Tuning Singlet Fission in Pi-Bridge-Pi Chromophores

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ABSTRACT: We have designed a series of pentacene dimers separated by homoconjugated or non-conjugated bridges that exhibit fast and efficient intramolecular singlet exciton fission (iSF). These materials are distinctive among reported iSF compounds because they exist in the unexplored regime of close spatial proximity but weak electronic coupling between the singlet exciton and triplet pair states. Using transient absorption spectroscopy to investigate photophysics in these molecules, we find that homoconjugated dimers display desirable excited state dynamics, with significantly reduced recombination rates as compared to conjugated dimers with similar singlet fission rates. In addition, unlike conjugated dimers, the time constants for singlet fission are relatively insensitive to the interplanar angle between chromophores, since rotation about σ bonds negligibly affects the orbital overlap within the π-bonding network. In the non-conjugated dimer, where the iSF occurs with a time constant > 10 ns, comparable to the fluorescence lifetime, we used electron spin resonance spectroscopy to unequivocally establish the formation of triplet-triplet multiexcitons and uncoupled triplet exciton through singlet fission. Together, these studies enable us to articulate the role of the conjugation motif in iSF.

Introduction: Understanding the fundamental dynamics of singlet fission (SF) chromophores with idealized properties for next-generation optoelectronic devices fuels the development of families of new materials.[1-6] This includes the important discovery of intramolecular singlet fission polymers and oligomers, where chromophore-chromophore interactions occur primarily through covalent bonds.[7-23] Several different bonding connectivity schemes have been demonstrated to activate singlet fission, where the triplet generation and decay kinetics have been shown to be highly sensitive to the manner in which neighboring chromophores are linked. The interaction of chromophores in iSF compounds differs significantly from the through-space interactions primarily found in molecular crystals, where the through-space coupling between the chromophore coupling is greatly influenced by the morphology.[24-26,28-30] For instance, multiexponential singlet fission rates are observed in disordered systems when compared to monoexponentional kinetics in iSF systems.[31,32]

Given the sensitivity of SF to structure, it remains unclear how through-bond interactions promote fast and efficient singlet fission, especially focusing on the most basic pentacene dimer model. To date, several groups have reported that connecting two pentacenes using conjugated bridges can be used to promote effi-

cient singlet fission, even when the proximity between the pentacenes is significantly decreased.[9,10,13,14] For example, when the bridge shown in Figure 1 is varied from one to three phenylene units, we have found that the rates of singlet fission and triplet pair recombination in pentacene dimers are drastically affected. The longer the conjugated bridge, the slower the rate of iSF and triplet pair recombination.[11] Similarly, Zirzlmeier et al. reported pentacene dimers that were connected through 6-position by *o-*, *m-*, *p-*diethynylbenzene spacers, which revealed that through-space and through-bond interactions play crucial role in singlet fission and triplet recombination dynamics. They also found that faster singlet fission was accompanied by faster triplet recombination.[9] Further, orthogonally connected dimers reported by Lukman et al. resulted in ultrafast singlet fission and were particularly sensitive to the polarity of the medium.[12,33] Recently, Liu et al. designed tetracene trimer through linear oligomerization which resulted in greatly enhanced iSF yield (96%) relative to a similar dimer. This SF enhancement was attributed to singlet exciton delocalization.[34] These studies all suggest that conjugation plays a significant role in driving singlet fission and triplet recombination. Such conclusion is further supported by the fact that singlet fission is slower in twisted dimers that lack bridging units, where conjugation is decreased due to reduced overlap of the pi orbitals.[35]
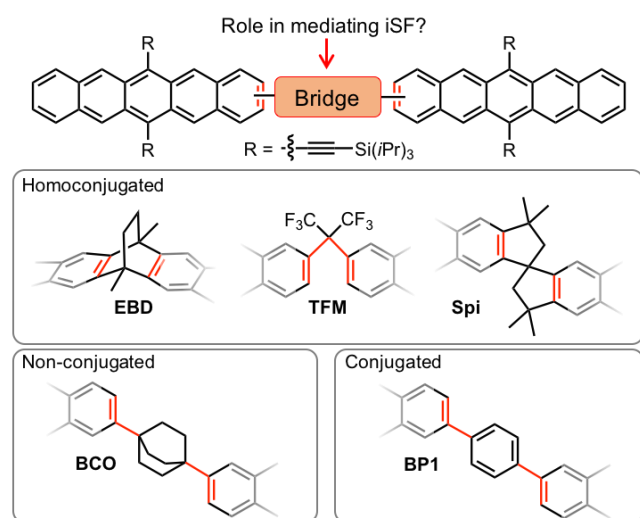
Figure 1. The pentacene-bridge-pentacene model showing the comparison between different bridging units. In the bottom representations, the pentacenes are omitted to highlight the nature of the bridging units.

Interestingly, many of aforementioned studies offer hints that conjugation may not be strictly necessary for singlet fission in pentacene-bridge-pentacene chromophores. A recent computational study suggests that singlet fission occurs by a direct mechanism in bipentacene, in contrast to the charge transfer mediated (stepwise) mechanism widely perceived to be dominant in intermolecular singlet fission of crystalline pentacene.[35] One of the key predictions from this study was that very weak chromophore-chromophore coupling could permit ultrafast singlet fission. The process is viable through an avoided crossing, when resonance between the singlet exciton and triplet pair states is reached through a vibrational mode. However, the ultimate limits of this hypothesis have not yet been tested, i.e., it is unknown what happens in the excited state when both through-space and through-bond interactions are extremely weak.

In this manuscript, we investigate how homoconjugated and non-conjugated bridging units affect the excited state dynamics of pentacene dimers. We particularly focus on understating how singlet fission and triplet pair recombination behave in the limit of weakly coupled pentacene dimers (Figure 1). In homoconjugated dimers, the two pentacene chromophores are separated by a saturated sp^3 carbon, thus the pentacene-pentacene coupling and/or electron delocalization is expected to be weaker than in conjugated systems (such as **BP1**, Figure 1).[11] We postulate that this π-sigma-π bonding scheme will make the excited state dynamics much less sensitive to subtle variations in the geometry of the bridge as compared to analogous conjugated dimers.[36] Additionally, these systems are suited to introduce more than one sp^3 carbon in the bridge to yield non-conjugated dimers, thus allowing us to probe the limits of weak coupling interactions.

Results and Discussion:

Materials Design: The chromophores shown in Figure 1 were designed as follows: In both the ethanobenzo[*b*]decacence derivative (**EBD**)[20-22] and the spirobi[cyclopenta[*b*]pentacene] derivative (**Spi**) the pentacenes are locked in a rigid fashion. The pentacenes in **EBD** are more planar than in **Spi**, where the two chromophores are nearly orthogonal to each other. In the bistrifluoromethyl derivative (**TFM**), the two pentacene units are connected by single saturated carbon, giving the pentacenes some freedom to rotate relative to one another. Finally, we use a bicyclooctane spacer (**BCO**) to mimic the distance imposed by the conjugated phenylene spacer in **BP1**, which has been previously reported.[11] Complete details of their synthesis and characterization are given in the supporting information.

Steady-State Optical Properties.

The UV-visible absorption spectra of the dimers are shown in Figure 2, and are plotted alongside the spectrum of TIPS-pentacene for comparison. In all cases the dimer spectra are qualitatively similar to the monomer spectra, allowing us to assign dimer transitions from the known spectrum of pentacene.[37] The absorption around 650 nm corresponds to an intra-monomer HOMO to LUMO excitation polarized along the short-axis of the monomer, and is slightly red-shifted in **Spi** (by ~12 nm), possibly due to a small interaction between pi systems of the monomers.

The intense absorption in the UV around 310 nm corresponds to a long-axis polarized transition and the weak absorption around 440 nm to an almost-forbidden

long-axis transition. Both the 650 nm and 440 nm transitions are accompanied by vibrational stretching progressions commonly seen in acene spectra. Some dimers exhibit a splitting of the 310 nm absorption, whereby the dipole moments along the long-axis of each monomer can combine in-phase or out-of-phase, giving two distinct absorptions. This is clearest when the long-axes of the monomers are approximately 90° apart (as for **Spi**) and absent if the long-axes are in the same (as for **BP1**). The redshift in the high-energy features in **BP1** is potentially due to greater interactions between the chromophores through a conjugated linker.

Although changes in the absorption spectrum (where present) can indicate the extent of chromophore interaction, the inter-chromophore coupling responsible for SF is not available from UV-vis spectra, since the relevant CT and TT states (or adiabatic states with that character, see SI) are generally dark and the UV-vis spectrum probes the adiabatic electronic states, not localized/diabatic states from whose coupling SF rates can be determined.[35,38]
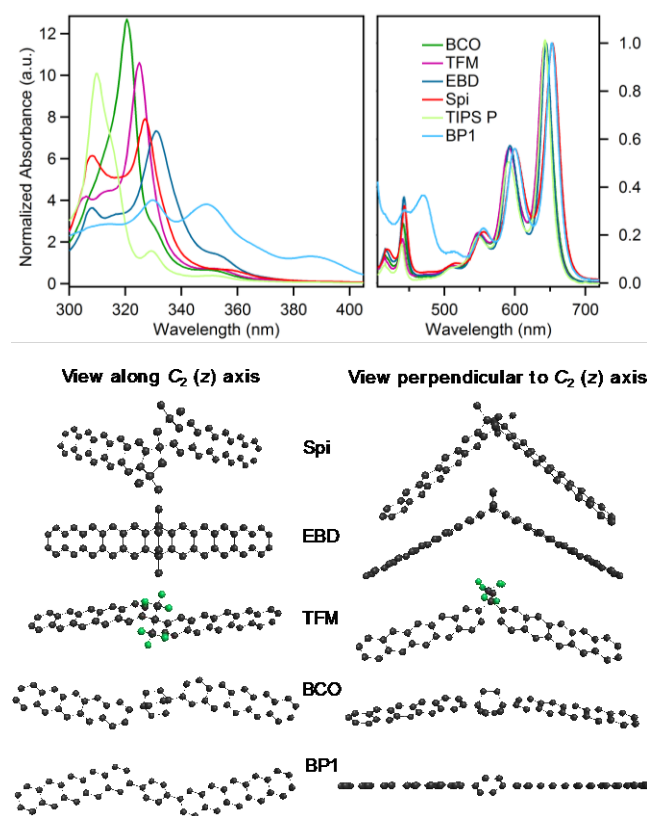

Figure 2. Top: UV-Visible absorption spectra with TIPS-pentacene and **BP1** included for reference. **Bottom:** Calcu-

lated structures using density functional theory. Hydrogens and TIPS substituents at the 6,13-position of pentacene are omitted for clarity.

Singlet Fission in Homoconjugated Dimers.

We use broadband transient absorption spectroscopy (TAS) to study the excited state dynamics of these molecules in dilute solution. The measurements are carried out in a standard nearly collinear transmission geometry. A 100 fs pump pulse is tuned to excite a vibronic feature associated with the lowest energy optical transition (~ 600 nm) and a supercontinuum white light was used as probe (additional details in the SI). Both femto- (mechanical delay) and nanosecond (electronic delay) broadband probes are employed in conjunction with this same pump pulse to extend the dynamic range of measurement from 100 fs – 100 μs. Figure 3 shows the resulting 2D color plots produced by photoexcitation of the pentacene dimers with a fluence of ~25 μJ/cm² in chloroform.

We find that efficient singlet fission occurs in all of the homoconjugated pentacene dimers (**EBD, TFM, Spi**). Moreover, despite the significantly different geometries, singlet fission rates are quite similar among the homoconjugated dimers as **EBD**, **TFM** and **Spi** undergo iSF with time constants of 10 ps, 50 ps and 55 ps, respectively. Singlet fission is assigned following the widely accepted criteria.[7,9-12,14,19,23,33-35,39-43] Briefly, the singlet decay is assigned by correlating the time constants associated with the decay of prompt fluorescence (using photoluminescence upconversion techniques, SI) to features in the transient absorption spectra. From this, we determine that the photoexcited singlet exciton is associated with photoinduced absorption bands near ~460 nm and 520 nm, and find that the singlet decays on <100 ps timescales.
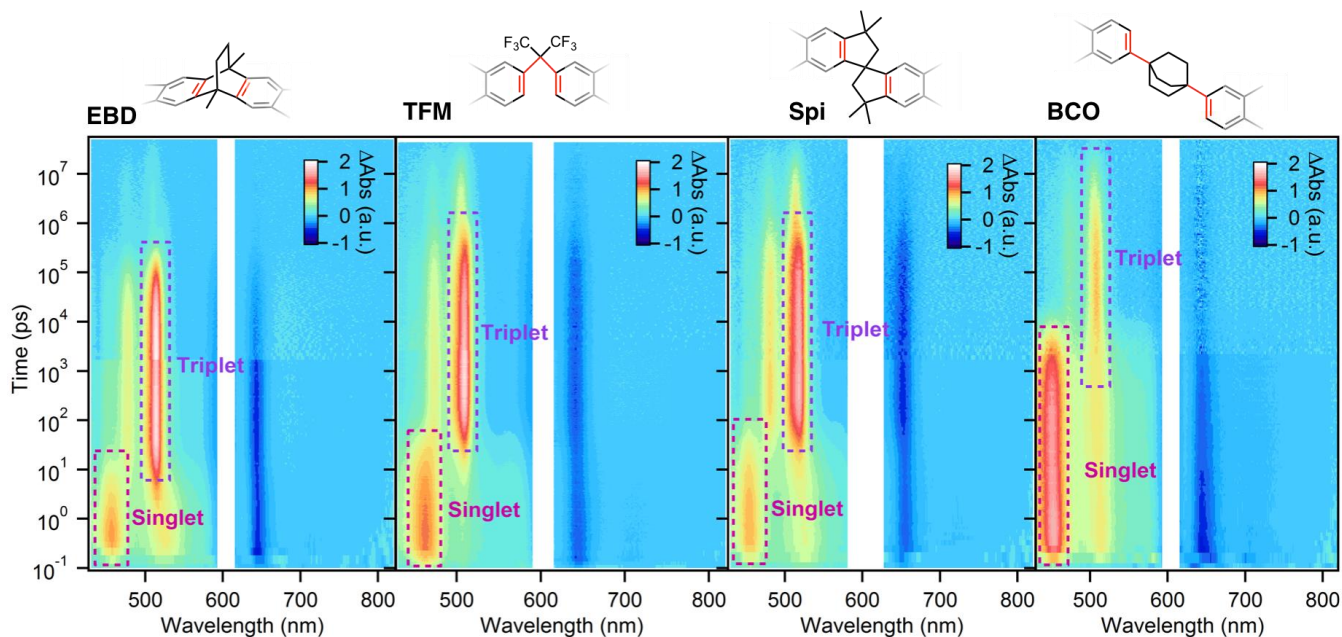
Figure 3. Transient absorption spectroscopy in dilute chloroform solution with 600 nm excitation (~25 μJ/cm²) reveals evolution of the photoexcited singlet into triplets with singlet fission and triplet pair recombination rates that depend strongly dependent on the properties of the bridge. In the structures of the bridges, red color indicates the connectivity of pentacene units, and the color scales have been normalized to facilitate comparison and are therefore reported in arbitrary units (a.u.). Data prior to ~2.7 ns is collected using a mechanical delay, while the same pump pulse and an electronically controlled probe were used to generate data after ~2.7 ns.

The triplet pair state also shows similar dynamics within the set of homoconjugated dimers and is assigned by comparing the products of singlet fission to triplet sensitization studies (SI). From this comparison, we find that the primary triplet feature in the transient absorption spectra is a prominent photoinduced absorption near ~510 nm. This feature can be used to monitor the triplet decay dynamics. Similar to other dimer systems, we find that the rise of the triplet pair is concomitant to the decay of the singlet, indicating that no parasitic processes or other intermediates are present, as has been widely suggested in the literature.[10-12,14,16,44] This allows us to quantify the yields using kinetic arguments, since the only significant competing relaxation process is a 12.3 ns radiative decay. Using these arguments, we calculate that the singlet fission yields exceed 198%. As will be discussed later, using electron spin resonance measurements, we also show that the triplet pairs that are formed from singlet fission remain spin coupled across the homoconjugated bridge. Similar to other dimers with long lived triplet pairs, this leads to a biexponential recombination process, with a dominant short lifetime component (< 1 μs) in ESR and TA representing the spin coupled state and a weaker component with a time constant of ~20 μs lifetime that is assigned to a minority species of free pentacene triplets formed *via* dissociation of the triplet pair. For **EBD**, **TFM** and **Spi** the spin coupled triplet pair lifetimes are extremely long, 174 ns, 531 ns, and 705 ns, respectively.

Akin to conjugated pentacene dimers, we suggest that iSF proceeds through a direct mechanism in homoconjugated dimers, without significant mediation from charge transfer (CT) states. This is based on the follow-

ing evidence: (i) the prohibitively high-lying energy of CT states with large center-center distances which we calculate using electronic structure theory methods, (see SI for details) compared to molecular crystals, where additional electronic bandwidth also help to bring singlet exciton and CT states into resonance (ii) the discovery of a viable direct mechanism based on vibrationally induced degeneracy between S_1 and TT, despite weak coupling,[35] and (iii) a weak and non-monotonic dependence of SF rates on solvent polarity or polarizability (SI).[11,35,41,45]

Here, the effect of changing the conjugation motif is highlighted by comparison to a previously reported conjugated dimer (**BP1**, Figure 4, Table 1). **BP1**, which constitutes two pentacenes connected by a *p*-phenylene bridge (Figure 1), is the conjugated dimer with the closest singlet fission time constant (20 ps) to the homoconjugated dimers investigated here.[11] From inspection, we clearly see that the electronic coupling between the chromophores is significantly affected by through-bond interactions; singlet fission in **BP1**, where pentacenes are connected through four sp^2 hybridized carbons, has a time constant similar to homoconjugated dimers, where pentacene chromophores are separated by just one sp^3 hybridized carbon.

Despite the faster time constants for triplet pair generation as compared to conjugated **BP1**, triplet pair recombination is > 10 times slower in **EBD**. Similarly, while singlet fission is slower by a factor of approximately 2.5, the triplet pair recombination is slower by a factor of > 30 in **TFM** and > 40 in **Spi**. These results indicate that singlet fission and triplet pair recombination are not governed by the exact same pentacene-pentacene

coupling relationship. This is an important observation because breaking the relationship between the rate of triplet generation (fast singlet fission) and decay rates (slow recombination) can play a fundamental role in optoelectronic devices, where maximizing the overall triplet pair lifetime is beneficial for harvesting that energy. While it has been observed in twisted dimers that reducing the coupling between pentacene chromophores preferentially extends the triplet pair lifetime,[35] this is the first family of materials with fast rates of iSF, and drastically different rates of triplet pair recombination. While it is worth noting that solid-state dynamics are relevant to devices, solution studies isolate through-bond singlet fission. In the solid-state, through-bond singlet fission can be complemented by through-space singlet fission, adding an additional SF channel. Though it must be noted that characterization of the through-bond SF in solution is informative to the properties of the new materials and their potential utility.

Table 1: Time constants for: rate of iSF (τ_{iSF}), triplet pair lifetimes ($\tau_{[TT]}$), and individual triplet decay ($\tau_{[T]}$, obtained from slower triplet decay component).

Compound	τ_{iSF} (ps)	$\tau_{(TT)}$ (ns)	$\tau_{(T)}$ (ns)
BP1[11]	20	16.5	---
EBD	10	174	24,300
TFM	50	531	23,000
Spi	55	705	19,600
BCO	~20,000	1,800	18,000
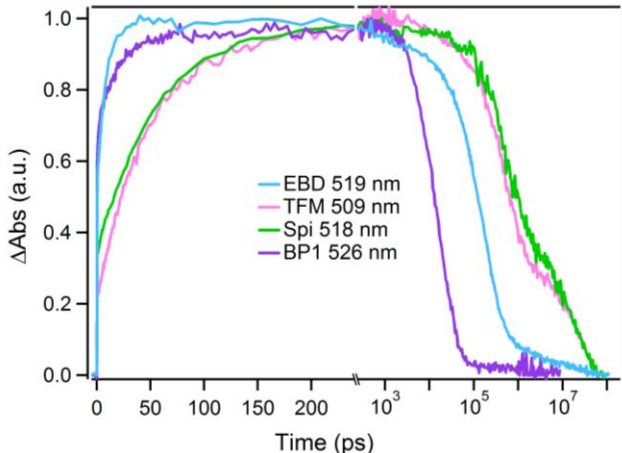
Figure 4. Normalized kinetics monitored at the maximum of the triplet photoinduced absorption of **TFM**, **EBD**, **Spi**, and **BCO** as dilute solutions in chloroform following 600 nm excitation (~25 μJ/cm²).

Singlet Fission in a Non-Conjugated Dimer.

Surprisingly, we find that **BCO**, a non-conjugated pentacene dimer separated by 4 sp^3 hybridized carbons, is capable of singlet fission (Figure 3). A similar methodology to other dimers was used to identify singlet fission

and assign the relevant rate constants. It is remarkable that singlet fission can proceed even in the limit of extremely weak electronic coupling, as evidenced by the long singlet lifetime (7.6 ns). Despite the similar interchromophore separation as conjugated **BP1**, the rate constant for singlet fission in **BCO** slower by a factor of nearly 1000. Again, this allows us to deduce the important role of conjugation in facilitating fast and efficient singlet fission.

Identification of Triplet-Triplet Pairs.

We establish that singlet fission is operative, producing triplet pairs as opposed to free triplet generation by intersystem crossing, by correlating transient absorption and electron spin resonance studies (Figure 5). Like other iSF dimers, transient absorption studies show that the triplet population decays biexponentially, indicating the presence of triplet pairs (TT) with an enhanced recombination rate (Figure 6) and a minority population of free triplets decay with the expected rate for an individual triplet. These biexponential decay dynamics have also been observed in other systems[11,14,39,40] and do not change as a function of concentration or other experimental parameters.

The biexponential dynamics in the TA experiments were further probed by transient electronic spin resonance (tr-ESR) measurements. tr-ESR spectroscopy has previously been used to identify coupled triplet-triplet pairs, (TT), and uncoupled triplets, T, in bipentacenes.[39] Figure 5 shows the 80K pulsed laser, continuous microwave tr-ESR spectra of **Spi** and **BCO** in toluene, using microwave frequencies of 9.681092 and 9.615778 GHz, respectively (additional details in the SI). The spectra are plotted as a function of g-factor to highlight the identical location of resonances, which arise from the g-factor and zero-field splitting parameters of individual pentacene triplets (g~2.0023, D~1100MHz and E~20MHz, in accordance with previous ESR studies of the pentacene chromophore[39,46,47]). Transition resonance peaks for magnetic fields applied along the x/y molecular axes are marked on the plot.

In both **Spi** and **BCO** the $^5(TT)_0$ quintet state is generated faster than the time resolution of the experiment. The absorptive/emissive resonances for the $^5(TT)_0 \rightarrow {}^5(TT)_\pm$ transitions are separated by (D-3E)/3, as is expected for strongly coupled triplets (J>D,E). After several hundred nanoseconds uncoupled triplets are generated, probably via a geometric relaxation that reduces the inter-triplet exchange coupling, J. This gives rise to absorptive/emissive $T_0 \rightarrow T_\pm$ transitions separated by D-3E. The absorption/emission structure is indicative of the selective population of T_0, as is expected for triplets generated by fission.[48]

We confirm the assigned spin multiplicities using pulsed laser, pulsed microwave measurements (additional details in the SI) of the $^5(TT)_0 \rightarrow {}^5(TT)_+$ and $T_0 \rightarrow T_+$ transitions, which yielded a Rabi nutation frequency ratio of 1.64±0.05, in agreement with the expected value

of $\sqrt{3}=1.73$ for strongly coupled triplet pairs.[39,49] The strong coupling regime in ESR measurements of these materials refers to exchange energies that are only $\gtrsim 20$ GHz. It is likely that the triplet-triplet pair coupling in **BCO** is actually weak on an electronic energy scale and this gives rise to the relatively large values of τ_{iSF} and $\tau_{(TT)}$.
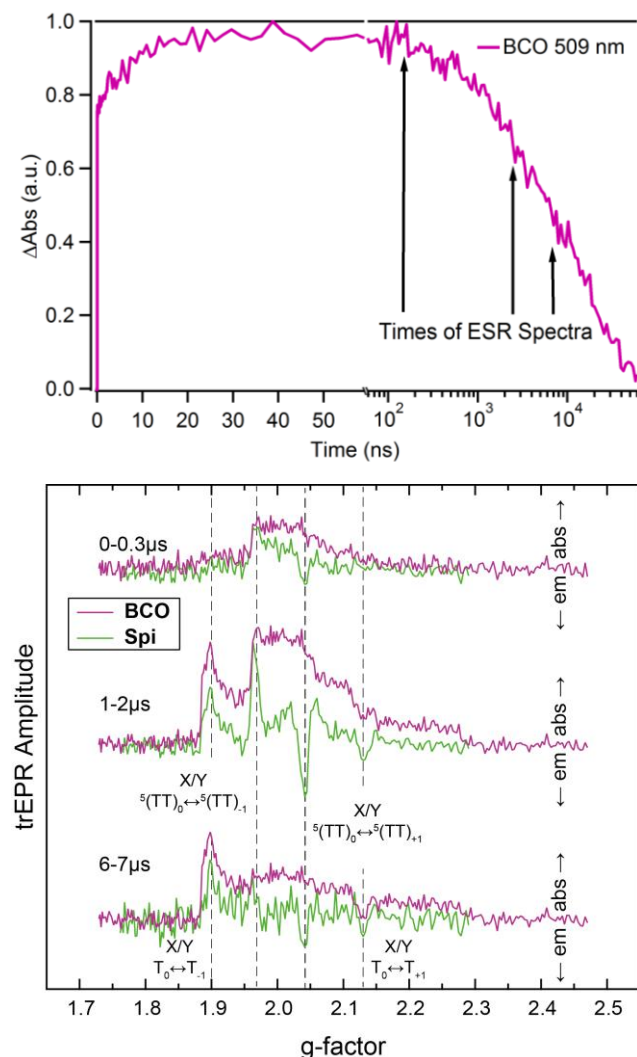
Figure 5: **Top:** Transient absorption kinetics near the triplet absorption maximum, with arrows indicating times selected for ESR spectra. **Bottom:** Transient ESR spectra of **Spi** and **BCO** in toluene at given time delays after laser excitation at 599 nm, ~70 μJ/pulse. Dashed lines mark locations of $(TT)_0$ and T_0 transition resonances.

These measurements allow us to confirm that no other parasitic decay channels besides radiative recombination are present in these dimers. Unlike in homoconjugated dimers, where the yield is nearly quantitative, radiative recombination in **BCO** is a significant loss channel. We estimate the singlet fission yield to be ~76% based on kinetic competition of SF with the typical ~12.3 ns radiative lifetime of TIPS-pentacene.[50] Importantly, the similarity between the triplet pair and free triplet transient spectra allows us to directly determined the SF yield using triplet sensitizations methods.[11] Indeed, a cross-sectional yield determination, where we compare the triplet signal at a given fluence to that produced by transfer of a known number of triplets from an external, well-characterized sensitizer, finds a yield of 63% (Supporting Information). If any other parasitic decay processes were occurring, the sensitization methods would yield a significantly lower value for the singlet fission yield. This compound shows that fully incoherent singlet fission can occur even in the limit of extremely weak electronic coupling, as long as the excited state lifetimes permit reasonable kinetic competition with ground state repopulation.

Conclusions: Through the evaluation of a family of materials, we have found that the conjugation motif of the interpentacene bridge is instrumental in mediating singlet fission in pentacene dimers. The concept of intrachromophore coupling interactions in pi-bridge-pi molecules was tested using homoconjugated and non-conjugated bridging moieties. In these systems, homoconjugated bridges can yield singlet fission rates that are faster than a conjugated bridge, while maintaining slower triplet pair recombination. We also found that SF can occur in the case of a non-conjugated bridge, although the process is much slower than SF in a similar sized conjugated bridge. We further characterized the formation of triplet pairs through singlet fission using ESR measurements. This study demonstrates the importance of the bridge design in such compounds and emphasizes that bridge effects must be play a key role in understanding SF and triplet pair recombination.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental methods, including details of the transient absorption spectroscopy and photosensitization experiments, synthetic details, electron spin resonance experiments and characterization of compounds used in this study.

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