On couplings and excimers: lessons from studies of singlet fission in covalently linked tetracene dimers†

Xintian Feng and Anna I. Krylov*

Electronic factors controlling singlet fission (SF) rates are investigated in covalently linked dimers of tetracene. Using covalent linkers, relative orientation of the individual chromophores can be controlled, maximizing the rates of SF. Structures with coplanar and staggered arrangements of tetracene moieties are considered. The electronic structure calculations and three-state kinetic model for SF rates provide explanations for experimentally observed low SF yields in coplanar dimers and efficient SF in staggered dimers. The calculations illuminate the role of the excimer formation in SF process. The structural relaxation in the S1 state leads to the increased rate of the multi-exciton (ME) state formation, but impedes the second step, separation of the ME state into independent triplets. The slower second step reduces SF yield by allowing other processes, such as radiationless relaxation, to compete with triplet generation. The calculations of electronic couplings also suggest an increased rate of radiationless relaxation at the excimer geometries. Thus, the excimer serves as a trap of the ME state. The effect of covalent linkers on the electronic factors and SF rates is investigated. In all considered structures, the presence of the linker leads to larger couplings, however, the effect on the overall rate is less straightforward, since the linkers generally result in less favorable energetics. This complex behavior once again illustrates the importance of integrative approaches that evaluate the overall rate, rather than focusing on specific electronic factors such as energies or couplings.

I. Introduction

Singlet fission (SF), a process in which one singlet excited state is converted into two triplet states, is of interest in the context of organic photovoltaic technology.1,2 By converting one absorbed high-energy photon into two lower-energy triplet excitons, the efficiency of a solar cell can be improved by reducing losses in the blue part of the solar spectrum. The reverse process, triplet-triplet annihilation producing an emitting singlet state, is exploited in frequency-upconversion materials that can harvest the lower-energy part of the solar spectrum.3,4 Owing to its technological significance, the mechanism of SF has been vigorously investigated.1,2 Yet, the design principles for materials capable of efficient SF remain elusive.

As illustrated in Fig. 1, SF involves at least two steps, conversion of the initially excited singlet state (S1 and S0) into a multi-exciton state (1ME) followed by the decoupling and spatial separation of the two triplets. Initial singlet state is derived from the bright singlet state of individual chromophores, S1(A)S0(B) and S0(A)S1(B); depending on the structure, it can be either localized on one chromophore or delocalized over several neighboring molecules. The electronic configuration of the 1ME state can be described as two triplet excitations...
residing on the nearby chromophores and coupled into a singlet state. From a quantum mechanical point of view, these two steps entail coupled electron-nuclear dynamics in a system comprising several (at least two) chromophores. Several other processes can compete with these two steps: radiationless relaxation from the initially excited or the ME state restoring the ground-state chromophore, annihilation of the triplets forming a singlet excitonic state, formation of charge-transfer states. In addition to these electronic processes, adiabatic nuclear dynamics can be important, e.g., the formation of excimers on the S1 surface or structural relaxation of the ME state can lead to significant changes in energies and couplings thus affecting the rates.

SF rates are controlled by energetics and couplings.5,6 To make SF thermodynamically feasible, the energy of the S1 state of the individual chromophore should be approximately double the energy of the T1 state. This criterion is satisfied in large conjugated molecules such as acenes (starting from tetracene), carotenoids, etc.1,2 Michl and coworkers noted the connection between the energetic drive for SF and diradical character, i.e., that triplet states can be lowered by increasing diradical character.7 This design principle8,9 has been used to engineer new systems capable of SF.10–14 Other suggested molecules await experimental validation.8,9

Electronically endoergic SF (ESF > 0) is possible due to the entropic factor.5,15 Note that the energies of the states can be affected by interactions between the chromophores in a molecular solid (e.g., Davydov’s splitting lowers the energy of the S1 state) as well as excited-state structural relaxation (e.g., excimer formation). Electronic couplings, which facilitate non-adiabatic transitions between the states, depend on the underlying wave functions and are strongly affected by morphology.1,2,16–18 The necessary condition to have a non-zero coupling is some degree of the overlap between the frontier orbitals. However, the non-zero overlap alone is not sufficient. Owing to the one-electron nature of the derivative operator,18 the coupling between pure excitonic and the ME configurations is zero, however, mixing the charge-resonance (CR) configurations into the respective adiabatic wave functions leads to non-zero couplings.1,2,17 Not all structures with large overlap have large mixing of CR configurations. A simple 4-electron-in-4-orbitals model1 predicts zero couplings at perfectly stacked configuration and suggests that parallel-displaced structures are optimal for SF.1,2 However, calculations of non-adiabatic couplings (NACs) in a model system showed that although the largest couplings are observed at the slip-stacked arrangement, the couplings are also quite large at perfectly stacked geometries.17,18 The role of other configurations (beyond the HOMO–LUMO active space) may also be important. As a recent example illustrating the complexity of the electronic structure, consider dimers from the crystals of the 1,3-diphenylisobenzofuran (DPBF) polymorphs.10–12 The calculations revealed, unexpectedly, that the largest couplings are exhibited by non-stacked (i.e., coplanar) dimers.19 In the case of the covalently linked dimers, the contribution of the linker to the couplings needs to be considered. Even if the arrangement of the chromophores that maximizes the couplings can be found, it does not necessarily translate into fast SF rates, because such a configuration may have poor energetics. Furthermore, the competing channels may be adversely affected by structural variations. Additional complexity arises due to the multi-step nature of the process. For example, lowering the energy of the ME state, which can be achieved by increasing ESF, speeds up the first step, but slows down the second (see Fig. 1).

In order to connect the electronic factors with macroscopic rates, we introduced a simple 3-state kinetic model5 based on Fermi’s golden rule and linear free energy approach,20,21 which argues that the activation energy for a process is proportional to the free energy difference of the reaction. The essential details of the model are outlined in Fig. 1 (here and in ref. 22 we redefined some of the quantities relative to ref. 5, to follow the standard convention of the signs of chemical reactions and to improve the clarity; however, the model itself is unchanged). The relevant electronic quantities are: ESF, ES, ED, and parameters ||γ|| and ||γ′||, which are proportional to the NACs between the S1/S1 and the 1ME states. The protocol for computing these quantities is described in Section II. ESF, the energy difference between the lowest S1 state and 1ME, determines the energetic drive for the formation of the multi-exciton state. Energy splitting between the excitonic pair, S1 and S1′ (Davydov’s splitting, ES), determines Boltzmann’s populations of the states from the initially excited singlet manifold (if the population of S1′ is significant, then the contribution of this state to SF should be also included). Energy difference between the ME state and two uncoupled triplets (multi-exciton stabilization energy, ES) arises due to the stabilization of the 1ME state relative to the two independent triplets through the configuration interaction with other singlet states. ES is a minimal energy that needs to be overcome for the ME state to acquire a pure (T1,T1) character, before the two triplets can separate. While large positive ES is beneficial for the 1ME state formation (step 1) because they lower ESF, it constitutes a penalty for the triplet separation step (step 2).

The rates for the first step, S1(AB) → 1ME and S1′(AB) → 1ME, are:

\[ r_1 \equiv r_1[S1(AB) \rightarrow 1ME] \sim \left( \frac{||\gamma'||}{\Delta E} \right)^2 e^{-\beta E_{SF}}, \]  

\[ r_1' \equiv r_1'[S1'(AB) \rightarrow 1ME] \sim \left( \frac{||\gamma'||}{\Delta E + E_D} \right)^2 e^{-\beta (E_{SF} - E_D)}, \]

where \( \beta = \frac{1}{k_B T} \), \( \alpha \) is a parameter from the free energy relationship, and \( \Delta E \) is the energy difference between the raw (uncorrected) RAS-SF energies of the S1 and 1ME states.19 The rate for the second step, 1ME → 2T1, is:

\[ r_2 \equiv r_2[1ME \rightarrow T1 + T1] \sim e^{-\alpha E_{SF}}. \]

As in the previous studies,5,19 we use \( \alpha = 0.5 \).

The quantity of interest is the total time \( \tau \) to reach State 3, which can be computed as first-passage time:23

\[ \tau = \frac{1}{r_1 + \frac{1}{r_2} + \frac{r_1}{r_2}} = \frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{K_{T1} r_2}. \]
where $K_1^0$ is an equilibrium constant for step 1. When $K_1^0 \gg 1$, the total time is just the sum of the inverses of individual rates:

$$\tau \approx \frac{1}{r_1} + \frac{1}{r_2}$$  \hspace{1cm} (5)

Efficient SF is identified by small $\tau$. Thus, we investigate variations of $r_1$ and $r_2$ in different tetracene dimers. Our model does not attempt to compute absolute rates. Instead, we compute rates relative to a reference system, so that the exact expressions for the prefactors in eqn (2) and (3) are not required. This strategy also takes advantage of error cancellation, i.e., one may expect that the errors of an electronic structure method applied to homologously similar compounds are systematic and, therefore, cancel out in the relative rate calculations. We note that the essential features of our model, the exponential dependence on energy differences and the quadratic dependence on the coupling, are also present in the kinetic model developed by Van Voorhis and co-workers.\(^4\) One difference between our model and that of Van Voorhis (or Marcus rate expression\(^24\)) is that we do not account for the kinetics in the inverted region that may occur for strongly exoergic processes. Thus, our model, in its current formulation, is only valid for endoergic and weakly exoergic SF. The physical foundations behind such phenomenological rate theories, the limits of their applicability, and their utility in understanding general trends and interpreting the experimental observations are reviewed in ref. 25.

Our strategy is as follows. We first compute relevant energies ($E_{SF}$, $E_0$, $E_d$) and couplings ($\|\gamma\|$ and $\|\gamma^*\|$) for the dimers. The details of the electronic structure protocol are given in Section II. We then compute the rates relative to the reference system (in this paper, two tetracenes in the orientation taken from the crystal structure). Since faster rates reduce the competition with parasitic processes, we equate faster rates with larger yields.

In the above variant, the model neglects triplet–triplet annihilation, radiationless relaxation to the ground state, geometric relaxation, and contributions to SF beyond dimers. As discussed below, some of these effects can be accounted for. For example, the effect of structural relaxation can be evaluated by computing relevant electronic parameters at the relaxed structures. The variations in the rates of radiationless relaxation leading to $S_0$ can be investigated by analyzing the corresponding couplings.

The utility of this approach has been illustrated by applications to several SF systems.\(^5,19\) The model has explained the relative rates in tetracene and pentacene and attributed three orders of magnitude difference to more favorable energetics (the couplings are very similar).\(^5\) The model predicted that the rate of SF in hexacene will be comparable to that in pentacene. A later experimental study\(^26\) reported 5–6 times slower rate of the $S_1$ population decay relative to pentacene. Although our model did not predict slower kinetics, the predicted rate (91–141 fs) was in qualitative agreement with the experimentally determined one (530 fs). The model has also explained\(^19\) the differences in the SF rates in the polymorphs of DPBF\(^31\) and DPH (1,6-diphenyl-1,3,5-hexatriene).\(^27\)

The focus of this work is on covalently linked tetracene dimers. Tetracene is a particularly interesting system because of slight endoergicity of SF. In the context of solar energy harvesting, small $E_{SF}$ is desirable because it minimizes efficiency losses due to the energy-levels mismatch. Since the rates are very sensitive to $E_{SF}$, small variations in states’ energies and the couplings due to the interactions between the chromophores may lead to a significant effect. Thus, understanding the relative rates in various tetracene-based systems presents a stringent test for a theoretical approach.

Early experimental studies of tetracene dimers were conducted by Bardeen and co-workers\(^28\) who reported low yields (3–5%) and three orders of magnitude slower SF rates (relative to tetracene) for the structures shown in Fig. 2. This finding can be rationalized by a small overlap between the individual chromophores, which are coplanar. This group also investigated a face-to-face tetracene dimer in which the two moieties are attached to a xanthene bridge\(^29\) and observed no evidence of SF, despite the strong electronic coupling between the fragments. The lack of SF was attributed to the formation of an excimer state lying too low in energy thus impeding the generation of free triplets.\(^29\) Formation of excimers on a picosecond timescale has also been observed in face-to-face and slip-stacked dimers of perylene.\(^30–32\) Interestingly, increasing the offset between the chromophores impeded the excimer formation, but did not result in SF.\(^31\) From the theoretical perspective, a possible role of excimers in SF and their energetics have been discussed by Zimmerman et al.\(^33\)

Contrary to the findings in covalently linked dimers, excimer formation in dilute solutions of pentacene and tetracene does not block the SF channel but rather serves as an intermediate step.\(^34,35\) The formation of excimer-like structure, described as frustrated photodimerization, has been invoked to explain the apparent lack of temperature dependence of the first SF step in tetracene and strong temperature dependence of the second SF step.\(^36\)

Recently, efficient SF has been observed in covalently linked pentacene dimers;\(^37\) this study suggested that the through-bond coupling between the linked chromophores might be important.

Dimers in which the tetracene moieties are not coplanar were recently synthesized at USC.\(^22\) Fig. 3 shows the structures of the two cofacial alkynyltetracene dimers called BET-B and BET-X. As one can see, the tetracene moieties are staggered, which suggests larger overlap than in the structures from Fig. 2. In BET-X, which is very similar to the face-to-face dimer from ref. 29, the rings are almost parallel, whereas in BET-B they are not. The experiments have shown that in neat film BET-B undergoes efficient SF within 1 ps with 154% ± 10% efficiency.

![Covalently linked tetracene dimers](Fig 2)
Interestingly, similar rates of the $1^\text{ME}$ state appearance were observed in neat films, solution, PMMA, and in BET-B doped DPT (diphenyltetracene) film.\textsuperscript{22} For the second step, the separation of triplets, possible triplet acceptors are needed. Thus, in PMMA where the dimers are isolated and immobilized, the $1^\text{ME}$ state simply decays to the ground state. However, in neat films and in the doped DPT films the $1^\text{ME}$ state can break into two independent triplets. The rates of the second step were $0.23 \pm 0.05$ ps\textsuperscript{-1} and $150 \pm 1$ ps\textsuperscript{-1} for BET-B in neat film and in doped DPT film, respectively. BET-X was found to be photochemically unstable in neat films and DPT;\textsuperscript{22} in solution, the initially excited singlet state in BET-X is shorter lived than the experiment time resolution (200 fs). The earliest-time transient-absorption spectra in BET-X were found to be similar to those observed in BET-B and assigned to the $1^\text{ME}$ state, suggesting similar initial dynamics, but with faster formation of the $2^\text{ME}$ state.\textsuperscript{22}

The calculations below analyze the electronic factors in these dimers and provide explanations to the observed trends. The structure of the paper is as follows. Section II outlines the computational details. The protocols of calculations are presented and discussed in Section III. Specifically, we discuss relevant structures in the ground and excited states and analyze energetics and the couplings on the SF rates. The effect of the covalent linker is also investigated. Our concluding remarks are given in Section IV.

### II. Theoretical methods and computational details

We employ the same protocol as in ref. 5, 17 and 19. For the sake of clarity, we rewrote the rate expressions, eqn (1)–(3), using slightly different quantities; however, the essential features of the model are unchanged. As shown in Fig. 1, we focus on the following states: initially excited excitonic pair, $S_1$ and $S_{1^\text{h}}$, the $1^\text{ME}$ state of a predominant $1^\text{T_1}$ character, and separated triplets, $T_1 + T_1$. The gap between $S_1$ and $S_{1^\text{h}}$ (Davydov's splitting) disappears when the two fragments are not interacting (e.g., at infinite separations between the fragments); in such a case, these states are just the $S_1$ states of the monomers. We use an adiabatic framework\textsuperscript{17} and compute all relevant states using the RAS-2SF (restricted-active-space double spin–flip) configuration interaction method.\textsuperscript{28,39} In this approach, different types of configurations (excitonic, charge-resonance, multi-excitonic) can mix and interact leading to complex adiabatic wave functions. To characterize the couplings between the resulting adiabatic states, we use density-matrix based formalism\textsuperscript{17,18} in which the NAC between the two states is proportional to the norm of the respective transition-density matrix, $\|\gamma\|$:

$$\gamma_{pq} = \langle \Psi|j|\Psi_i \rangle,$$  

$$\|\gamma\| = \sqrt{\sum_{pq} \gamma_{pq}^2}.$$  

The RASCI-2SF method has been successfully employed to model various aspects of SF.\textsuperscript{5,17,19,40–43}

Following the protocol developed in ref. 5, we employ the cc-pVTZ basis\textsuperscript{44} from which f-functions are removed, cc-pVTZ(-f). The RAS-2SF calculations were performed using the ROHF quintet references and the 4-electrons-in-4-orbitals active space.

The key electronic energies, $E_{S_d}$, $E_{T_d}$, and $E_{d}$, were computed as follows:

$$E_{S_d} = E(1^\text{ME}) - E(S_1),$$  

$$E_{T_d} = E(S_1) - E(T_1),$$  

$$E_{d} = E(2^\text{ME}) - E(1^\text{ME}).$$

To account for dynamical correlation, the raw RAS-2SF $E_{S_d}$ energies were corrected by a simple energy-difference correction\textsuperscript{17,19} (note that in relative rate calculations of tetracene dimers, the correction cancels out exactly).

The rates were computed using eqn (1)–(3) relative to the tetracene A–C dimer structure.\textsuperscript{17} In the tables below, logarithmic relative rates are reported. In this paper, we neglect entropic contributions and focus exclusively on the electronic factors.

The dimer structures in Fig. 2 and 3 were optimized by $\omega$B97X-D with the cc-pVDZ basis set. The crystalline BET-B/X structures (denoted as ‘cry’) are based on the X-ray structures from ref. 22 for which the CH bonds were optimized using the same level of theory. The excimer structures for BET-B and BET-X were optimized by TDDFT with $\omega$B97X-D/cc-pVDZ following the $S_1$ and $T_1$ states. The structure of the $2^\text{ME}$ state was optimized by $\omega$B97X-D/cc-pVDZ.

The degree of overlap between the frontier orbitals of tetracenes in various structures was computed as follows. First, fragment's molecular orbitals were computed by the explicit polarization (XPOL) method,\textsuperscript{45,46} where each tetracene moiety in a dimer (Tc) or a linked dimer (BET-B/X) is treated as one fragment (the linkers are removed in these calculations), with electrostatic inter-fragment interaction described by the Löwdin charges. Then the orbital overlap between the relevant MOs of the two tetracene units is calculated as $\langle H_{A_i}|H_{B_i} \rangle$ and $\langle L_{A_i}|L_{B_i} \rangle$, where $H_{A,B}$ and $L_{A,B}$ are the HOMO and the LUMO of fragments A and B, respectively.

To analyze the effect of the covalent linker, we prepared additional model structures as follows. Starting from the above BET-X and BET-B structures, we replaced the linkers...
(benzene or xanthene) by the hydrogen atoms (the CH bonds were optimized with oB97X-D/cc-pVDZ). These structures are denoted ‘TcCC-BET-B/X’. Similarly, we prepared the structures in which the benzene/xanthene moiety and the two ethynyl groups were replaced by hydrogens; these structures are denoted ‘Tc-BET-B/X’. These model structures are shown in Fig. S2 in ESL.†

All calculations were performed with the Q-Chem electronic structure program. 47, 48

III. Results and discussion

A. Structures

The most important difference between the structures from Fig. 2 and 3 is that in the former the tetracene rings are coplanar, whereas in the latter they are staggered.

We considered several model structures of BET-B and BET-X (see Section II for details). The first set was taken from the crystal structures of BET-B and BET-X (which has two types of crystals, BET-X1 and BET-X2). In the discussion below, these structures are denoted by ‘cry’. The second set, denoted by ‘i’, consists of the fully optimized structures (for BET-B, we considered 3 conformers). The main difference between the two sets of structures is the distance and the angle between the tetracene rings. Interestingly, in BET-B fully optimized dimers the tetracene moieties are closer to each other and more parallel, relative to the crystal structure. This is accompanied by a slight bending of the CC linkers. The reason for this becomes apparent when analyzing the crystal structure of BET-B shown in Fig. 4—as one can see, the molecules are packed such that the tetracene rings from the neighboring dimers form a nearly perfect π-stacked motif. Thus, in the crystal, the inter-dimer dispersion interaction, which favors more open dimer structures, compensates intra-dimer dispersion favoring structures with bent linkers and shorter intra-dimer tetracene distances.

The dimer structures derived from the crystal structure are representative of the neat film, whereas the fully optimized structures provide realistic models for dimers in solutions, PMMA, and DPT. In addition to the ground-state structures, we also considered excited-state optimized geometries for the S1, T1, and 5ME states, which are representative of excimers.

![Fig. 4](The arrangement of two BET-B molecules in the crystal structure of BET-B.22)

Table 1 summarizes the key features of the ground-state and excited-state structures. Specifically, we consider the distance between the tetracene moieties (d), the angle between their long axes (z), the bent angle of the ethynyl linkers (β), and the deformation of the xanthene bridge (γ); see ESI† for the exact definitions of these parameters. We note that twist angle z has a large effect on the electronic couplings. 17 The differences between the structures are subtle. The distance between the tetracene planes decreases slightly in the isolated ground-state and excimer structures of BET-B relative to the crystal structure. We also note a large change in z between the crystal structure of BET-B and the S1 excimer—the tetracene units become better aligned. In the 5ME excimer, the angle increases again.

B. Energetics, couplings, and rates

Table 2 presents the results for the structures shown in Fig. 2. As one can see, all structures show the decrease in r1 for up to three orders of magnitude. The analysis of the individual components shows that energetics in these linked dimers is more favorable than in tetracene (E_SF is less endoergic), however, the couplings are more than 30 times smaller. We also note that Davydov’s splittings are rather large, which, once again, illustrates that strong electronic interactions between the chromophores do not imply favorable S1/1ME couplings.

<table>
<thead>
<tr>
<th>System</th>
<th>E_SF</th>
<th>E_b</th>
<th>E_d</th>
<th>log(r1)</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc</td>
<td>0.396</td>
<td>0.021</td>
<td>0.140</td>
<td>0.084</td>
<td>0</td>
</tr>
<tr>
<td>cis-I</td>
<td>0.136</td>
<td>0.001</td>
<td>0.098</td>
<td>5.2 × 10^{-4}</td>
<td>-0.72</td>
</tr>
<tr>
<td>trans-I</td>
<td>0.134</td>
<td>0.001</td>
<td>0.093</td>
<td>3.8 × 10^{-4}</td>
<td>-0.84</td>
</tr>
<tr>
<td>cis-II</td>
<td>0.141</td>
<td>0.005</td>
<td>0.121</td>
<td>1.7 × 10^{-3}</td>
<td>-0.23</td>
</tr>
<tr>
<td>trans-II</td>
<td>0.159</td>
<td>0.001</td>
<td>0.122</td>
<td>7.3 × 10^{-4}</td>
<td>-0.72</td>
</tr>
<tr>
<td>cis-III</td>
<td>0.102</td>
<td>0.000</td>
<td>0.029</td>
<td>5.8 × 10^{-7}</td>
<td>-3.44</td>
</tr>
<tr>
<td>trans-III</td>
<td>0.098</td>
<td>0.000</td>
<td>0.027</td>
<td>1.4 × 10^{-3}</td>
<td>-0.04</td>
</tr>
</tbody>
</table>

Ground-state energy differences (oB97X-D/cc-pVDZ): E(trans-I) − E(cis-I) = 0.36 kcal mol^{-1}; E(trans-II) − E(cis-II) = 0.20 kcal mol^{-1}; E(cis-III) − E(trans-III) = 0.37 kcal mol^{-1}. 

The reason for this becomes apparent when analyzing the crystal structure of BET-B shown in Fig. 4—as one can see, the molecules are packed such that the tetracene rings from the neighboring dimers form a nearly perfect π-stacked motif. Thus, in the crystal, the inter-dimer dispersion interaction, which favors more open dimer structures, compensates intra-dimer dispersion favoring structures with bent linkers and shorter intra-dimer tetracene distances.
Experimentally, three orders of magnitude slower rates for dimers I–III relative to tetracene were observed. The calculations based on electronic factors alone reproduce this trend, but show a smaller effect. We note that including the entropic effect will result in additional slowdown (the entropy contribution is proportional to the exciton delocalization and the number of possible triplet acceptors). Table 3 presents the results for BET-B and BET-X structures from ref. 22. We consider the structures of the dimer from the X-ray (denoted by ‘cry’) and of fully optimized isolated dimers (denoted by ‘i’). The former are representative of the neat film structures, whereas the latter provide realistic models for dimers in solutions, PMMA, or DPT.

The calculations reveal that the couplings are favorable in all dimer structures. Couplings are larger in fully optimized dimer structures relative to the ones from the crystal structures because of better overlap between the rings. The analysis of the couplings shows that the presence of the linker is important (more on this below).

\[ E_{up} \] is more favorable in BET-X(i) > BET-B(cry) > BET-B(i) > BET-X(cry2) > Tc > BET-X(cry1). Better energetics in BET-B relative to Tc are mostly due to the lowering triplet energy and, consequently, the \(^1\text{ME}\) state (this can be seen from the raw energies shown in ESI†). For example, relative to Tc, in BET-B(cry) the \(^1\text{S}\) state is lower by 0.14 eV, whereas \(^1\text{ME}\) is lowered by 0.5 eV. As one can see, a more parallel arrangement of the tetracene moieties in BET-B(i) leads to a larger Davydov splitting, and, consequently, preferential stabilization of \(^1\text{S}\) and less favorable \(E_{up}\). Likewise, the BET-X structures show large \(E_d\) and less favorable \(E_{up}\). The trends in couplings and energetics often oppose each other, since the couplings often increase when the overlap between the tetracenes increases. For example, BET-B(i) and BET-X(cry) exhibit larger couplings and less favorable energetics than BET-B(cry). Likewise, the couplings in all three BET-X structures are larger than in the reference tetracene system.

The rate of the first step of intra-dimer SF in BET-B(cry) is faster by almost two orders of magnitude than in tetracene suggesting that SF occurs on picosecond timescale, in agreement with the experimental observations. We note that for such fast process one may need to consider the contribution to fission from the initially excited state, \(^1\text{S}\). Due to more favorable energetics, these rates are even faster (see ESI†).

We note that the intra-dimer rate of SF is somewhat higher (up to 10 times) in BET-B(cry) than in BET-B(i), suggesting that one may expect faster rates in neat films. However, to make unambiguous comparison between the neat film and isolated dimer, the contributions from inter-dimer fission should be considered. We will address this question in future work.

On the basis of the data from Table 3, both crystal structures of BET-X are expected to have \(r_2\) that are more than an order of magnitude slower than in BET-B(cry), but slightly faster than in neat tetracene. Thus, one would expect that BET-X may also undergo SF. Experimentally, BET-X crystals were found to be photochemically unstable, suggesting that additional photochemical channels are operational. Thus, in the discussion below we focus on the structures of isolated dimers and experimental results for PMMA and solution.

As discussed above, transient absorption of BET-B reveals the formation of the \(^1\text{ME}\) state with ~2 ps time constant in PMMA and in DPT. In the latter, independent triplets were also detected. In BET-X, it was found that the initially excited singlet state is shorter lived than the experiment time resolution (200 fs). The earliest-time transient-absorption spectra in BET-X were found to be similar to those observed in BET-B and assigned to the \(^1\text{ME}\) state, suggesting faster formation of the \(^1\text{ME}\) state. Below we analyze whether triplets could, in principle, be harvested from BET-X and conclude that this system is not favorable for SF due to possible trapping in an excimer-type structure, which slows down the second step (\(r_2\) and facilitates radiationless relaxation to the ground state.

In order to assess relative rates of the radiationless relaxation to the ground state, we computed \(r_2\) for the \(^1\text{ME} \rightarrow \text{S}\) transition for BET-B(i) and BET-X(i). The respective values are 0.076 and 0.160; therefore, one may expect twice higher rates of the \(^1\text{ME} \rightarrow \text{S}\) transition in BET-X(i). Thus, a combination of slower \(r_1\) and higher rates for the radiationless relaxation to the ground state might be responsible for a fast excited-state decay in BET-X.

Finally, we consider the effect of excimer formation on SF rates. We computed optimized geometries on the \(^1\text{S}\) surface for BET-B and BET-X (see Table 1). As expected, both structures are characterized by shorter distances between the tetracene moieties relative to the respective crystal structures. BET-X shows larger relaxation relative to BET-B (the structures in Table 1 suggest that a larger geometric relaxation in BET-X is mostly due to a more flexible bridging moieties). Table 4 collects relevant electronic factors and rates. As expected, excimer formation leads to the increase in \(E_{up}\) and lowering of the \(E_d\) state. Unexpectedly, we found that \(E_{up}\) actually becomes more favorable, because of the considerable relaxation of the \(^1\text{ME}\) state along this displacement.

<table>
<thead>
<tr>
<th>System</th>
<th>(E_{up})</th>
<th>(E_d)</th>
<th>(E_{up})</th>
<th>(E_{up})</th>
<th>(E_d)</th>
<th>(E_{up})</th>
<th>(E_{up})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc</td>
<td>0.396</td>
<td>0.021</td>
<td>0.140</td>
<td>0.084</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>BET-B(cry)</td>
<td>0.015</td>
<td>0.152</td>
<td>0.313</td>
<td>0.044</td>
<td>1.90</td>
<td>-1.11</td>
<td>0</td>
</tr>
<tr>
<td>BET-B(i)</td>
<td>0.315</td>
<td>0.098</td>
<td>0.323</td>
<td>0.087</td>
<td>0.41</td>
<td>-0.65</td>
<td>0</td>
</tr>
<tr>
<td>BET-X(cry1)</td>
<td>0.447</td>
<td>0.069</td>
<td>0.553</td>
<td>0.172</td>
<td>0.13</td>
<td>-0.38</td>
<td>0</td>
</tr>
<tr>
<td>BET-X(cry2)</td>
<td>0.364</td>
<td>0.043</td>
<td>0.356</td>
<td>0.121</td>
<td>0.31</td>
<td>-0.77</td>
<td>0</td>
</tr>
<tr>
<td>BET-X(i)</td>
<td>0.020</td>
<td>0.312</td>
<td>0.226</td>
<td>0.195</td>
<td>0.96</td>
<td>-2.47</td>
<td>0</td>
</tr>
</tbody>
</table>
In order to validate the RAS-2SF results, we also computed relaxation of the $T_1$ state at the excimer structure by TDDFT. We found that the computed energy drop of the ME state is indeed roughly equal to twice the value for the triplet. We found that at the $S_1$-excimer structure, the rates of the first step, the ME formation, are comparable to or faster than the rates computed at the Franck–Condon geometries. However, the rates of the second step, triplet separation, are considerably impeded, due to the ME stabilization and the increase in $E_b$. Thus, the excimer serves a trap of the transient $1\text{ME}$ state. Again, we observe that the decrease in $r_2$ is two orders of magnitude larger in BET-X($S_1$) than in BET-B($S_1$). The analysis of the couplings (see Table 4) suggests that the excimer formation leads to the faster rate of radiationless relaxation and the effect is more pronounced in BET-X($S_1$). Thus, the calculations suggest that triplet harvesting from BET-X would be hampered by faster rates of radiationless relaxation and slower rates of the triplet separation step relative to BET-B. Both effects are enhanced by the excimer formation.

An interesting question is what is the impact of the geometric relaxation of the $1\text{ME}$ state. As one can see from Table 4, the $1\text{ME}$ state is considerably stabilized at the $S_1$-excimer geometry. We expect that it may relax even further. This geometric relaxation of the $1\text{ME}$ state will increase energetic penalty for the separation of triplets. We were not able to optimize the structure of the $1\text{ME}$ state (we note that it is very similar to the C-DFT optimized structure of $T_1T_1$), but it does not capture the effect of other electronic configurations, which are present in the adiabatic $1\text{ME}$ state. The energy diagram in Fig. 5 shows energies of the $S_1$, $1\text{ME}$, and $5\text{ME}$ states relative to $S_0$ (at its equilibrium geometry) at the Franck–Condon geometry and the optimized geometries of the $S_1$ and $5\text{ME}$ states. As one can see, the relaxation of the ME state can be quite substantial, up to 0.85 eV (BET-B), which likely will impede the separation of the triplets. Thus, if the lifetime of the ME state is sufficiently long and if the structure is conductive to excimers’ formation, the ME state can be trapped in an excimer-like structure. Another observation is that the structures of the $S_1$ and ME excimers are apparently rather different, leading to different energy ordering of the relevant states. For example, in the $S_1$-excimer structure, the ME state is stabilized more in BET-X relative to BET-B, whereas the ME excimer is lower in BET-B. The comparison of the optimized geometries of the $5\text{ME}$ state (see Table 1) reveals that the distance between the tetracene moieties is slightly larger in BET-X and BET-B and that the xanthene bridge is strongly bent.

We note that our results also lend an indirect support to the mechanistic hypotheses put forward by Schmidt and coworkers. They posited that in solid tetracene a multi-exciton state relaxes, forming an excimer-like structure and acquiring small oscillator strength via intensity borrowing from $S_1$. The structural relaxation, which they described as frustrated photodimerization, lowers the energy of the ME state below vertical $S_1$ energy making the first SF step temperature independent and resulting in strong temperature dependence of the second step. As discussed below, at the excimer-like structures, both BET-X and BET-B show non-zero oscillator strength, 0.001, for the $S_0 \leftrightarrow 1\text{ME}$ transition. As one can see from Fig. 5, unconstrained optimization on the $1\text{ME}$ surface (using DFT) results in the $1\text{ME}$ state dropping by 0.53 eV below the vertical energy $S_1$ state in BET-B. In solid tetracene, the relaxation of the ME state is likely to be incomplete. Based on the computed energetics for a model Tc dimer (see Table 3), relaxation of 0.4 eV would be sufficient to support Schmidt’s hypothesis.

### Table 4 Relevant electronic factors and relative rates of the $S_1 \rightarrow 1\text{ME}$ and $1\text{ME} \rightarrow 2T_1$ steps in BET-B and BET-X dimers at the $S_1$-optimized structures.

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{\text{SF}}$</th>
<th>$E_b$</th>
<th>$E_d$</th>
<th>$|\gamma|^2$ ($S_1-1\text{ME}$)</th>
<th>$\log\left[\frac{r_1}{r_1(\text{FC})}\right]$</th>
<th>$\log\left[\frac{r_2}{r_2(\text{FC})}\right]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET-B($S_1$)</td>
<td>0.439</td>
<td>0.229</td>
<td>0.771</td>
<td>0.195</td>
<td>0.014</td>
<td>0.21</td>
</tr>
<tr>
<td>BET-X($S_1$)</td>
<td>−0.070</td>
<td>0.475</td>
<td>0.757</td>
<td>0.191</td>
<td>0.172</td>
<td>3.28</td>
</tr>
</tbody>
</table>

**Fig. 5** Excitation energies of the $S_1$, $1\text{ME}$, and $5\text{ME}$ states relative to $S_0$ (at its equilibrium geometry) at the Franck–Condon (FC) geometry and at the optimized geometries of the $S_1$ and $5\text{ME}$ states. Left: BET-B. Right: BET-X.

### C. The role of covalent linker in BET-B

In this section, we further analyze the effect of the structure on the energetics and couplings. In particular, we compare the trends in couplings with those in orbital overlaps and also consider the role of the covalent linkers. To extend the set of representative structures, we consider three optimized structures...
shown in Fig. 6, in addition to the crystal structure of BET-B. The structures differ by the degree of the overlap between the tetracene moieties. We denote them as 33, 22, and 23. The lowest-energy one is BET-B(33); it is the same structure as BET-B(i) in the discussion above. It is most similar to the BET-B(cry). In addition, we included the S1-optimized excimer structures in the analysis (denoted as ‘ex’).

Orbital overlaps for these structures are given in Table S2 in ESL.† As expected, the excimer structure features the largest overlap between the frontier orbitals. Conversely, the X-ray structure in which the rings are less parallel, has smaller overlap than 33. However, the differences between the three optimized structures, 33, 23, and 22, are less obvious. For example, BET-B(33) has smaller overlap than 22 and 23, due to the interplay between different types of displacements and nodal structures of the MOs.17

Fig. 7 shows the correlation of the computed overlaps with the couplings. As one can see, the correlation is not perfect. The differences in overlaps between the two limiting cases, such as the X-ray and excimer structures, correlate with the differences in the couplings. However, for other structures the trends in couplings differ from the computed overlaps. Thus, the orbital overlaps alone should not be taken as a reliable proxy for the electronic couplings.

Fig. 8 shows the couplings and rates computed for model structures in which the covalent linker is removed (see Section II). The top panel shows the couplings, whereas the middle and bottom panels show rates relative to the tetracene dimer from the crystal structure \( \log[r/r_{(Tc)}] \). As one can see, the couplings are larger in the presence of the linker. The effect is most pronounced in the structure with the smallest overlap, BET-B(cry). For this structure, we also observe that both the benzene ring and the –CC– part of the linker are significant. Our results on the role of the covalent linker are in line with the experimental findings for pentacene dimers,37 which showed that the through-bond interaction is important. Such through-bond interactions are turned off when the linkers are removed and the couplings are driven by the overlaps.

The effect of the linker on the rate is more complex, because of its effect on energetics. The energy contribution from the linker disfavors SF, as one can see from the middle panel of Fig. 8, which shows the energy contribution to the relative rates. The overall rate (Fig. 8, bottom panel) shows that the linker slows down SF relative to the unlinked tetracenes at the identical geometric arrangement.

Finally, we would like to discuss the nature of the 1ME state in BET-B and BET-X in crystal and excimer-like structures. In contrast to the 3ME state, only asymptotically 1ME can be described as pure \( ^1(T_1T_1) \). At typical chromophore orientations, the adiabatic wave function of 1ME contains small contributions (4–6%) from other singlet configurations, such as CR and excitonic configurations.17,43 Indirectly, the wave function composition can be inferred from variations in \( E_b \) (larger values are indicative of an increased mixing of other singlet configurations into the 1ME state), \( |\gamma| \) (admixture of CR configurations leads to increase in \( |\gamma| \)), and transition dipole moments (the oscillator strength of the \( S_0 \leftrightarrow 1ME \) transition is zero for the pure \( ^1(T_1T_1) \) state). We observe relatively large \( E_b \) in BET-X and BET-B, especially at the excimer-like structures. We also found that at the X-ray structure, the oscillator strength is 0.0004 and 0.0007 for BET-B and BET-X, respectively. At the S1 excimer geometries, the oscillator strength increases to ~0.001 for both species. This small oscillator strength acquired by the 3ME state is likely responsible for weak steady-state emission observed in BET-X in rigid media.22 The wave function analysis43,49 shows that the weight of the \( ^1(T_1T_1) \) configuration in the multi-exciton state is roughly 80% (at the crystal structure). Thus, the weight of other singlet configurations is indeed larger than observed in unlinked pairs of chromophores (4–6%).17,43 Such large
This mixture of other configurations explains why in BET-B, the transient absorption of the \( ^{1}\text{ME} \) state is noticeably different from the absorption of a pure triplet state.\textsuperscript{22}

**IV. Conclusion**

We presented electronic structure calculations of electronic factors controlling SF rates in several covalently linked tetracene dimers. In the dimers with coplanar moieties, the calculations predict slower rates relative to neat tetracene, in qualitative agreement with experimental findings.\textsuperscript{28} In contrast, the BET-X and BET-B dimers in which the tetracene rings are staggered,\textsuperscript{22} the electronic factors are favorable for SF. The calculations predict faster (relative to neat tetracene) intra-fragment SF (i.e., formation of the \( ^{1}\text{ME} \) state) in both BET-X and BET-B. Relative to the coplanar dimers,\textsuperscript{28} the computed rate of SF in BET-B is faster by more than 3 orders of magnitude. Fast SF in BET-B is confirmed by the recent experimental study.\textsuperscript{22} Early excited-state dynamics in BET-X is similar to that in BET-B. The calculations reveal that the second step of SF, the separation of the \( ^{1}\text{ME} \) state into independent triplets, is significantly impeded in BET-X. Furthermore, almost perfect sandwich-like arrangement of the tetracene moieties in BET-X leads to the increased couplings with the ground state. In addition, the excimer formation, which is more favorable in BET-X, enhances both effects. Thus, the calculations suggest that the BET-X type of structures, which are more conductive to excimers formation, lead to a slower rate of the second step and more efficient radiationless relaxation (to \( S_0 \)).

We also analyzed the effect of the fragments orbital overlaps and covalent linkers on the couplings and rates of SF. We found a limited correlation between the overlaps and couplings. In all considered structures, the presence of the linker leads to larger couplings, however, the effect on the overall rate is less obvious, since the linkers generally result in less favorable energetics. This complex behavior once again illustrates the importance of integrative approaches\textsuperscript{5,6} that evaluate the overall rate, rather than focusing on specific electronic factors, such as energies or couplings. Using such kinetic models is important because couplings and energies are affected by morphology in different ways.

**Acknowledgements**

We are grateful to Prof. S. E. Bradforth and Dr. S. Das for their critical comments about the manuscript. We also would like to thank Prof. Mark Thompson and Ms. Nadia Korovina for stimulating discussions. Support for this work was provided by the Scientific Discovery through Advanced Computing (SciDAC) program funded by U.S. Department of Energy, Office of Science, Advanced Scientific Computing Research and Basic Energy Sciences. A. I. K. also acknowledges support through the DE-FG02-05ER15685 grant (DOE).

**References**


40 P. M. Zimmerman, F. Bell, D. Casanova and M. Head-Gordon, Mechanism for singlet fission in pentacene and tetracene: from single exciton to two triplets, J. Am. Chem. Soc., 2011, 133, 19944–19952.


