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# Singlet fission in a flexible bichromophore with structural and dynamic control

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#### Abstract

Singlet fission (SF), i.e., the splitting of a highenergy exciton into two lower-energy triplet excitons, has the potential to increase the efficiency for harvesting spectrally broad light. The path from the photo-populated singlet state to free triplets is complicated by competing processes that decrease the overall SF efficiency. An in-detail understanding of the whole cascade as well as the nature of the photoexcited singlet state are still major challenges. Here, we introduce a pentacene dimer with a flexible crownether spacer enabling a control of the interchromophore coupling upon solvent induced self-aggregation as well as cation binding. The systematic change of solvent polarity and viscosity, excitation wavelength as well as available conformational phase space allows us to draw a coherent picture of the whole SF cascade from the fs to us timescales. High coupling leads to ultrafast SF ( $<2\,\mathrm{ps}$ ), independent of the solvent polarity, and to highly coupled correlated triplet pairs. The absence of a polarity effect indicates that the solvent coordinate does not play a significant role and that SF is driven by intramolecular modes. Low coupling results in much slower SF ( $\sim 500 \,\mathrm{ps}$ ), that depends on viscosity, and leads to weakly coupled correlated triplets pairs. These two triplet pairs

could be spectrally distinguished and their contribution to the overall SF efficiency, i.e., to the population of free triplets, could be determined. Our results reveal how the overall SF efficiency can be increased by conformational restrictions and control of the structural fluctuation dynamics.

#### Introduction

Singlet fission (SF), i.e., the splitting of a singlet exciton into two triplet excitons,<sup>1,2</sup> offers promising perspectives to overcome the intrinsic efficiency cap for converting spectrally broad light into electricity,<sup>3</sup> by limiting the thermal losses.<sup>4</sup> The climate crisis and the need for efficient solar energy harvesting have stimulated a spectacular revival of interest for this process, that was first reported in 1965.<sup>5</sup> Studies on crystalline solids,<sup>6–12</sup> polymers<sup>13–16</sup> and molecular dimers<sup>17–28</sup> resulted in an overall picture of SF that can be described as a three step process:<sup>29–32</sup>

$$S_1S_0 \rightleftharpoons [^m(TT) \rightleftharpoons {}^m(T \cdots T)] \rightleftharpoons T_1 + T_1$$
(1)

A key factor for efficient and rapid SF is the conservation of angular momentum during the transition from the photo-populated singlet excited state,  $S_1S_0$ , to the spin-correlated triplet pair <sup>1</sup>(TT) with an overall singlet character. The latter can evolve to <sup>1</sup>(T···T) by spatial separation and thus a decrease of electronic coupling and exchange interaction. Since electronic coupling varies continuously, <sup>1</sup>(TT) and <sup>1</sup>(T···T) should be considered as limiting cases and are often merged into a single species, TT.<sup>30,32,33</sup> However, different spectral features and dynamics justify the distinction between these two triplet pairs.<sup>30,32</sup>

These pairs can undergo spin conversion or dephasing to the uncorrelated free triplet pair,  $T_1+T_1$ , depending on the exchange interaction and, thus, on the energy spacing between the <sup>1,3,5</sup>(TT) states.<sup>34–37</sup> However, the dynamics towards  $T_1+T_1$  are complicated by the existence of various competing channels that are detrimental to the overall SF efficiency. Depending on the spin character of the correlated triplet pair, two spin-allowed decay channels can be operative:<sup>1,38</sup>

 $^{1}(TT) \rightarrow S_{0}S_{0}$  Singlet channel: loss of  $\leq 100\%$  of T signal  $^{3}(TT) \rightarrow T_{1}S_{0}$  Triplet channel: loss of  $\leq 50\%$  of T signal (2)

To unravel these complex mechanistic aspects, it is advantageous to consider the simplest multichromophoric material, a covalently bound dimer.<sup>26</sup> Such dimers simplify the study of SF by eliminating the possibility of energy transfer to nearby chromophores and allows for a systematic variation of the interchromophore geometry and solvent environment. Pentacenebased dimers are probably the most studied SF systems for which the interchromophore distance has been systematically tuned over a wide range.<sup>17,20–23,36,39–43</sup> These investigations revealed a fast appearance of triplet spectral features in strongly coupled pentacene dimers, followed by a decay on a ps-ns timescale, i.e. much faster than expected for a  $T_1$  state.<sup>17,26,39</sup> In contrast, the build up of the triplet features in weakly coupled dimers was found to be slower and their decay bimodal, with the slowest component matching the decay of the  $T_1$ state measured in sensitization studies.<sup>21,22,39</sup> Time-resolved electron-spin resonance experiments evidenced a strong influence of the coupling on the spin conversion dynamics of the correlated triplet pairs.<sup>36</sup> Two distinct assignments of the slow component of the bimodal triplet decay were proposed: (i) the decay of the "lone triplet"  $T_1S_0$ ;<sup>36</sup> or the decay of free triplet pairs  $T_1+T_1$ .<sup>20-23,39-44</sup> These two interpretations presuppose significantly different SF mechanisms.



Scheme 1: Preparation and structures of **Ref** and **18C6**. i) acetyl chloride,  $Et_3N$  in  $CH_2Cl_2$ ; ii) macrocycle **9** (see SI), <sup>t</sup>BuOK in THF. See SI for full synthetic details.

Here we focus on three important aspects of the SF cascade: i) the effect of the coupling between the chromophores on the nature of the photo-populated  $S_1S_0$  state and its dynamics; ii) the contributions of solvent and intramolecular modes to the SF coordinate; and iii) the origin of the bimodal triplet For this, we synthesized a bichrodecay. mophore, named 18C6, consisting of two TIPSpentacene subunits linked via amide bridges to a crownether (Scheme 1); its preparation involves a straightforward synthetic protocol with simple starting materials (stable diazo reagents, 1.4-dioxane) and high concentration conditions for the macrocyclization and amide formation steps (see SI for full preparation details).<sup>45–48</sup> As will be shown, the interchromophore distance can be controlled by the solvent as well

as by the addition of  $Ba^{2+}$  to form a hostguest complex with the macrocycle. In contrast to stiff backbones, the geometrical flexibility of the crownether allows for structural fluctuations, which can decrease the exchange interaction and allow for spin conversion. This comes however at the cost of multiple structural sub-populations. To unravel the complicated excited-state dynamics, we performed a systematic comparative study involving: (i) excitation wavelength  $(\lambda_{ex})$  dependence allowing for the photo-selection of different sub-populations; (ii) solvent viscosity  $(\eta)$  dependence revealing the impact of structural fluctuations; (iii) change of the conformational phase space by solvent dependent interchromophore aggregation and  $Ba^{2+}$  binding. This spectroscopic study is complemented by molecular dynamics (MD) simulations to estimate the structure of the various sub-populations present under different experimental conditions.

#### Results

#### Structural control

Solvent-dependent aggregation. The absorption spectra change significantly upon going from the reference monomer **Ref** to **18C6** (Figure 1A, see SI section 2.3 for the photophysics of **Ref**). These changes, which report on the coupling between the chromophores, depend markedly on the solvent. In HEX and ACN, the absorption spectrum of 18C6 is broader and red shifted, while the intensity ratio between the 0-0 and first vibronic bands,  $I_{0-0}/I_{0-1}$ , is smaller. By contrast, in the medium polar tetrahydrofuran (THF), the position, width and  $I_{0-0}/I_{0-1}$  are nearly the same for 18C6 and Ref. The differences observed in HEX and ACN point to a close proximity of the pentacene subunits in these solvents and to an arrangement consistent with the spectral signature of a H-type dimer.<sup>49–52</sup> In THF, the similarity between the monomer and the dimer spectra suggests a weak interchromophore coupling as well as a negligible impact of the crownether on the  $S_1 \leftarrow S_0$  transition. These spectral changes in HEX and ACN and not in THF can be assigned to self-aggregation. Indeed, the propensity of aromatic molecules to aggregate has been shown to be the weakest in medium polar solvents and the strongest in high and low polarity solvents as it depends on the interplay between chromophore-solvent and chromophore-chromophore interactions.  $^{53-56}$  Since SF involving charge-transfer interactions has been reported to be sensitive to solvent polarity,  $^{43}$  this non-linear dependence of aggregation on the solvent polarity allows structural effects to be disentangled from mechanistic effects.

Insight into the conformational space available to **18C6** in a given solvent was obtained from the potentials of mean force (PMFs) between the two pentacene subunits, w(r), determined by MD simulations. These PMFs, illustrated in Figure 1B, reflect the free energy of **18C6** as a function of the center-of-mass distance between the two chromophores, r. They reveal that many interconverting conformations coexist at room temperature. These structures cannot be all differentiated from their absorption spectrum, as a sufficiently large coupling is needed to result in detectable spectral changes. Quantum-mechanical calculations on perylene predict that the absorption spectrum departs from that of the monomer at center-to-center distance  $r \lesssim 0.7$  nm.<sup>57</sup> We can thus assume that the stationary absorption spectra can only distinguish strongly coupled dimers, whose spectrum differ significantly from that of **Ref**, from weakly coupled dimers, which comprise all conformers with  $r \gtrsim 0.7 \,\mathrm{nm}$ . Therefore, red-edge illumination in HEX and ACN should predominantly excite strongly coupled dimers, whereas irradiation at shorter wavelength should not allow any photo-selection.

Figure 1C illustrates a few representative snapshots from the MD simulations. According to the PMFs, the strongly coupled dimers should have a structure similar to that of the r = 0.38 nm conformer. The local minimum associated with this conformer is deepest in ACN, intermediate in HEX and least favourable in THF. The PMFs therefore suggests that the relative population of strongly coupled conformers



Figure 1: (A) Comparison of the absorption and emission spectra of the reference monomer **Ref** (blue) and **18C6** (red) in the low, intermediate and high polarity solvents, n-hexane (HEX), tetrahydrofurane (THF) and acetonitrile (ACN), respectively. The formation of **18C6** $\subset$ **Ba**<sup>2+</sup> (green) upon addition of Ba(ClO<sub>4</sub>)<sub>2</sub> in ACN can be followed by changes in the absorption and emission spectra. (B) Potentials of mean force (PMFs) describing the free energy as a function of the interchromophore centre of mass distance. The free energy of the absolute minimum of each PMF is arbitrarily set to 0. (C) Representative snapshots from molecular dynamics simulation at local minima of the PMFs. The TIPS groups are transparent for the sake of clarity.

decreases from ACN to HEX and THF. We will show later that results are fully consistent with the TA spectra in different solvents. In THF, **18C6** is predicted to exist mainly with the pentacene subunits at  $r \sim 1$  nm and separated by solvent molecules. Such weak coupling agrees well with the stationary absorption spectrum.

Additional information on the interchromophore coupling was obtained from the effective transition dipole moment,  $|\vec{\mu}_{abs}|$ , associated with the lowest energy absorption band. In the case of **Ref**,  $|\vec{\mu}_{abs}|$  is the same in all three solvents (see SI section 2.5.5), whereas for **18C6**, it is significantly smaller in ACN and HEX. This suggests that the nature of the excited state of **18C6** is different in THF, where weakly coupled dimers predominate, than in ACN and HEX, where strongly coupled dimers are present. Such a decrease of  $|\vec{\mu}_{abs}|$  upon self-aggregation cannot be described by only

considering the two local excited states,  $|LE\rangle$ , and their dipole-dipole interactions as in the Kasha excitonic model.<sup>58</sup> The decreased  $|\vec{\mu}_{abs}|$ is attributed to the contribution of dark excited states such as the charge transfer states,  $|CT\rangle$ , and/or the correlated triplet pair states,  $|TT\rangle$ , to the wavefunction of the photo-populated state of strongly coupled conformers. We will use the nomenclature applied by Scholes and coworkers for amorphous nanoparticle suspensions, and designate the strongly coupled, Haggregate-like conformers as H-dimers and the weakly coupled, monomer-like conformers as M-dimers.<sup>30</sup> By analogy, their first singlet excited state will be designated as  $(S_1S_0)_H$  and  $(S_1S_0)_M$ , respectively.  $(S_1S_0)_H$  consists of multiple states depending on the nature of the excitonic coupling, whereas  $(S_1S_0)_M$  is doubly degenerate.

The emission spectra of 18C6 and Ref are

almost identical, suggesting that the fluorescence of **18C6** originates from the M-dimers and that, if an excimer is formed, its lifetime is too short and/or its radiative rate constant too small to contribute to the fluorescence spectrum. Contrary to **Ref**, the fluorescence decay of **18C6** measured by time correlated single photon counting is multiexponential in all solvents, in agreement with the presence of various sub-populations with different interchromophore coupling (Figure S9).

Host-Guest Complex. In order to change the conformational phase space even more drastically, we exploited the tendency of the unsaturated crownether to strongly bind divalent cations. As illustrated in Figure 1A, the formation of the  $18C6 \subset Ba^{2+}$  host-guest complex upon addition of  $Ba(ClO_4)_2$  is accompanied by an increase and a blue shift of the absorption band as well as an increase of  $I_{0-0}/I_{0-1}$ . MD simulations suggest that complexation involves the rotation of the amide groups with the oxygen atoms participating in the binding of the cation. As the bound cation can also interact with the solvent, long distance conformers are favoured by a larger solvation energy (Figure 1B,C). As shown previously,<sup>59</sup> the electron donating character of the amide is decreased upon cation binding, explaining the difference between  $18C6 \subset Ba^{2+}$  and Ref. The higher emission intensity upon excitation at the isosbestic points furthermore to a significant increase of the fluorescence quantum yield upon complexation.

#### Singlet-fission dynamics

Now that we have a better idea of the relevant conformations of the bichromophore in the ground state, we focus on their sub-nanosecond excited-state dynamics, dominated by SF, as measured by combined UV-Vis (335-740 nm) and near IR (670-1650 nm) ultrafast transient absorption (TA) spectroscopy.

**Reference monomer.** Excitation of **Ref** in HEX (Figure S4) and ACN (Figure 2A) at 650 nm (0-0 band) leads to the prompt

appearance of excited-state absorption (ESA) features around 470, 550 and 1500 nm, which together with the ground-state bleach (GSB) and the stimulated emission (SE), can be attributed to the population of the  $S_1$  state. In HEX, these bands decay on the ns timescale in agreement with the fluorescence lifetime (Figure S2). Afterwards, a weak ESA band, that can be assigned to the  $T_1$  state, is visible at 500 nm. In ACN, a shift of the ESA and SE bands occurring during the first few ps, absent in HEX, can be attributed to solvent relaxation.<sup>60</sup> The subsequent decay of the  $S_1$  state population is significantly faster than in HEX, due to the smaller  $S_1 \leftarrow S_0$  gap (see SI section (2.3) and, consequently, the  $T_1$  band is not visible. However, the spectrum and lifetime of the  $T_1$  state in ACN could be obtained by triplet energy transfer from naphthalene diimide. The  $T_1$  state is characterised by a prominent band at 498 nm and a lifetime on the us timescale (Figure S6).

18C6 dimer and  $18C6 \subset Ba^{2+}$  in ACN. The TA spectrum recorded with 18C6 in ACN 200 fs after 650 nm excitation resembles that of **Ref**, but is, however, not identical (Figure 2B). During the first two ps, where solvent relaxation is observed with **Ref**, the intensity of the singlet ESA band decays partially and new bands, which can be attributed to the triplet state,<sup>30</sup> appear at 498, 875 and 993 nm. As these triplet ESA features are absent in the early TA spectra of **Ref**, this process is attributed to the population of the overall singlet, correlated triplet pair,  $^{1}(TT)$ , via SF. The intensity of the GSB does not increase during this process, contrary to what could be expected for a transition from a state with one subunit excited,  $(S_1S_0)$ , to a state with two subunits excited,  $^{1}(TT)$ . This can be explained by the large coupling in the Hdimers and by a delocalization of the excitation over both subunits in the  $(S_1S_0)_H$  state. Contrary to the  $T_1$  state of **Ref**, a significant part of the triplet population decays to the ground state on the hundreds of ps timescale, visible as a concurrent decay of the GSB and triplet bands.

SF is considerably slowed down upon increas-

ing the interchromophore distance via cation binding (Figure 2C). The early TA spectra recorded with  $18C6 \subset Ba^{2+}$  in ACN show only the occurrence of solvent relaxation as with **Ref**. SF takes place on the hundreds of ps timescale as indicated by the NIR triplet bands at 875 and 993 nm as well as the visible ESA band which shifts towards 498 nm. Compared to 18C6, not only SF is slower, but also the decay of the triplet pair population is slowed down, as shown by a nearly constant GSB intensity within the 0-2 ns time window of these measurements.



Figure 2: Femtosecond transient absorption spectra measured with **Ref** (A), **18C6** (B), and **18C6\subsetBa<sup>2+</sup>** (C) in ACN upon 650 nm excitation. The inset highlights the wavelength region in the near infrared where triplet absorption can be observed. The stationary absorption and stimulated emission spectra are shown in A to indicate the contribution of ground-state bleach (red) and stimulated emission (blue).

*Excitation-wavelength dependence.* The above results were obtained upon 650 nm excitation, where both H- and M-dimers absorb. TA measurements in ACN were repeated with pump pulses at 675 and 690 nm. A marked

excitation wavelength,  $\lambda_{ex}$ , dependence of the early excited-state dynamics of **18C6** can be observed, as illustrated by the TA spectra recorded at 2 ps (Figure 3A). The contribution of the triplet ESA around 500 nm increases significantly with  $\lambda_{ex}$ , suggesting that SF is faster or more efficient upon red-edge illumination, i.e. upon selective excitation of H-dimers. Because of the presence of many different conformers, each kinetic process cannot be quantified by a single rate constant. As a consequence, global analysis of the TA data with a target model, that would allow obtaining the spectra of the individual species/states involved as well as the rate constants associated with the different transitions,  $^{61,62}$  is not possible. Because of this and the strong overlap of the singlet and triplet ESA bands, the impact of  $\lambda_{ex}$  on the SF dynamics was visualised by looking at the ratio of the intensity-normalized time-profiles around 498 nm (triplet excited state, Figure 3D) and around 535 nm (singlet excited state, Figure 3C)  $R_{\rm T/S} = \Delta A_{\rm T} / \Delta A_{\rm S}$  (Figure 3E). The rise of  $R_{T/S}(t)$  reflects the transition from the photopopulated singlet state,  $(S_1S_0)$ , to the correlated triplet pair,  $^{1}(TT)$ . In the case of **18C6** the rise of  $R_{T/S}(t)$  is a good proxy for the SF dynamics, which is however not generally true and depends on the spectral characteristics of the two transient species (see SI section 2.6).

Increasing the excitation wavelength results in a higher  $R_{T/S}$  already at 2 ps, as shown in Figure 3A and E. Similar wavelength dependence can be observed in HEX, whereas no difference can be detected in THF on this timescale (Figure 3A and E). This result is fully consistent with the co-existence of H- and Mdimers in ACN and HEX, and with the predominance of the latter in THF, as inferred from the stationary absorption spectra and the MD simulations.

Intensity normalization of the  $R_{T/S}(t)$  profiles in ACN reveals that the  $\lambda_{ex}$  dependence observed during the first few ps is not due to different rise times but only to different amplitudes of this rise (Figure S13). This supports our above assumption about two main subpopulations, namely the strongly (H) and the weakly (M) coupled dimers. Therefore, rededge illumination in ACN and HEX increases the probability to excite H-dimers, which undergo fast SF (<2 ps). On the contrary, a higher fraction of M-dimers, with slower SF dynamics ( $\sim 500 \text{ ps}$ ), is excited at shorter wavelength.

SF in H-dimers: role of the solvent and intramolecular modes. The SF dynamics and efficiency in various covalently linked pentacene dimers was reported to be sensitive to the solvent polarity. This was attributed to changes of the relative energies of the  $|\text{LE}\rangle$ and  $|\text{CT}\rangle$  states.<sup>17,19,40,43,63,64</sup> Depending on the molecular system, either a two-step process via a distinct symmetry-broken charge separated (SB-CS) intermediate, <sup>19,63,64</sup> or a onestep SF involving significant  $|\text{CT}\rangle$  admixing to the  $(S_1S_0)_{\text{H}}$  state is invoked.<sup>19,64,65</sup>

Here, the solvent has a strong influence on the conformation of the bichromophore, and hence on the coupling and on SF. In order to disentangle the direct polarity effect of the solvent on the SF dynamics from this indirect conformational effect, we now only consider the H-dimers present in ACN and HEX. Figure S11 reveals that the rise of  $R_{T/S}(t)$  in ACN matches closely the early ESA peak shift at 470 nm measured with **Ref** and assigned to solvent relaxation. This suggests that, in ACN, SF in H-dimens occurs on the same timescale as diffusive solvent motion. However, intensity normalisation of  $R_{T/S}(t)$  in ACN and in HEX shows that, although  $R_{T/S}(t)$  reaches significantly larger values in ACN than in HEX independently of  $\lambda_{ex}$ , the rise dynamics are the same in both solvents. One can thus conclude that the SF dynamics in H-dimers does not depend on the solvent polarity, and that the observed similarity of timescale for polar solvation and SF in ACN is most likely a coincidence. Here, the solvent only determines the probability to excite H-dimers, which is higher in ACN than in HEX. The identical SF dynamics in these solvents indicate that the possible larger admixture of  $|CT\rangle$  state to the photoexcited state in ACN, as suggested by the smaller transition dipole moment, does not play a decisive role in the SF dynamics of these H-dimers. Similarly, SB-CS, triggered by asymmetric solvation of the two chromophores, is not involved. This result is consistent with our recent investigation on a bichromophore similar to **18C6** but with perylene instead of pentacene. We found that SB-CS in strongly coupled dimers is overruled by relaxation along an interchromophore coordinate towards the excimer.<sup>59</sup>

This independence on solvent polarity points to intramolecular modes as the main constituents of the SF coordinate. It has has been suggested that SF in crystalline pentacenes occurs upon relaxation of the photo-populated singlet state towards the excimer. During relaxation, the singlet excited state becomes quasi degenerate with the triplet pair state allowing for a non-adiabatic transition in  $\sim 70$  fs.<sup>66</sup> According to this hypothesis, SF in the 18C6 H-dimers could take place upon structural relaxation of the photo-populated singlet state,  $(S_1S_0)_H$ . The absence of an excimer emission can be explained by SF occurring before this state is significantly populated, the rate limiting step being relaxation rather than the SF step itself.

SF in M-dimers: the role of structural *fluctuations.* In THF,  $R_{T/S}(t)$  does not exhibit the initial  $\sim 2 \,\mathrm{ps}$  rise, in agreement with a predominance of M-dimers in this solvent. Here, SF is not ultrafast, but occurs on the hundreds of ps timescale. The slow rising component of  $R_{T/S}(t)$  is also present, but with a smaller amplitude, in ACN and HEX. It can be associated with 'static' SF in dimers with a correspondingly small coupling and/or with 'dynamic' SF occurring after conformational fluctuations of dimers with an initially smaller coupling. This modulation of the coupling involves relatively large amplitude motion of the pentacenes and can, thus, be expected to depend on the solvent viscosity,  $\eta$ . To confirm this, TA measurements were repeated in dodecane (N10,  $\eta = 0.9 \,\mathrm{cP}$ ) and tetradecane (N14,  $\eta = 2.1 \,\mathrm{cP}$ ). As these longer alkanes have the same polarity as HEX ( $\eta = 0.3 \,\mathrm{cP}$ ), the distribution of populations is expected to be similar, but the interconversion by structural fluctuations slower.

As illustrated in Figure 4,  $R_{T/S}(t)$  at early time is nearly the same in all three alkanes,



Figure 3: Excitation wavelength ( $\lambda_{ex}$ ) dependence of transient absorption (TA) spectra of **18C6** in HEX (top), THF (middle) and ACN (bottom). (A) Comparison of visible TA spectra at 2 ps with the wavelengths used for the time profiles. (B) Near infrared TA spectra at different time delays upon excitation at 675 nm. (C,D) Time profiles of the singlet (S) and triplet (T) features. (E) Ratio of triplet and singlet time profiles,  $R_{T/S}(t)$ , tracking the conversion via SF as well as the decay via the singlet annihilation channel.

pointing to a similar distribution of conformers. The small difference at 2 ps (inset) is most likely due to a shift of the absorption band associated with a variation of the refractive index and leading to the photo-selection of slightly different sub-populations (Figure S8). Normalisation of  $R_{T/S}(t)$  shows that the fast rising component is insensitive to  $\eta$  (Figure S14). Consequently, SF in H-dimers is not only independent of polarity, but also of viscosity. If the structural relaxation towards the excimer invoked above is the rate limiting step, it does not involve large amplitude motion.

The slower rising component of  $R_{T/S}(t)$  associated with SF in M-dimers, slows down further upon increasing  $\eta$ . One can thus conclude that SF on this timescale occurs upon large-amplitude structural fluctuations towards sufficiently coupled conformations. The  $\lambda_{ex}$  dependence of  $R_{T/S}(t)$  in THF is absent at early times but becomes visible on the timescale at which the viscosity dependence appears. This suggests that although no H-dimers are present in THF, some photo-selection is still possible with the less coupled dimers.

To sum up, SF in **18C6** can be discussed in terms of two sub-populations, strongly coupled H-dimers and weakly coupled M-dimers. The fraction of these sub-populations probed in TA depends on  $\lambda_{ex}$  as well as on the solvent. Excitation of the H-dimers to the delocalised  $(S_1S_0)_H$  state leads to ultrafast SF  $(<2\,\mathrm{ps})$  driven by non-diffusive structural motion. In M-dimers, excitation is rather localized on one chromophore and sampling of the conformational phase space is required to achieve appropriate coupling. For the  $18C6 \subset Ba^{2+}$  complex, close contact between the pentacene subunits is energetically unfavourable and only the  $(S_1S_0)_M$  state is photo-populated, resulting in slow SF ( $\sim 500 \, \mathrm{ps}$ ).

## Nature and dynamics of the triplet pairs

#### Different types of triplet pairs and triplet annihilation via the singlet channel.

The NIR triplet band at 993 nm measured 2 ps after excitation of **18C6** in ACN and HEX is characterised by a shoulder on its blue side (black arrow in Figure 3B), which disappears

on the hundreds of ps timescale, together with a partial decrease of the GSB. Similar spectral features were reported earlier,<sup>30</sup> and attributed to two main types of correlated triplet pairs. The shoulder was assigned to strongly coupled correlated triplet pairs,  $^{1}(TT)$ , populated from the  $(S_1S_0)_H$  state. By contrast, the  $^{1}(T \cdots T)$  pairs populated from the  $(S_{1}S_{0})_{M}$ state are weakly coupled and longer lived. This hypothesis is supported here by the presence of the shoulder in ACN and HEX only, where the  $(S_1S_0)_H$  state is populated, but not in THF. Recent quantum-chemical studies predict absorption of the correlated triplet pair in the 700-900 nm region with an oscillator strength increasing with the interchromophore coupling.<sup>67</sup>

The normalized TA profiles at the triplet maximum (Figure 3D) illustrate the influence of the interchromophore coupling on the decay of the triplet population. In ACN and HEX, the triplet band decays faster when H-dimers are photo-selected by red-edge excitation. Mechanistically, the sub-ns decay of the triplet signal is assigned to the internal conversion of the  $^{1}(TT)$  pairs via the singlet channel (eq.2), in line with previous studies that point to a faster decay with increased coupling.<sup>26,39</sup> This decay in ACN is even faster than that of the  $S_1$  state of the parent  $\mathbf{Ref}$  (Figure S15). This can be accounted for by a smaller energy gap, since the  $^{1}(TT)$  state of **18C6** is lower than the S<sub>1</sub> state of **Ref**, as well as by a higher density of vibrational states in the bichromophore.<sup>68</sup>

Even though the triplet signal is decaying after about 100 ps in ACN,  $R_{T/S}(t)$  is still increasing, independently of  $\lambda_{ex}$ . This rise is due to the build up of <sup>1</sup>(T···T) via the slow SF occurring in the M-dimers. Since the latter is controlled by large-amplitude structural fluctuations, the decay of <sup>1</sup>(TT) and the rise of <sup>1</sup>(T···T) can be distinguished by increasing the viscosity. As illustrated in Figure 4, the decay of  $\Delta A_S$  on the hundreds of ps time-scale slows down with increasing viscosity due to a slower  $(S_1S_0)_M \rightarrow^1(T···T)$  SF, whereas the early decay of  $\Delta A_S$  due to  $(S_1S_0)_H \rightarrow^1(TT)$  is not affected.

Separation, decorrelation and decay of the triplet pairs. Most of the  $^{1}(TT)$  population decays through the singlet channel,



Figure 4: (Left) Viscosity dependence of the fs-ps transient absorption dynamics of **18C6** in HEX, N10 and N14 upon 650 nm excitation: triplet-singlet ratio ( $R_{T/S}(t)$ , top), singlet (S, middle) and triplet absorption (T, bottom). (Right) Relative population of the singlet and triplet excited states of **18C6** in HEX, N10 and N14 extracted from ps-µs transient absorption upon excitation at 532 nm. The concentrations are normalized to the total concentration at early times (grey).

which is detrimental to a large free triplet yield. Spatial separation of the nascent triplet pairs, mainly  ${}^{1}(T \cdots T)$ , allows escaping this process and lengthens their lifetime sufficiently to enable spin conversion towards free triplets,  $T_1+T_1$ . Since the pentacenes are covalently linked, they cannot separate completely but sample the available conformational space before returning to a closer contact conformation at a later time (secondary encounter). The duration of these excursions out of the contact distance depends on the solvent viscosity and on the free-energy surface. The fate of the triplet pair upon secondary encounter depends on its underlying spin dynamics, which determines if  $T_1+T_1$  rephases to <sup>1</sup>(TT), <sup>3</sup>(TT), or  $^{5}(TT)$ .  $^{34,35,69,70}$ 

Although all these different triplet pairs cannot be distinguished spectrally with TA, some insight into the underlying spin dynamics can be obtained by looking at the influence of the accessible conformational space and the solvent viscosity on the time evolution of the triplet signal. We thus turned to ps-µs TA upon 532 nm excitation to investigate the fate of the  ${}^{1}(T \cdots T)$  pairs. Figures S18-S28 show that, in all solvents, the singlet ESA features around 470 and 550 nm decay entirely within a few tens of ns. Afterwards, the TA spectra exhibit only the triplet ESA bands and the GSB. A modelfree analysis of these spectra, based on spectral decomposition,  ${}^{62,71}$  was applied to extract the time evolution of the singlet and triplet excitedstate populations (see SI section 2.7).

The decay of the triplet population is bimodal for  $18C6 \subset Ba^{2+}$  in ACN as well as for 18C6, irrespective of the polarity and viscosity of the solvent (Figures 4, 5, S15) The two decay components are separated by a plateau and the slow decay component matches the decay of the T<sub>1</sub> state of **Ref** populated by triplet sensitization (Figure S16).

The TA spectra can be reproduced as a linear combination of three components: (i) the singlet excited-state spectrum; (ii) the early triplet spectrum related to the fast decay component; and (iii) the late triplet spectrum associated with the plateau and the slow decay (Figure 5). In all cases, the late triplet spectrum (green) is slightly red shifted compared to the early triplet spectrum (blue). This trend was already observed with triplet pairs, which can separate spatially by triplet energy hopping and therefore do no longer couple.<sup>23</sup>

Interpretation of bimodal decay. As discussed in the introduction, the origin of the bimodal decay is debated, with the two main hypotheses being compared in Figure 6A. Hypothesis 1 (H1) attributes the plateau and the subsequent slow decay component to the lone triplet,  $S_0T_1$ , populated via the triplet channel after secondary encounters, whereas hypothesis 2 (H2) assigns them to  $T_1+T_1$  after the loss of spin correlation of the <sup>1</sup>(TT) and <sup>1</sup>(T···T) pairs.

Two of our experimental observations are in favour of H1 over H2. First, according to H1,  $R_{\rm pl}$ , defined as the late triplet population relative to maximum triplet population cannot exceed 0.5, whereas it can be as high as 1 with H2. Here, even with **18C6** in THF and



Figure 5: Ps-µs transient absorption measurements with 18C6 in THF (top) and  $18C6 \subset Ba^{2+}$  in ACN (bottom). Left: basis spectra (red: singlet excited state; blue: early triplet; green: late triplet) used to reproduce the TA spectra. Right: time evolution of the overall excited-state population (gray) and of its individual constituents: singlet (red), early triplet (blue) and late triplet (green) excited-state populations.

especially with  $18C6 \subset Ba^{2+}$ , where only Mdimers are present,  $R_{\rm pl}$ , determined from the height of the plateau relative to the maximum triplet signal, is less than 0.5 (Table 1). It is furthermore smaller for  $18C6 \subset Ba^{2+}$  than for  $18C6 \subset Ba^{2+}$  should favour decoherence rather than the decay via the singlet channel.

Second, as shown in Figure S16, the decay of the late triplet population occurs on the same timescale as that of the  $T_1$  state of **Ref** and does not show any correlation with solvent viscosity (Figure 4 and S17). This observation is not compatible with the late triplet signal being due to  $T_1+T_1$  (H2). Indeed, the conformational space in alkanes allows for close contact. Consequently, the  $T_1+T_1$  pairs can undergo secondary encounters, enabling their decay via the singlet or triplet channels, and, thus, leading to a decrease of the overall triplet population. Due to these possible reencounters, the late triplet decay should not only be faster than that of the  $T_1$  state of **Ref**, but should also be significantly faster in HEX than in N14, contrary to the observation.

SF yield as a function of distance and



Figure 6: (A) Comparison of the singlet fission cascade based on the two hypotheses suggested in literature. Species which cannot be spectrally differentiated are represented with the same color. The present study supports hypothesis 1. (B) Schematic representation of the impact of conformational space and solvent viscosity on the interchromophore coupling, which governs the singlet fission yield. Coupling increases from left to right. The orange dots stand for weakly coupled dimers whose excited-state dynamics is strongly entangled with structural fluctuations (represented as dashed lines); the red dots designate highly coupled dimers, whose excited-state dynamics is faster than that associated with diffusive structural changes.

Table 1: Comparison of the triplet concentration at the plateau relative to the maximum triplet concentration,  $R_{\rm pl}$ , and to the initial concentration of the photopopulated singlet state,  $\Phi_{\rm S_0T_1}$ . Doubling the latter gives a lower limit of the singlet fission quantum yield,  $\Phi_{\rm SF}$ , based on eq. 2. Values for quantitative SF based on hypothesis 1 are given for comparison.

	$R_{\rm pl}$	$\Phi_{S_0T_1}$	$\Phi_{\rm SF}$
ACN	-	-	$\sim 0.1$
$\mathrm{ACN} + \mathrm{Ba}^{2+}$	0.41	0.34	>0.68
$\mathrm{THF}$	0.49	0.17	>0.34
HEX	0.30	0.18	>0.36
N10	0.35	0.24	>0.48
N14	0.36	0.27	>0.54
quantitative	$\leq 0.5$	$\leq 1$	2

viscosity. According to H1, the fraction of photo-populated molecules which decay via the triplet channel,  $\Phi_{S_0T_1}$ , allows estimating a lower limit of the singlet fission quantum yield,  $\Phi_{SF}$ , defined as the triplet yield associated with the  $T_1+T_1$  pairs.<sup>36</sup> If we assume a quantitative decay of  $T_1+T_1$  via the triplet channel,  $\Phi_{SF}$  is equal to twice  $\Phi_{S_0T_1}$ , which is reflected by the height of the plateau compared to the concentration of the photo-populated singlet state (Table 1). A detailed description on how  $\Phi_{\rm SF}$  is extracted is given in the SI (section 2.8).

 $\Phi_{\rm SF}$  is governed by a trade off between the rate of triplet pair formation and the triplet pair survival, both functions of the interchromophore distance and coupling (Figure 6B). For **18C6** in ACN, where H-dimers are predominant, triplet formation is fast, but the survival probability of the resulting <sup>1</sup>(TT) pairs is low due to fast annihilation along the singlet channel (red dots in Figure 6B). Consequently,  $\Phi_{\rm SF}$ is estimated to be only around 0.1, much lower than the theoretical limit of 2.

In THF, where mostly M-dimers are present,  $\Phi_{\rm SF}$  is significantly enhanced due to the increased survival probability of <sup>1</sup>(T···T) formed at larger distances (orange dots in Figure 6B). However, large-amplitude conformational fluctuations are required for SF to take place in M-dimers. As the latter occur on the same timescale as the intrinsic decay of the S<sub>1</sub> state, part of the excited-state population is lost, explaining the deviation from the maximum yield of 2. The highest  $\Phi_{\rm SF}$  is observed with **18C6** $\subset$ **Ba**<sup>2+</sup> in ACN, where close contact conformers are structurally excluded and the triplet formation is further slowed down. This higher yield for  $18C6 \subset Ba^{2+}$  in ACN compared to THF shows that, in this case, the effect of the longer triplet survival surpasses that of the slower SF and the ensuing loss via the intrinsic decay of S<sub>1</sub>.

In alkanes, where both H- and M-dimers are excited, the SF yield increases with solvent viscosity. A higher viscosity can have two opposite effects with different impact on H- and Mconformers. First, it can slow down the separation of  $^{1}(TT)$  pairs generated from  $(S_{1}S_{0})_{H}$ , hence decreasing the triplet survival probability and  $\Phi_{\rm SF}$ . This trend is however not experimentally observed probably since  $^{1}(TT)$  decays nearly quantitatively via the singlet channel even in the least viscous solvent. Second, higher viscosity also slows down structural fluctuations of M-dimers that lead to conformations with increased coupling. Given that the triplet pairs can be populated over a wide range of distances, diffusion-controlled fluctuations of  $(S_1S_0)_M$  occur until the coupling between the TIPS-pentacenes is large enough for SF to take place without further diffusion. Therefore, the interchromophore distance, and, thus, the survival probability of the triplet pair are on average higher in viscous than non-viscous solvents (Figure 6B). A similar effect is known for bimolecular photoinduced electron transfer, where high viscosity favours remote electron transfer and thus produces longer-lived ion pairs.<sup>71</sup> As illustrated in Figure 4 and S17, the rise of the triplet signal slows down with increasing viscosity, whereas  $\Phi_{\rm SF}$  becomes larger. Therefore, as with  $18C6 \subset Ba^{2+}$  in ACN, the effect of a higher survival probability, here due to triplet formation at a geometry with low coupling, outweighs the effect of a slower triplet population.

#### Conclusion

By using a flexible crownether-like backbone, we could study SF in a TIPS-pentacene dimer over a wide range of interchromophore distances. This was achieved by exploiting the

influence of the solvent and the formation of a host-guest complex on the conformational phase space. MD simulations as well as stationary spectroscopic measurements point to a distribution of conformers that can be sorted into strongly coupled H-dimers and weakly coupled M-dimers. Their slightly different absorption spectra allow for photo-selection in  $\lambda_{ex}$  dependent experiments. We could spectrally and kinetically differentiate two types of triplet pairs.  $^{1}(TT)$ , and  $^{1}(T \cdots T)$ , differing by their coupling. SF in H-dimers populates the  $^{1}(TT)$ state on the sub-ps timescale with solvent polarity and viscosity independent dynamics. The absence of polarity effect reveals that the solvation coordinate does not play a significant role and that SF in these strongly coupled dimers is driven by intramolecular modes. SF in Mdimers occurs on the hundreds of ps timescale and populates the  ${}^{1}(T \cdots T)$  state. This process is governed by large amplitude structural changes that modulate the coupling and thus depend on viscosity.

The <sup>1</sup>(TT) pairs decay mainly via internal conversion to the ground state with only a minor fraction (~ 10%) evolving to  $T_1+T_1$ via conformational changes and spin conversion. The latter channel is predominant for the <sup>1</sup>(T···T) pairs. However, the ensuing  $T_1+T_1$ pairs have a limited lifetime due to the occurrence of structural fluctuations enabling secondary encounters and annihilation via the singlet or triplet channel giving  $S_0T_1$ . This mechanism, proposed by Campos and Sfeir et al. to account for the bimodal decay of the triplet population, <sup>36</sup> is confirmed here by our viscosity dependent measurements.

The structure-property relationships acquired from the systematic study of this flexible crownether-based dimer can be summarised as follows. Close contact  $\pi$ -stacked H-dimer should be prevented and the center-to-center distance should be kept slightly below about 1 nm to achieve an optimal balance between the rate of triplet formation and the triplet pair survival. In addition to the structural restriction, we could show that solvent viscosity can be used to dynamically control the average coupling of the ensuing triplet pair and increase  $\Phi_{SF}$ . Further fine tuning toward an optimal coupling, and thus higher SF yield, should be feasible thanks to a judicious selection of solvent according to polarity and viscosity. Additionally, the band gap of pentacene should not be reduced by functionalization, in order to avoid a shortening of the singlet lifetime as well as a potential acceleration of the singlet and triplet decay channels, which is detrimental to the overall  $\Phi_{\rm SF}$ .

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Supporting Information Available: Synthesis and characterization of Ref and 18C6, experimental details, details on the molecular dynamics simulations, photophysical properties of Ref, additional spectroscopic data on 18C6, analysis of the picomicrosecond transient absorption spectra, estimation of the SF yield. The data can be downloaded from https://doi.org/10.26037/ yareta:7dwzkrfo6zd4domn3tlbuvrloe This material is available free of charge via the Internet at http://pubs.acs.org/.

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### Graphical TOC Entry

