Supporting Information for

Excited-State Dynamics of 5,14- vs. 6,13-Bis(trialkylsilylethynyl) Substituted Pentacenes: Implications for Singlet Fission

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Table of Contents:

Section S1. Supplemental materials and methods
Section S2. Comparison of local molecular packing of 5,14-TIPS-, 5,14-TES-, 6,13-TIPS-, and 6,13-TES-pentacene
Section S3. Substitution of the pentacene core can profoundly influence both singlet and triplet state energies
Section S4. Steady-state absorption and structural characterization of amorphous and crystalline 5,14-TIPS-pentacene films
Section S5. Transient absorption of dilute solutions of 5,14-TIPS-pentacene in toluene
Section S6. Comparison of transient absorption of isolated-molecule triplet excitations with the long-time transient absorption signal in amorphous 5,14-TIPS-pentacene film
Section S7. Global target analysis of transient absorption of amorphous 5,14-TIPS-pentacene and factors complicating an accurate analysis of triplet yields
Section S8. Global target analysis of transient absorption of crystalline 5,14-TIPS-pentacene

Section S9. Contribution of photo-dimerization and photo-oxidation to transient absorption signals and derivation of quantum yield for the sum of these processes

Section S10. Steady-state absorption and structural characterization of crystalline 5,14-TES-pentacene films

Section S11. Global target analysis of transient absorption of crystalline 5,14-TES-pentacene

Section S12. Steady-state absorption and structural characterization of crystalline 5,14-TIBS-pentacene films

Section S13. Global target analysis of transient absorption of crystalline 5,14-TIBS-pentacene

Section S14. References
**Section S1: Supplemental materials and methods**

**Single crystal structure**

The crystal structure of 5,14-bis(triethylsilylethynyl)pentacene has been reported previously.\(^1\)

**Nanoparticle preparation**

The nanoparticle preparation has been described in detail previously.\(^2,3\) Briefly, an 800 μM solution of each pentacene derivative in tetrahydrofuran was prepared. 200 μL of the solution was rapidly injected into a 20 mL glass scintillation vial containing 9.8 mL of vigorously stirring distilled water. A 21 gauge disposable needle and 1 mL disposable syringe were used to inject the pentacene derivative/THF solution. The aqueous colloidal nanoparticle suspensions were concentrated by combining four 10 mL batches together and subjecting the total solution to rotary evaporation at 18 mbar and 35 °C for a period of ca. 40-45 min.

**Steady-state absorption spectroscopy**

Absorption spectra were measured on an Agilent Cary 60 UV-Vis spectrophotometer (Agilent Technologies, Santa Clara, California). Spectra were typically obtained with a scan rate of 600 nm/min, a 1 nm step size, and 0.1 s averaging time.

**Femtosecond transient absorption spectroscopy**

For femtosecond transient absorption spectroscopy measurements, nanoparticles suspensions were contained in a 1 mm path length glass spectrophotometer cell (Starna Cells, Inc., Atascadero, California) secured in a filter holder and fixed in place at the sample position. The optical density of the nanoparticle suspensions was generally kept below ca. 0.25 at the excitation wavelength.

**Nanosecond transient absorption spectroscopy**

Nanosecond transient absorption spectroscopy was performed using a home-built laser flash photolysis instrument reported previously.\(^4\) Briefly, the excitation source was a ~10 ns pulsed laser operating at 30 Hz generated by pumping a dye laser cavity (Photon Technology International, Edison, New Jersey) using a frequency-doubled Nd:YAG laser (Continuum, San Jose, California). A pump wavelength and fluence of 642 nm and ~200 μJ cm\(^{-2}\), respectively, were used for the measurements. The output of a tungsten halogen lamp (Spectral Products, Putnam, Connecticut) was used as the probe. Spectral resolution of 10 nm effective bandwidth was obtained by dispersing the probe using a monochromator (CM110, Spectral Products, Putnam, Connecticut). The dispersed probe beam was then detected using a Si photodiode (Thorlabs, Newton, New Jersey). Dielectric filters were used to block scatter from the pump. Samples were prepared at a concentration of 2 × 10\(^{-5}\) M in toluene and were gently stirred over the course of the measurements. Sample solutions were additionally saturated with nitrogen gas to displace and remove dissolved oxygen.
Grazing incidence wide-angle X-ray scattering

Grazing incidence wide-angle X-ray scattering (GIWAXS) experiments were conducted at the G2 (11.2) station at the Cornell High Energy Synchrotron Source. The X-ray beam was aligned between the critical angles of the film and substrate, at 0.17° with respect to the substrate. The scattered intensity was collected using a 640-element one-dimensional diode array. All GIWAXS images have been background subtracted.
Section S2: Comparison of local molecular packing of 5,14-TIPS-, 5,14-TES-, 6,13-TIPS-, and 6,13-TES-pentacene

**Figure S1.** Local molecular packing of (a) 5,14-TIPS-Pn, (b) 5,14-TES-Pn, (c) 6,13-TIPS-Pn, and (d) 6,13-TES-Pn. The local molecular packing was derived from the single crystal structure file for each respective compound.

**Figure S1** shows that, while sub-Angstrom differences exist, the local molecular packing for 5,14-TIPS- and 5,14-TES-Pn generally speaking are very similar, and the local molecular packing for 6,13-TIPS- and 6,13-TES-Pn also are very similar. In fact, a number of 6,13-TAS-Pn derivatives adopt a similar local molecular packing.\textsuperscript{2,5}
Section S3: Substitution of the pentacene core can profoundly influence both singlet and triplet state energies

The singlet energy measured for unsubstituted pentacene,\textsuperscript{6} 5,14-bis(triisopropylsilylethynyl)pentacene (see e.g. Section S4), and 6,13-bis(triisopropylsilylethynyl)pentacene\textsuperscript{2} in toluene are 2.15, 1.96, and 1.93 eV, respectively. Clearly, substitution of the pentacene core affects the singlet energy.

Although it has been suggested that substitution of the pentacene core does not affect the triplet energy, this cannot be the case. See also \textsuperscript{7,8}. Direct measurements of the triplet energy of unsubstituted pentacene and 6,13-bis(triisopropylsilylethynyl)pentacene confirm that core substitution impacts the triplet energy; values of 0.85 and 0.78 eV are obtained for the triplet energy of unsubstituted pentacene\textsuperscript{9} and 6,13-bis(triisopropylsilylethynyl)pentacene\textsuperscript{10}, respectively.
Section S4: Steady-state absorption and structural characterization of amorphous and crystalline 5,14-TIPS-pentacene films

Figure S2. (a) Steady-state absorption of a dilute solution of 5,14-TIPS-Pn in toluene (grey), an as-cast 5,14-TIPS-Pn film (orange), and a solvent-vapor annealed 5,14-TIPS-Pn film (brown). (b) GIWAXS of an as-cast 5,14-TIPS-Pn film. (c) GIWAXS of a solvent-vapor annealed 5,14-TIPS-Pn film.

Figure S2a displays the absorption spectra of a dilute solution of 5,14-TIPS-Pn in toluene, an as-cast 5,14-TIPS-Pn film, and a solvent-vapor annealed 5,14-TIPS-Pn film. The solvent-vapor annealed film exhibits a redshifted vibronic progression with respect to that of the monomer. While
the origin band of the compound in toluene peaks at ca. 634 nm, the origin band of the solvent-vapor annealed film peaks at ca. 654 nm. Thus, the origin band of the solvent-vapor annealed film is redshifted by ca. 480 cm⁻¹, which we consider a signature of strong excitonic coupling (i.e., chromophores are strongly coupled and excitons are evenly delocalized about these chromophores). The absorption spectrum of the as-cast film, on the other hand, exhibits properties intermediate between that of the compound in toluene and the solvent-vapor annealed film. Namely, the origin band of the as-cast film peaks at ca. 639, a modest redshift of ca. 120 cm⁻¹ with respect to the compound in toluene. Thus, the majority of chromophores in the as-cast film are weakly coupled, and primary excitations are highly localized. Notably, the origin band of the as-cast film exhibits a shoulder in the proximity of the origin band of the solvent-vapor annealed film. We assign the shoulder to some fraction of strongly-coupled chromophores in the as-cast film. Additional evidence in support of this assignment is provided in a subsequent supporting section.

**Figure 2b** displays the GIWAXS results for an as-cast 5,14-TIPS-Pn film. No features are observed, indicating that the film lacks any long-range order and is largely amorphous.

**Figure 2c** displays the GIWAXS results for a solvent-vapor annealed 5,14-TIPS-Pn film. Diffraction peaks are observed indicating the film is crystalline, adopting its known crystal structure (CCDC # 172477) with the a-axis normal to the substrate.
Figure S3. Transient visible absorption singlet excitations photogenerated in a dilute solution of 5,14-TIPS-Pn in toluene. (a) Surface plot of transient visible absorption. The experiments were performed with incident pump wavelength of 635 nm and incident pump fluence of 230 µJ cm⁻². The scale bar is indicated beside the plot. (b) Selected transient spectra. Spectra time delays are indicated in the legend. (c) Selected transient kinetics. The kinetics of the singlet photoinduced absorption and combined ground-state bleach and stimulated emission features were taken as the average over the spectral range 420 to 569 nm and 620 to 651 nm, respectively. These data have been normalized over the time range from 5 to 10 ps. A fit from a global target analysis overlays these transient absorption data. Specifically, the data were modeled according to a global target
analysis that includes two components that account for a dynamic Stokes shift arising from a combination of intramolecular structural relaxation and/or solvation dynamics and decay to the ground state, i.e., $S_1 \rightarrow S_0$. The analysis returns two time constants of ca. 3 ps and $>>500$ ps.

**Figure S3a** displays the transient absorption of the dilute solution of 5,14-TIPS-Pn in toluene, and selected transient spectra are presented in **Figure S3b**. The transient spectra exhibit very modest changes over the course of the measurement, which we attribute to a dynamic Stokes shift arising from combination of intramolecular structural relaxation and/or solvation dynamics. Notably, the signal is essentially constant over the course of the measurement (**Figure S3c**), and does not evolve into a lineshape consistent with triplet excitations (see a subsequent supporting section). Thus, intersystem crossing, i.e., $S_1 \rightarrow T_1$, is relatively slow in 5,14-TIPS-Pn and does not occur on the timescale of the measurements reported in this work. Considering that different alkyl substituents have very little to no impact on the electronic structure and dynamics of bis(trialkylsilyl)ethynyl substituted pentacenes, we conclude that intersystem crossing is negligible for all of the 5,14-TAS substituted pentacene derivatives on the timescale of the measurements reported in this work.
Section S6: Comparison of transient absorption of isolated-molecule triplet excitations with the long-time transient absorption signal in amorphous 5,14-TIPS-pentacene film

Figure S4. Transient visible absorption spectrum of triplet excitations photogenerated in a dilute solution of 5,14-TIPS-Pn in toluene compared with the 400 ps transient absorption spectrum measured for the amorphous 5,14-TIPS-Pn film. Asterisks have been placed above signals arising from a thermal artifact that results in the discrepancy between the two datasets.

Figure S4 displays the transient visible absorption spectrum of triplet excitations photogenerated in a dilute solution of 5,14-TIPS-Pn in toluene compared with the 400 ps transient absorption spectrum measured for the amorphous 5,14-TIPS-Pn film. While there is some discrepancy between the two datasets, which is especially notable at ca. 620 nm, the data otherwise agree very well. The slight discrepancy between the two datasets can be explained by considering that some fraction of chromophores in the film are strongly coupled, which promotes rapid internal conversion to the ground state on the few picosecond timescale, leading to a thermal artifact on the 400 ps timescale that gives rise to at positive- and negative-going features at ca. 620 and 660 nm, respectively (see subsequent supporting section). Given the otherwise good agreement between the data, we take these results to indicate that triplet excitations are the long-lived population in the amorphous 5,14-TIPS-Pn film.
Section S7: Global target analysis of transient absorption of amorphous 5,14-TIPS-pentacene and factors complicating an accurate analysis of triplet yields

In this section, we perform a global target analysis of the transient absorption of amorphous 5,14-TIPS-Pn films, and discuss factors complicating an accurate analysis of triplet yields.

We begin by performing a global target analysis of the transient absorption of the amorphous 5,14-TIPS-Pn films. Two five-component kinetic schemes were used to model the data (Figure S5). Each of these schemes is based on the idea that there are two different decay pathways in the amorphous 5,14-TIPS-Pn films,\textsuperscript{7,11} which we will show evidence for below. Specifically, we find that one of these decay pathways is at singlet fission sites where molecules adopt the local packing of the single crystal structure. The other decay pathway is at sites where molecules do not have a preferred packing arrangement. Both of the kinetic schemes are the same with respect to this part of the model.
Figure S5. Kinetic schemes used for global target analysis of amorphous 5,14-TIPS-Pn films. (a) Five-component triplet pair separation model. (b) Five-component parallel decay model.

The difference in the kinetic schemes (Figure 5a,b) is in how we treat the singlet fission dynamics at sites where molecules do not have a preferred packing arrangement. In the first scheme, denoted “triplet pair separation” model, we treat the singlet fission dynamics at these sites as occurring from one site population and in a manner that accounts for the dissociation of triplet pairs at these sites onto a third molecule (i.e., TT → T ... T). In contrast, in the second scheme, denoted “bifurcation” model, we treat the singlet fission dynamics at these sites as occurring from two site populations, one that generates triplet pairs that decay quickly (i.e., TTₜ) and the other that generates triplet pairs that are long-lived (i.e., TTₗ).

The results of the analysis are displayed in Figure S6 and Table S1.

Figure S6. Species-associated spectra derived from global target analysis of amorphous 5,14-TIPS-Pn films. (a,b) Spectra for “triplet pair separation” model attributed to sites where molecules
adopts local packing of the single crystal structure and sites where molecules do not have a preferred packing arrangement. (c,d) Spectra for “bifurcation” model attributed to sites where molecules adopt local packing of the single crystal structure and sites where molecules do not have a preferred packing arrangement.

**Table S1.** Time Constants Derived for Five-Component “Triplet Pair Separation” and “Bifurcation” Models

| Component | “Triplet Pair Separation” Model | “Bifurcation” Model | Time Constant (ps) |
|-----------|---------------------------------|---------------------|--------------------|
| 1         | $\tau_{S1S0,\text{equil}}$     | Same as TPS model   | $\leq 0.1$         |
| 2         | $\tau_{TT,\text{equil}}$       | Same as TPS model   | 6                  |
| 3         | $\tau_{S1S0,\text{non-equil}}$ | Same as TPS model   | 0.6                |
| 4         | $\tau_{TT,\text{non-equil}}$   | $\tau_{TT(S),\text{non-equil}}$ | 40                |
| 5         | $\tau_{T\ldots T,\text{non-equil}}$ | $\tau_{TT(L),\text{non-equil}}$ | $> 500$           |

The first two species-associated spectra and time constants are remarkably reminiscent of singlet fission in crystalline material (Section S8), and so we assign these spectra and time constants to singlet fission at sites where molecules adopt the local packing of the single crystal. While the spectrum of the singlet excitons at these sites, i.e., SAS-1, is not clearly resolved, likely due to the small amount of this population and mixing of components at early timescales, the spectrum of the triplet pairs generated at these sites, i.e., SAS-2, and their lifetime are nearly identical to that observed for the crystalline 5,14-TIPS-Pn films (Section S8).

There is less certainty in the discussion of the species spectra associated with singlet fission sites with no preferred local packing (Figures S6b,d). While the spectra derived from the two models are distinct, it is unclear which is more physically appropriate. For example, the spectra derived in the “triplet pair separation model” in Figure S6b exhibit signatures expected for dissociating triplet pairs. That is, a redshift of the prominent triplet pair photoinduced absorption at ca. 560 nm is observed following triplet pair separation, and the weaker triplet pair photoinduced absorption band at ca. 750 nm is reduced in intensity. In the case of the spectra derived for the “bifurcation” model in Figure S6d, we observe species-associated spectra for the short- and long-lived triplet pairs. The short-lived triplet pairs exhibit signatures similar to that observed previously in amorphous solids of 6,13-TIPS-Pn,7 and also look similar to the spectra of the triplet pairs generated at sites that adopt the local packing of the single crystal (Figure S6a,c). In contrast, the long-lived triplet pairs exhibit spectra very similar to isolated triplet excitations (Section S6), as we observed previously in amorphous solids of 6,13-TIPS-Pn.7 Given that it is unclear which model is physically most appropriate, and given that, from a mathematical standpoint, the two five-component kinetic schemes fit the data equivalently, we therefore preclude further discussion of this aspect of the global target analysis. For future work, it will be important to find a way to overcome the poor photostability of these 5,14-TAS substituted pentacenes which challenges obtaining high signal-to-noise data and acquiring data over a longer time window to facilitate determining which model is most physically appropriate.

For the present work, it is sufficient to note that significant triplet losses are observed in the amorphous 5,14-TIPS-Pn film as a result of the decay pathway through sites that adopt the
local packing of the single crystal structure. Whether the “triplet pair separation” or “bifurcation” model applies for the sites that have no preferred local packing does not change the fact that there are additional sites that adopt the local packing of the single crystal (Figure S6a,c and Table S1) that are responsible for a large amount of triplet losses. Normalizing the raw transient absorption data to a time window of 200 fs to 1 ps (Figure 2c) enables us to estimate a long-time triplet yield of ca. 48%, significantly less than unity and significantly less than the triplet yield observed in amorphous 6,13-TIPS-Pn (i.e., 132 – 154%). We thus conclude that 5,14-TAS substitution is unfavorable for harvesting triplets generated via singlet fission.

We conclude by noting that a strictly quantitative analysis of losses in amorphous 5,14-TIPS-Pn is circumvented by the following challenges: (i) the presence of singlet fission sites that adopt the local packing of the single crystal structure, which may depend on materials processing conditions and which complicates a quantitative analysis of triplet yields through a simple early-time normalization procedure, and (ii) uncertainty over the most correct physical model to describe the singlet fission dynamics which has implications on the interpretation of changes in the transient absorption signal amplitude in the vicinity of the ground-state bleach feature.
In this section, we elucidate the excited-state dynamics of crystalline solids of 5,14-TIPS-Pn. We chose to first study the excited-state dynamics of aqueous crystalline 5,14-TIPS-Pn nanoparticle suspensions, because they provide the equivalent photophysical picture as films and circumvent issues associated with transient absorption work on crystalline films of 5,14-TIPS-Pn, including optical orientation effects, thermal artifacts, pump scatter, and low signal-to-noise ratios (due to low signal amplitudes). The identical global target analysis of crystalline 5,14-TIPS-Pn films is then provided for comparison.

Figure S7a displays the transient absorption of the crystalline 5,14-TIPS-Pn nanoparticle suspensions, and selected transient absorption spectra are presented in Figure S7b.

Figure S7. Transient visible absorption of an aqueous suspension of crystalline 5,14-TIPS-Pn nanoparticles. (a) Surface plot of transient visible absorption. The measurements were performed with incident pump wavelength of 655 nm and incident pump fluence of 230 µJ cm⁻². The scale bar is indicated beside the plot. (b) Selected time-averaged transient spectra. Spectra time delays are indicated in the legend.

The transient absorption data of the crystalline nanoparticles strongly resemble the transient absorption data of the crystalline films (Figure 3, main text). Namely, we observe spectral features
consistent with primary singlet excitons at early times and two spectroscopically distinct triplet pairs at intermediate time delay. Similar to the crystalline films, we also observe a small thermal effect at the longest time delays measured, although the amplitude of the features is strongly suppressed in the crystalline nanoparticles. Critically, in the crystalline nanoparticle transient absorption data pump scatter in the vicinity of the ground-state bleach feature is strongly suppressed and, for the same incident pump fluence, the signal-to-noise is considerably higher than the film measurements owing, in part, to a larger amplitude signal. We take these results to indicate that the crystalline film and nanoparticle singlet fission dynamics are equivalent and attribute the differences in the transient spectra of the different electronic populations, especially apparent in panel b, to the presence and absence of optical orientation effects in the film and nanoparticle transient absorption measurements, respectively.

We next proceed to perform a global target analysis on the transient absorption data of the crystalline 5,14-TIPS-Pn nanoparticles. The four-component, sequential kinetic scheme employed in the global target analysis is displayed in Figure S8.

![Four-component kinetic scheme](image)

**Figure S8.** The four-component kinetic scheme used in the global and target analysis. This pseudo-three-component scheme accounts for: (i) the decay of primary singlet excitons into nascent triplet pairs, i.e., SAS-1 or $S_1S_0$ and SAS-2 or $TT^*$, (ii) the decay of the nascent triplet pair into a second, spectroscopically distinct triplet pair, i.e., SAS-3 or TT, that we posit is mediated by intermolecular structural relaxation, and (iii) a thermal effect caused by the internal conversion of the triplet pair population directly to the ground state and subsequent dissipation of excess electronic energy into the nuclear kinetic energy degrees of freedom of the bath, i.e., SAS-4 or $(S_0S_0)^*$. It should be noted that in the absence of the thermal artifact, a three-component kinetic scheme would apply; that is, the physics of actual relevance to the singlet fission dynamics of the crystalline 5,14-TIPS-pentacene nanoparticles (i.e., the evolution of the electronic populations) are best described by a three-component kinetic scheme.

Below we expound upon the main evidence supporting the use of a four-component kinetic scheme.
**Figure S9**, for example, compares selected transient kinetics traces along with associated fits and residuals derived from an analysis of the data according to three- and four-component kinetic schemes.
**Figure S9.** Selected transient kinetics traces in the vicinity of the triplet pair photoinduced visible absorption, ground-state bleach feature, and triplet pair photoinduced near-infrared absorption at 529, 656, and 740 nm, respectively, along with fits, rms values, and residuals from the global and target analysis. (a,c,e) Fits, rms values, and residuals associated with the three-component kinetic scheme. (b,d,f) Fits, rms values, and residuals associated with the four-component kinetic scheme. The grey blocks in each panel highlight regions where the residuals are improved by the inclusion of a fourth component.

As indicated by the improved fits and residuals, especially apparent on the sub-picosecond timescale, along with the overall reduced rms value, a four-component kinetic scheme clearly provides a better representation of the data.

**Figure S10** displays the species-associated spectra derived from the four-component global target analysis; the time constants derived according to the analysis are displayed in **Table S2**.

![Figure S10](image)

**Figure S10.** Species-associated spectra derived from a four-component global and target analysis of the transient absorption of the crystalline 5,14-TIPS-pentacene nanoparticles, with three time constants floating and one fixed. Species-associated spectra SAS-1 (black) is attributable to primary singlet excitons. SAS-2 (blue) and SAS-3 (grey), exhibit similar spectral features, and are attributable to two spectroscopically distinct triplet pairs. SAS-4 (red) is attributable to a thermal artifact. Asterisks are included in the plot to highlight spectral regions where SAS-1 and SAS-2 components exhibit appreciable mixing.
Table S2. Time Constants Derived for the Singlet Fission Dynamics in Crystalline 5,14-TIPS-pentacene Nanoparticles, With Three Floating and One Fixed $^a$

| $\tau_1$ (ps) | $\tau_2$ (ps) | $\tau_3$ (ps) | $\tau_4$ (ps) |
|---------------|---------------|---------------|---------------|
| 0.138         | 0.146         | 2.4           | $>> 500$      |

$^a$ The time constant associated with the thermal artifact, which following its formation is essentially constant over the course of the measurement, was fixed at 100,000 ps.

As can be seen in Figure S10, the component assigned to primary singlet excitons, SAS-1, exhibits spectral properties overall consistent with that of singlet excitations (Section S5). That is, intensity is observed at short wavelengths in the vicinity of ca. 450-500 nm, and a prominent stimulated emission band is observed at ca. 720 nm. The following two components, SAS-2 and SAS-3, exhibit qualitatively similar spectral properties. Differences are also apparent, although a detailed analysis of these particular data is complicated by component mixing between SAS-1 and SAS-2, as highlighted by the asterisks in the figure. Additional evidence of component mixing between SAS-1 and SAS-2 is evident by considering that the time constants associated with each component are very similar.

To overcome the issue of component mixing observed in the global target analysis above, we inspected the transient absorption kinetics of the crystalline 5,14-TIPS-Pn nanoparticles. Figure S11 displays transient absorption kinetics associated with the primary singlet exciton photoinduced absorption ($S_1S_0$ PIA), the triplet pair visible photoinduced absorption (TT PIA1), the overlapping ground-state bleach and stimulated emission features (GSB/SE), and the triplet pair near-infrared photoinduced absorption (TT PIA2) and highlights three distinct periods of evolution.
Figure S11. Transient absorption kinetics of an aqueous suspension of crystalline 5,14-TIPS-Pn nanoparticles. (a) Transient kinetics associated with the photoinduced absorption of primary singlet excitons and a short-wavelength photoinduced absorption band associated with triplet pairs (i.e., $S_1S_0$ PIA and TT PIA1, respectively). The kinetics of $S_1S_0$ PIA and TT PIA1 features were taken as the average over the spectral range 450 to 520 nm and 510 to 600 nm, respectively. Both datasets were normalized over the time range from ca. 200 to 350 fs. The dynamics in this time
range are assigned to the decay of primary singlet excitons into triplet pairs. (b) Transient kinetics associated with overlapping ground-state bleach and stimulated emission features (i.e., GSB/SE) and short- and long-wavelength triplet pair photoinduced absorption bands (i.e., TT PIA1 and TT PIA2, respectively). The kinetics of TT PIA1 and TT PIA2 features were taken as the average over the spectral range 510 to 600 nm and 700 to 760 nm, respectively, while the kinetics of the overlapping GSB/SE features was taken as the average over the spectral range from 620 to 690 nm. The transient kinetics associated with TT PIA1, GSB/SE, and TT PIA2 features have been normalized over the time range from 200 to 350 fs, 400 to 560 fs, and 560 to 680 fs, respectively. The dynamics in this time range are assigned to an intermolecular structural relaxation between two types of triplet pair intermediates. (c) The same data as in panel b, highlighting the decay at long time assigned to internal conversion of triplet pairs to the ground state.

In panel a, transient kinetics associated with the photoinduced absorption of primary singlet excitons and a short-wavelength photoinduced absorption band associated with triplet pairs (i.e., S1S0 PIA and TT PIA1, respectively) is plotted. Given the simultaneous decay of the S1S0 PIA and growth of the TT PIA1 bands, we attribute these dynamics to the relaxation of primary singlet excitons into triplet pairs. The dynamics are effectively complete within ca. 300 fs (grey region), and are well described according to a single-exponential fit function with a time constant of ca. 100 fs (see below).

Figure S11b displays a period of evolution in the transient absorption data that we assign to an intermolecular structural relaxation between two types of triplet pair intermediates. We previously showed that intermolecular structural relaxation can modify the transient absorption bands of excitonic populations, especially when a significant excess of electronic energy is dissipated into nuclear kinetic energy degrees of freedom of the bath. Figure S11b shows that, over the course of this period of the dynamics, while the overlapping GSB/SE features remains essentially constant, the TT PIA1 and PIA2 bands decay and grow, respectively. The decay and growth of TT PIA1 and PIA2 bands, respectively, are well described according to a single-exponential fit function with a time constant of ca. 400 fs (see below). The final period of evolution in the transient absorption data is displayed in Figure S11c, which also plots TT PIA1, GSB/SE, and TT PIA2 bands with the final period of evolution highlighted. All signals decay to approximately zero amplitude on a timescale of a few picoseconds. We assign the dynamics over the course of this period of evolution to internal conversion of the triplet pair directly to the ground state.

Figure S12 displays the results of modeling the short- and intermediate-time delay transient absorption evolution.
Figure S12. (a) The kinetics of the S1S0 PIA feature was taken as the average over the spectral range 450 to 520 nm. The data were fit with a single exponential function with the resulting time constant indicated. (a) The kinetics of TT PIA1 (VIS) and TT PIA2 (NIR) features were taken as the average over the spectral range 510 to 600 nm and 700 to 760 nm, respectively. Both datasets were fit simultaneously with a bi-exponential function with the first time constant fixed at 100 fs and the second resulting time constant indicated.

Modeling the decay of the primary singlet exciton photoinduced absorption with a single-exponential function, we obtain a time constant of ca. 100 fs (Figure S12a), which describes the decay of primary singlet excitons into triplet pairs (i.e., S1S0 → TT). Modeling both the decay and growth of the short- and long-wavelength triplet pair photoinduced absorption bands with a bi-exponential fit function, where the first time constant is fixed at 100 fs, we obtain a second time constant of ca. 400 fs, which describes the intermolecular structural relaxation between triplet pairs (i.e., TT* → TT).

We next proceed to model the data according to the same four-component global target analysis (Figure S8), but fixing the first two time constants according to the values derived above. Figure S13 displays the species-associated spectra derived from the four-component global target analysis; the time constants used in and derived in the analysis are displayed in Table S3.
Figure S13. Species-associated spectra derived from a four-component global and target analysis of the transient absorption of the crystalline 5,14-TIPS-pentacene nanoparticles, with one time constant floating and three fixed. The species-associated spectra labels are equivalent as in Figure S8, i.e., SAS-1 = S1S0, SAS-2 = TT*, SAS-3 = TT, and SAS-4 = (S0S0)*. Here, mixing between components is suppressed considerably (compare e.g. Figures S10 and S13).

Table S3. Time Constant Derived for the Singlet Fission Dynamics in Crystalline 5,14-TIPS-pentacene Nanoparticles, With One Floating and Three Fixed $^{a,b}$

| $\tau_1$ (ps) | $\tau_2$ (ps) | $\tau_3$ (ps) | $\tau_4$ (ps) |
|---------------|---------------|---------------|---------------|
| 0.10          | 0.40          | 2.4           | $>>$ 500      |

$^a$ The time constant associated with the thermal artifact, which following its formation is essentially constant over the course of the measurement, was fixed at 100,000 ps.

$^b$ The first and second time constants were also fixed according to the values derived above, i.e., 0.1 and 0.4 ps, respectively.

As can be seen in Table S3, fixing the time constants associated with the first two components has little effect on the time constant associated with the decay of triplet pairs to the ground state. Fixing the first two components according to the values derived above also suppresses the mixing between these two components (Figure S13). The spectrum associated primary singlet excitons (SAS-1) looks more similar to that of isolated-molecule singlet excitations (Section S5). While again, the triplet pair spectra SAS-2 and SAS-3 look qualitatively similar, subtle differences become obvious when the component mixing has been suppressed. Specifically, the overall amplitude of the TT VIS PIA is larger for TT*, whereas the overall amplitude of the TT NIR PIA transition is larger for TT. Furthermore, subtle spectral shifts and differences in vibronic structure are obvious in the TT VIS PIA, with the TT* band exhibiting a smaller 0-0/0-1 ratio and redshifted spectral features. These trends are consistent with intermolecular structural relaxation within a single electronic population, which is expected to subtly change the structure and transient absorption of the
electronic population. The last component associated with the thermal artifact, \((S_0S_0)^*\), exhibits a derivative lineshape especially prominent in the vicinity of strong ground-state bleach features, clearly consistent with a thermal artifact induced by the rapid dissipation of a substantial amount of electronic energy into the bath in the form of nuclear kinetic energy degrees of freedom.

We next turn to the singlet fission dynamics in the crystalline 5,14-TIPS-Pn film. The results of an identical analysis are shown in Figure S14 and Table S4.

![Figure S14. Species-associated spectra derived from a four-component global and target analysis of the transient absorption of the crystalline 5,14-TIPS-pentacene film, with one time constant floating and three fixed. The species-associated spectra labels are equivalent as in Figure S8, i.e., SAS-1 = S1S0, SAS-2 = TT*, SAS-3 = TT, and SAS-4 = (S0S0)*.](image)

**Table S4. Time Constant Derived for the Singlet Fission Dynamics in Crystalline 5,14-TIPS-pentacene Nanoparticles, With One Floating and Three Fixed.**

| \(\tau_1\) (ps) | \(\tau_2\) (ps) | \(\tau_3\) (ps) | \(\tau_4\) (ps) |
|-----------------|-----------------|-----------------|-----------------|
| 0.10            | 0.40            | 1.9             | >> 500          |

\(a\) The time constant associated with the thermal artifact, which following its formation is essentially constant over the course of the measurement, was fixed at 100,000 ps.

\(b\) The first and second time constants were fixed according to the values derived above, i.e., 0.1 and 0.4 ps, respectively, for crystalline 5,14-TIPS-Pn nanoparticles.

The species-associated spectra for the crystalline films are qualitatively similar to those derived for the nanoparticles (Figures S13 and S14). Namely, a stimulated emission band peaking at ca. 720 nm is observed in the spectrum of the primary singlet exciton (i.e., SAS-1), and a TT photoinduced absorption band peaking at ca. 520 nm is observed in the spectrum of the fully-relaxed triplet pair (i.e., SAS-3). Critically, the time constant derived for the decay of TT to the ground state is essentially equivalent to the value derived in the case of the crystalline nanoparticles (Tables S3 and S4).
While the transient absorption of the crystalline nanoparticles and film is qualitatively similar, as noted above, distinct differences are observed between these datasets as a result of the fact that the 5,14-TIPS-Pn core orients normal to the substrate surface (Section S4), much like unsubstituted pentacene.\textsuperscript{17} This causes the amplitude of the TT PIA band to reduce considerably, as is evidenced by comparing the larger GSB signal amplitude with respect to the TT PIA band amplitude in the case of the crystalline nanoparticles and film. Another difference between these datasets is the noticeably larger amplitude associated with the thermal artifact in the crystalline films (i.e., SAS-4 in Figures S13 and S14). This is likely related to a number of factors, including that the volume expansion of the crystalline nanoparticles may be resisted by the surrounding solvent matrix, and that the nanoparticles can diffuse in and out of the focal volume of the experiment. We note that in this particular experiment on the crystalline nanoparticles, the solution was not stirred, and so even further suppression of this thermal artifact may be possible. In summary, even though the spectra are changed as a result of orientation effects and a more significant thermal effect, we find that the singlet fission dynamics for the crystalline 5,14-TIPS-Pn nanoparticles and films are equivalent, consistent with reports for a number of other material systems.\textsuperscript{2,3,5,7,12,13}
Section S9: Contribution of photo-dimerization and photo-oxidation to transient absorption signals and derivation of quantum yield for the sum of these processes

It is well known that pentacenes have the capacity to photo-dimerize and photo-oxidize, especially at the highly-reactive 6 and 13 positions of the pentacene core. Given that 5,14-TAS-pentacene derivatives are not protected at this position, photochemical processes are a real concern. In this supporting section, we discuss what role (if any) these photochemical processes play on the transient absorption signals and subsequently derive the quantum yield for the sum of any photochemical processes in transient absorption measurements on crystalline films of 5,14-TIPS-pentacene.

First, we discuss what role (if any) photo-dimerization and photo-oxidation play on the transient absorption signals. Over the course of measurements on the crystalline films, permanent photobleaching of the sample was indeed observed as an incremental decrease of the overall signal amplitude in successive scans. Critically, the extent of the permanent photobleaching can be quantified by the extent to which the signals decrease. Given that the ground-state bleach feature is one of the strongest signals of the crystalline 5,14-TIPS-pentacene films (see main text), we compare the amplitude of that feature at the beginning of a series of measurements with the amplitude observed in the final measurement. Over the course of 10 minutes of laser exposure, we observed this feature to reduce in amplitude by 34% (Figure S15). This indicates that permanent photobleaching of the sample has occurred.

![Figure S15](image_url)

**Figure S15.** Transient absorption measurements of a crystalline film of 5,14-TIPS-pentacene. The entire series of measurements (9 scans) was performed over the course of 10 min (or 600 sec). The first and final scan (shown) had a signal amplitude in the vicinity of the ground-state bleach feature of ca. -0.0026 and -0.0017, respectively, as determined by averaging the data from 0 to 0.9 ps. Lines corresponding to these values overlay the data.
Although permanent photobleaching was observed over the course of 10 minutes of laser exposure, permanent photobleaching was not observed in single measurements. This means that the dynamics we observe cannot result from solid-state “butterfly” dimerization. Because the product of the solid-state “butterfly” dimerization is an acene of lower conjugation length, we know that the end product will have an absorption spectrum peaking in the UV, far away from where the pentacene absorbs. And so, if the dynamics we were observing in the transient absorption measurement were a result of solid-state “butterfly” dimerization, we would observe a permanent ground-state bleach for the pentacene, which is not what we observe.

To evaluate the extent to which photochemical processes contribute to the transient absorption signal, we derive the photochemical quantum yield in crystalline 5,14-TIPS-pentacene films for a single light excitation event. The photochemical quantum yield (per pulse) can be derived according to the following expression:

\[ \Phi_{\text{photochem\_per\_pulse}} = \frac{N_{\text{photochem\_events\_per\_pulse}}}{N_{\text{chromophores\_excited\_per\_pulse}}} \]

where \( \Phi_{\text{photochem\_per\_pulse}} \) is the quantum yield of photoisomerization per pulse, \( N_{\text{photochem\_events\_per\_pulse}} \) is the fraction of isomerization events per pulse, and \( N_{\text{chromophores\_excited\_per\_pulse}} \) is the fraction of chromophores excited per pulse. This expression can be solved for \( N_{\text{photochem\_events\_per\_pulse}} \) to yield:

\[ N_{\text{photochem\_events\_per\_pulse}} = N_{\text{chromophores\_excited\_per\_pulse}} \times \Phi_{\text{photochem\_per\_pulse}} \]

We also have the following expression, that relates the extent of photodimerization within the beam volume to \( N_{\text{photochem\_events\_per\_pulse}} \). Specifically:

\[ \Phi_{\text{photochem\_beam\_volume}} = \text{Repetition Rate} \times \tau_{\text{photochem\_beam\_volume}} \times N_{\text{photochem\_events\_per\_pulse}} \]

where \( \Phi_{\text{photochem\_beam\_volume}} \) is the extent of photochemical decay of the sample in the beam volume, the repetition rate is that of the light source, \( \tau_{\text{photochem\_beam\_volume}} \) is the time it takes for photochemical decay of the sample to occur in the beam volume to the extent of \( \Phi_{\text{photochem\_beam\_volume}} \), and \( N_{\text{photochem\_events\_per\_pulse}} \) is defined above. Substituting the expression for \( N_{\text{photochem\_events\_per\_pulse}} \) into the expression above, we have for \( \Phi_{\text{photochem\_beam\_volume}} \):

\[ \Phi_{\text{photochem\_beam\_volume}} = \text{Repetition Rate} \times \tau_{\text{photochem\_beam\_volume}} \times N_{\text{chromophores\_excited\_per\_pulse}} \times \Phi_{\text{photochem\_per\_pulse}} \]

Solving this expression for \( \Phi_{\text{photochem\_per\_pulse}} \), we have:

\[ \Phi_{\text{photochem\_per\_pulse}} = \Phi_{\text{photochem\_beam\_volume}} / \left( \text{Repetition Rate} \times \tau_{\text{photochem\_beam\_volume}} \times N_{\text{chromophores\_excited\_per\_pulse}} \right) \]

All of the values on the right-hand side of the expression above are either known or measurable. \( \Phi_{\text{photochem\_beam\_volume}} \) is determined by evaluating the reduction of the ground-state bleach amplitude over the course of the series of measurements. That is, over the course of 10 min or 600 sec of
laser exposure (which is the value of $\tau_{\text{photochem \ beam \ volume}}$), the ground-state bleach amplitude reduced from an initial value of $2.6 \times 10^{-3}$ to a value of ca. $1.7 \times 10^{-3}$. Thus, the extent to which the signal amplitude was reduced, which is equivalent to the value of $\Phi_{\text{photochem \ beam \ volume}}$ is 0.34. The value for the repetition rate of the light source is 1000 Hz. Lastly, $N_{\text{chromophores \ excited \ per \ pulse}}$, as defined above, can be evaluated as the absolute ground-state bleach amplitude at the onset of the series of measurements. This value is $2.6 \times 10^{-3}$. Plugging these values into the expression above, we obtain a value of 0.0002 or 0.02% for $\Phi_{\text{photochem \ per \ pulse}}$. Given this exceedingly low value of $\Phi_{\text{photochem \ per \ pulse}}$, we therefore take any photochemical processes, such as photo-dimerization and photo-oxidation, to represent a very minor decay pathway.

Lastly, we note that, according to the 0.02% value derived above for $\Phi_{\text{photochem \ per \ pulse}}$, the absolute signal we expect to observe for permanent photobleaching associated with photochemical processes is ca. $6 \times 10^{-7}$. This value is beyond the detection limit of even the most sensitive transient absorption instrumentation,\textsuperscript{18} meaning it is not possible to detect in our measurements.
Section S10: Steady-state absorption and structural characterization of crystalline 5,14-TES-pentacene films

Figure S16. (a) Steady-state absorption of a solvent-vapor annealed 5,14-TES-Pn film (red). For reference, the steady-state absorption of a dilute solution of 5,14-TIPS-Pn is overlaid in grey. Note we previously showed that the alkyl substituent of 6,13-trialkylsilylethylene substituted pentacenes negligibly changes the electronic structure of the monomer, and presume the same to be the case.
for the compounds studied here. (b) GIWAXS of a solvent-vapor annealed 5,14-TES-Pn film and (c) corresponding plot tracking the integrated intensity as a function of the reciprocal vector q.

**Figure S16a** displays the absorption spectrum of a solvent-vapor annealed 5,14-TES-Pn film. The solvent-vapor annealed film exhibits a redshifted vibronic progression with respect to that of the monomer reference. Similar to crystalline 5,14-TIPS-Pn (see **Section S4**), the origin band of the solvent-vapor annealed 5,14-TES-Pn film peaks at ca. 654 nm, which is redshifted by ca. 480 cm\(^{-1}\) with respect to the monomer. Again, we consider the excitonic redshift (and band broadening) a signature of strong excitonic coupling (i.e., chromophores are strongly coupled and excitons are evenly delocalized about these chromophores).

**Figures 16b and 16c** display the GIWAXS results for a solvent-vapor annealed 5,14-TES-Pn film. Diffraction features are observed indicating the film is polycrystalline with random out-of-plane orientation as evidenced by the diffraction rings in the 2-D pattern. Plotting the azimuthally integrated intensity as a function of reciprocal space indicates that the solvent-vapor annealed film does not adopt the known crystal structure as evidenced by the differences in the diffraction patterns. These films appear to adopt a new, as yet reported polymorph.
Section S11: Global target analysis of transient absorption of crystalline 5,14-TES-pentacene

In this section, we report the results of a global target analysis of the transient absorption of the crystalline 5,14-TES-Pn film. The results of the analysis are shown in Figure S17 and Table S5.

![Species-associated spectra derived from a four-component global and target analysis of the transient absorption of the crystalline 5,14-TES-Pn film, with one time constant floating and three fixed. The species-associated spectra labels are equivalent as in Figure S8, i.e., SAS-1 = S1S0, SAS-2 = TT*, SAS-3 = TT, and SAS-4 = (S0S0)*.](image)

**Figure S17.** Species-associated spectra derived from a four-component global and target analysis of the transient absorption of the crystalline 5,14-TES-pentacene film, with one time constant floating and three fixed. The species-associated spectra labels are equivalent as in Figure S8, i.e., SAS-1 = S1S0, SAS-2 = TT*, SAS-3 = TT, and SAS-4 = (S0S0)*.

**Table S5.** Time Constant Derived for the Singlet Fission Dynamics in Crystalline 5,14-TES-pentacene Nanoparticles, With One Floating and Three Fixed $^{a,b}$

| $\tau_1$ (ps) | $\tau_2$ (ps) | $\tau_3$ (ps) | $\tau_4$ (ps) |
|--------------|--------------|--------------|--------------|
| 0.10         | 0.40         | 1.7          | $>>$ 500     |

$^a$ The time constant associated with the thermal artifact, which following its formation is essentially constant over the course of the measurement, was fixed at 100,000 ps.

$^b$ The first and second time constants were fixed according to the values derived above, i.e., 0.1 and 0.4 ps, respectively, for crystalline 5,14-TIPS-Pn nanoparticles.
Section S12: Steady-state absorption and structural characterization of crystalline 5,14-TIBS-pentacene films

Figure S18. (a) Steady-state absorption of an as-cast 5,14-TIBS-Pn film (cyan). For reference, the steady-state absorption of a dilute solution of 5,14-TIPS-Pn is overlaid in grey. Note we previously showed that the alkyl substituent of 6,13-trialkylsilylhexynyl substituted pentacenes negligibly changes the electronic structure of the monomer, and presume the same to be the case for the compounds studied here. (b) GIWAXS of an as-cast 5,14-TIBS-Pn film.

Figure S18a displays the absorption spectrum of an as-cast 5,14-TIBS-Pn film. The as-cast film exhibits a redshifted vibronic progression with respect to that of the monomer reference. In contrast to crystalline 5,14-TIPS- and 5,14-TES-Pn (see Sections S4 and S10), the origin band of the as-cast 5,14-TIBS-Pn film peaks at ca. 671 nm, which is redshifted by ca. 870 cm$^{-1}$ with respect to the monomer reference. Similar to crystalline 5,14-TIPS- and 5,14-TES-Pn, we consider the excitonic redshift (and band broadening) a signature of strong excitonic coupling (i.e., chromophores are strongly coupled and excitons are evenly delocalized about these chromophores).

Figure S18b displays the GIWAXS results for an as-cast 5,14-TIBS-Pn film. Diffraction peaks are observed indicating the film is crystalline and exhibits preferential out-of-plane
orientation, but no crystal structure has been solved for this material so we cannot extract information regarding molecular packing. We note that the as-cast (and crystalline) 5,14-TIBS-Pn film was chosen for study as it exhibited the least scatter in optical measurements.
**Section S13: Global target analysis of transient absorption of crystalline 5,14-TIBS-pentacene**

In this section, we report the results of a global target analysis of the transient absorption of the crystalline 5,14-TIBS-Pn film. The results of the analysis are shown in **Figure S19** and **Table S6**.

**Figure S19.** Species-associated spectra derived from a four-component global and target analysis of the transient absorption of the crystalline 5,14-TIBS-pentacene film, with one time constant floating and three fixed. The species-associated spectra labels are equivalent as in **Figure S8**, i.e., SAS-1 = S1S0, SAS-2 = TT*, SAS-3 = TT, and SAS-4 = (S0S0)*.

**Table S6.** Time Constant Derived for the Singlet Fission Dynamics in Crystalline 5,14-TIBS-pentacene Nanoparticles, With One Floating and Three Fixed \(^{a,b}\)

| \(\tau_1\) (ps) | \(\tau_2\) (ps) | \(\tau_3\) (ps) | \(\tau_4\) (ps) |
|----------------|----------------|----------------|----------------|
| 0.10           | 0.40           | 3.6            | >> 500         |

\(^a\) The time constant associated with the thermal artifact, which following its formation is essentially constant over the course of the measurement, was fixed at 100,000 ps.

\(^b\) The first and second time constants were fixed according to the values derived above, i.e., 0.1 and 0.4 ps, respectively, for crystalline 5,14-TIPS-Pn nanoparticles.
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