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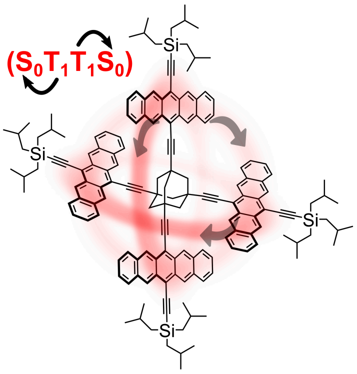
COMMUNICATION

A tetrameric pentacene is designed as a model system to explore the influence of exciton delocalization on singlet fission and to study subsequent triplet decorrelation via exciton diffusion following intramolecular singlet fission in dilute solution. Using transient absorption spectroscopy, we document the delocalization of singlet and triplet excitons amongst the four pentacenes.



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Chromophore multiplication to enable exciton delocalization and triplet diffusion following singlet fission in tetrameric pentacene

Chromophore multiplication to enable exciton delocalization and triplet diffusion following singlet fission in tetrameric pentacene

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Abstract: A tetrameric pentacene **PT** has been used to explore the effects of exciton delocalization on singlet fission (SF). We document, for the first time, triplet decorrelation via intramolecular triplet diffusion following SF. Transient absorption spectroscopy is used to document different decorrelation mechanisms (triplet diffusion versus structural changes) for **PT** and its dimeric equivalent **PD** based on the rate and activation barrier of the decorrelation step. Charge-separation experiments using tetracyano-p-quinodimethane (**TCNQ**) to quench triplet excitons formed through SF demonstrate that enhanced intersystem crossing, i.e., spin catalysis, is a widely underestimated obstacle to quantitative harvesting of the SF products. The importance of spatial separation of the decorrelated triplet states is emphasized, and independent proof that the decorrelated triplet pair state consists of two (T_1) states per molecule is provided.

Singlet fission (SF) depends on the interaction of a photoexcited singlet state (S_1) with a neighboring ground-state (S_0) chromophore, and results in the spontaneous splitting of (S_1) into a pair of correlated triplets (T_1T_1).[1] To harvest both triplet excitons (T_1T_1) must, however, transition into a pair of uncorrelated triplets (T_1+T_1). This decorrelation step is usually mediated by spin mixing with a quintet spin-correlated triplet pair, $^5(T_1T_1)$,[2] as outlined in several excellent reviews.[3]

Successful SF requires a minimum of two chromophores, and dimers such as **PD** (**Figure 1**) have been studied in dilute solution to outline many of the mechanistic aspects of intramolecular SF (iSF). The power of organic synthesis is key and allows the electronic coupling between chromophores to be tuned through control of relative distance and orientation, as well as conjugation.[4] Despite the success of dimers in dissecting the role of, e.g., charge transfer, quintet and excimer states,[2b, 5] further breakthroughs in SF are currently hampered by the intrinsic limitations outlined below.

In solids, intermolecular coupling allows diffusion of the initial singlet excitation over several molecules.[3c] Moreover, triplet decorrelation implies a distinct change in the coupling between triplets,[2a, 6] facilitated by triplet diffusion.[6-7] The analogous diffusion is, however, impossible in molecular dimers, and triplet-triplet annihilation of (T_1T_1) usually governs recovery of (S_0S_0).[8] Thus, oligomers and polymers have evolved as model systems for probing triplet diffusion.[9] Nevertheless, after SF in a polymer, triplet diffusion from correlated triplets is hindered by strong coupling. This ultimately results in rapid recombination, rather than the desired formation of free triplets.

The present work documents the influence of chromophore multiplication on iSF. Chromophore multiplication differs from oligomerization: All chromophores remain electronically independent because of the non-conjugated spacer in **PT**. The adamantane scaffold is ideal for investigating chromophore multiplication via tetrameric **PT** (**Figure 1**).[10] Using photophysical analyses and comparisons to dimeric **PD** and monomeric **PM**, supplemented with theoretical calculations, we identify differences in excitation behavior, SF, and triplet decorrelation that result from chromophore multiplication. This work concludes by solution-state "harvesting" of the products of SF via charge-separation experiments with the electron acceptor tetracyano-p-quinodimethane (**TCNQ**). Importantly, charge-separation experiments provide independent evidence that the decorrelated triplet pair state must consist of two non-interacting triplets on the *same molecule*, rather than a single triplet *per molecule*. These studies demonstrate that enhanced intersystem crossing (EISC) hinders quantitative harvesting of the triplet products of SF. Thus, spatial triplet separation is now firmly established as a prerequisite for harvesting the two triplet excitons from SF efficiently.

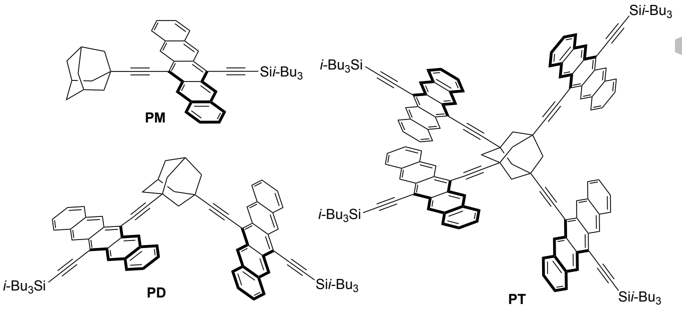

Figure 1. Structures of **PM**, **PT**, and **PD**.

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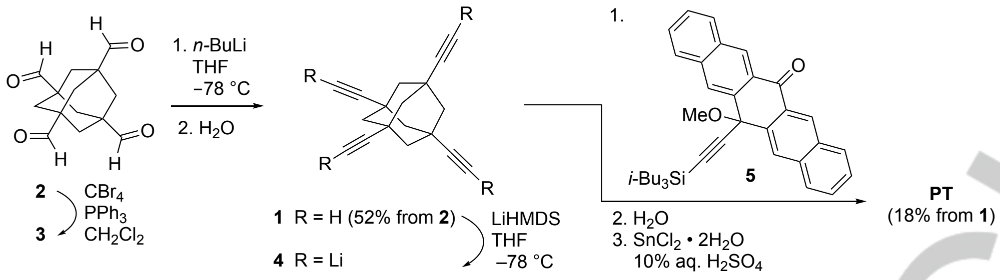

Scheme 1. Synthesis of **PT**

Tetraethynyladamantane **1** was the key building block for pentacene tetramer **PT** (**Scheme 1**). The work of Hokura and Neamura gives, to our knowledge, the only published procedure for **1**,[11] but it has several challenging steps. Thus, an alternative synthetic route was developed. Starting from 1-bromoadamantane, aldehyde **2** was formed in five steps (see SI), and dibromoolefination gave intermediate **3**. Exhaustive elimination effected with BuLi, followed by aqueous workup, gave **1** via a Corey-Fuchs-like reaction. Lithiation of **1** with LiHMDS gave intermediate **4**, to which a solution of ketone **5** was added. The reaction was subsequently quenched at low temperature via the addition of H_2O. Without further purification, the intermediate was subjected to reductive aromatization.[12] Purification via column chromatography gave tetramer **PT**. Tetramer **PT** has reasonable solubility (ca. 4 mg mL^{-1}) in typical organic solvents (THF, CH_2Cl_2, $CHCl_3$, toluene), but slowly decomposes over several days in solution upon exposure to air and light. In the absence of air (O_2), solutions are stable for 3–5 days, and **PT** is stable as solid under normal laboratory conditions.

X-ray crystallographic analysis of **PT** documents the symmetrical structure and shows that there is no appreciable intramolecular π-overlap between in the solid state (**Figure 2**, see also SI). Each pentacene moiety shows π-stacking with that of a neighboring molecule with an interplanar distance between acene cores of 3.6 Å (**Figure S1**). π-Stacking is limited to two acenes, however, and there is no long-range π-overlap.

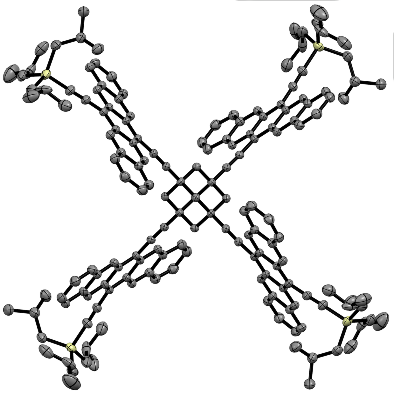

Figure 2. Solid-state structure of **PT** showing the spatial arrangement of the pentacene units (H atoms omitted; ORTEPs at 30% probability).

Steady-state spectroscopy confirms that the pentacene moieties of **PD** and **PT** are electronically independent in the ground state: The intensities of the absorption bands evolve linearly as a function of the number of chromophores (**Figure S6**). Closer inspection, however, reveals that the FWHM (full width at half maximum) decreases as a function of the number of pentacenes (**Table S1**). Upon normalization, the relative intensities of the fundamental 0-*0 transitions increase relative to those of the 0-*1, 0-*2, and 0-*3 transitions, and the increase depends on the number of pentacene groups (**Figures 3A**, **3C**). Thus, the Franck-Condon overlap for the 0-*0 transition increases with the number of chromophores. Fluorescence measurements show that the quantum yield is significantly lower in **PD** and **PT** than in **PM** (**Table S2**). The Stokes shifts decrease in the order of **PM** > **PD** > **PT** (**Figures 3B, 3D**), with a concurrent sharpening of the fluorescence spectra regardless of solvent polarity. In other words, the polarity of the excited singlet states is largest for **PM** and smallest for **PT**.

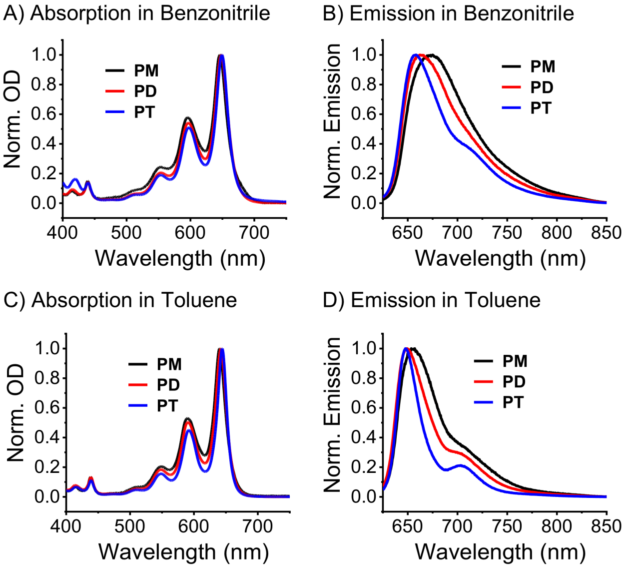

Figure 3. Normalized steady-state absorption and fluorescence (excitation at 590 nm) data of **PM**, **PD**, and **PT**.

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Femtosecond (fsTA) and nanosecond (nsTA) transient absorption experiments were used to investigate the excited-state dynamics. A change in dipole moment upon excitation is associated with solvent relaxation during the first picoseconds after excitation, which is typically manifested as a blue shift of singlet excited-state features in the NIR (**Figure 4B**).[5a] The energy gain upon relaxation (ΔE) decreases from **PM** to **PD** and to **PT** (**Figure 4B**), consistent with the emission behavior. We conclude that the polarity of the singlet-excited state decreases with the number of pentacenes, consistent with delocalization of the singlet-excited state over all four pentacene moieties. Calculations support this hypothesis, showing only small splitting between the four singlet-excited states that formally result from four locally excited pentacene singlets (see SI). Minimal splitting, coupled with thermal motion, leads to time-averaged delocalization (by Dexter energy transfer) of the singlet-excited state. Note that this observation is supported by the fact that no Davidov splitting is observed in the experimental absorption spectra. Excited states S_1-S_3, which all have significant intensity, lie within 0.02 eV. Only S4, which is dark, is split significantly (0.14 eV) from the other three. The same is true for the four triplet states that formally result from localized pentacene triplet states. Thus, thermal mixing gives way to time-averaged delocalization and reduced polarity on the timescale of solvent reorganization.

On a longer timescale, the excited-state dynamics of **PD** and **PT** are similar (**Figures 4A**, **S7–S8**), and singlet decay for both is significantly faster than for **PM** (**Table S3**). In benzonitrile (BN), the singlet excited state lifetimes are 6.2 ns (S_1), 402 ps (S_1S_0), and 129 ps ($S_1S_0S_0S_0$) in **PM**, **PD**, and **PT**, respectively, and reflect the statistical likelihood of iSF. Delocalized over four chromophores, iSF in **PT** offers six different pairs of pentacenes in a favored orientation: [($\mathbf{T_1T_1}S_0S_0$), ($\mathbf{T_1}S_0\mathbf{T_1}S_0$), ($\mathbf{T_1}S_0S_0\mathbf{T_1}$), ($S_0\mathbf{T_1}S_0\mathbf{T_1}$), ($S_0\mathbf{T_1T_1}S_0$), ($S_0S_0\mathbf{T_1T_1}$)]. This leads to a higher rate of iSF for **PT** than **PD**, as well as a concurrent increase in the rate constant of SF (k_{SF}) by a factor of ~3, from 2.3×10^9 s^{-1} (**PD**) to 6.8×10^9 s^{-1} (**PT**). This finding is in line with results for oligomeric pentacenes.[9b] Solvent polarity also dictates k_{SF} with values in toluene of 1.2×10^9 s^{-1} and 3.3×10^9 s^{-1} for **PD** and **PT**, respectively, suggesting a superexchange mechanism.[5a, 8a] Finally, ($S_1S_0S_0S_0$) and (S_1S_0) decay, and the characteristic pentacene triplet-excited state features evolve. Concurrent with singlet decay, ground-state bleaching intensifies by a factor of ca. two. This suggests nearly quantitative iSF for **PD** and **PT** (**Figures 4A, S7–S8**), while **PM** produces <1% triplet (**Figure S9**). The triplet-excited state decay is triexponential for **PD** and **PT** (**PD**/**PT**), including the singlet correlated triplet pairs $^1(T_1T_1)$/$^1(T_1T_1S_0S_0)$, the quintet correlated triplet pairs $^5(T_1T_1)$/$^5(T_1T_1S_0S_0)$, and the decorrelated triplet pairs (T_1+T_1)/(T_1+T_1+S_0+S_0).[13] Triplet decorrelation lifetimes stand out. The $^5(T_1T_1)$ lifetime of **PD** and $^5(T_1T_1S_0S_0)$ of **PT** are 91 and 70 ns, respectively. If a localized pair of spin-correlated triplets undergoes decorrelation via structural changes, then rates and yields of decorrelation should be essentially equal for **PT** and **PD** because of the analogous geometrical relationships between the pentacene chromophores. This is not the case, however, as the triplet excitations in $^5(T_1T_1S_0S_0)$ are free to diffuse within the tetramer, which statistically affords more rapid decorrelation for **PT**. This is also supported by the small splitting between the four relevant triplet states of **PT**, as supported by theoretical calculations (vide supra). Temperature-dependent nsTA measurements for **PD** and **PT** in BN have been performed (**Figures S13–S19**) to provide the activation energy (E_A) for triplet decorrelation (**Figure 5**). Triplet decorrelation arises via a change in coupling between the two triplet states. In the solid state this occurs as two triplets diffuse away from each other. In a dimer, changes in coupling would be effected by, for example, bond rotations. Triplet decorrelation in **PD** faces a barrier of ca. 13 meV, consistent with the geometric rearrangement. Decorrelation in **PT**, however, lacks any appreciable temperature dependence ($E_A = 0$), and an alternative mechanism must thus be operative: Decorrelation occurs through diffusion of a triplet excitation to any of the pentacenes in a ground-state configuration with a slightly different conformation than that of the initially excited triplet.

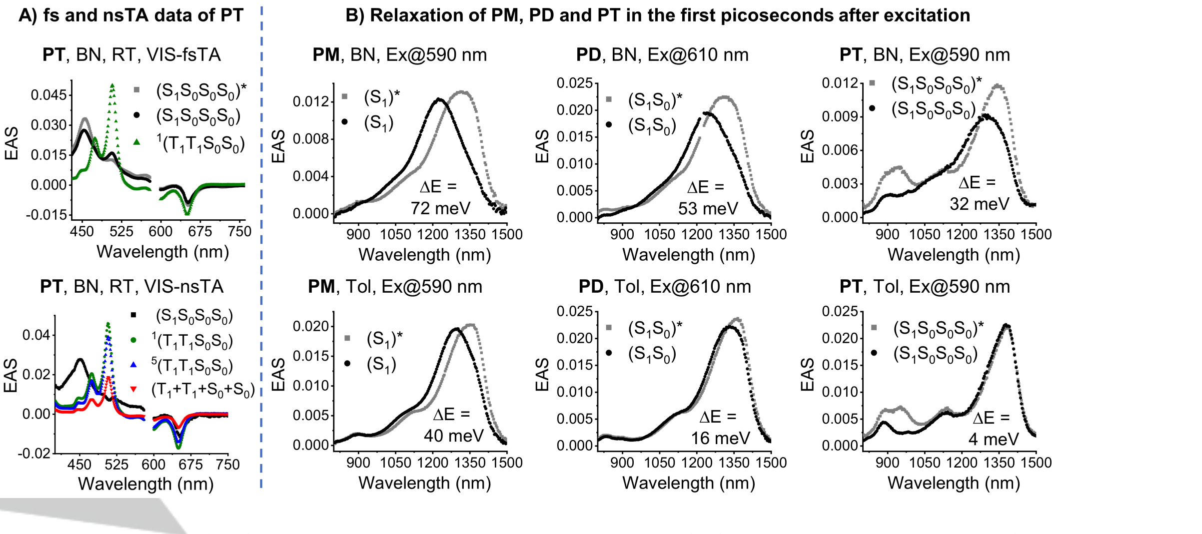


Figure 4. A) Evolution associated spectra (EAS) of the TA data of **PT** in argon-saturated benzonitrile (BN). See **Figure S7** for more details. B) EAS of the blue shift of the fsTA NIR singlet feature of **PM**, **PD** and **PT** in argon-saturated BN and toluene (Tol). Ex = excitation wavelength.

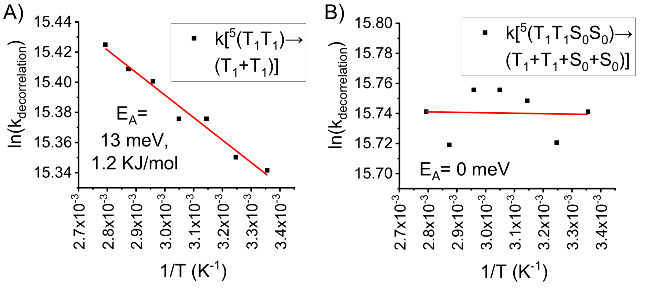


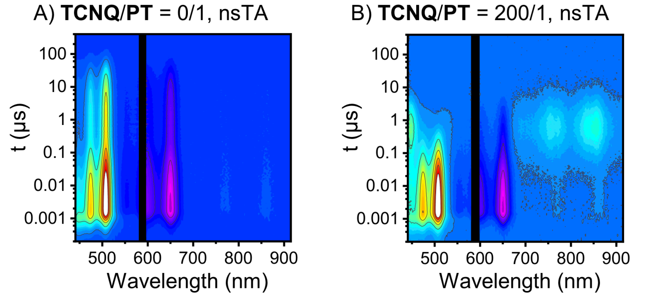
Figure 5. Arrhenius plots of the triplet decorrelation rate k_{decoor} for **PD** and **PT**. See **Table S5** for details.

For SF to be implemented in solar energy conversion schemes, it is imperative that both triplets can be harvested. Charge-separation experiments with the acceptor tetracyano-p-quinodimethane (**TCNQ**) were attempted toward achieving this goal; an excess of **TCNQ** (6.3–200 equiv.) was used relative to **PD** or **PT** to guarantee pseudo first-order reaction conditions. In the presence of **TCNQ**, both **PT** and **PD** show accelerated decay of the triplet features at 508 nm (**Figure S24**) and concomitant growth of new features at 700–900 nm, which are spectroscopic fingerprints of **TCNQ**$^{•-}$ (**Figures S20–S24**).[14]

Sequential analyses of the nsTA data yields good fits of the transient kinetics using five transient species for **PD**/**PT**: $(S_1S_0)/(S_1S_0S_0S_0)$, $^1(T_1T_1)/^1(T_1T_1S_0S_0)$, $^5(T_1T_1)/^5(T_1T_1S_0S_0)$, $(T_1+T_1)/(T_1+T_1+S_0+S_0)$ and the charge-separated state ($P^{•+}$ + **TCNQ**$^{•-}$), in which ($P^{•+}$) is the one-electron oxidized form of pentacene (**Figures S26–S31**). A sequential fit demonstrates that the charge-separated state ($P^{•+}$ + **TCNQ**$^{•-}$) is predominantly populated by a diffusion-controlled reaction of **TCNQ** with $(T_1+T_1)/(T_1+T_1+S_0+S_0)$. Nevertheless, a minor contribution stems from interactions of **TCNQ** with the quintet state $^5(T_1T_1)/^5(T_1T_1S_0S_0)$.

Target analyses of the corresponding data for **PT** and **PD** were then performed assuming that two charge separated states ($P^{•+}$ + **TCNQ**$^{•-}$) evolved from $^5(T_1T_1)/^5(T_1T_1S_0S_0)$ or $(T_1+T_1)/(T_1+T_1+S_0+S_0)$, to yield $[(P^{•+}+P^{•+})/(P^{•+}+P^{•+}+S_0+S_0)$ + 2 × **TCNQ**$^{•-}$] (**Figure S33**). Under this assumption, the quantum yield for electron transfer (ET) to **TCNQ** was ca. 50% relative to $(T_1+T_1)/(T_1+T_1+S_0+S_0)$. In other words, one, rather than two, charge-separated state was generated per $(T_1+T_1)/(T_1+T_1+S_0+S_0)$. The fact that $(P^{•+}+T_1)/(P^{•+}+T_1+S_0+S_0)$ is harder to oxidize than $(T_1+T_1)/(T_1+T_1+S_0+S_0)$ is not fully compatible with our observations. Considering that only a single triplet in $(T_1+T_1)/(T_1+T_1+S_0+S_0)$ is oxidized, the spectroscopic signatures of the charge-separated state ($P^{•+}$ + **TCNQ**$^{•-}$) should be discernable in concert with those of the second triplet, which is definitely not the case. Rather, the triplet decay goes hand-in-hand with the formation of the ($P^{•+}$ + **TCNQ**$^{•-}$) features, i.e., both triplets in $(T_1+T_1)/(T_1+T_1+S_0+S_0)$ deactivate simultaneously. Nevertheless, charge separation is only 50%. We conclude that ($P^{•+}$) accelerates deactivation of the triplet-excited state of the neighboring pentacene, namely a rate increase of ISC induced by a neighboring unpaired electron, i.e., enhanced intersystem crossing (EISC) or spin catalysis.[15] Finally, a revised target analysis considered the formation of only one charge-separated state per $^5(T_1T_1)/^5(T_1T_1S_0S_0)$ or $(T_1+T_1)/(T_1+T_1+S_0+S_0)$ to afford $[(P^{•+}+S_0)/(P^{•+}+S_0+S_0+S_0)$ + **TCNQ**$^{•-}$] (**Figures 6, S35–S39**), which gives a quantum yield for ET of essentially 100% relative to $(T_1+T_1)/(T_1+T_1+S_0+S_0)$ for all data sets. Thus, only one of the two triplets is quenched, and the other is deactivated to the ground state due to EISC.

In conclusion, we show that the tetrameric structure of the **PT** is an excellent model system for SF in solids beyond the two-chromophore approximation of dimers. Solvent-dependent experiments establish that the singlet-excited state of **PT** is delocalized (from a time-averaged perspective) over four pentacenes by thermal mixing, as observed in crystalline chromophores.[3c] Similar to (T_1T_1) found in **PD**, coupling in $(T_1T_1S_0S_0)$ for **PT** is sufficiently weak to facilitate triplet decorrelation. The mechanisms of triplet decorrelation in **PD** and **PT** are, however, different. In **PD**, temperature-dependent TA measurements demonstrate that decorrelation is triggered by geometric rearrangements, while in **PT** triplet diffusion occurs most likely by a Dexter-type energy transfer resulting in time-averaged delocalization. These conclusions are supported by both experiment and theory. Experiments with **TCNQ** demonstrate that, following formation of the decorrelated triplet pair, trapping of one triplet by charge separation leads to an accelerated decay of the second triplet to the ground state by EISC. This establishes that efficient, spatial diffusion of the triplet states is a crucial parameter toward harvesting both triplet excitons.


A) **TCNQ**/**PT** = 0/1, nsTA

B) **TCNQ**/**PT** = 200/1, nsTA

C) **PT** [1.25x10^{-5}M] + **TCNQ** [2.50x10^{-3}M], nsTA, target analysis

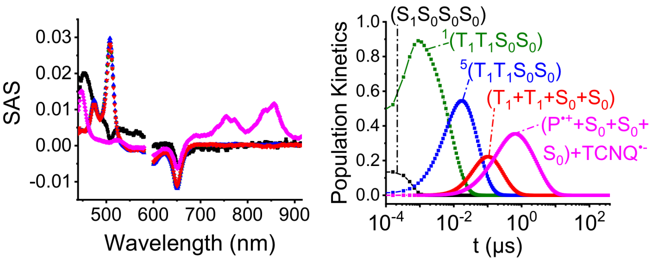


Figure 6. A) nsTA raw data for **PT** in Ar-saturated BN. B) nsTA raw data for **PT** and **TCNQ** in Ar-saturated BN. C) Species associated spectra (SAS) and corresponding population kinetics of the nsTA data shown in (B) as obtained by target analysis. See **Figure S34** for the kinetic model and **Table S14** for rate constants.

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Keywords: time-resolved spectroscopy • pentacene oligomers • singlet fission • triplet decorrelation • charge transfer

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