

Persistent Multiexcitons from Polymers with Pendent Pentacenes

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ABSTRACT: Singlet fission has emerged as a key mechanism of exciton multiplication in organic chromophores, generating two triplet excitons from a single photon. Singlet fission is typically studied in crystalline films or in isolated dimers. Here, we investigate an intermediate regime where through-space interactions mediate singlet fission and triplet pair recombination within isolated polymer chains. Specifically, we investigate how appending pentacenes to a polynorbornene backbone can lead to macromolecules that take advantage of through-space π - π interactions for fast singlet fission and rapid triplet pair dissociation. Singlet fission in these systems is affected by molecular dynamics, and triplet-triplet recombination is a geminate process where the rate of recombination scales with molecular weight. We find that these pendent pentacene polymers yield free triplets with lifetimes that surpass those of crystalline chromophores in both solution as isolated polymers and in thin films.

Introduction

Singlet fission (SF), a process that converts one singlet exciton into two triplet excitons, has become a focal point of solar research as it is one of the principal mechanisms enabling single-junction solar cells to exceed the thermochemical limit.¹⁻³ Pentacene and its derivatives are prototypical SF chromophores since they fulfill the energetic requirement that a triplet exciton be approximately half or less than the energy of the singlet exciton.⁴ Singlet fission is a multichromophore process, and in the solid state, it is facilitated by intermolecular π - π interactions (xSF). As a result the structural arrangement of the chromophores plays a crucial role in determining the rate of SF and subsequent triplet pair separation and recombination.⁵⁻¹⁰ Achieving the necessary inter-chromophore interactions through crystal engineering to enable efficient xSF in the solid-state is nontrivial and represents a crucial challenge in the field.¹¹ Surprisingly, Walker *et al.* recently reported that the precise orbital overlap required for singlet fission to occur in crystalline media is not necessary in solution.¹² Their study revealed that diffusion-mediated collisions of 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS pentacene) at high concentrations led to singlet fission in dynamic solutions. This approach suffers from the need for diffusional collision in solution, as singlet fission is slow and concentration dependent.

Recent approaches have attempted to mimic the local order of crystalline systems through physical macromolecular chemistry strategies to access effective local interchromophore interactions for singlet fission.¹³⁻¹⁷ Building on the success of semicrystalline nanoparticle singlet fission materials, whose through-space interactions allow for

highly mobile free triplets,^{13,15} Seferos and co-workers developed micelles based on self-assembled pentacene functionalized poly(ethylene glycol) (PEG).¹⁶ Changing the connectivity of the pentacene on the PEG chain and the size of the micelle both affected the rate of triplet formation and recombination.

To overcome the limitations of xSF, intramolecular singlet fission (iSF) can provide another alternative to crystalline systems, where iSF is mediated by chromophore-chromophore coupling interactions through-bond rather than through-space.¹⁸⁻²⁶ In fact, linear conjugated polymers of tetracene have been implemented in devices as a proof-of-concept of the first polymer-based singlet fission solar cells.²⁷ However, transport of free triplets is constrained by the few number of chromophores in small molecule iSF systems. Furthermore, the yield of free triplets in the few reported iSF polymer systems is poor due to the formation of strongly bound, correlated triplet pairs that do not separate.²⁰

In light of these studies, we envisioned a new class of polymers featuring pendent acene chromophores, where the structural parameters can enable dynamic through-space interactions allowing for singlet fission to occur (Figure 1a). This design concept allows for a locally high concentration of chromophores that mimic crystalline systems, whereby the π - π overlap of chromophores promotes rapid dissociation and migration of the triplets along the pendent units along the polymer. Unlike micelles or other high concentration systems, the structure of these polymers and resulting singlet fission dynamics do not strongly depend on concentration, sample preparation, or other external factors. Specifically, we investigate pendent pentacenes from a polynorbornene

backbone (Figure 1b and details in SI).^{28,29} Connecting the chromophores to a polymer backbone allows for the synthesis of macromolecules that can be easily chemically modified. One could vary the structure of the attached chromophore, the inter-chromophore distance, or the distance between the chromophore and the backbone. It is postulated that this architecture will allow for dissociation of triplets generated from singlet fission due to the chromophores translational motion, and the close proximity of the pentacenes will allow the triplets to move along the pendent moieties, similar to crystalline systems. It must be noted that singlet fission polymers are rare, and less than five polymers have been found to exhibit singlet fission yields >150%, albeit without the formation of free triplets.^{20,27,30,31} The model presented here opens up the possibility for the development of families of singlet fission polymers, exploiting the pendent polymer architecture.

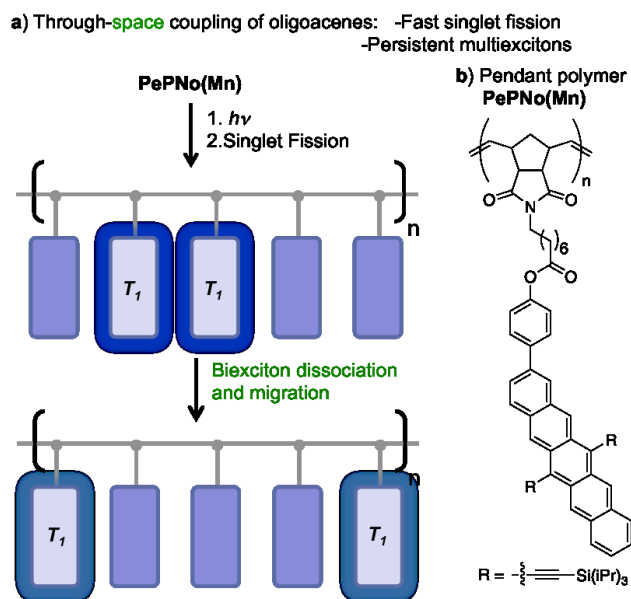


Figure 1. (a) Model for pendent SF chromophore units on a non-conjugated polymer backbone where the chromophores take advantage of through-space interactions to undergo singlet fission and subsequent triplet dissociation. (b) Structure of the polynorbornene with pendent pentacene units (**PePNo**), having average number molecular weight (**Mn**).

Results and Discussion

Polymer design and solution dynamics. Five norbornene polymers with pendent pentacene units **PePNo** with various molecular mass were synthesized ($M_n = 8, 10, 16, 24, 29$, and 33 kg/mol). Gel permeation chromatography (GPC) was used to determine the relative length and dispersity of the polymers (Table S2). As expected, the weight average molecular weights of the polymers increased as the catalyst loading decreased. The dispersity of the polymers ranged between 1.1 and 1.6. To

verify the molecular weight, MALDI-TOF analysis was performed on the lowest molecular weight polymer, **PePNo8**. We see a distribution of molecular weights centered around 4.7 kDa (Figure S20).

We found that singlet fission is indeed an efficient process in these polymers, leading to a high yield of mobile free triplets with lifetimes that exceed those found in crystalline systems.¹¹ Moreover, only two triplets are generated per polymer chain regardless of the number of pendent pentacenes, and singlet fission takes place within individual chains. Since all five polymers exhibit similar steady state absorption and singlet fission characteristics, we will focus on **PePNo24** as the prototype for discussion of these fundamental dynamics in solution and **PePNo29** for dynamics in films. We will then examine how these molecular weight differences affect triplet recombination.

Linear absorption spectroscopy in the UV-visible region and small angle neutron scattering (SANS) were used to confirm that the polymer was not aggregated in toluene, the primary solvent used in this study.¹² SANS shows that the polymer chains are compact, slightly anisotropic, globule-like, and not aggregated (radius of gyration $R_g = 4.2$ nm, see Figure S12 and SI for details). The monomer and polymer show near identical UV-Vis traces in toluene. Upon addition of a non-solvent to the polymer solution, a bathochromic shift is clearly visible, characteristic of aggregation, further demonstrating that the polymer is not aggregated in toluene (Figure S9). Moreover, drop casted films of **PePNo29** exhibited a similar UV-Vis trace to the monomer in toluene (Figure S11). This modest change in absorption spectrum upon film formation suggests relatively weak interchromophore interaction.

Singlet fission dynamics. To investigate the excited state dynamics of **PePNo24**, we turn to transient absorption (TA) spectroscopy. For pentacene based materials, the procedures for identifying singlet fission rates and yields are well established.¹⁹ We summarize them here and provide more detailed discussions of the factors that affect the rate constants and yield. At early times after photoexcitation, the transient spectrum of **PePNo24** exhibits a prominent but rapidly decaying photoinduced absorption feature at ~ 475 nm that we assign to a transition from the bright singlet (S_1) to a higher energy singlet level (S_n) (Figure 2b). The singlet assignment is based on the similarity of the polymer transient spectrum to the monomer in dilute solution (Figure 2a and 2c), in which no singlet fission is expected, as well as the similarity of its decay dynamics to time-resolved photoluminescence measurements (Figure 4a). This singlet feature decays rapidly into a triplet feature, characterized by its excited state absorption feature at 525 nm that has been widely observed in previous reports of triplet spectra in pentacene derivatives. This assignment is confirmed by photosensitization studies in which an energy transfer process is used to directly populate individual triplets on the polymer (Figure 2d and S1). We verify that triplet formation is through singlet fission and not intersystem crossing since we determine the yield of triplets to be near-quantitative (see Figure S21 and details in SI). This observation also confirms the absence of any major unidentified decay channels during singlet fission. Additionally, the singlet fission dynamics are fully concentration independent, indicating that all these dynamics originate from intra-chain chromophore interactions (Figure S4).

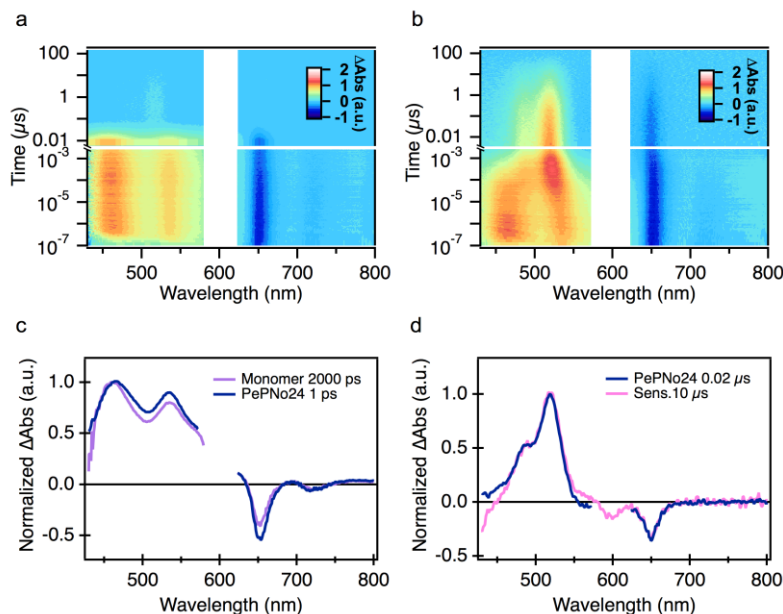


Figure 2. Transient absorption data of **PePNo24** and pentacene monomer. (a) Transient absorption spectrum of pentacene monomer in toluene excited at 600 nm ($\sim 50 \mu\text{J}/\text{cm}^2$). (b) Transient absorption spectrum of **PePNo24** in toluene excited at 600 nm ($\sim 50 \mu\text{J}/\text{cm}^2$). (c) Spectral cut of **PePNo24** singlet feature compared to the spectral cut of the monomer singlet. At early times the singlet on **PePNo24** resembles the monomer singlet spectrum. (d) Spectral cut of **PePNo24** at late times, after singlet fission has occurred, compared to the sensitization spectral cut (sensitization details in SI).

Analysis of singlet decay. The fast decay of the singlet and concomitant rise in the triplet signal are comparable to what is observed in the solid state⁵ and covalently linked dimers in solution.¹⁹ Using global analysis methods, we determined that the rise of the triplet population reflects the heterogeneity of the dynamic ensemble. The spectral evolution of **PePNo24** can be characterized using a three-state sequential model, with an initial time constant of 30 ps, followed by a slower time constant of 486 ps before the final population of triplets is obtained (Figure 3 and S2). We note that this simplified model reproduces the essential features of the data (Figure S3), implying a small number of stable conformations dominate the ensemble. Still, we expect a large amount of heterogeneity between individual polymer chains. A summary of the singlet fission time constants is given in Table S1. We assign the transient species that decays on 30 ps time scale to the singlet as it is nearly identical to the singlet spectrum of the monomer. The state that evolves after 500 ps can be unambiguously assigned to the triplet, based on photosensitization measurements (see SI for details).

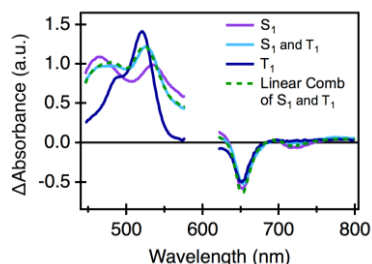


Figure 3. The deconvoluted spectra of **PePNo24** obtained using Global Analysis overlaid with the linear combination of the singlet and triplet traces.

At intermediate times (50 – 500 ps), spectral deconvolution yields a spectrum that can be reproduced using a linear combination of the S_1 and T_1 associated spectra. This suggests that both singlets and triplets exist in the polymer ensemble, reflecting the distribution of dynamic conformations of the pendent pentacenes. That is, the fast singlet decay corresponds to singlet fission from well-ordered or aligned chromophores along the chain, whereas the slow singlet decay arises from aberrant pentacenes with unfavorable alignment to undergo singlet fission. The observed line shape results from the coexistence of the triplets

produced from aligned pentacenes undergoing rapid singlet fission and the singlets on the aberrant pentacenes.

Photoluminescence (PL) measurements were used to confirm that the slow singlet decay arose from disordered chromophores and rule out the presence of an additional state, such as an excimer which has been suggested as a mediator of singlet fission in similar systems.^{32,33} The PL decay of **PePNo24** shows the bright singlet exciton converting into a dark state with a small population of singlet at late times as this system is near-quantitative (Figure 4a). The PL shows a decay of the signal with a time constant of 480 ps, which is consistent with the time constant observed for the intermediate state obtained from global analysis. We note that PL measurements are sensitive to a very small minority of singlets that appear to persist longer than can be identified using TA alone. These can be identified in the weak PL tail that persists out to several nanoseconds. Still, their lifetime (~ 1.5 ns) is still much shorter than the radiative lifetime (~ 13 ns) of TIPS pentacene, implying that they eventually migrate to SF sites. We rule out delayed PL as the cause of this signal since the energetics of this system do not permit repopulation of the singlet from the triplet pair within this time scale.

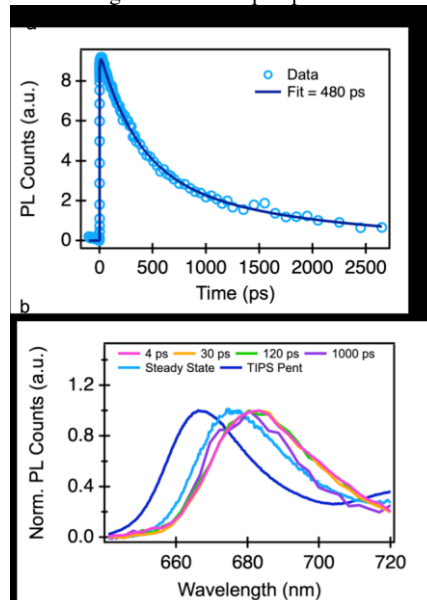


Figure 4. Photoluminescence spectroscopy of **PePNo24** in toluene. (a) PL decay at 680 nm spectra of the pentacene singlet with a lifetime of 480 ps (excitation wavelength 600 nm). (b) Normalized transient emission spectra taken at different time points, and steady state emission of **PePNo24** and TIPS pentacene. For transient PL measurements, crystal phase matching was calibrated in the range of 600 – 720 nm.

The transient emission spectra of the polymer taken at different times were also examined and showed no trace of an excimer signal (Figure 4b). The early time spectra show a peak at 680 nm that is characteristic of the bright singlet emission in pentacene materials. This peak decreases in intensity over time as SF occurs but shows no change in line shape. Furthermore, the steady state emission spectrum of **PePNo24** is nearly identical to monomeric TIPS-pentacene although red shifted (see SI Figure S10 for further discussion), ruling out a long lived spectrally shifted species that may be difficult to detect in transient measurements. Taken together, this data confirms that there is no detectable redshifted peak characteristic of excimers in the emission spectra.³³

While regions of less ordered chromophore alignment are apparent in the solution phase data from the associated slow SF time constant, SF in thin films of our pendent polymer is greatly enhanced (see SI Figure S7 and S8 for further discussion). Similar to the solution data, we observe a signal at ~475 nm at early times that we assign to a transition from the bright singlet (S_1) to a higher energy singlet level (S_n) (Figure 5a). Unlike in solution, the decay of the singlet in the thin film is fully completed within 5 ps, with two discernable characteristic time constants of ~0.8 and 4 ps. These data imply that areas of poor orbital overlap are minimized when the dynamical motion of the individual polymer chains is suppressed and electronic coupling between adjacent chains is enhanced.

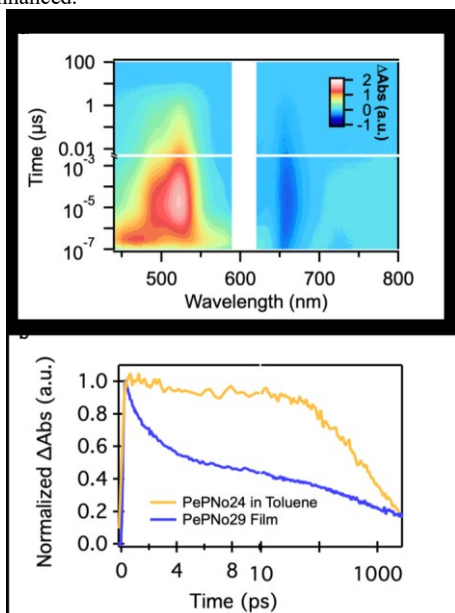


Figure 5. Singlet fission in **PePNo29** films. (a) Transient absorption spectrum of **PePNo29** excited at 600 nm (~50 $\mu\text{J}/\text{cm}^2$). (b) Kinetic traces (450 nm) showing the singlet decay of the polymer in film and solution. Singlet fission occurs significantly faster in films than in solution.

Triplet recombination and molecular weight dependence. Facile tunability of polymer molecular weights enabled us to probe the influence of chain length on the triplet exciton dynamics. Using five different molecular weight polymers (**PePNo8**, **PePNo10**, **PePNo16**, **PePNo24**, and **PePNo33**), we demonstrate that singlet fission in **PePNo** results in two mobile triplet excitons that annihilate to give one long lived triplet exciton. The triplet decay can be represented with a biexponential decay function with a molecular weight dependent component and a molecular weight independent component (Figure 6a). The picture of mobile triplets that migrate along the chain is supported

by the molecular weight dependence of the primary triplet decay component. Numerical models of triplet-triplet annihilation are used to verify that the time constants should scale linearly with increasing polymer length. In fact, the problem of the average recombination time of two triplets on a rigid polymer can be mapped onto a problem of two random walkers, initially sitting on two neighboring sites and constrained to independently diffuse over a discrete straight line containing L sites (number of monomers). Assuming reflective boundaries at the edges of the line (polymer), it can be shown that the average recombination time is equal to $\tau_{rec} = \tau_D(L - 1)$, where τ_D is the typical time for an excitation to diffuse from one site to the next.³⁴ This result was also checked with numerical simulations. Here, the longer lifetime of the triplets on longer polymer chains indicates that a longer effective chain length for triplets to diffuse (Figure 4b). An approximately linear trend is observed where the lifetime of the two triplets increases as molecular weight increases (orange line) until saturation (τ_{max}) occurs between $M_n = 15 - 20$ kg/mol. This design allows for facile tuning of triplet lifetimes. See supplementary information and Figure S6 for NIR transient measurements.

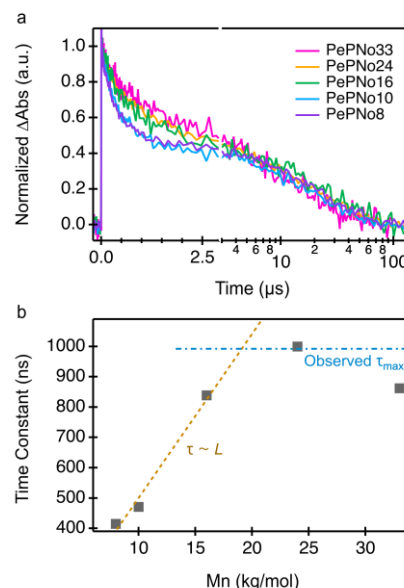


Figure 6. Triplet dynamics as a function of polymer molecular weight in toluene. (a) Kinetic traces (520 nm) of the five different molecular weight polymers. A molecular weight dependent singlet decay is seen at earlier times, followed by a molecular weight independent triplet decay. (b) A graph of time constants of the triplet lifetime vs. the number average molecular weight (M_n). The lines are guides to the eye to identify the regions where the triplet pair lifetime is proportional to the length (L) and the region in which it saturates (τ_{max}).

As the recombination is power independent over a large range of absorbed fluences (Figure S5), all recombination appears to occur *via* a secondary geminate process, i.e. separation followed by convergence of a pair of triplet excitons to yield a triplet exciton and a ground state.³⁵ The slower component is constant for different polymer chains, with a time constant of 22 μs that reflects the characteristic lifetime (determined using photosensitization) of individual triplets that are unable to annihilate with other triplet excitons. This suggests that at late times only a single triplet exciton is left on the polymer chains and that the primary triplet loss mechanism is annihilation of two triplets into a hot triplet state $-^3(TT) \rightarrow T_1^* + S_0$. This process has been identified as a major loss mechanism in organic light emitting diodes.^{36,37} As the T_2 excited triplet level is expected to be energetically inaccessible, these results imply that the role of vibronic states needs to be considered in models of triplet annihilation. Notably, this decay mechanism sets an upper limit for the relative amplitude of the 20 μs component at 50%,³⁸ very similar to what is observed here.

Conclusion

We designed pendent polymers that can undergo SF in dilute solution. Using a polymer scaffold allows us to fine-tune SF and triplet decay dynamics. The convergent synthesis is easily scalable and results in a stable polymer. The pendent pentacene chromophores undergo singlet fission on individual polymer chains with no significant interaction observed between different polymer chains. Singlet fission occurs with two different time constants depending on the position of the monomers upon excitation and yields mobile triplets, with a molecular weight dependent decay time constant. The mobile triplets appear to recombine geminately to produce one hot triplet exciton and one ground state molecule, causing the final product to be an individual triplet with roughly half the initial amplitude. Fast singlet fission is observed in films, with reduced contribution from disordered regions with poor electronic coupling. The tunability of this system and the ability to investigate it in both solution and solid-state provides a clear path for further study, such as random and block copolymers where excitonic interactions can be fine-tuned. Further work is being done on incorporating different chromophores and on developing a theoretical model for the polymer dynamics in solution.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Supporting Information includes synthetic methods and characterization, spectroscopic data and analysis, Supplementary Figures 1–20, and Supplementary Tables 1–2.

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Notes

The authors declare no competing interests.

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