Intra- and Intermolecular Singlet Fission in Covalently Linked Dimers

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Supporting Information

ABSTRACT: Electronic factors controlling singlet fission (SF) rates are investigated in four-chromophore model systems comprising two covalently linked dimers of tetracene. By using adiabatic framework and wave function analysis tools, we show that the lowest singlet multie exciton states are localized on the individual molecules. The intermolecular ME states, in which the triplet excitons reside on separate moieties, are higher in energy and are not accessible from the lowest singlet excitonic state. Although the electronic states from the excitonic/charge-resonance band are delocalized over the four chromophores, the calculations suggest that the essential electronic properties controlling the rates of SF depend largely on the electronic properties of the individual covalently linked chromophores, owing to the strong through-bond couplings.

1. INTRODUCTION

Singlet fission (SF), a process in which one singlet excited state is converted into two coupled triplet states, is of interest in the context of organic photovoltaic technology.1,2 Although design principles for materials capable of efficient SF remain elusive, it is clear that the morphology of a molecular solid is an important factor affecting the two steps in the SF photophysical mechanism, that is, the formation of an intermediate state of multiexcitonic character and its splitting into two noninteracting triplets.

Due to the inherent difficulties with controlling morphology in molecular solids, the idea of using covalently linked dimers, in which the relative orientation of the two chromophore moieties can be tuned up at will by the rational design of the linker, shows much promise in the search for efficient SF materials.3–13 Among different chromophores capable of SF, tetracene is an interesting system because of slight endoergicity of SF: close level matching is more attractive from the efficiency point of view.

Recently, dimers with staggered tetracene moieties have shown promising SF ability. In particular, ortho-bis(5- ethynyltetracenyl) benzene (BET-B) was found to exhibit efficient SF on the time scale of 1–10 ps in neat films, in solution, and when doped into 5,12-diphenyltetracene (DPT).8 These rates are an order of magnitude faster than the SF rate measured in neat tetracene. Figure 1 shows the structure of BET-B. On the basis of calculations,9 fast SF rates were attributed to the improved energetics and couplings relative to the neat tetracene. The analysis of electronic states illuminated the role of the covalent linker: it facilitates through-bond interactions between the tetracene moieties leading to the noticeable changes in the wave function composition of the relevant states relative to the unlinked tetracenes at the same configuration. This system demonstrated that, by using the linked dimers scaffold, one can control both through-space and through-bond interactions between the chromophores. Thus, one may be able to tune the electronic properties of the individual chromophore dimers to maximize SF rates.

One interesting aspect of BET-B revealed by calculations9 is that the distance and the overlap between the rings depends strongly on the competition between inter- and intramolecular dispersion interactions between the π-systems on the tetracene moieties. For example, geometry optimization of isolated BET-B results in the structure in which the two ethynyl units in the linker are slightly bent and the two rings are more parallel than in the X-ray structure (Figure 1). The driving force for this distortion is intramolecular dispersion interaction. Interestingly, in the X-ray structure, the distance between the tetracene moieties from the adjacent BET-B molecules (A and A′) is nearly the same as between the rings from the same BET-B molecule (A and B). Also, the adjacent tetracene moieties from the two different BET-B molecules are more parallel than the intramolecular pair. These structural features of (BET-B)2 lead to an important mechanistic question: whether SF in the neat...
film of BET-B involves intra- or intermolecular fission, or both. While intramolecular SF has been characterized in several systems,\textsuperscript{10–14} the competition between intra- and intermolecular pathways in dimers’ aggregates has not been investigated.

In this paper, we analyze the electronic structure of the two BET-B molecules and assess the relative importance of intramolecular SF. As in our previous work,\textsuperscript{9,15–17} we employ an adiabatic framework for calculating relevant states and their couplings. In the context of SF, relevant electronic states of a system comprising two chromophores (A and B) are derived from excitonic (EX, or local excitations, LE), charge-resonance (CR), and multie exciton (ME) configurations.\textsuperscript{15} We analyze the character of many-electron adiabatic states in terms of EX, CR, and ME configurations using a wave function analysis tool based on localized orbitals and spin correlators.\textsuperscript{18,19}

We address the following questions:

- What is the degree of delocalization of the relevant electronic states, and what impact does it have on the SF properties?
- How are electronic states of the single BET-B molecule affected by intermolecular interactions? We consider energies, couplings, and the characters of the states.
- How do the SF mechanism and rates in the dimer compare to those in isolated BET-B?

2. THEORETICAL METHODS AND COMPUTATIONAL DETAILS

The structures of BET-B and (BET-B)\textsubscript{2} were taken from the crystal structure, and positions of all hydrogens were optimized with \textit{ω}B97X-D. BET-B has C\textsubscript{2} symmetry, whereas the dimer has C\textsubscript{s} symmetry. The Cartesian geometries of all structures are given in the Supporting Information.

We employ an adiabatic framework for calculating all relevant states by using the restricted-active-space spin-flip configuration interaction (RASCI-SF or RAS-SF) method\textsuperscript{20–22} with single, double, and quadrupole spin-flip. In the systems with two chromophores (such as tetracene dimer and BET-B molecule), we use RAS-2SF and a quintet reference state. In the system with four teracenes, (BET-B)\textsubscript{2}, we use RAS-4SF and a high-spin reference state with eight unpaired electrons. We quantify the electronic couplings between the states by using respective one-particle transition-density matrices.\textsuperscript{15,23} We then analyze the characters of the adiabatic states in terms of EX, CR, and ME configurations using a wave function analysis tool based on localized orbitals and spin correlators.\textsuperscript{18,19}

The weights of different configurations in RAS-SF calculations are used to compute state-specific energy corrections,\textsuperscript{18,24} as described below (section 2.1).

As in our previous studies of SF,\textsuperscript{9,17} we estimate the effects of changes in electronic structure on the SF rates by using a simple kinetic model.\textsuperscript{16} The rate of 1ME state formation is given by the following expression derived by using the linear free energy approach and the Fermi golden rule

\[
\tau_{\text{1}} = \alpha \left[ S_{\text{i}}(\text{AB}) \rightarrow \text{1ME} \right] \sim \left( \frac{||\mu||}{\Delta E} \right)^{2} e^{-a||\beta||} \tag{1}
\]

where $\beta = \frac{1}{kT}$, $\alpha$ is a parameter from the free energy relationship, and $\Delta E$ is the energy difference between the raw (uncorrected) RAS-SF energies of the S\textsubscript{i} and 1ME states.\textsuperscript{17} The rates are computed relative to the reference system, a single BET-B molecule (note that alpha cancels out in relative rate calculations). When several target 1ME states are available (as it happens in (BET-B)\textsubscript{2} where the two lowest 1ME states are degenerate), the respective rates are summed. When the gap between the lowest excitonic pair (EX\textsubscript{1} and EX\textsubscript{2}) is comparable with kT, the rates from both states are computed and averaged using Boltzmann’s populations.

The cc-pVDZ basis was used in all calculations reported here. We note that this is a smaller basis than in refs 8 and 9, where we employed a mixed basis (cc-pVTZ-f on carbons and cc-pVDZ on hydrogens). Core electrons were frozen in RAS-SF calculations. All calculations were performed using the Q-Chem electronic structure program.\textsuperscript{25,26}

2.1. Raw RAS-SF Energies and Energy Correction. The RAS-SF configuration expansion contains all important determinants needed to describe EX/LE, CR, and ME configurations; thus, it provides a balanced description of electronic states relevant to SF. Although RAS-SF wave functions are of good quality, the dynamic correlation is largely missing. Consequently, the absolute excitation energies are not sufficiently accurate. In our previous work,\textsuperscript{9,15–17} we used simple empirical correction to account for missing dynamical correlation. Here we employ a more rigorous energy correction

![Figure 1. Two different views of the structure of the two BET-B molecules taken from the crystal structure. The distance between the covalently linked tetracene rings (units A and B) is 3.34 Å, the distance between A and A’ is 3.40 Å. A and B rings are staggered (the angle between their long axes is 45°), whereas A and A’ are parallel (zero angle) but shifted along the long axis by 1.5 Å (about 0.6 of benzene’s ring width).](image-url)
scheme based on state-specific wave function composition. The wave function analysis scheme for multichromophore assemblies\textsuperscript{18} allows one to decompose the total adiabatic wave function in terms of EX/LE, CR, and ME configurations.

The energy correction scheme in terms of wave function composition was described in detail in refs 18 and 24. The expression for the corrected energies is

\[ E[\Psi] = E_0[\Psi] + \sum_X \omega_X E_C[\Psi^X] \] (2)

where \( X \) corresponds to a specific type of excitation contribution and \( E_C[\Psi^X] \) are correction energies associated with each \( X \) contribution with \( \omega_X \) weight. The different types of excitations considered here are EX/LE, CR, and ME configurations.

2.1. Corrected Energies for BET-B. For a bichromophoric system, the weights of different configurations are given by \( \omega_{LE} \) and \( \omega_{CR} \). CR numbers \( \omega_{S}\)S and \( \omega_{SS} \) and ME indices \( \omega^{TT} \) (triplet–triplet) and \( \omega^{SS} \) (singlet–singlet). We note that in BET-B the two tetracene moieties are equivalent by symmetry; thus, the weights of LE and CR configurations are symmetric and it is sufficient to consider their sums, \( \omega^{LE} \) and \( \omega^{CR} \). For low-lying excited singlet states of a bichromophoric system, eq 2 assumes the following form:

\[ E[\Psi] = E_0[\Psi] + \omega^{LE} E_C[\Psi[LE]] + \omega^{TT} E_C[\Psi[TT]] + \omega^{SS} E_C[\Psi[SS]] + \omega^{CR} E_C[\Psi[CR]] \] (3)

Based on our previous studies,\textsuperscript{18,19} the SS contributions in the decomposition of low-lying states are usually rather small. Here we approximate the correction to these contributions (\( E_C[\Psi[SS]] \)) as twice the correction of singlet local excitons (\( E_C[\Psi[LE]] \)). Higher contributions like QQ (quintet–quintet) are not considered. Hence,

\[ E[\Psi] = E_0[\Psi] + (\omega^{LE} + 2\omega^{SS})E_C[\Psi[LE]] + \omega^{TT} E_C[\Psi[TT]] + \omega^{CR} E_C[\Psi[CR]] \] (4)

To obtain the correction energy to the CR contributions, we compare the energies of RAS-SF CR diabatic states (computed as described in our previous work\textsuperscript{24}) to the excitation energy of the CT state computed with constrained DFT (C-DFT) with \( \omega B97X-D \). The C-DFT state corresponds to the A\textsuperscript{B} configuration, while the RAS-SF CR diabatic states for symmetric dimers correspond to “+” and “−” linear combinations of the A\textsuperscript{B} and A\textsuperscript{B} configurations. Therefore, in order to compare C-DFT with the RAS-SF energies, we take the average of the two lowest RAS-SF CR diabatic states:

\[ E_C[\Psi[CR]] = E_{CT}^{\omega B97X-D} - \frac{1}{2} (E_{CR1}^{\text{RAS-SF}} + E_{CR2}^{\text{RAS-SF}}) \]

\[ = -1.693 \text{ eV} \] (5)

The correction energies to the TT contributions are obtained from the energies of the lowest quintet state (\( Q_1 \)) of BET-B as

\[ E_C[TT] = E_{Q_1}^{\omega B97X-D} - E_{Q_1}^{\text{RAS-SF}} = -0.462 \text{ eV} \] (6)

Finally, the energy correction to LE contributions is obtained by enforcing the RAS-SF corrected energy for the lowest EX singlet state of BET-B to be equal to the excitation energy of the lowest excited singlet computed with \( \omega B97X-D \)

\[ E_C[LE] = E_{S_1}^{\omega B97X-D} - (E_{S_2}^{\text{RAS-SF}} + \omega_{S}^{TT} E_C[TT] + \omega_{S}^{CR} E_C[CR])) \]

\[ = -0.939 \text{ eV} \] (7)

where \( E_{S_1}^{\omega B97X-D} \) is the excitation energy of the lowest excited singlet of the BET-B molecule computed with \( \omega B97X-D \) and the \( S_1 \) label corresponds to the lowest EX singlet of BET-B obtained with RAS-SF (see Table S1).

2.1.2. Corrected Energies for (BET-B)\textsubscript{2}. The expression for corrected energies for (BET-B)\textsubscript{2} is

\[ E[\Psi] = E_0[\Psi] + (\omega^{LE} + 2\omega^{SS})E_C[\Psi[LE]] + \omega^{TT} E_C[\Psi[TT]] + \omega^{CR} E_C[\Psi[CR]] \]

\[ + \omega^{CR} E_C[\Psi[CR']] \] (8)

where CR’ corresponds to charge resonances between the two BET-B molecules and \( E_C[\Psi[CR']] \) is obtained as

\[ E_C[CR'] = (E_{S_1}^{\omega B97X-D} - (E_{S_2}^{\text{RAS-SF}} + \omega_{S}^{LE} + 2\omega_{S}^{SS} E_C[\Psi[LE]]) + \omega_{S}^{TT} E_C[TT] + \omega_{S}^{CR} E_C[CR])/\omega_{S}^{CR'} \]

\[ = -1.522 \text{ eV} \] (9)

where here \( E_{S_1}^{\omega B97X-D} \) is the excitation energy of the lowest excited singlet of (BET-B)\textsubscript{2} computed with \( \omega B97X-D \) and the \( S_1 \) label corresponds to the lowest EX singlet of (BET-B)\textsubscript{2} obtained with RAS-4SF (see Table S1). Higher configurations with the TTS form have been included in the \( \omega^{TT} \) weights.

2.2. Comparison of Energies and Anticipated Error Bars. Here we discuss anticipated error bars of the corrected energies. Let us revisit tetracene, to illustrate the origin of the problem. Table 1 shows excitation energies for tetracene. As one can see, RAS-SF considerably overestimates experimental energies and the errors are different for the singlet and triplet states: they are 0.88 and 0.28 eV, respectively, in the cc-pVDZ (1.41 and 0.53 eV in a triple-ζ quality basis). Thus, the errors in relative energies of the singlet and multichromophore states in dimers (and larger aggregates) will be significant, as illustrated by \( E_{S_1} = 2\times E_{T_1} \) given in the last row of Table 1.

In our previous work,\textsuperscript{15–17} we used simple empirical correction following the idea from ref 29: raw RAS-SF energies of \( S_1 \) and \( S_2 \) states were shifted down by 1 eV, energies of the triplets were shifted down by 0.2 eV, and energies of the ME states were shifted down by 0.4 eV (twice the value for the triplet). Since we always compute rates relative to the reference tetracene system, the correction was canceling out exactly. That is, the relative rates computed using the old fixed-value correction are identical to the rates computed using the raw
RAS-SF energies. In this approach, the effects of possible contributions of CR configurations and mixing of LE and TT configurations were not accounted for. The new energy correction scheme is based on wave-function compositions of the adiabatic states and, therefore, accounts for these effects. However, the correction relies on the reference values. We chose to use ωB97X-D/cc-pVQZ as our reference method because we could not find a more reliable approach, which is still affordable. Thus, our corrected RAS-SF energies are going to be as good as ωB97X-D/cc-pVQZ is.

As one can see from Table 1, the errors of ωB97X-D/cc-pVQZ against the experimental excitation energies of BET-B in solution (2.42 eV) are 0.615 and 0.279 eV, respectively. These values give an estimate of the error bars in the absolute excitation energies computed using our scheme: 0.62 eV for S1/S1, 0.28 eV for T1/T1, and 0.56 eV for ME. The errors in the S1−1ME gap are much smaller, about 0.06 eV. To evaluate the accuracy of absolute excitation energies, we can compare the computed corrected value of S1 of 2.61 eV with the experimental excitation energies of BET-B in solution (2.42 eV) and in neat film (2.32 eV). Thus, the computed S1 state is blue-shifted by about 0.2 eV. The agreement could be improved by using higher-quality reference data for computing energy correction.

3. RESULTS AND DISCUSSION

In the context of SF, relevant electronic states of a system comprising two chromophores (A and B) are EX, CR, and ME states.18 The former can be described as a linear combination of excited states (Si) of the individual fragments (c1Si(A)-S0(B) + c2Si(B)S0(A)); these states carry the oscillator strength of the transition giving rise to the initially excited bright state (the distribution of the oscillator strength and the energy splitting between these states depends on the relative orientation of the chromophores). Because EX states are derived from the excited states of the individual chromophores, they are often referred to as LE states. At small interchromophore distances, adiabatic wave functions of the excitonic states also include CR configurations (A′B′ and A′B). The ME states are derived from the simultaneously excited triplet states of the individual chromophores (T1(A)T1(B)), which can be coupled into the overall singlet, triplet, or quintet state. The quintet state usually has pure multie exciton character, whereas the 1ME state can mix with other singlet configurations (EX and CR), which lowers its energy and affects the electronic couplings with other singlet states.15,18,19 At large interchromophore separation, the energy of the EX states equals the energy of the Si state of the individual chromophore and the energy of the ME states equals twice the energy of T1. The first step of SF entails a nonadiabatic transition from the EX to the 1ME manifold. Once 1ME is formed, two triplets can, in principle, separate by Dexter energy transfer,6,30 provided that possible triplet acceptors are available. The energy splitting between 1ME and ME arises due to stabilization of the 1ME state by configuration interaction; it represents the energy penalty that needs to be overcome for two triplets to separate. This quantity is called multie exciton binding energy.15

This relatively simple picture becomes increasingly complex for larger chromophore aggregates. The number of EX states increases proportionally to the number of chromophores, and the excitonic band develops.31,32 Importantly, these states are quite delocalized29,33 the calculations in tetracene derivatives34 and pentacene18 show delocalization over more than 10 molecules and an average electron−hole distance greater than 6 Å. The ME states, on the other hand, are more localized.18 Thus, many computational studies of SF focus on model dimers whose structures are taken from the available X-ray structures.

Here we compute the manifold of low-lying excited states in BET-B and (BET-B)2 and describe their characters in terms of the LE, ME, and CR configurations. Figure 1 shows labels marking the individual chromophores used throughout this study. In BET-B, A and B refer to the two tetracene rings. In (BET-B)2 states localized on one of the BET-B molecules are denoted by either A/B or A′/B′, whereas the interchromophore states are marked by mixed labels, i.e., A′B′, A′/B′, etc.

In the case of the BET-B molecule, we consider two lowest excitonic states (S1(AB) and S1(AB)), using the notations from our previous work5,18−17 as the singlet and quintet ME states. Table 2 shows energies and properties of these states.

Table 2. Electronic Properties of BET-B4

| state         | E0 (eV) | f1 | α1e | α1cr | α1tt | α1ss | ||γ|| |
|---------------|--------|----|-----|------|------|------|-------|
| S1(AB)        | 2.69   | 0.307 | 0.80 | 0.14 | 0.00 | 0.06 | 0.056 |
| S1(AB)        | 3.09   | 0.932 | 0.88 | 0.02 | 0.01 | 0.09 | 0.092 |
| 1ME           | 2.49   | <0.001 | 0.00 | 0.20 | 0.79 | 0.00 |       |
| 1ME           | 2.90   | 0.00  | 0.00 | 1.00 | 0.00 |       |       |

*||γ|| denotes coupling with the 1ME state.

The energies were computed from the raw RAS-SF energies by using the energy correction computed by eq 4,18 which accounts for dynamical correlation. As one can see, both excitonic states include some CR contributions. Noticeably, the 1ME state has a quite substantial contribution from the CR configurations (20%), which is responsible for nonvanishing oscillator strength and for significant coupling with the excitonic states, evaluated in terms of the squared norm of the symmetrized one-particle transition-density matrix (||γ||)2,8,9 The multiexciton binding energy for BET-B is 0.41 eV.

The (BET-B)2 dimer has C2 symmetry. Consequently, the canonical MOs are delocalized over both BET-B molecules and even qualitative assignment of state characters of the computed adiabatic states cannot be easily performed by analyzing the wave function amplitudes. However, the state characters can be unambiguously determined and quantified using a recently introduced approach based on localized MOs and spin-correlators.18 Frontier fragment orbitals for the (BET-B)2 system within the RAS2 space in RAS-4SF calculations mainly correspond to the HOMOs and LUMOs of the four tetracene moieties with small delocalization toward the covalent bridge (Figure 2). Qualitatively, the manifold of the low-lying singlet adiabatic excited states in the system with four chromophore units is mainly derived from the 16 diabatic configurations: four EX states, six ME states, and six CR states. We computed the 16 singlet adiabatic states of (BET-B)2 and assigned their character using our wave function analysis scheme.18 We also computed the six lowest high-spin 3ME states. The results for all 1ME and 3ME states and for the lowest seven EX/CR states are collected in Table 3. These states constitute the lowest-energy manifold (the next singlet state appears at 3.22 eV).

All computed 1ME/3ME states can be described as singlet-and quintet-coupled pairs of triplet states residing on two tetracene fragments. As one can see, the two lowest 1ME states, which are degenerate, are of intramolecular type. They are...
energetically separated from the next four 1ME states, which are of the intermolecular type, by a gap of ~0.3 eV. The intramolecular 1ME states have considerably larger mixing of the CR configurations, which is responsible for their energy lowering and also larger couplings with the EX states. This behavior can be explained by through-bond interactions within each BET-B molecule, which lowers the energy and increases the intramolecular couplings. The two lowest EX/CR states are located at 2.61 and 2.64 eV; EX₁ is dark, and EX₂ is bright. We note that both states are delocalized and feature noticeable intramolecular couplings. The two lowest EX/CR states are derived from a mixture of LE and CR on the two outer tetracene units (B and B°), whereas the two highest computed states are predominantly of CR character.

There are six quintet ME states, which are nearly degenerate (2.79−2.84 eV). Similarly to BET-B, their wave functions are dominated by the TT configurations. The absence of other configurations in these states explains small splittings of the energies, in contrast to the 1ME manifold. Thus, through-bond interaction has much less of an effect on the 1ME states relative to the 3ME ones. We observe that five out of six 3ME states have mixed intra- and intermolecular character. The highest 3ME state is almost a pure TT (intermolecular) state. The multie exciton binding energy of the lowest 3ME state is 0.34−0.39 eV, which is very close to the value obtained for BET-B. In contrast, the four highest intermolecular 3ME states are practically degenerate with the 3ME band, leading to the vanishing multie exciton binding energies.

Figure 3 shows the energy diagram for BET-B and (BET-B)₂. As one can see, in (BET-B)₂, the transition to the lowest two 1ME states from the lowest EX pair is exoergic by 0.17 eV, whereas the four intermolecular 1ME states are higher in energy (by 0.16 eV). Thus, most likely, SF in BET-B aggregates proceeds via intramolecular 3ME states, as in the isolated covalent dimer. Although we anticipate that our computed absolute excitation energies might have substantial errors, we estimate the errors in the S₁−3ME gap to be about 0.06 eV (see section 2.2 for discussion). Thus, we believe that the relative ordering of the lowest EX states relative to the 1ME manifold is described correctly by the present calculations.

The interaction between the two BET-B molecules lowers the excitation energies of the lowest 3ME and EX states in (BET-B)₂ with respect to the transition energies in BET-B by 0.05 and 0.08 eV, respectively. The larger effect for the excitonic state is consistent with its delocalized character. Thus, the overall driving force for SF is slightly reduced in the dimer with respect to the BET-B monomer (by 0.03 eV). The couplings are also slightly reduced, probably because of the delocalized character of the excitonic states. Nevertheless, these changes are rather small to significantly affect the rates. The computed rates for the transition from the EX₁/EX₂ pair to the two lowest ME states in (BET-B)₂ are almost the same as in

**Table 3. Electronic Properties of (BET-B)₂**

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<th>state</th>
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<tr>
<td>3′ME₅</td>
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<td>0</td>
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<td>0.09</td>
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<td>0.12</td>
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<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.21</td>
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<tr>
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<td>0.01</td>
<td>0.22</td>
<td>0.21</td>
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<tr>
<td>CR₁</td>
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<td>0.11</td>
<td>0.12</td>
<td>0.07</td>
<td>0.06</td>
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<tr>
<td>CR₂</td>
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<td>0.10</td>
<td>0.06</td>
<td>0.06</td>
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<td>0.56</td>
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<td>CR₃</td>
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<td>0.07</td>
<td>0.72</td>
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<td>0.75</td>
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*"$\|\gamma\|$ and $\|\gamma'\|$ denote couplings with the two lowest EX states (EX₁ and EX₂), respectively.*
BET-B: \( \log(\frac{r_1(BET-B)}{r_1(BET-B)}) = -0.4 \). We also estimated the rate of transitions to the intermolecular \(^1\)ME states; as expected, the rate is considerably lower (by about 3 orders of magnitude) relative to the rate to the lowest (intramolecular) \(^1\)ME states. An intriguing thought is that if these states are populated, either via transitions from the lowest EX state or from higher excited states, one might expect more efficient separation of the triplets due to vanishing multiexciton binding energies.

Thus, our calculations suggest that SF in neat films of BET-B is predominantly intramolecular and is similar to that in the isolated dimer. These results explain and rationalize why the SF rates in BET-B are virtually the same in solution, neat film, and when doped in DPT. Although the electronic structure of the dimers (and larger aggregates) of BET-B is rather complex and features many more states, the energies and character of the relevant states, the lowest excitonic and ME states, are similar to those of the isolated dimer. The manifold of the intermolecular ME states lies higher in energy; also, because intermolecular \(^1\)ME states have less CR character, they feature smaller electronic couplings.

We note that relatively weak couplings for the intermolecular \(^1\)ME states in \((BET-B)_2\) might be not only because there is no through-bond interaction, which is stronger than the through-space one, but also because the A and A’ tetracene moieties are shifted by about 0.6 benzene rings (Figure 1), which is unfavorable for couplings. In order to test how the interplay between through-space and through-bond inter- and intra-molecular interactions can be affected by different packing of dimers in a molecular solid or aggregate, we analyzed electronic states of \((BET-B)_2\) in three additional model structures varying by the offset between the A and A’ chromophores. In the first

![Figure 3. Energy levels of BET-B (left) and \((BET-B)_2\) (right). Bright states are marked in red; quintet ME states are marked in blue; all other states are marked in black.](image1)

![Figure 4. Excitation energies of \((BET-B)_2\) in model structures differing by the overlap between the middle tetracene moieties (A and A’, see Figure 1). Left: The tetracene rings are perfectly stacked (shift of 0.00 Å). Middle: The tetracenes are shifted along the long axis by half of a benzene ring (shift of 1.23 Å); this structure is similar to the crystal structure. Right: The tetracenes are offset by one benzene ring along the long axis (shift of 2.46 Å).](image2)
structure, the two middle tetracenes are perfectly stacked; this structure is 0.22 eV higher than the dimer from the crystal structure. In the second structure, the two BET-B molecules are shifted such that the two tetracenes are offset by exactly half of the benzene ring (this structure is similar to the crystal structure; its energy is only 0.02 eV higher). In the third structure, the tetracenes are offset by one benzene ring (this structure is 0.09 eV above the original X-ray structure).

Figure 4 shows the energies of the ME and EX/CR manifolds in the three structures; the detailed analysis of the state characters and energies is given in the Supporting Information. The first observation is that the electronic properties of the half-ring offset structure are rather similar to the model X-ray dimer. In the structures with zero and full-ring offset tetracenes, the state ordering changes significantly. The most striking observation is broadening of the ME band and strong stabilization of the lowest exciton state (in the structure with stacked tetracenes, this state develops significant (46%) CR character). These EX/CR states drop significantly below the ME band, which is conducive to exciton trapping in the excimer-like states. Based on the recent study of two different linked tetracene dimers,9,10 we expect that such a type of molecular packing will be detrimental to SF. Interestingly, strong perturbation to the state ordering and the EX/CR band does not affect the wave function composition of the lowest 1ME states—they retain their pure intramolecular character. We conclude that small variations in molecular packing of BET-B-like dimers, which feature strong through-bond coupling between the two linked tetracenes, will not change the balance between intra- versus intermolecular couplings; that is, we expect that the lowest ME states are likely to be localized on individual dimers, despite relatively good overlap between the π-systems of the tetracenes from different molecules. This is a characteristic feature of BET-B deriving from the strong through-bond coupling between the chromophores. Since the strength of the through-bond interactions can be turned on and off by structural variations, as was illustrated in a recent study of pentacene dimers,10 other isomers of BET-B with weak coupling might feature a different pattern. The calculations on different model structures suggest that the design of the SF materials based on covalently linked chromophores can indeed focus on the electronic properties of the individual molecules and electronic couplings facilitated by the linker, rather than on molecular solid morphology.

Excited-state nuclear relaxation might play an important role in the SF of crystalline BET-B, by affecting state energies and electronic couplings and, ultimately, SF rates.9 Although these effects have not been considered in the present study, the results obtained for different intermolecular displacements suggest that excited-state structural relaxation could drive the excited system into a trap state, hindering the SF process. On the other hand, as discussed above, these trap states correspond to intermolecular eximers, while the lowest ME states are of intramolecular nature. Hence, relaxation within the ME manifold following the initial photoexcitation might favor SF over the formation of low-energy eximers. We expect that the competition of different deactivation pathways will be strongly dependent on the activation of specific vibrational modes.

4. CONCLUSION

In this paper, we investigated electronic properties of the two BET-B molecules, each consisting of the two covalently linked tetracene chromophores. The analysis of the electronic states reveals that the lowest 1ME states, which are well separated in energy from the higher ME states, are of local, intramolecular character, due to strong through-bond interactions. In contrast, the excitonic states are more delocalized. The 1ME states in which two triplet excitons reside on different molecules are not readily accessible from the lowest excitonic state (although they might be populated from higher-excited excitonic states). The important practical implications are (i) the electronic structure of the individual covalently linked dimer is the most essential factor for the design of efficient SF materials; (ii) the theoretical modeling of SF using small dimer systems is reasonably justified. Our calculations and wave function analysis also provide valuable reference data for the development of excitonic models for multichromophore assemblies.35–42

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b07666.

Details of electronic structure calculations, relevant Cartesian geometries, raw excitation energies, energy correction calculations, and detailed wave function analysis (PDF)

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Notes

The authors declare no competing financial interest.

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