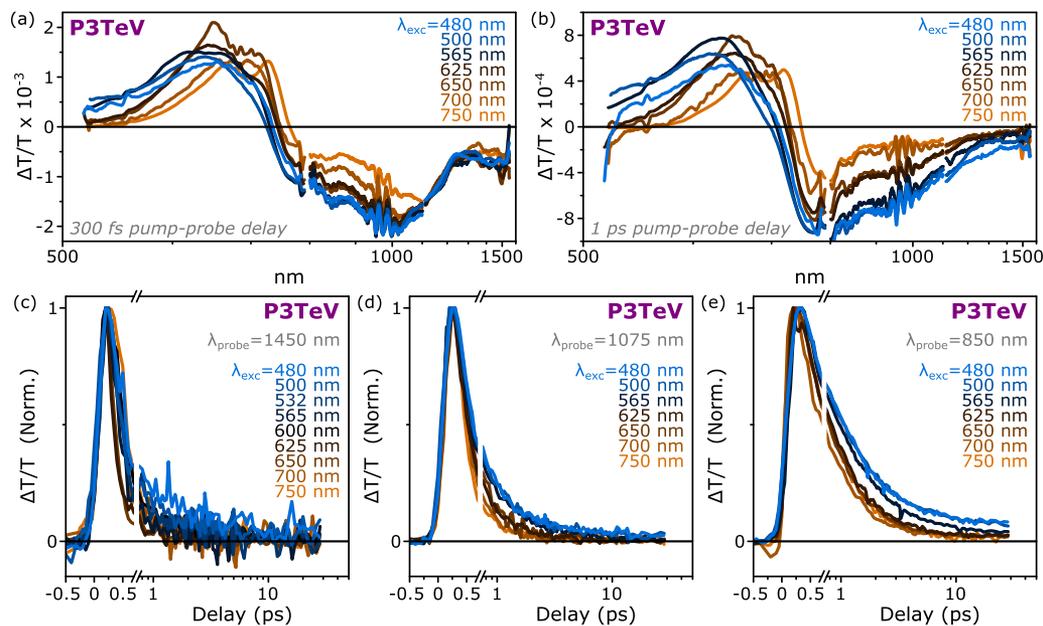


FIG. 6. Excitation-wavelength dependence of P3TeV transient absorption. (a) Spectra immediately after the instrument response (300 fs) were scaled to match intensity in the region >1100 nm, revealing a systematic increase in intensity 700–1000 nm with an increase in pump photon energy. (b) The increase in intensity remains evident on longer time scales (1 ps). (c)–(e) Decay kinetics integrated over a 20-nm window centered on the indicated wavelength reveal a systematic increase in lifetime with increasing pump photon energy. The enhancement is most pronounced in the central region of TT absorption, 850 nm. Corresponding spectra are presented in the [supplementary material](#), Fig. 4.

DISCUSSION

We must first address the recent study by Datko *et al.*⁶⁴ of closely related P3DTV and P3DSV (similar to P3TV and P3SV, but with C₁₀ rather than C₁₂ side chains), which calls the findings of our earlier study³¹ and the premise of this current work into question. Datko *et al.* measure resonance Raman spectra which suggest significant wavepacket motion along the excited-state potential energy surface, including multiple return visits to the Franck-Condon point. They further note that the polymer is highly non-emissive under excitation into the main absorption band, but that following dilution and high-energy excitation, clear photoluminescence can be observed at energies well above the nominal absorption band edge (i.e., emission ~450–700 nm, despite an absorption edge ~675 nm). The excitation spectrum of this emission reveals a broad lineshape reminiscent of unaggregated P3HT in solution, and the authors suggest that this corresponds to unaggregated P3DTV chains. On the basis of these observations, the authors claim that the fast electronic dynamics reported by ourselves and others can be explained entirely through large-amplitude vibrational relaxation along a single excited-state potential energy surface, coupled with efficient nonradiative decay directly to the ground electronic state.

However, this model is not able to fully account for the reported behavior. The explanation of dynamics presented by Datko *et al.* takes no account of the earlier observation of SE on very early time scales (notably using sub-20-fs transient absorption),³¹ the decay of which coincides with the formation of the prominent peak we and others assigned to 2A_g.^{31,67–69} There is likewise no mention of the unique excited-state absorption band we reported >1200 nm (PIA1 here, beyond their reported probe spectral range), which decays in parallel with the SE.³¹ As in the electronically similar carotenoids,^{10,62,63,76,77} these observations directly demonstrate that the primary state observed in transient absorption measurements (PIA ~1000 nm) is distinct from the electronic state initially photoexcited, i.e., there should exist a low-lying “dark” S₁ state. Moreover, while the authors observe a comparable excitation wavelength dependence in the probe range <800 nm,⁶⁴ they do not measure this effect beyond ~750 nm and provide no explanation for the reported close match of the “additional” photoinduced absorption intensity to the sensitized triplet spectrum.³¹

The alternative, nonfission model proposed relies primarily on the two observations mentioned above—significant wavepacket motion and enhanced above-gap emission upon dilution. It is well established in polyenes that photoexcited S₂ undergoes significant vibrational relaxation prior to conversion into the dark S₁ (2A_g) state,^{61,78} for instance in the canonical carotenoids.^{76,79,80} Indeed, this relaxation is a necessary precursor to the internal conversion as in the Franck-Condon geometry, the 2A_g state lies energetically above 1B_u.^{61,78} Additionally, Datko *et al.* resolved clear Raman overtones, indicating that the wavepacket is able to return to the Franck-Condon point multiple times prior to decay of the initial photoexcited state.⁶⁴ This observation was used to argue that the same state should be present for the full ~1 ps lifetime. Our reported internal conversion time scale³¹ of ~50 fs is also enough, though, for multiple periods of the reported modes (periods < ~25 fs). The Raman observations thus remain entirely consistent with the earlier^{31,67–69} polyene-based model of electronic relaxation 1B_u → 2A_g.

The argument in Datko *et al.* regarding aggregation is heavily based on an earlier single-molecule spectroscopy study by Hu *et al.*,⁸¹ using yet another PTV derivative with short hexyl sidechains and lower regioregularity. That work reproduced the extremely low PL quantum yield for excitation into the main PTV absorption band (<10⁻⁴),^{67,82} but observed in diluted films a ~20× increase in emission intensity due to emission from states ~0.5 eV above the optical band gap.⁸¹ It was suggested that the reduction in interchain aggregation reduces nonradiative decay or slows relaxation into the 2A_g state although it is worth noting that this result still suggests a quantum efficiency of only ~10⁻³. Datko *et al.* measure a similar effect in solution,⁶⁴ which arises from excitation of a species absorbing 350–550 nm. They argue that this band represents free, unaggregated polymer chains and that the entire primary absorption band 500–700 nm is due to aggregated chains, regardless of concentration. Furthermore, because an additional red-shifted absorption peak was seen upon film formation or after aging solutions for multiple days (the latter effect was never observed in our previous solution study,³¹ possibly due to the use of longer C₁₂ solubilizing chains), Datko *et al.* assign the prominent vibronic peaks in the solution spectrum to the 0–1 and 0–2 transitions. In this interpretation, the 0–0 absorption origin is suppressed, except in thin films or larger aggregates. On this basis, the authors argue for H-type aggregation of the P3DTV chains.

It is very unlikely, though, for H-type coupling to result directly in such a significant redshift (~0.7 eV). Not only does H-type coupling typically result in blueshifts⁸³ (albeit not always⁸⁴), the very large exciton coupling strength that such a shift implies would also suppress the 0–1 and 0–2 absorption peaks,⁸³ but this effect is not observed. Since exciton coupling alone cannot explain the spectral behavior, there must be another effect at play. The detailed study of thienylenevinylene oligomers (OTVs, 2–12 repeat units, each with two C₆ solubilizing chains) by Apperloo *et al.* provides an important insight.⁷⁵ Unsurprisingly, that work found significant reduction in the optical band gap with increasing conjugation length, with most reported soluble PTV polymers exhibiting absorption consistent with the 8–12-unit oligomers.^{31,64,67,81,85} All the reported OTVs, regardless of length, exhibited similar temperature dependence in absorption, namely, a sharpening of peaks and strong relative increase in 0–0 intensity upon cooling. The latter effect is the opposite of the behavior of H-aggregates.⁸³ Instead, the main absorption transition in these materials is best described in terms of intrachain J-type coupling, in which increased planarization results in enhanced delocalization along the polymer backbone. The cooling-induced red-shift in OTVs is relatively small, suggesting that the conjugation extends along nearly the full oligomer length even at room temperature.⁷⁵ This planarization effect is well known in P3HT, where it is induced through interchain packing,⁸⁶ and similar cooperative planarization has been reported in MEH-PPV.⁸⁷ In the latter, importantly, even in the planarized “red phase,” the electronic interactions are found to be primarily intrachain rather than interchain. This means that even in systems where high concentration favors interchain interactions to form such red-shifted states, the spectra and photophysics may still be characteristic of the intrachain electronic properties. In the case of the PTVs, the study by Hu *et al.*⁸¹ found that the tendency toward planarity is much greater than in polythiophenes. It is thus reasonable to propose that extended-chain structures can exist in solution even without aggregation

and that the reported aggregation effects⁶⁴ may be instead treated in terms of extended (nonemissive) vs collapsed (emissive) chain segments.

As for the emission at high energies detected upon dilution, we find that it can be entirely explained—is indeed expected—in the polyene framework as a simple function of conjugation length. It is well established in polyenes that the energies of the bright $1B_u$ state and the dark $2A_g$ state exhibit different conjugation length dependence:^{56,57,61,88,89} relaxed $2A_g$ only falls below $1B_u$ above a certain chain length. Any polyene with sufficiently short conjugation would be expected to be emissive. In agreement with this framework, Apperloo *et al.* observed clear photoluminescence from the trimer and dimer OTVs, only trace emission from the tetramer and no emission from the longer molecules,⁷⁵ an effect very unlikely to be related to aggregation. The excitation response of the “bright” material in Hu *et al.*⁵¹ and Datko *et al.*⁶⁴ is strikingly consistent with the absorption of trimers, which are the longest OTVs with appreciable PL quantum efficiency. These dilution/single-molecule experiments most likely probed a very small subpopulation (not observable in absorption) of trimerlike conjugation lengths. We conclude that the vibrational and photoluminescence results presented by Datko *et al.* are fully consistent with the established polyene framework used to describe PTVs.^{31,67–69} The earlier assignment of the fast dynamics to parallel internal conversion into dark $2A_g$ and intrachain singlet fission into weakly coupled TT pairs remains robust,³¹ and we are justified in relying on that earlier work for our current interpretation.

On that basis, we find that heteroatom substitution has only subtle effects on the primary photophysics of intramolecular singlet fission in these polymers. The same basic behavior is observed regardless of the heteroatom atomic mass: rapid internal conversion $1B_u \rightarrow 2A_g$ following band-edge excitation, which under excess-energy excitation competes with the formation of short-lived TT states. Within the limits of the instrument used, the rates of these processes are scarcely affected; the similar relative weight for all polymers of “additional” excited-state absorption following excess-energy excitation confirms that the rates must be similar. This is not surprising for such a fast singlet fission system. Taking a typical 1 ns time scale for a process mediated by spin-orbit coupling, the heavy-atom effect should accelerate that at most to ~ 27 ps for P3SV and ~ 4 ps for P3TeV, still orders of magnitude slower than $2A_g$ formation or singlet fission. We note that in principle the TT and $2A_g$ states may exhibit a more complex relationship than we have suggested here, for instance existing in dynamic equilibrium as has been proposed between S_1 and TT in some covalent dimers.¹⁸ That can be directly ruled out in P3TV based on the large energetic difference between TT and S_1 (~ 1 eV, see above), but the similarity in decay lifetime and uncertainty in state energies in P3SV and P3TeV mean that currently there remains a possibility in the new materials. Similarly, we cannot entirely rule out that excess-energy excitation populates a highly vibrationally excited region of the $2A_g$ surface that is susceptible of singlet fission. If the rate-limiting step is the $1B_u \rightarrow$ “hot” $2A_g$ internal conversion rather than “hot” $2A_g \rightarrow$ TT, then these measurements—even the sub-20-fs experiments in our previous work—would be unable to distinguish these pathways. However, in the absence of a clearly detected intermediate, we consider this less likely than the previously proposed model, and within the

limitations of our measurements, $2A_g$ and TT are populated in parallel.

Only on longer time scales do we observe any clear influence of heteroatoms. The nanosecond data in Fig. 2 demonstrate that the triplets on these polymers are indeed sensitive to spin-orbit coupling from the heteroatom. We posit that the minor differences on the few-picosecond time scale in Fig. 4 have a similar origin. On these time scales, the TT states formed by singlet fission are undergoing rapid geminate recombination to the ground state. The ability of the TT pair to annihilate rapidly is linked to its overall singlet character,^{3–5,90} and the persistence of triplets out to longer time scales typically arises from spatial separation^{12,24,70,91} or spin evolution^{7,8,37,92} out of the initial singlet TT state. Typically, the spin-dependent process occurs on ~ 1 – 10 ns time scales,⁹³ but the heavier Se and Te atoms may enable faster spin evolution within TT, causing more population to survive the regime of rapid annihilation. Together, these results—little impact on prompt singlet fission dynamics but an influence on the fate of triplets—suggest that heteroatom substitution may be a useful new tool to selectively manipulate the dynamics of triplets formed by singlet fission. The interaction responsible, spin-orbit coupling, is not restricted to polyenes, and we thus expect that the same concept can be applied to the entire library of singlet fission systems. It may offer a pathway to minimize losses from geminate triplet-pair recombination, an especially great challenge following intramolecular singlet fission. Moreover, the direct tunability of the final triplet lifetime offers up the tantalizing possibility of enabling efficient phosphorescence following singlet fission, resulting in a singlet fission photomultiplier for improved photovoltaics,⁹⁴ made from a single material without the need for intervening nanocrystals.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for details of transient absorption system, pump intensity dependence, and the full transient absorption data.

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