

# Mechanism of singlet fission in carotenoids from a polyene model system

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## Abstract

Singlet fission (SF) is the process of formation of multiple excitons (triplet) from a locally excited singlet state. The mechanism of SF in polyacenes have been shown to proceed via a charge transfer intermediate state. However, carotenoids are not understood in the context of SF. This is possibly due to the complicated multireference nature of the low-lying excited states of carotenoids and the presence of a dark  $2^1A_g$  state below the optically bright  $1B_u$  state. In this work, we show that the dark  $A_g$  state in polyenes / carotenoids, along with the charge transfer states, play a pivotal role in the SF process. We notice that the relative importance of these states vary with change in geometry and the overall presence of multiple pathways is crucial to the success of SF process in carotenoid aggregates and disordered geometries.

Singlet fission (SF) is the process of formation of two free triplet states residing on separated monomers from an initially excited singlet state localized on a single monomer (chromophore).<sup>1,2</sup> This process proceeds via formation of coupled triplet state (coupled-TT) on multiple chromophores in near vicinity, and its subsequent diffusion to free triplets on distant chromophoric sites.<sup>3</sup> This first step of the SF process is schematically shown in Fig. 1. SF can only occur in the presence of multiple chromophores and the SF phenomena has been observed in crystals, aggregates, thin films and in disordered states such as biological medium.<sup>4-6</sup> SF is characterized by the observation of more than 100% triplet quantum efficiency, which denotes the formation of two excitons by the action of a single photon. SF process have been extensively observed in acene systems.<sup>4,5,7,8</sup>

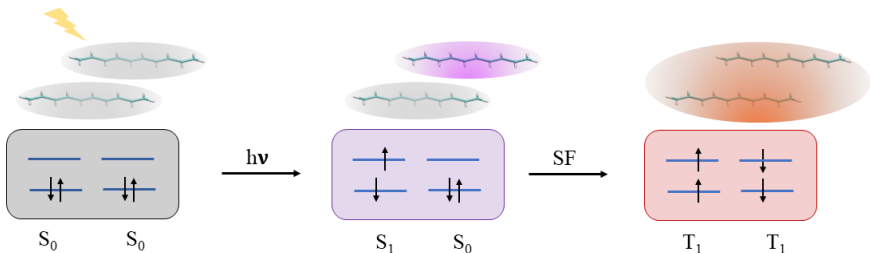


Figure 1: Schematic representation of the first step of SF process - formation of coupled-TT state.

While SF process has been known for a long time, its mechanism is only recently being studied.<sup>8-10</sup> In polyacenes, the coupled-TT state formation is mediated by a charge transfer (CT) excited state, where CT occurs between the two monomers where the coupled-TT state resides.<sup>9,11,12</sup> Since the CT state is sensitive to the relative orientation of the monomers, the efficiency of SF process depends on the crystal packing and geometry.<sup>13-15</sup> Therefore, many of the experimental observations in acenes have been explained within this model.

Carotenoids exhibit SF phenomena in H-aggregates and also in biological phases with significant disorder.<sup>6,16-19</sup> In J-aggregates, singlet fission is observed for dipolar carotenoids, although it has not been observed for non-polar carotenoids.<sup>17</sup> This apparent insensitivity to structural features of SF in carotenoids remains unexplained. Furthermore, the carotenoid

monomer transitions are significantly different from the acenes. The first excited state in carotenoids is an optically dark  $2^1A_g$  state followed by a second optically active  $^1B_u$  state (HOMO-LUMO excitation).<sup>20</sup> This unexpected ordering of the excited states is due to multireference nature of the conjugated polyenes/carotenoids.<sup>21,22</sup> Therefore, to address these intricacies of SF in carotenoids one has to extend the model to include both  $A_g$  and  $B_u$  states.

Carotenoids spectra and low-lying excited states are similar to conjugated polyenes due to the predominant importance of the conjugated backbone. In our work we consider a conjugated polyene model system, decapentaene to understand mechanism of SF in carotenoids. The choice of decapentaene as a model system is the position of its  $A_g$  state below the  $B_u$  state. All polyenes shorter than decapentaene have a first excited  $B_u$  state. We probe the importance of  $A_g$  states as well as CT states as effective conduits for the formation of the coupled-TT state from the initial optically active state localized on a single polyene. We will show that depending on the relative geometries of the monomers, a variety of pathways via  $A_g$  and CT states are indeed effective intermediates for SF.

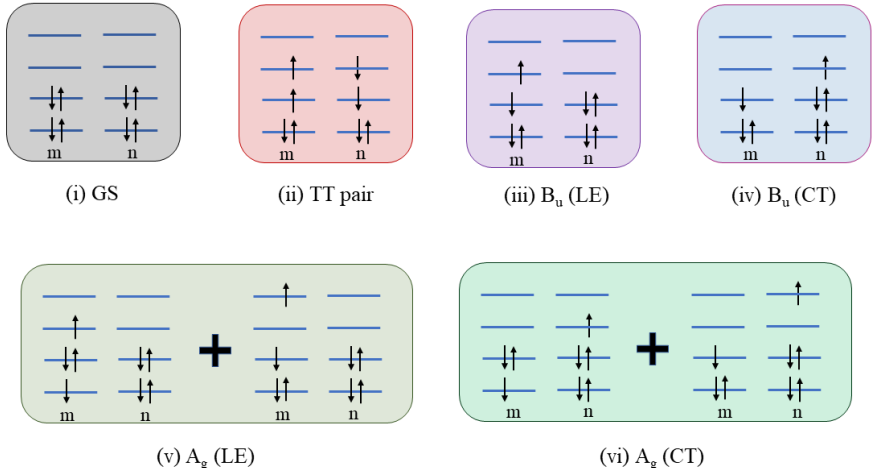


Figure 2: Electronic configuration of the prototype low-lying states of polyene / carotenoid systems. The locally excited states are denoted as LE and the charge transfer states as CT. The  $A_g$  and  $B_u$  states refer to the symmetry of the excited states on the monomers.

The predominant electronic configurations for the low-lying excited states of polyene dimers are shown in Figure 2. The different types of states that are possible are: (i) ground

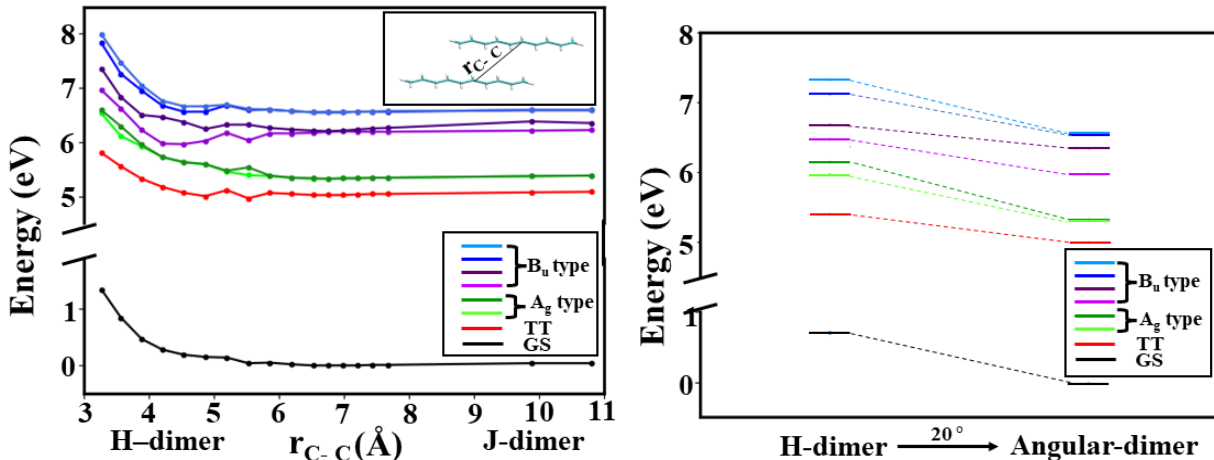
state (GS) which is predominantly closed shell in nature; (ii) coupled-TT state with two triplet states localized on monomers  $m$  and  $n$ , such that the total spin of the system is an effective singlet; (iii) optically active  $B_u$  states that are localized on single monomer (i.e., locally excited or LE) and is characterized by a single electron excitation from  $\text{HOMO}_m$  to  $\text{LUMO}_m$ ; (iv) CT state involving a  $\text{HOMO}_m \rightarrow \text{LUMO}_n$  excitation (we denote this as  $B_u(\text{CT})$ ); (v)  $A_g$  state that is localized on a single monomer (LE) and characterized by a two electron excitation  $\text{HOMO}_m \rightarrow (\text{LUMO} + 1)_m$  and  $(\text{HOMO} - 1)_m \rightarrow \text{LUMO}_m$ ; and (vi)  $A_g$  state with a CT component, i.e., two electron excitation with  $\text{HOMO}_m \rightarrow (\text{LUMO} + 1)_n$  and  $(\text{HOMO} - 1)_m \rightarrow \text{LUMO}_n$ . It is important to note that with respect to the ground state, the  $B_u$  and  $B_u(\text{CT})$  states are one electron excitations, while the  $A_g$ ,  $A_g(\text{CT})$  and TT states are two electron excitations.

The SF process has to satisfy certain energetic and coupling criteria to occur efficiently. Since SF requires the formation of two triplet excited states from one excited singlet state, the individual monomers must satisfy the basic rules of conservation of energy,<sup>1,23</sup> i.e.,

$$E(S_1 - S_0) \geq 2E(T_1 - S_0). \quad (1)$$

While this is a necessary condition, it is not a sufficient one as can be suspected from the sensitivity of SF efficiency on geometry and crystal packing in some SF materials. For the energy transfer to occur effectively, the coupling term between the initial and final states,  $\langle \Psi_i | \hat{H} | \Psi_f \rangle$ , has to be significant.<sup>10,24</sup> When one considers the  $B_u$  ( $S_1$ ) state as the initial state and coupled-TT as the final state, this can only be viewed as a two electron transfer process and the coupling term between these states is quite small. Therefore, it is presumed that the SF process occurs predominantly through an intermediate. In Refs 25–27, using various nonadiabatic approaches, it has been proposed that the intermediate state contains large CT components in case of the polyacenes. The CT state can be viewed as an one electron transferred state from  $S_1$  state and also connected to the coupled-TT state via one

electron transfer. Therefore, the coupling terms of CT state with both  $S_1$  and coupled-TT states are significantly large ( $\approx 100$  meV) to allow SF process via the CT state.



(a) Excited state ordering from J-H structure of de- (b) Effect of rotation on the excited state ordering. capentaene dimers.

Figure 3: (a) Potential energy surfaces of low-lying states of decapentaene dimers calculated at the (8e,8o) active space SA-CASSCF/6-31G(d) level of theory. In the inset on the upper left corner the  $r_{C-C}$  is shown, which is plotted along the x-axis. (b) Comparison of the relative state ordering in an angular geometry with H-dimer geometry.

When this same approach is considered for the carotenoids/polyenes, the energy conservation condition for the monomers is satisfied (shown in SI). In the dimer geometries, the lowest excited state is the coupled-TT state as expected (Fig. 2).  $A_g$  states reside in between the coupled-TT and  $B_u$  states. Therefore, energetically the  $A_g$  states are in the correct region to act as effective intermediates. It should be noted that the CT states also satisfy this energy criterion in the polyene/carotenoid systems.

To evaluate the possibility of  $A_g$  states as intermediates one should also calculate the coupling terms. However, before the quantitative estimates, let us look at the qualitative features of these  $A_g$  states. The excited  $A_g$  state cannot be viewed from predominantly one electron HOMO-LUMO type transition. Excited  $A_g$  state is a multireference state with two electron transitions (with respect to ground state) - one transition from HOMO  $\rightarrow$  LUMO+1 and another from HOMO-1  $\rightarrow$  LUMO.<sup>21,22</sup> Therefore, it requires at least two configurations to be qualitatively described. It can, alternatively, be viewed as two spin

flips on a 1-D Heisenberg lattice (linear chain) of antiferromagnetically coupled spins.<sup>28</sup> The antiferromagnetic couplings ensure the formation of bond pairs between adjacent sites, i.e.,  $p_z$  orbitals. Thus, the ground state has alternating up and down spins to maximize favorable interactions. When two spins are flipped at distant locations two magnons are formed at these locations, i.e., it is a bimagnon state with  $\uparrow\uparrow$  and  $\downarrow\downarrow$  configurations. This bimagnon  $A_g$  state looks qualitatively similar to the coupled-TT state with the noteworthy difference that the  $A_g$  state has 2 magnons located on the same polyene (or chain) while coupled-TT is on different polyenes. Due to these similarities, one can expect to obtain large coupling between the  $A_g$  state and coupled-TT state. Furthermore, it is well known that carotenoids in photosynthetic systems show fast non-radiative transitions between the  $B_u$  state and the  $A_g$  state.<sup>29</sup> Therefore,  $A_g$  states seems to have significant transition probabilities from both  $B_u$  state as well as coupled-TT state and therefore, can act as an intermediate for SF in carotenoids / polyenes.

The dimer model structures are constructed from the decapentaene monomers. The dimer is created by forming slip stacked geometry of decapentaene and optimized at B3LYP/6-31G(d) level of theory. The H-dimer geometry and all intermediate geometries are created by reducing the slide, i.e., increasing the slip angle between the dimers, while the J-dimer structure is created by increasing the slide, i.e., reducing the slip angle. The slip angles of the H and J-dimer structures used are  $70.37^\circ$  and  $31.66^\circ$ , respectively. This is in accordance with the definitions of aggregates in Ref. 30. Fig. 3(a) shows the excited states and their nature along the H to J slipped geometries. The first excited state is a coupled-TT state, followed by 2  $A_g$  states and finally 4  $B_u$  states with different amounts of CT character. In H-dimer, the  $B_u$  states are all optically active, while in J-dimer the third  $B_u$  state is optically active. From the many degenerate excited states in the J-dimer, it is evident that due to large slide motion, the dimers are quite far apart and non-interacting, i.e., the states retain mostly the monomer characters. In H-dimer the degeneracies are lifted, i.e., the excited states in the monomers interact with each other giving rise to Davydov splitting. We further notice

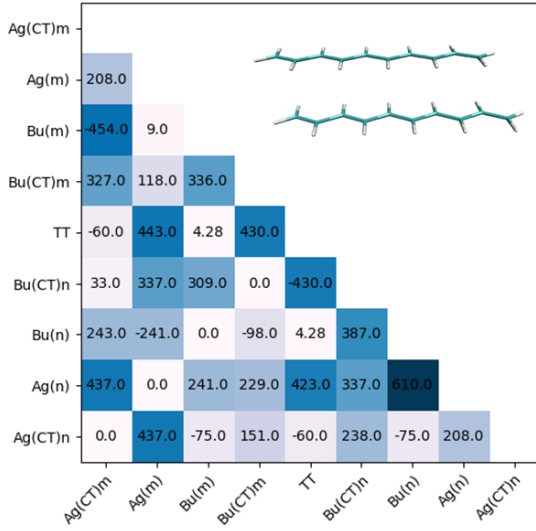
the effect of small rotation ( $20^\circ$ ) on the H-dimer and observe that the relative ordering of the states are similar (Fig. 3(b)). There are limited interactions between the states and degeneracies are somewhat lifted at least for the  $B_u$  states.

In order to compare the different states as intermediates in the SF process, diabatic representation of each of the states are constructed by considering the spin adapted configurations as shown in Fig. 2. For the configurations, the orbitals from (8e,8o) CASSCF/6-31G(d) calculations are taken after Pipek Mezey localization on respective monomers. The couplings coefficients between these diabatic states were calculated following the procedure in Ref. 25,26 and extended to include the  $A_g$  states. The equations used for the couplings are included in SI.

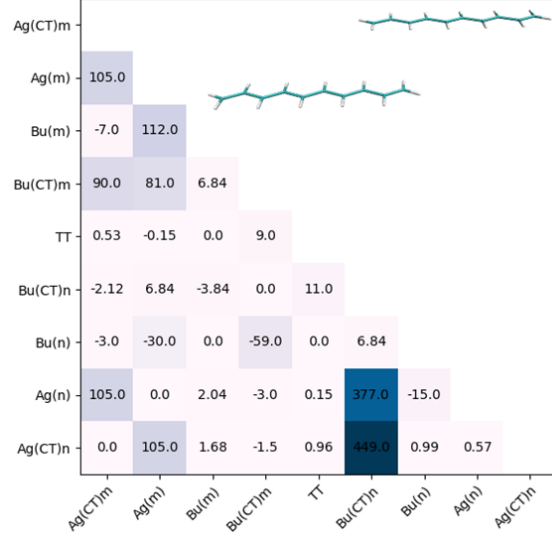
The heat maps of the coupling terms between the different states are given in Fig. 3, at H-dimer, J-dimer, intermediate (H-J) and rotated geometries. On cursory inspection, one can notice the numerous high coupling terms ( $> 100$  meV) in all geometries, except for J-dimer.

In H-dimer, there is a large coupling between the optically active local excited  $B_u$ (LE) state and the  $A_g$  states with or without CT components as well as  $B_u$ (CT) state. Therefore, one can expect the excitation to decay from  $B_u$  state to  $A_g$ ,  $A_g$ (CT) and  $B_u$ (CT) states. Following this, there are large couplings between  $B_u$ (CT) and  $A_g$  states with the subsequent coupled-TT state. Therefore, the SF process can occur through both  $B_u$ (CT) and  $A_g$  states as intermediate in the H-dimer. The signature of  $A_g$  state as an intermediate between  $B_u$  and TT state is in good agreement with experimental observation from transient absorption studies.<sup>16</sup>

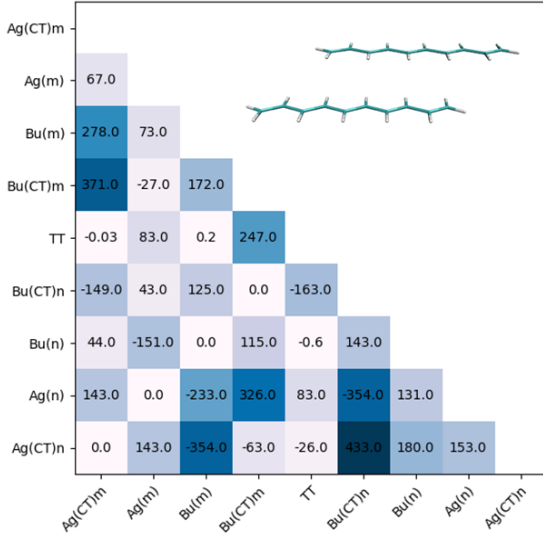
For J-dimer, the coupling matrix looks markedly different from the other geometries. It has only few large coupling terms. There are coupling terms between  $B_u$  state to  $A_g$  state but no large coupling with the TT state. Therefore, while there is a feasible pathway from  $B_u$  to  $A_g$  state, it cannot decay onwards into the TT state. Therefore, our model predicts that SF process will not occur in J aggregate geometry in non-dipolar polyenes. This is in good



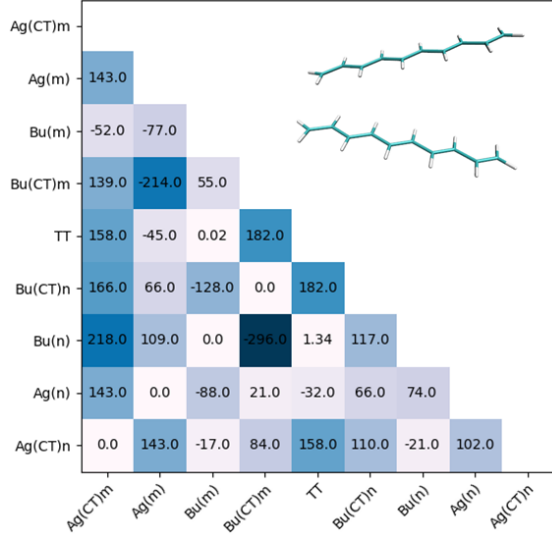
(a) H-dimer



(b) J-dimer



(c) Intermediate between H and J dimer



(d) Rotated dimer

Figure 4: Off-diagonal elements of the coupling matrices for (a) H-dimer, (b) J-dimer, (c) H/J-dimer (intermediate geometry), and (d) Angular-dimer. The values of the couplings are in meV and higher coupling values are denoted by darker colors. The corresponding geometries are shown for each case.

agreement with experimental observations.

In the intermediate structure between H and J geometries, the optically active  $B_u$  state is most strongly coupled with  $A_g(CT)$  and  $A_g$  states, and moderate coupling with  $B_u(CT)$  state. When one considers the coupling with TT state, it is only with  $A_g$  and  $B_u(CT)$ .



Therefore, in this case the predominant pathway is via  $A_g$  with some contributions from  $B_u$ (CT) state.

The angular geometry shows strong SF probabilities via CT states only, with both  $B_u$  and  $A_g$  characters. Therefore, it shows that disordered geometries are also capable of undergoing SF. The insensitivity of geometry on SF process in carotenoids can be explained within our model.

To summarize, from the energetic criterion in the monomer, i.e., comparison of energies between first optically active  $S_1$  and  $T_1$  states, it appears that SF phenomena is feasible in carotenoids and decapentaene as the model system. In order to explain the effect of geometry on SF in polyenes / carotenoids, we obtain the excited state energies at various geometries. In all the geometries, except J-dimer, significant Davydov splitting is observed, and therefore, we surmise that the excited states on the monomers are strongly interacting. We extend the diabatic model in Ref 25,26 to include all the low-lying excited states and calculate the coupling between these excited states. It shows that there are numerous efficient conduits for SF in H-dimer, e.g.,  $A_g$  state and CT states with both  $A_g$  and  $B_u$  nature. In case of rotated geometry, the most important pathways are both  $A_g$  and CT state with  $B_u$  nature. The model also shows that there are no efficient pathways in J-dimer. It should be noted that J-aggregates with polar carotenoids have shown signatures of SF phenomena and to capture that one might have to include polar groups in the theoretical study.

Therefore, this model for the first time shows the importance of  $A_g$  state as the intermediate for SF process and explains the experimental observations quite succinctly. It explains the experimental observation of  $A_g$  like peaks at intermediate timescales in transient absorption spectra on the way to a coupled-TT state formation. The presence of  $A_g$  states as intermediates along with CT states for the polyene system, shows the crucial difference of SF mechanism in carotenoids as compared to acenes.

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## Supporting Information Available

Detailed computational methods used in the work is given, along the geometries of the dimers that are referred to in the manuscript. The couplings between the different types of excited states and their formulae are given.

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