

Triplet Population Dynamics of Single Conjugated Polymer Molecules and Nanoscale Assemblies

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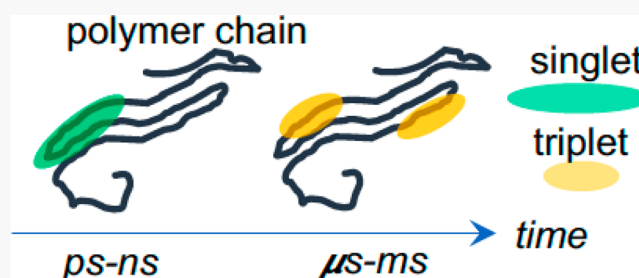


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ABSTRACT: The formation of long-lived triplet excited electronic states has important ramifications for conjugated organic materials used in optoelectronic devices. In the case of polymers, unravelling various structural factors mediating triplet processes is difficult because of heterogeneity effects due to intrinsic molecular weight polydispersity and large conformational degrees of freedom. Conformation-dependent electronic coupling between chromophore segments also modulates relaxation branching ratios that may vary substantially from molecule to molecule. However, ensemble-level spectroscopy experiments typically average over distinct responses, which disguises important qualities of the overall material photophysical landscape. Suppression of heterogeneity by diluting polymers into inert solid hosts permits single molecule level investigations of conformation-dependent triplet dynamics thereby avoiding the most insidious consequences of ensemble averaging. Interestingly, the multichromophoric nature of polymers can lead to significant likelihoods of multiple coexisting triplets, where population dynamics are revealed from fluorescence quenching dynamics on time scales comparable to triplet lifetimes (i.e., μ s to ms). Stochastic photodynamic models are then used to extract key kinetic constants, including bimolecular triplet–triplet annihilation, that tend to exhibit pronounced dependences on polymer conformational ordering. Furthermore, simple processing strategies to selectively control chain conformation and packing order in hierarchical polymer assemblies can be combined with experiment and modeling to uncover the evolution in triplet processes from single molecule to bulk material levels. We posit that molecular-level control can be harnessed to more accurately manage triplet yields and interactions over a large range of time scales, which has potential uses in multiexciton harvesting schemes, such as singlet fission.



1. INTRODUCTION

Conjugated organic polymers have many practical advantages as organic semiconductor materials for light energy harvesting applications.^{1–3} Interestingly, the relaxation pathways of excited states following photon absorption are largely dictated by the conformational and packing qualities that regulate the number, relative size, and coupling interactions between discrete segments (chromophores) on polymer chains.^{4,5} Photoexcitation cycling in these closed-shell systems occurs within the singlet ($S = 0$) manifold followed by rapid excitation energy funneling between chromophore sites depending on the strength and directionality of electronic coupling. Singlet relaxation processes are usually complete in less than a nanosecond but come to a halt if the spin of an unpaired, excited electron changes.⁶ Conversion of excited singlets to lower-energy, spin-forbidden triplets ($S = 1$) effectively traps chromophores for much longer than the singlet lifetime, which not only prevents subsequent excitation but also increases susceptibility to degradation via oxygen-related photochemistry.⁷ Importantly, processing conditions (namely, solvent) modulate the delicate interplay between structural and electronic coordinates in these multichromophoric molecules,

which has been both a boon and detriment to optoelectronic applications.^{8,9}

Along these lines, much of the current understanding of excited spin conversion events in polymers is based on simpler (i.e., single chromophore) systems. Furthermore, entering the triplet manifold is traditionally regarded as a loss channel, although a recent paradigm shift has occurred, where triplets are now viewed as an energy currency. For example, strategies such as triplet fusion and thermally assisted singlet repopulation have demonstrated promise for improving performance metrics of organic light-emitting diodes (OLEDs).^{10–12} Moreover, singlet fission (i.e., two triplets produced for one singlet excitation) has emerged as a viable multiexciton generating mechanism capable of overcoming predicted theoretical (Shockley-Queisser) performance limits of organic solar cells.^{13,14} Despite the appeal

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of harvesting multiple triplets per photon absorbed, the repertoire of known singlet fission active materials is limited. In fact, most current triplet harvesting schemes rarely involve polymers despite their desirable attributes for large-scale processing, which is readily traced to their large variability in triplet photophysical behaviors. Specifically, triplet signatures often appear in polymer dilute solutions but vanish in the solid state (i.e., thin films).^{15,16} These observations have stimulated studies into the various factors deciding the long-term fate of excitation energy in polymers that all point to conformational and packing qualities governing electronic coupling between chromophore segments.⁴ Unfortunately, intrinsic molecular weight polydispersity effects together with the large conformational degrees-of-freedom of polymers muddle this critical structure–function information due to the coalescence of many distinct responses at the ensemble level. This situation may lead to incomplete physical pictures and inconsistencies in predictive capabilities for guiding material design and optimization. It is mainly for these reasons that polymers as triplet generating and harvesting platforms have not garnered widespread interest for advancing new functionalities and improving performance.

Despite these difficulties, bountiful opportunities do exist for utilizing polymers to selectively corral triplets as well as manage interactions between these and other species of different overall spin and charge (e.g., excitons and polarons). We demonstrate that such control is possible often without costly and time-consuming synthetic or processing procedures. This is accomplished by investigating triplet processes at the single molecule level, which may be extended to hierarchical assemblies to uncover their evolution over multiple size scales. Because absorptive probes are usually not feasible at this level, triplet population dynamics are instead revealed from fluorescence quenching dynamics. These techniques offer very high sensitivity and further expose the true stochastic nature of triplet photophysics and intrinsic heterogeneity effects. Robust photodynamic models are then employed to extract useful kinetic details of triplet population dynamics on time scales comparable with their lifetimes (i.e., nano- to millisecond time scales). Proven self-assembly methods can be combined with these tools to unravel the evolution of triplet processes with polymer structure from molecular to materials levels, which serve as the basis for unlocking the mysteries surrounding the disappearance of triplet features in the solid state or upon polymer aggregation.^{17,18}

2. TRIPLET PROCESSES AT THE SINGLE MOLECULE LEVEL: SINGLE AND MULTICHROMOPHORIC SYSTEMS

Disentangling competing exciton decay processes in polymers requires taming their large degrees of conformational freedom and polydispersity effects. These attributes have long plagued ensemble-level photophysical studies by averaging over many distinct structures leading to ambiguous responses. Fortunately, diluting and immobilizing polymer chains in glassy inert hosts limits heterogeneity to the single molecule level and removes many competing relaxation channels (i.e., lower intermolecular contacts) encountered in bulk thin films.¹⁹ Individual polymer chains may then be interrogated using background-free single molecule fluorescence spectroscopic probes.

Evidence of triplets at the single molecule level was first reported in seminal studies of conjugated organic molecules.^{20–22} Namely, fluorescence intensity trajectories of spatially isolated molecules displayed telegraphic-like, random

switching between “on” and “off” emitting levels. Typical on times varied with excitation light intensity, whereas off times were more sensitive to the surroundings (i.e., oxygen). It was concluded that transitioning to nonemissive triplet states was responsible for this fluorescence intermittency (“flickering”) behavior, which can be explained most straightforwardly using a three-level photophysical model. Figure 1a illustrates this

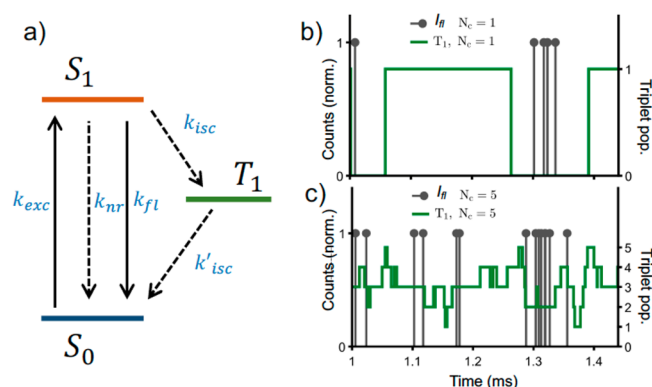


Figure 1. (a) Three-level state diagram depicting the singlet ground and excited electronic states (S_0 and S_1 , respectively) and the lowest-energy triplet excited state (T_1). Simulated fluorescence intensity transients of a single chromophore (b) and five chromophores (c).

framework for a single chromophore that may be further simplified by assuming the steady-state approximation for the short-lived S_1 state. Now, the system is reduced to an effective two-level model, where the chromophore spends most time in either S_0 or T_1 states.

$$S_0 \rightleftharpoons T_1 \quad (1)$$

The forward rate constant for entering T_1 (off state) is given by $k_{exc}\Phi_{ISC}$, where k_{exc} is the excitation rate constant, and Φ_{ISC} is the triplet intersystem crossing (ISC) quantum yield. The chromophore then returns to the on state by relaxing via k'_{ISC} (reverse ISC). Excitation intensities (k_{exc}) regulate the frequency T_1 is populated, which, along with varying surroundings (e.g., ambient vs oxygen depleted),²³ makes the model straightforward to validate experimentally. Figure 1b depicts a simulated fluorescence transient of a single chromophore with time-dependent transitions between on and off fluorescence intensity (I_{fl}) levels and corresponding triplet occupancies.

Extending this simple model to multichromophoric polymers is less straightforward depending on the nature of conformation-dependent coupling interactions between chain segments. For example, elongated conformations are associated with weak coupling, where the entire molecule can be effectively described as a collection of independent chromophores.²⁴ On the one hand, in this case, fluorescence emission occurs from multiple emitters, and each chromophore may transition to triplets independently of their neighbors, which is illustrated in Figure 1c assuming the same three-level description for each chromophore. On the other hand, collapsed chain conformations (often referred to as self-aggregation) are associated with strong interchromophore coupling, and the photophysical landscape is dominated by rapid excitation energy funneling often to as little as one site on the chain.^{25,26} Interestingly, if the chromophore site at the bottom of the energy funnel transitions to a triplet, then fluorescence abruptly switches off. Despite the

presence of multiple absorbers, outcomes resemble the single chromophore case in Figure 1b implying a single triplet accepts all singlet excitation energy, which has significant mechanistic implications.

The substantially longer lifetimes of triplets present another twist on these scenarios, where the likelihoods of multiple coexisting excitonic species becomes appreciable if energy funneling does not outcompete all other processes. Moreover, higher-order (specifically, bimolecular) decay contributions must be considered that should exhibit stronger sensitivity to chain conformational characteristics. Singlet–Triplet annihilation, namely, triplet(s) acting as an energy sink for an entire polymer chain, is frequently invoked to explain intermittency in collapsed conformations. In this view, only the singlet is “annihilated”, since energy transfer to triplets simply excites to higher energy levels followed by rapid internal conversion back to the lowest-energy triplet (T_1). While experimental evidence is compelling,^{27,28} sparingly few mechanistic details are actually known about this process, which is commonly assumed to be long-range (Forster) or short-range (Dexter) resonant energy transfer. Interactions between more than one triplet (namely, triplet–triplet annihilation) also become possible, but resolving kinetic details is complicated in polymers regardless of the functional form.

Figure 2 depicts the basic framework of a coupled, multichromophoric photodynamic model containing first- and

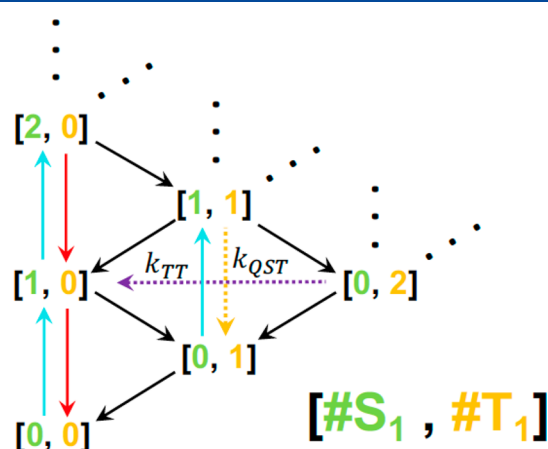


Figure 2. States and ladders diagram of a multichromophoric system describing population and depopulation of different exciton spin-state configurations. This form of the model only considers the number of excited singlet (S_1) and triplet (T_1) determining a population configuration rather than the specific locations of each state along the chain. Exciton interaction and annihilation processes are included in this model describing singlet–triplet and triplet–triplet annihilation.

second-order exciton decay processes surpassing many limitations accompanying the simple three-level view in Figure 1. Importantly, this description maintains the intrinsic stochasticity of triplet dynamics but, only the number of singlets and triplets on each molecule $[\#S_1, \#T_1]$ determines the overall configuration. It is common to assume that, because singlets are much shorter-lived compared to triplets, configurations of more than one singlet (e.g., $[2,0]$) can be neglected under typical experimental conditions (<1 kW/cm²). Singlet–Triplet and triplet–triplet annihilation now become possible upon populating $[1,1]$ and $[0,2]$ configurations, respectively, but very little is directly known about their dependences on polymer structure. While direct evidence of singlet–triplet annihilation can be

more intuitively inferred from fluorescence quenching dynamics of single polymers, triplet–triplet annihilation has proven more difficult, because it involves interactions between two nominally “dark” excited states. Simple spin statistics also predict multiple triplet–triplet annihilation products that may be difficult to detect directly from fluorescence emission. Historically, contributions of this bimolecular channel have been inferred from delayed fluorescence, though it is the least likely of all annihilation channels.²⁹ Additionally, pulse radiolysis investigations of solvated polymers represent a substantial body of work in the study of triplets and their interactions, where it has been suggested that a single polymer chain (i.e., high molecular weight (M_w)) may support up to 30 triplets at a time.³⁰ Table 1 presents a brief summary of relevant excitonic processes with their respective rate constants used in the coupled photodynamic model.

Table 1. Summary of Possible First- and Second-order Exciton Formation, Decay, and Interactions in Single Polymer Chains

process	rate	reaction
absorption/excitation	k_{exc}	$S_0 + h\nu \rightarrow S_1$
singlet nonradiative decay	k_{nr}	$S_1 \rightarrow S_0$
emission	k_{fl}	$S_1 \rightarrow S_0 + h\nu$
intersystem crossing	k_{isc}	$S_1 \rightarrow T_1$
reverse intersystem crossing	k'_{isc}	$T_1 \rightarrow S_0$
triplet–triplet annihilation (singlet product)	$k_{\text{TT}}/9$	$2T_1 \rightarrow S_0 + S_1$
triplet–triplet annihilation (triplet product)	$k_{\text{TT}}/3$	$2T_1 \rightarrow S_0 + T_1$
singlet–triplet annihilation (quenching)	k_{QST}	$S_1 + T_1 \rightarrow S_0 + T_1$

Because fluorescence transients typically lack sufficient time resolution to resolve dynamics comparable with triplet lifetimes (e.g., micro- to milliseconds), specialized approaches are required to go beyond resolution limits of most multichannel scalars. To this end, fluorescence correlation spectroscopy (FCS) and excitation intensity modulation spectroscopy (EIMS) techniques represent the most effective and commonly employed tools for interrogating triplet processes at the single molecule level.

Figure 3 illustrates simulated FCS and EIMS responses for single and multichromophoric systems (i.e., $N = 1$ and $N = S$, respectively) in the absence of bimolecular exciton decay pathways for simplicity. FCS relies on autocorrelating photon arrivals, $G(\tau)$, which exhibit characteristic dynamics when triplet states are involved. This effect is shown in Figure 3a with distinct decays emerging due to triplet occupation captured by the second-order form of $G(\tau)$.³³

$$G(\tau) = \frac{I(t)I(t+\tau)}{I^2} \quad (2)$$

Characteristic times τ reflect triplet decay kinetics, which, in the regime of low-excitation intensities, are consistent with the first-order reverse intersystem crossing process.³⁴

EIMS is a quasi continuous wave (CW) technique, where rectangular-shaped excitation pulses excite single molecule fluorescence, and responses are synchronously averaged.^{35–37} This technique offers greater flexibility for probing triplet dynamics in equilibrium and nonequilibrium scenarios by varying pulse height (intensity) and duration according to

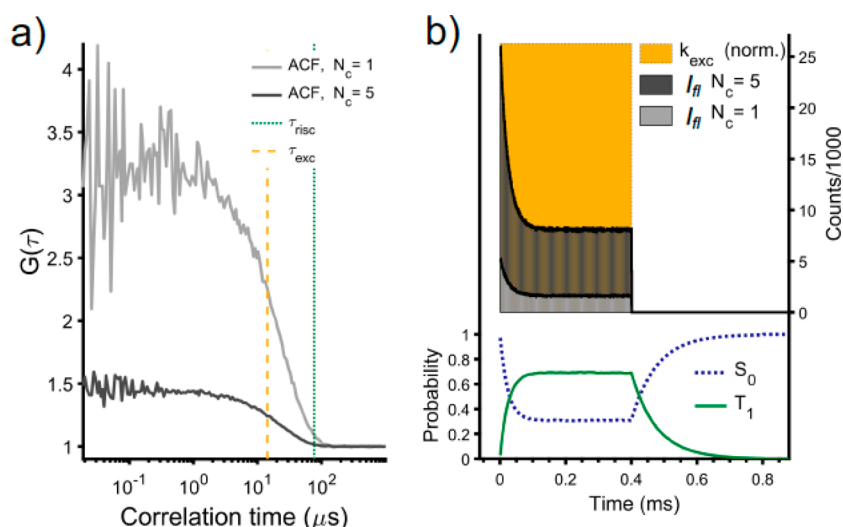


Figure 3. Examples of FCS (a) and EIMS (b) responses for the case of single and multichromophore systems. FCS curves are displayed as an autocorrelation (ACF) of fluorescence photons generated under CW excitation. EIMS responses for both systems are generated using rectangular-shaped pulsed excitation waveforms (gold). Values of first-order triplet formation and decay rate constants were taken from refs 31 and 32.

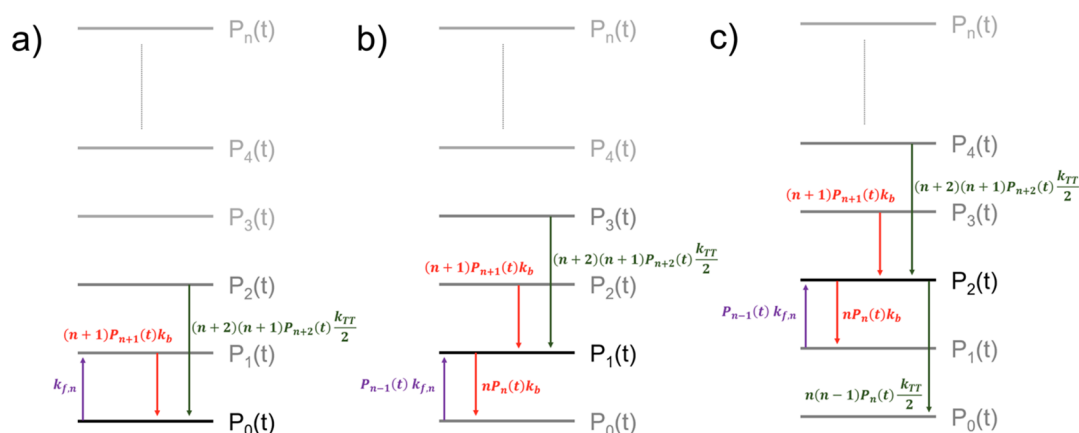


Figure 4. Schematic representation of triplet population dynamics for nonzero probability of zero (a), one (b), and two (c) triplets in the conjugated polymer. Reproduced with permission from ref 39. Copyright 2019 Springer Nature.

expected triplet decay time scales. Furthermore, EIMS is also less susceptible to errors and artifacts commonly encountered in FCS (e.g., detector after-pulsing). Figure 3b shows an example EIMS experiment from the same single and multichromophore case as seen for FCS (Figure 3a). EIMS responses reflect intensity decay from a triplet-free level (I_0) to a steady-state level (I_{ss}), where triplet populations have equilibrated with those of the ground state (i.e., $(1-[0,0]) \geq [0,1]$).

Unlike the simple three-level system, applying the full multichromophoric model to simulate either quenching dynamics requires direct numerical integration of all rate equations. However, certain approximations are often invoked to greatly simplify this task. For example, analytic solutions may be obtained by assuming rates of multitriplet configurations (i.e., $[0,2]$) reach a steady-state condition immediately after photon absorption. The entire model is then reduced to an effective two-level system, which tacitly assumes infinitely fast triplet–triplet annihilation, where all chromophores spend the most time in $[0,0]$ or $[0,1]$ states.³⁷ This limit is usually only strictly valid in the regime of low-excitation intensities (i.e., low k_{exc}) and polymers with low triplet yields. However, when triplet yields are large ($>10\%$), the assumption of one triplet existing at a time on a polymer chain (e.g., nonzero $[0,2]$ populations) may be

invalid. Tachiya and co-workers first considered the possibility of multiple coexisting triplets and finite triplet–triplet annihilation by applying the well-known Smith-Ewart differential difference equation approach to simulate population dynamics of n triplets.³⁸ This formalism only considers dynamics within the triplet manifold and requires three principle rate constants to transition between triplet configurations (see Figure 4), namely, the (forward) triplet formation, $k_{f,n}$, reverse intersystem crossing, and triplet–triplet annihilation rate constant, k_{TT} .

Relating population dynamics of n triplets to fluorescence intensities is accomplished by eq 3

$$I(t) \propto \sum_{n=0}^{\infty} \frac{P_n(t)}{1 + nk_{QST}\tau_f} \quad (3)$$

where the quenching depth is determined by the singlet–triplet annihilation rate constant k_{QST} and fluorescence lifetime τ_f . Because only the latter quantity is measured experimentally, k_{QST} must be estimated and usually treated as an ad-hoc adjustable parameter. In the limit of infinitely fast triplet–triplet annihilation, eq 2 reduces to the same form as obtained when setting the rate of the $[0,2]$ configuration to zero.³⁸

To facilitate general comparisons across the range of polymers and limiting forms of the multichromophoric model, we introduce a new kinetic Monte Carlo (KMC) approach for solving all coupled rate equations of the coupled photodynamic model in Figure 2 and Table 1. We implemented Gillespie's direct method from a completely stochastic perspective (additional details are provided in the Supporting Information). Similar to earlier numerical simulations, KMC simulations are functionally zero-dimensional, meaning only the total number of species on each chromophore defines the state. Most importantly, solutions of the KMC approach are in the form of explicit fluorescence photon emission count rates (i.e., dI_{f}/dt) that are also devoid of accumulated error usually incurred from numerical approximations. This aspect better facilitates direct comparisons to experimental FCS or EIMS responses as opposed to extrapolating singlet population dynamics via eq 2. We specifically take advantage of exact KMC methods to shed new light on the large variability of triplet signatures depending on the polymer structure, conformation, and aggregation state.^{40,41}

3. RESULTS AND DISCUSSION

3.1. Elucidating Triplet Processes of Polymer Molecules and Assemblies at the Single Molecule Level: The Limiting Case of Infinitely Fast Triplet–Triplet Annihilation. Much of the early work involved in advancing the basic understanding of triplet photophysics in polymers focused on poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV). MEH-PPV is particularly advantageous for single molecule level studies of conformation-dependent excitation energy transfer due to its relatively large fluorescence quantum yields.^{26,42} Despite low triplet yields (i.e., <5%), Barbara and co-workers first demonstrated that triplet dynamics could be resolved from single MEH-PPV chains using combinations of FCS and EIMS techniques.³⁷ Figure 5a portrays a typical EIMS response from a single MEH-PPV chain using a stair-step shaped excitation pulse sequence to excite fluorescence emission.

EIMS or FCS responses of MEH-PPV chains also show a broad range of behaviors (i.e., large variations in quenching depths and dynamics) consistent with conformational heterogeneity effects. Importantly, quenching dynamics were predominately single exponential in nature, which was primarily used to justify the limit of infinitely fast triplet–triplet annihilation. Now, fluorescence quenching activity is determined solely by adjusting k_{QST} to obtain good agreement with experiment. Values ranged from $\sim 10^8$ – 10^{10} s^{−1} similar to early reports, although mechanistic details are much more elusive.³⁷ Resolving the onset of exciton–exciton annihilation is still possible in this system, although this requires increasing the excitation intensity or the number of chromophores in the excitation volume. While the former option should eventually result in nonzero multitriplet populations, photodegradation is also accelerated, whereas the latter approach can be accomplished simply by varying the polymer molecular weight or fabricating nanoscale polymer assemblies. Reprecipitating nanoparticles of MEH-PPV in aqueous solution is a simple method for producing what are effectively small pieces of a bulk thin film but without long-range heterogeneity effects.⁴³ The kinetics of nanoparticle formation are very rapid due to the fact that water is a nonsolvent, resulting in typical sizes being limited to ~ 10 – 100 nm corresponding to ~ 2 – 20 individual polymer molecules. These structures now provide a basis for establishing how increased interchain

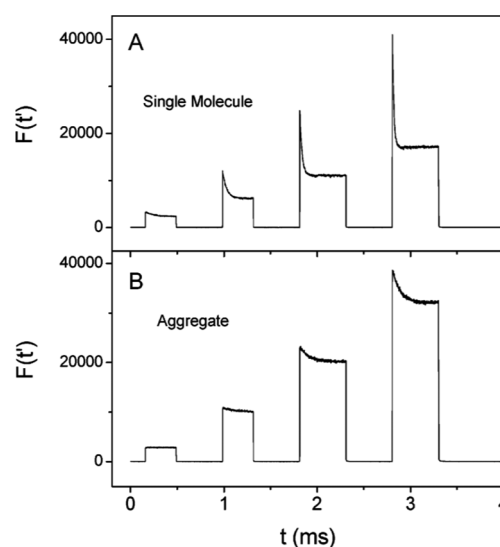


Figure 5. Representative intensity modulation transients of (a) MEH-PPV single molecules and (b) MEH-PPV nanoparticles excited with 488 nm light at 298 K. A 0.5 OD neutral density filter was placed in the detection path for nanoparticle transient measurements to obtain comparable intensities to the single molecules. Adapted with permission from ref 44. Copyright 2005 American Chemical Society.

contacts influence triplet processes while maintaining relatively small size scales. Figure 5 compares EIMS responses from an isolated MEH-PPV molecule with a single nanoparticle suspended in a poly(vinyl alcohol) host.

Severely attenuated triplet-induced quenching dynamics and modulation depths are most apparent in MEH-PPV nanoparticles that were initially assigned as enhanced triplet–triplet annihilation yields (i.e., larger k_{TT}).⁴⁴ Related assignments of triplet–triplet annihilation were also reported from studies of MEH-PPV thin films⁴⁵ and pulse radiolysis in solution presumably from more interchain contacts acting as triplet conduits. Assuming the limit of infinitely fast triplet–triplet annihilation still applies, the substantially lower triplet population density in nanoparticles necessitates particularly large values of k_{QST} to achieve similar levels of dynamic fluorescence quenching as found in single chains. A further implication of this assumption is that effective quenching length scales must be substantially larger than typical accepted values of Förster radii (i.e., >10 nm).

To better assess the impact of these proposed effects, we use the KMC method to simulate EIMS responses of single MEH-PPV chains and nanoparticles with different bimolecular rate configurations. Figure 6 shows cursory EIMS simulations undertaken for a fixed number of chromophores ($N = 5$) and excitation intensities (k_{exc}) using previously reported values for first-order triplet formation and decay components of MEH-PPV.^{46,47} The effect of exciton–exciton annihilation on fluorescence quenching characteristics is demonstrated by displaying two limiting cases of no triplet–triplet annihilation ($k_{\text{TT}} = 0$) and a finite value chosen to be fast enough to prevent delayed emission, since that behavior has not been experimentally observed. For each of these limits of k_{TT} , we also compare the effect of k_{QST} using a value similar to the singlet lifetime (qualitatively there is little change in the simulation with faster k_{QST} due to increased singlet quenching preventing triplet quenchers from coming into existence). In each example, the EIMS response (dark gray) is superimposed with the

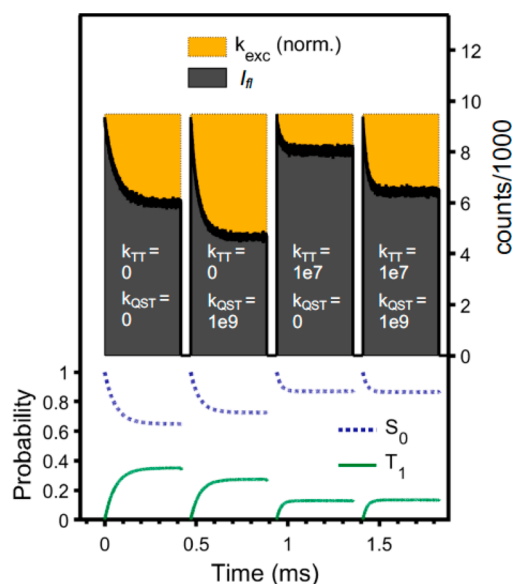


Figure 6. Simulated EIMS sweeps using the KMC approach to solve the coupled multichromophore photophysical model. Excitation intensities and number of chromophores were held constant ($k_{\text{exc}} = 4.8 \times 10^5 \text{ s}^{-1}$, $N = 5$) while evaluating the effect of exciton–exciton annihilation. These rate constants are displayed on quenching curves along with corresponding excitation pulse profiles with each rate constant (set to first-order units by dividing by the number of chromophores).

corresponding excitation light pulse (gold). Furthermore, the time-dependent probabilities of S_0 ($[0,0]$) and T_1 ($[0,1]$) are displayed below the EIMS responses to compare the effect on exciton populations. When both $k_{\text{TT}} = k_{\text{QST}} = 0$, fluorescence quenching modulation occurs only from the finite probability that a triplet forms on any chromophore, which cannot be excited again until the triplet relaxes. On the one hand, when singlet–triplet annihilation becomes active ($k_{\text{TT}} = 0$), noticeable increases (decreases) in quenching depths (probabilities) are observed but with no change in dynamics time scales. On the other hand, nonzero k_{TT} values produce significantly faster quenching dynamics, but faster triplet population losses result in lower quenching depths. Likewise, including singlet–triplet annihilation only increases the quenching depth but leaves dynamics unchanged, similar to the case of $k_{\text{TT}} = 0$.

These results indicate that larger k_{TT} values cannot fully account for the observed trends in MEH-PPV nanoparticles. Instead, it is more plausible that triplet formation kinetics are disrupted (i.e., attenuated) possibly from the presence of charges (polarons) originating from the fact that the peripheries of these structures are exposed to protic media upon formation.⁴⁸ This notion is supported from related EIMS studies investigating exciton–polaron interactions (e.g., singlet–polaron and triplet–polaron) in single polymer molecules embedded within unipolar charge (hole) injection devices. Upon forward biasing beyond the device “turn-on” voltage, triplet-induced quenching responses were significantly altered in the presence of injected polarons.⁴⁹ Interestingly, holes were found to impact singlet populations as well as triplets as seen from diminished initial intensities (i.e., triplet-free conditions).⁴⁹ Accounting for the presence of charges becomes an increasingly important factor when bridging the gap between single molecule and bulk levels, although additional work is needed in this area to fully understand exciton–polaron interactions.

3.2. Single Molecule Level Perspectives of Multitriplet Interactions: Heavy Atom and Aggregation Effects.

Conjugated polymers with large fluorescence and low triplet yields have many practical advantages for the single molecule level, including respectable signal-to-noise ratios. However, these systems do not afford many opportunities to peer deeper into exciton–exciton interactions (i.e., triplet–triplet annihilation) at the single molecule level. Polychalcogenophenes are an interesting class of conjugated polymers that have seen use in devices and tend to form π -stacked aggregates with the packing order and size determined primarily by the regioregularity of monomer linkages.⁵⁰ The presence of larger chalcogen atoms (e.g., sulfur, selenium, and tellurium) also increases spin–orbit coupling, resulting in faster triplet formation and decay kinetics.^{51,52} These materials are perhaps most renowned for their efficient and multidirectional charge and energy transport making them excellent benchmarks for solar cells and transistor applications.^{53,54} Poly(3-alkylthiophenes), in particular, are frequently employed for optoelectronic devices, and their triplet processes have been investigated extensively at the ensemble level. Importantly, these polymers exhibit the most pronounced variations in triplet features with the local environment in addition to being considerably less emissive than other archetype systems, such as MEH-PPV. Nonetheless, Palacios et al. investigated triplet population dynamics in single chains of regioregular poly(3-octylthiophene) (P3OT) using EIMS.⁵⁵ Typical fluorescence quenching depths were significantly larger than those seen in MEH-PPV and other polymers under similar excitation conditions, a strong indication of larger triplet yields. P3OT triplet lifetimes were estimated directly from EIMS quenching curves generated with very low excitation intensities and found to be ca. 16 μs , in good agreement with transient absorption spectral dynamics.⁵⁵ These authors further demonstrated the high efficacy of triplet-induced quenching by comparing both oxygen-rich and oxygen-depleted samples, with the former exhibiting much stronger average fluorescence counts.⁵⁵

Performing similar measurements on related polychalcogenophenes further exposes the role of heteroatom as well as side-group substitution on spin–orbit coupling and packing characteristics, respectively. Poly(3-hexylthiophene) (P3HT) shares similar characteristics as P3OT, although it has more desirable solid-state packing qualities beneficial for devices. Triplet processes have been studied extensively in many P3HT variants (e.g., different molecular weights, regioregularities, etc.) mainly by ensemble-level transient absorption spectroscopy. While chain regioregularity and alkyl substitution effects are well-studied, relatively little work has been performed involving the effect of the chalcogen atom. To this end, Pensack et al. performed detailed transient absorption studies of P3HT and its seleno- and telluro-substituted derivatives in dilute solutions and observed a large increase in triplet formation rates along with substantial reductions in fluorescence yields with larger heteroatoms.⁵² Importantly, aggregation in polychalcogenophenes is notorious for causing large fluctuations in triplet photophysics, which was ruled out in this case on the basis of solution concentrations and lack of characteristic features in absorption spectra.⁵²

Single molecule level studies of heavy atom effects in polymers are much rarer due to the diminished solubility of polymers containing large heteroatoms and, more importantly, drastically lower fluorescence yields. Datko et al. studied isolated single chains of P3HT alongside those of poly(3-hexylselenophene)

(P3HS) of similar molecular weight on both short and long time scales to capture the full range of heavy atom-mediated triplet dynamics.⁵⁶ Because triplets are inextricably tied to oxygen-related photochemistry, it is first useful to assess how typical triplet residence times impact photodegradation. Fluorescence transients of single P3HS and P3HT chains dispersed in polystyrene were investigated while exposed to the ambient environment, and intermittency characteristics (i.e., “on/off” time distributions) can be used to compare the efficacies of triplet-induced oxygen sensitization causing longer time flickering behavior. Intriguingly, P3HS chains exhibited significantly longer average on times despite having larger reported triplet yields. This effect was explained by the fact that, while the heavier selenium atom expedites triplet formation,⁵⁶ it also facilitates deactivation by increasing reverse intersystem crossing back to the S_0 state. Comparing the expected triplet residence times to known diffusion behavior (or, encounter frequencies) of oxygen in polymer films indicates that P3HS chains are far less likely to sensitize reactive species. With experimental kinetic parameters, these behaviors were simulated in the limit of the three-level model using a hidden Markov chain approach (see Figure 7) that shows good agreement with measured transients.⁵⁶

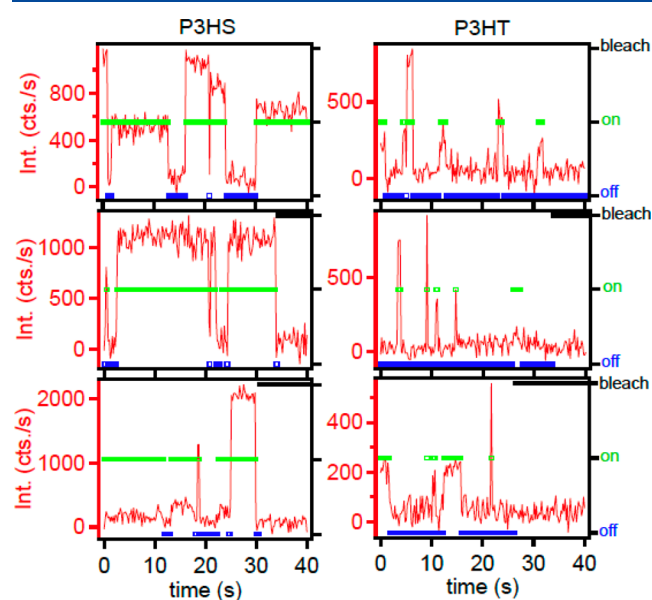


Figure 7. Simulated fluorescence intensity transients based on exponentially distributed on and off transition probabilities for single P3HS and P3HT chains. Transients were simulated using a conventional Monte Carlo approach assuming that on intensity levels follow the empirical log-normal behavior. State occupancies are shown on the right axis of each graph represented by different levels accessed in the course of the transient (not to scale). Reproduced with permission from ref 56. Copyright 2018 American Chemical Society.

Taking these studies to faster time scales, EIMS investigations of P3HS and P3HT single chains were performed, which included a new hybrid approach to obtain better estimates of the actual triplet lifetime in both molecules. Moreover, when combined with the multichromophoric photodynamic model, EIMS probes can be used to more accurately determine triplet population dynamics and average occupancies, which is not possible from fluorescence transients and the limit of infinitely fast triplet–triplet annihilation. Figure 8a shows a typical response from a single P3HS chain superimposed with a stair-

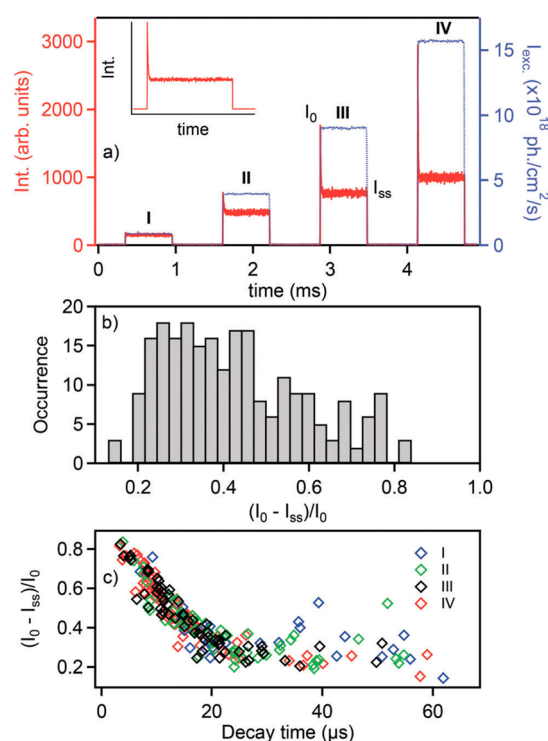


Figure 8. (a) Representative MCA transient from a single P3HS chain (red trace) using 568 nm (2.18 eV) excitation with Roman numeral labels for each pulse in the sequence with increasing intensity. (inset) MCA transient from a single pulse. Prompt (I_0) and steady state (I_{ss}) intensities are noted, and histograms of modulation quenching depths are shown in (b). (c) Scatter plots of quenching depths vs decay time constants for each excitation pulse intensity in the pulse cycle. Reproduced with permission from ref 57. Copyright 2017 Royal Society of Chemistry.

step shaped excitation pulse sequence. Triplet-induced fluorescence quenching dynamics were significantly faster in P3HS than typically observed in related polymers, which was attributed to both larger triplet formation rates and faster relaxation dynamics. Figure 8b displays distributions of quenching depths (normalized to the initial intensity I_0) reflecting intrinsic heterogeneity effects on triplet photophysics with the average modulation depth being ~ 0.4 . Measured decay times appear in Figure 8c for each pulse in the total sequence (labeled I–IV in increasing intensity) demonstrating triplet quenching dynamics features are virtually independent of the excitation intensity over the range studied. This result suggests that bimolecular contributions (i.e., triplet–triplet annihilation) are not appreciably consistent with shorter triplet lifetimes or possibly lower mobilities. Because P3HS molecular weights are relatively small (ca. 30 kDa), the ability of P3HS chains to self-aggregate is limited, meaning that, if triplet–triplet interactions can occur, they would also be limited to intrachain type implying lower encounters.⁵⁷

To obtain clearer views of triplet relaxation characteristics in the absence of competing processes, a hybrid approach was used, where two excitation pulses of the same intensity were used to (i) generate a steady-state level of triplets, then, (ii) re-excite with a second pulse with varying temporal delays. By comparing ratios of I_0 between the first and second pulses with each time delay, it is possible to estimate triplet lifetimes that are less susceptible to complications (i.e., other dynamic fluorescence

quenchers), since the excitation light switches off from the first pulse, and populations relax in the dark.

Figure 9a illustrates the delayed two-pulse excitation scheme employed for estimating triplet lifetimes, and average responses

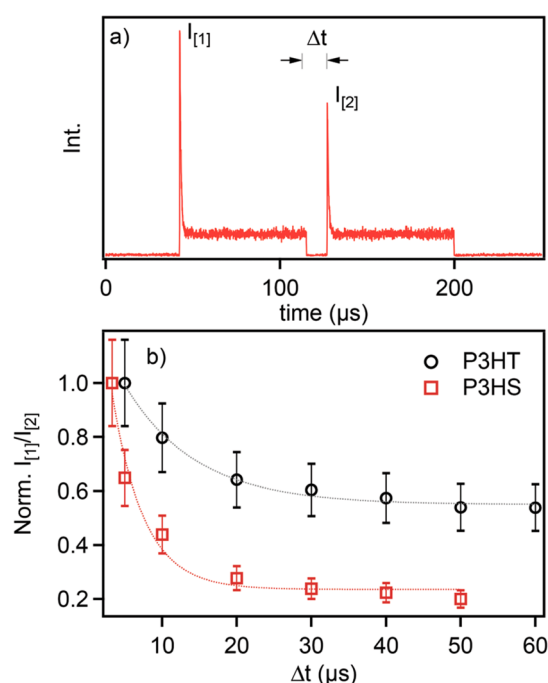


Figure 9. (a) Variable delay two-pulse experiment of triplet relaxation time scales in the dark (i.e., T_1-S_0). (b) Comparisons of triplet relaxation kinetics for average responses of single P3HT and P3HS chains. Reproduced with permission from ref 57. Copyright 2017 Royal Society of Chemistry.

from many single P3HS and P3HT chains are shown in Figure 9b. The results indicate much faster relaxation of triplet quenchers in P3HS compared to P3HT (~ 4 vs ~ 10 μ s, respectively) consistent with findings from longer time fluorescence transients in the presence of oxygen.⁵⁷ With estimates of first-order triplet formation rate constants from transient absorption spectra and from single molecule triplet lifetimes (Figure 9b), triplet population dynamics were simulated assuming finite triplet–triplet annihilation.³⁹ These calculations required adjusting k_{QST} within the range of values reported earlier, although quenching by more than one triplet is now possible, since appreciable population buildup occurs in both polymers.³⁹ Figure 10 shows the results of these simulations with the time-dependent evolution of triplet populations for P3HT (a) and P3HS (b). While k_{QST} mostly affects quenching depths, estimates of k_{TT} values can be more difficult to determine reliably. Here, the lower limit of k_{TT} was set to the experimentally measured reverse intersystem crossing rate constant k'_{ISC} , which reproduced experimental trends remarkably well-consistent with expected lower intrachain triplet encounters.³⁹ Because this model is integrated over all time, it is possible to evaluate both the average duration to reach a steady-state condition as well as the number of triplets present in each polymer. Population relaxation dynamics reached a steady-state condition much faster in single P3HS chains compared to P3HT samples (i.e., ~ 3 vs ~ 25 μ s, respectively). Consequently, expected average triplet levels are significantly lower in P3HS than found in P3HT (see Figure 10c) confirming

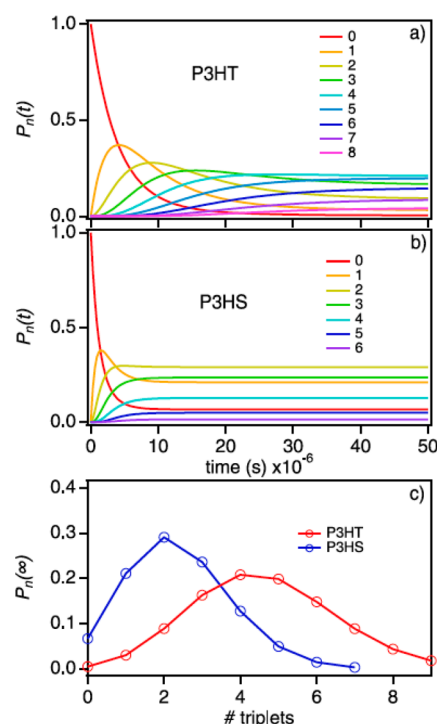


Figure 10. Time-dependent populations of triplets in P3HT (a) and P3HS (b) for multiple triplet configurations. (c) Steady-state triplet populations ($P_n(\infty)$) for each polymer. Reproduced with permission from ref 56. Copyright 2019 Springer Nature.

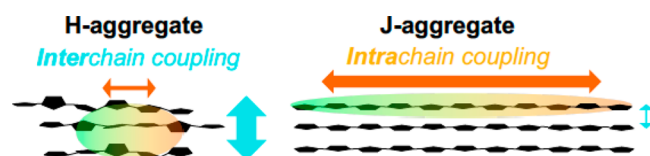
trends found in fluorescence transients measured on longer time scales.

These results offer new perspectives of the importance of heavy atoms to tune triplet levels, which can be harnessed by synthetic approaches or including additives (e.g., transition-metal complexes). However, the complete picture of triplet photophysics in polymers also requires consideration of polymer conformational and packing qualities regulating electronic coupling strength and directionality between segments. Along these lines, it is noteworthy that triplet-induced fluorescence quenching signatures vanished in P3HS samples at the onset of aggregation.⁵⁷ This effect mirrors that found in thin films of this and other polymers that may involve several factors, including enhanced triplet–triplet annihilation, diminished triplet yields, or polaron formation and subsequent quenching of triplets.⁴⁰ In a more recent example, investigations of conjugated polymers proposed to undergo singlet fission observed sudden losses in triplet signatures once chains began aggregating.⁴¹

The correlation between aggregation and the disappearance of triplets has been confirmed in multiple experimental studies; however, the mere formation of aggregates alone is not sufficient to fully explain large modifications in photophysical branching ratios. Chain ordering characteristics also play a critical role in mediating triplet formation and interactions, but it is exceptionally difficult to discern these effects in most ensemble-level studies. For this reason, we turn to self-assembly-based approaches to tune aggregation intra- and interchain order dictating the directionality and strength of excitonic coupling. A key question moving forward in understanding conformational and packing ordering effects is whether triplet exciton coupling and interactions follow similar, well-known rules as their singlet counterparts.⁵

3.3. Unraveling Conformational Ordering Effects on Multitriplet Interactions. The propensity of P3HT to form extended aggregate π -stacks has generated considerable interest for improving exciton and charge transport in devices as well as advancing the basic understanding excitonic coupling interactions.⁵ Specifically, intrachain order (specifically, monomer planarity) within aggregated chain segments has a large influence on the directionality and strength of exciton coupling. For example, high intrachain order enhances intrachain exciton coupling and coherence lengths in addition to suppressing interchain coupling. This scenario resembles classic J-aggregate-type excitonic features, where intensities are concentrated in the electronic origin (0–0) transition, which is actually rare for polymers, since polydispersity and associated heterogeneity effects can easily disrupt intrachain order.^{5,18} Consequently, most polymer aggregates display H-aggregate-type coupling due to intrachain localization leading to stronger interchain coupling. In this case, spectral line widths are usually much broader together with larger Stokes shifts, since transition strengths are shifted away from the electronic origin.⁵ Scheme 1 portrays a cartoon schematic of P3HT aggregates representing the two limiting regimes of excitonic coupling.

Scheme 1. Cartoon schematics^a



^aCartoon schematics of H- and J-type aggregates of P3HT. Arrows highlight intra- (orange) and interchain (cyan) coupling directions with sizes reflecting the relative strength. Reproduced from ref 39. Copyright 2019 American Institute of Physics.

Here, we show that self-assembled P3HT aggregate nanostructures are excellent model systems for uncovering the evolution of triplet interactions in aggregates without the usual complications from polydispersity and ensemble averaging. Nanofibers of P3HT were fabricated to produce H- and J-type limiting forms that were then investigated using EIMS techniques to unravel the roles of intra- and interchain order

on triplet population dynamics characteristics, especially bimolecular processes, such as triplet–triplet annihilation.

Figure 11a,b shows transmission electron micrographs of both P3HT nanostructures, where typical widths of H-aggregates are ca. 15 nm compared to ~ 40 nm for J-aggregates. On the one hand, P3HT J-aggregate represents ultrapurified fractions with very few stacking faults making them unique among similar nanoscale polymer forms.¹⁸ On the other hand, H-type aggregates are fabricated in anisole (a poor solvent), where no weight fractionation occurs, leading to smaller (underdeveloped) aggregated regions within the nanofiber along with a significant amorphous fraction. Furthermore, intrachain order is severely limited in aggregated regions because of a large fraction of interpenetrating nonaggregating chains, which resembles typical morphologies of P3HT thin films. These stark differences in nanomorphology and intrachain order of π -stacked segments are especially apparent in both spectra and photophysics. For example, J-aggregate-type nanofibers exhibit dominant electronic origin transitions (0–0) along with small Stokes shifts (~ 100 cm^{-1} or less) and line widths, whereas intensities shift to vibronic sidebands in addition to broader line widths and larger Stokes shifts in H-aggregates due to greater disorder (Figure 11c,d).¹⁸

Figure 12 next shows the typical stair-step excitation pulse sequence used (a) and representative EIMS sweeps from single H- (b) and J-type (c) P3HT nanofibers. Comparing quenching characteristics reveals yet another glaring dissimilarity between these structures. P3HT J-aggregates show considerably larger quenching depths in contrast to H-aggregates that tend to exhibit faster quenching dynamics. These trends putatively indicate larger triplet yields in the former and greater triplet–triplet annihilation yields in the latter systems.

Cursory modeling of EIMS behaviors was performed in the limit of one triplet, but these simulations were not able to reproduce either behavior very well.⁵⁹ Specifically, preliminary simulations of P3HT J-aggregates in the limit of infinitely fast triplet–triplet annihilation required inflated estimates of k_{QST} (e.g., approaching $\sim 10^{11}$ s^{-1}) to replicate observed quenching depths. In a later study, J-aggregate triplet quenching was evaluated in the limit of finite triplet–triplet annihilation revealing high probabilities of more than one triplet and correspondingly lower values of k_{QST} , since more than one triplet may quench fluorescence.³⁹ With experimental estimates of all

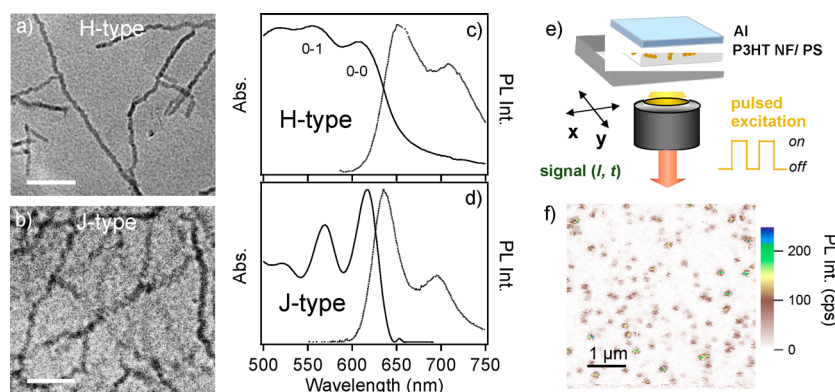


Figure 11. TEM images of H- (a) and J-type (b) P3HT nanofibers (scale bar = 200 nm). Absorption and PL spectra of H- (c) and J-type (d) P3HT NF dispersions. (e) Diagram of excitation intensity-modulated single-particle PL imaging and spectroscopy on P3HT nanofibers. (f) Representative photoluminescence (PL) image of single NFs dispersed within the polystyrene (PS) host matrix. (scale bar = 5 μm). Adapted with permission from ref 58. Copyright 2014 American Chemical Society.

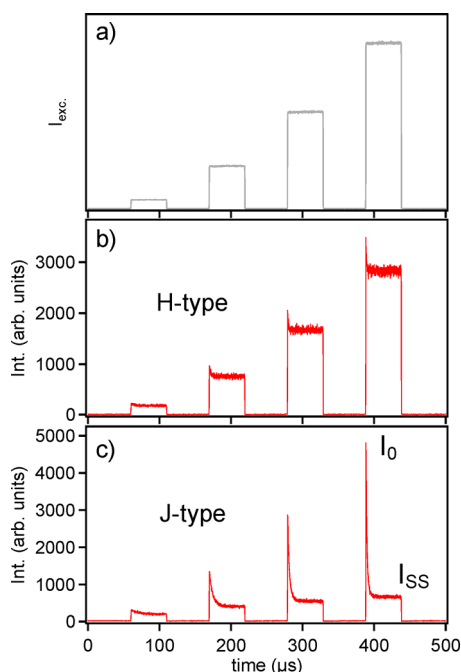


Figure 12. (a) Rectangular laser pulse excitation profile. (b, c) Representative EIMS sweeps of H-type and J-type P3HT nanofibers, respectively. Adapted with permission from ref 58. Copyright 2014 American Chemical Society.

first-order triplet formation and decay constants, the full multichromophoric model was extended to perform least-squares fitting of many single J-aggregate EIMS sweeps. To arrive at physically meaningful estimates of k_{TT} , this parameter was allowed to vary over several orders of magnitude while keeping the lower limit set to the reverse intersystem crossing rate constant. By calculating triplet population dynamics for all times, it was possible to estimate (specifically, count) the number of triplets present once steady-state conditions were reached. Figure 13 displays results from this procedure with an example EIMS response from a single P3HT J-aggregate excited with a variable-intensity pulse sequence along with estimates of the triplet expectation value (i.e., $\langle T_1 \rangle$) generated from extrapolating populations at long times (i.e., $P_n(\infty)$, where n is the number of triplets).

In related studies of triplet and energy transfer effects in single P3HT chains, Lupton and co-workers investigated the effect of molecular weight and chain folding and found that fluorescence counts saturate for larger P3HT chains. It was concluded that all excitation energy is transferred to a single triplet, which effectively limits the ability to utilize photogenerated singlets.²⁸ Interestingly, reported fluorescence spectra showed prominent electronic origin intensities with higher molecular weight in addition to the observation of photon antibunching, indicating single chromophore behavior.²⁸ These traits closely resemble those of J-aggregates, yet strong interchain coupling (characteristic of H-aggregates) was instead invoked to explain this facile singlet–triplet annihilation mechanism. Estimates of k_{QST} were not furnished, but an effective quenching distance of 30 nm was inferred based on the expected size of self-aggregated P3HT chains and corresponding experimental observations. This exceptionally large value is consistent with earlier predictions using k_{QST} to phenomenologically describe triplet quenching in the limit of infinitely fast triplet–triplet annihilation.

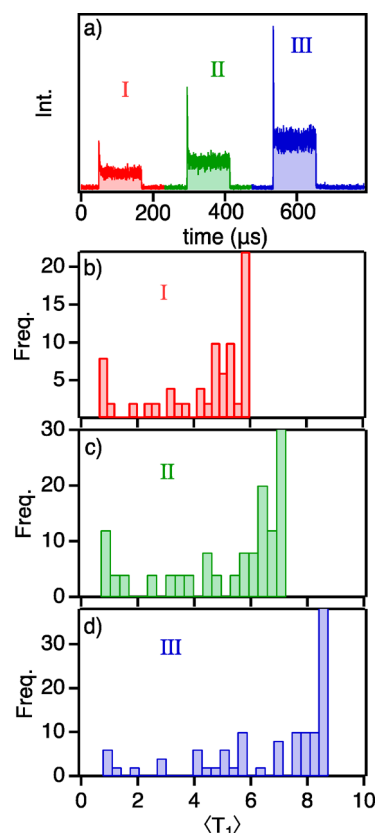


Figure 13. (a) Illustration of a three-pulse sequence used to estimate T_1 for ~ 40 P3HT J-aggregate nanoparticles. (b–d) T_1 values for excitation intensities of $\sim 2 \times 10^{20}$, 5×10^{20} , and 7×10^{20} photons/s/cm². Reproduced with permission from ref 39. Copyright 2019 American Institute of Physics.

While P3HT J-aggregates show strong evidence of multiple coexisting but non-interacting triplet populations, EIMS responses of H-aggregate type nanofibers (see Figure 12b) indicate substantial contributions from triplet–triplet annihilation (i.e., small quenching depths with rapid relaxation dynamics). It is important to stress that, unlike MEH-PPV nanoparticles, alterations in triplet formation mechanisms do not lead to this type of response. The fact that interchain exciton coupling dominates in these structures suggests that triplet–triplet annihilation is an interchain-mediated interaction. We do not attempt to assign or quantitate the exact nature of coupling between triplets, although, based on well-established rules governing interchain coupling of singlet excitons,⁵ we assume that dipolar interactions probably dominate at room temperature.

Because P3HT H-aggregate nanofibers possess similar morphological qualities as thin films, these trends offer new explanations for the unexpected disappearance of triplets in solid forms of many aggregating polymers. Namely, stronger interchain coupling should lead to greater triplet–triplet annihilation yields and rapid losses of triplet populations.⁶⁰ Interestingly, theoretical studies found that H-aggregate couplings actually suppress exciton–exciton annihilation contrary to expectations from J-aggregates.⁶¹ It is possible that contributions from polarons are also involved in triplet–triplet annihilation in H-aggregates, which may be significant, since both aggregated and amorphous domains coexist within the

same nanofiber, which is known to promote polaron formation.^{58,62,63}

We now explore how variable triplet–triplet annihilation impacts fluorescence quenching in P3HT nanofibers using the KMC approach to simulate results directly comparable to experimental EIMS trends between H- and J-type P3HT structures. This is accomplished by using first-order singlet and triplet formation and decay kinetic parameters while varying k_{TT} , which is summarized in Figure 14. Contributions from

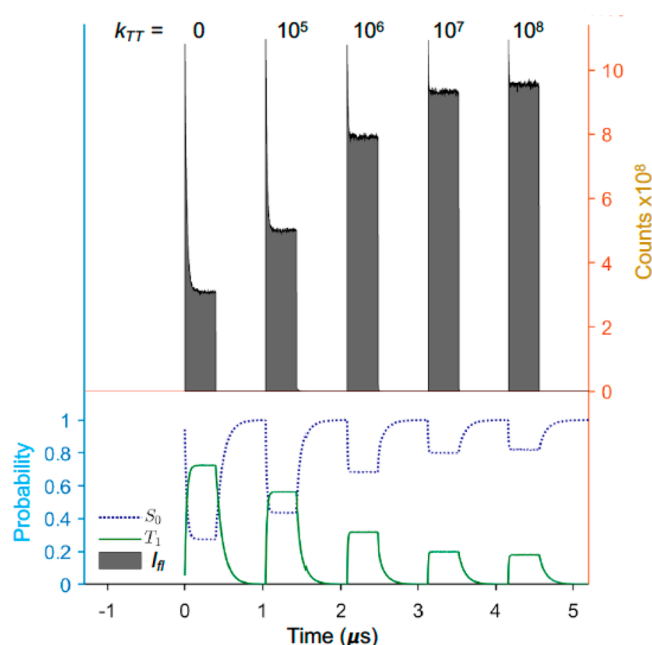


Figure 14. KMC simulations of EIMS dynamics using experimentally measured first-order exciton formation and decay rate constants of P3HT dilute solutions for a model system of $N = 5$ chromophores. Examples of typical values are $k_{ISC} = 8.3 \times 10^8 \text{ s}^{-1}$, $k'_{ISC} = 1.1 \times 10^5 \text{ s}^{-1}$, $\tau_{fl} = 2.0 \times 10^{-9} \text{ s}$, and excitation intensities were the same for each response ($k_{exc} = 7 \times 10^5 \text{ s}^{-1}$). k_{TT} values are in units of inverse seconds.

singlet–triplet annihilation have little influence on observed quenching behaviors, and we set k_{QST} to zero in these simulations. When k_{TT} is small, large fluorescence quenching depths are observed due to significant triplet population buildup as seen from corresponding triplet probabilities. This behavior exactly reproduces typical EIMS responses of P3HT J-aggregates, where the dominant intrachain nature of excitonic coupling suppresses interchain coupling and, consequently, triplet–triplet annihilation. Conversely, increasing k_{TT} causes faster triplet population decay leading to smaller quenching depths and faster dynamics, exactly the same characteristics as P3HT H-aggregate nanofiber responses. These results suggest that polymer aggregates with high intrachain order may accommodate many triplets simultaneously. The fact that chain ordering characteristics may be easily tuned by simply varying processing conditions and solvent demonstrates significant potential for polymers as multiexciton generating and harvesting platforms.

4. CONCLUSIONS

The ability of single-molecule spectroscopic probes to uncover stochastic triplet processes in heterogeneous conjugated polymer chains offers valuable perspectives into the interdependence between chain conformational characteristics and

exciton population dynamics. When combined with stochastic multichromophoric kinetic modeling, these relationships may be quantified, making it possible to reconcile variations with processing conditions. Furthermore, comparing different polymer structural forms reveals how triplets evolve between the molecular and material levels. This information is often hidden from view in conventional ensemble-level spectroscopies that may lead to inconsistencies in the predictive capabilities of physical models describing triplet processes. Perhaps the most useful finding of single molecule level studies is the highly influential role of polymer chain conformation and ordering characteristics on deciding triplet formation and relaxation channels and branching ratios. Moreover, many established “rules” for controlling excitonic coupling between singlet excitons also appear to be obeyed for their triplet counterparts, which has the added intuitive appeal that both spin states have the same orbital parentage. The proposed relationships between polymer chain order and triplet encounter and annihilation frequencies lends itself to further study by selectively controlling intra- and interchain order. In particular, the apparent relationship between intrachain order and efficacies of triplet–triplet annihilation sheds new light on the absence of triplet features in many aggregating thin films due to greater disorder and stronger interchain coupling. On the contrary, suppressing interchain coupling in the limit of high intrachain order (i.e., J-aggregate type π -stacked chains) creates new opportunities for storing many triplets for relatively long times, which should prove useful for triplet harvesting schemes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c01696>.

Outline of kinetic Monte Carlo simulations and parameters. The following files are available free of charge. Kinetic Monte Carlo SI addendum (PDF)

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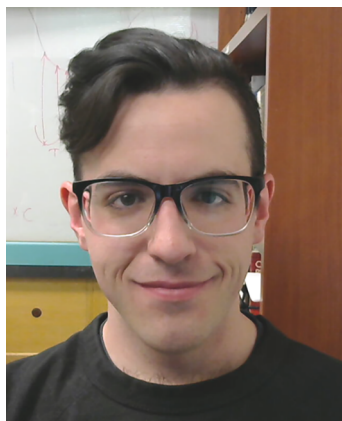
Notes

The authors declare no competing financial interest.

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