

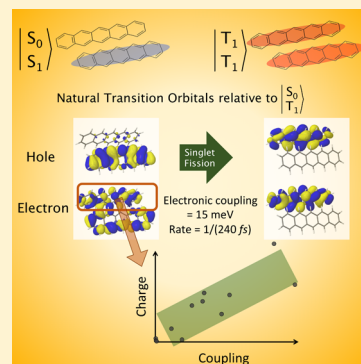
# First-Principle Characterization for Singlet Fission Couplings

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**S** Supporting Information

**ABSTRACT:** The electronic coupling for singlet fission, an important parameter for determining the rate, has been found to be too small unless charge-transfer (CT) components were introduced in the diabatic states, mostly through perturbation or a model Hamiltonian. In the present work, the fragment spin difference (FSD) scheme was generalized to calculate the singlet fission coupling. The largest coupling strength obtained was 14.8 meV for two pentacenes in a crystal structure, or 33.7 meV for a transition-state structure, which yielded a singlet fission lifetime of 239 or 37 fs, generally consistent with experimental results (80 fs). Test results with other polyacene molecules are similar. We found that the charge on one fragment in the  $S_1$  diabatic state correlates well with FSD coupling, indicating the importance of the CT component. The FSD approach is a useful first-principle method for singlet fission coupling, without the need to include the CT component explicitly.



Singlet fission is the process in which the singlet excitation energy in a molecule is split into two triplet excitons



With singlet fission, a high-energy photon absorption can generate two lower-energy triplet excitons. In solar energy devices, each exciton has a chance to drive for charge separation that leads to photocurrent. Due to the potential in increasing quantum yields in solar energy conversion,<sup>1,2</sup> singlet fission has attracted much attention recently.<sup>2–11</sup> The triplet yield in a thin film of 1,3-diphenylisobenzofuran, a molecule that has been regarded as a promising candidate for singlet fission,<sup>12</sup> was reported as  $200 \pm 30\%$ . A multiexciton state, presumably the product state of singlet fission ( $T_1T_1$ ), was observed right upon excitation in a pentacene thin film.<sup>9</sup> In another work, triplet excitons was observed at  $\sim 80$  fs time scales accompanied by a very similar decay in the singlet excited states.<sup>8</sup>

Suitable candidates for singlet fissions should have the  $S_1$  state energy more than twice the  $T_1$  energy. Previous computational works have predicted such a property over a number of molecules.<sup>10,13</sup> Using a restricted active space double spin flips (RAS-2SF) scheme, a transition state has been identified for a pair of pentacenes near crystal packing.<sup>5</sup> The electronic coupling for singlet fission has also been discussed frequently in the literature.<sup>2,3,14–16</sup> In the weak-coupling limit, the rate for singlet fission is given by the Fermi's golden rule

$$k_{if} = \frac{2\pi}{\hbar} |V_{if}|^2 (\text{FCWD}) \quad (2)$$

where the electronic coupling  $V_{if}$  is the off-diagonal Hamiltonian matrix element between the initial and final diabatic states and FCWD is the Franck–Condon weighted density of states. Singlet fission involves a change in the occupancy of two electrons, and the coupling is essentially a two-electron exchange-like integral, which is typically small.

The coupling strengths reported are between 0.1 and 4 meV,<sup>2,3,14,15</sup> too small to reproduce subpicosecond singlet fission rates. It was found that the coupling can arise from an indirect, charge-transfer (CT)-mediated component.<sup>3,4,7,15–18</sup> CT state population is also observed directly on the singlet excitation in time-dependent nonadiabatic dynamic simulations.<sup>19–21</sup>

Until now, the CT contribution has been estimated with model Hamiltonians or perturbations with a small number of CT states included in the basis. However, it is not always clear whether the configurations included in the model are sufficient. Additional problems may arise in including more configurations because the diabatic nature of the state needs to be maintained in order to properly model the process. Therefore, it remains a challenging problem to characterize the diabatic states properly and to quantify the influence of the CT contribution.

In the present work, we aim to calculate the singlet fission coupling from spin-localized states as its diabatic states. We generalize the fragment spin difference (FSD) scheme to calculate singlet fission coupling, which was originally developed for triplet energy transfer.<sup>22,23</sup> While singlet fission is mainly discussed throughout the present work, we note that the triplet–triplet annihilation (TTA), the reverse process where a singlet high-energy exciton can be created by two low-energy triplet excitations, shares essentially the same electronic coupling,  $\langle S_1S_0|H|T_1T_1\rangle$ . TTA has been a useful way to up-convert photon energies without the need for coherent input light.<sup>24–26</sup> The computational methods developed and discussed in the present work are applicable to TTA.

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Singlet fission involves change of spin states in both fragments, where FSD may be applicable for calculating its coupling strength. In its original form, FSD takes two eigenstates and forms diabatic states that are with the largest spin localization. To localize the spin population, the spin population is first defined as

$$\sigma_{mn}(\mathbf{r}) = \rho_{mn}^{\alpha}(\mathbf{r}) - \rho_{mn}^{\beta}(\mathbf{r}) \quad (3)$$

where  $\rho_{mn}$  is the one-particle transition density matrix. The spin difference in the donor and acceptor region is calculated as

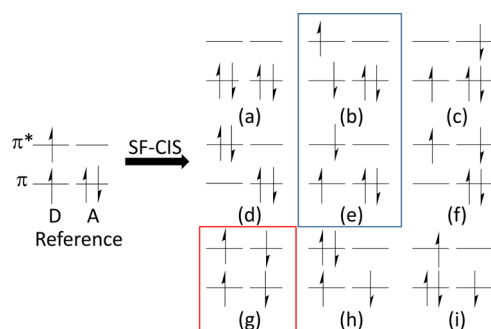
$$\Delta s_{mn} = \int_{\mathbf{r} \in D} \sigma_{mn}(\mathbf{r}) d\mathbf{r} - \int_{\mathbf{r} \in A} \sigma_{mn}(\mathbf{r}) d\mathbf{r} \quad (4)$$

where D and A are the donor and acceptor regions. In FSD, diabatic states are formed with a linear combination of the two eigenstates that are with the largest difference in their  $\Delta s$  values. In other words, the eigenvector of the  $\Delta s$  matrix gives the diabatic states. The FSD coupling is obtained from the off-diagonal Hamiltonian matrix element between the two diabatic states

$$V_{\text{FSD}} = \frac{\Delta s_{12} \Delta E_{12}}{\sqrt{(\Delta s_1 - \Delta s_2)^2 + 4\Delta s_{12}^2}} \quad (5)$$

where  $|1\rangle$  and  $|2\rangle$  are the two eigenstates in the linear combination for finding the diabatic states, and  $\Delta E_{12}$  is the energy difference between the two eigenstates.

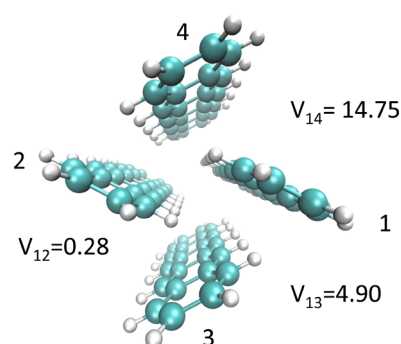
FSD requires a vertical excitation that generates the initial and final states simultaneously. The spin-flip configuration interaction singles (SF-CIS) scheme was proposed and tested in the present work. The spin-flip scheme starts with a high-spin configuration, and the desired low-spin configurations are obtained as spin-flipped excitations.<sup>27–29</sup> SF-CIS is the SF variant of the traditional spin-conserving CIS method. As shown in Figure 1, both  $|T_1T_1\rangle$  and  $|S_1S_0\rangle$  states can be



**Figure 1.** Configurations involved in SF-CIS starting from  $|T_1S_0\rangle$ , a state with triplet population localized at the donor. Shown are simplified four-orbital schemes with two ( $\pi$  and  $\pi^*$ ) orbitals from each fragment. The blue box indicates the configurations for the  $S_1S_0$  state (b,e), and the red is the  $T_1T_1$  state (g).

generated from  $|T_1S_0\rangle$  with spin-flipped excitations. In this case, the ideal  $\Delta s$  values relative to the reference  $|T_1S_0\rangle$  state are +2 for  $|T_1T_1\rangle$  and –2 for  $|S_1S_0\rangle$ , quite similar to that of triplet energy transfer. Thus, we further test FSD for singlet fission couplings.

To calculate the intermolecular electronic coupling, a thin-film pentacene<sup>30</sup> that resembles the experimental condition<sup>8</sup> was used. An array of four neighboring molecules from the X-ray structure is shown in Figure 2. The FSD coupling was calculated with SF-CIS states and DZ\* basis sets, performed



**Figure 2.** Singlet fission couplings calculated (in meV) for three pairs of molecules. The couplings are denoted as  $V_{ij}$ , where the singlet fission starts with the  $i$ th molecule excited.

with a developmental version of Q-Chem.<sup>31</sup> The singlet fission coupling values in three pairs of molecules are reported in Figure 2. The 1–2 dimer is a slip-stacked structure that has a  $\pi$ – $\pi$  interaction. The 1–3 and 1–4 dimers are in a herringbone structure with a CH– $\pi$  interaction. The initial singlet excitation can be in either of the two molecular fragments. We include both values in Table 1. Among the couplings, the largest one is between molecules 1 and 4, ( $V_{14}$ ) 14.75 meV, and the smallest is for  $V_{12}$ , 0.28 meV.

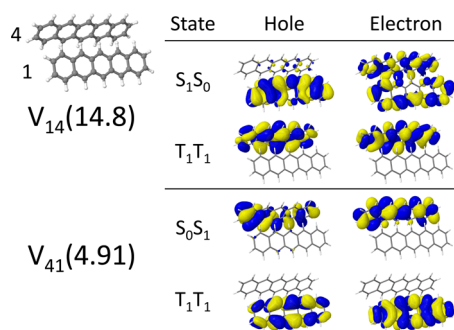
In the golden rule rate expression (eq 2), the FCWD is essentially the probability of a thermally relaxed initial state finding a resonant state in the final state. In Förster energy transfer, the FCWD is approximated as an integration of spectral overlap of donor emission and acceptor absorption. In our earlier work,<sup>23</sup> the triplet energy transfer rate was estimated similarly, that is, with the phosphorescent spectrum for the donor and a mirror image of phosphorescence of the acceptor to simulate the triplet “absorption”. It was shown that such an approach is both reasonably solid and practical.<sup>23</sup> For the present system, we estimated the density of states for  $S_1$  to  $T_1$  and  $S_0$  to  $T_1$  transitions similarly. We have derived spectral parameters from both experimental spectra (0–0 transition energies, vibronic progression frequencies, and spectral line widths) and density functional theory computation (structural differences). With other details given in the Supporting Information, for singlet fission in pentacene, the FCWD is estimated to be  $1.96 \text{ eV}^{-1}$ . With the coupling obtained (14.75 meV), the theoretical singlet fission lifetime is 239 fs. With the transition-state structure found previously,<sup>5</sup> the coupling is calculated as 37.30 meV, and the corresponding singlet fission lifetime is 37 fs, again confirming the theoretical plausibility of singlet fissions of experimental results.<sup>2,8,32</sup>

The diabatic states were further analyzed with the natural transition orbitals (NTOs).<sup>33</sup> As seen in Figure 3, there exists a CT component in the diabatic states of the 1–4 pair with initial  $S_1$  excitation starting from pentacene 1. On the other hand, when the  $S_1$  excitation is switched to pentacene 4, the coupling  $V_{41}$  is smaller (4.91 meV), and the CT component is invisible in the isosurface plots. The magnitude of the CT component in the diabatic states can be quantified by the net charge in one of the fragments. In Table 1, the charge on the donor in the  $S_1S_0$  diabatic state is also listed. It is seen that for large coupling cases, the corresponding  $q_D(S_1)$ 's are also large. The  $\Delta s$  values are also listed for the diabatic states. For the  $T_1T_1$  state, most of the values are close to the ideal value 2, indicating that the transition from the reference state  $T_1S_0$  to  $T_1T_1$  has a localized spin population change (in the acceptor). However, for  $S_1S_0$ ,

Table 1. Singlet Fission Couplings ( $V$  in meV) and Corresponding Lifetimes (fs) for Pentacene Pairs

structure	D <sup>a</sup>	A	$V_{\text{FSD}}$	rate <sup>-1</sup>	$q_{\text{D}}(\text{S}_1)^b$	$\Delta s(\text{S}_1\text{S}_0)$	$\Delta s(\text{T}_1\text{T}_1)$
thin-film phase <sup>30</sup>	1	2	0.28		0.0011	-1.96	2.00
	1	3	4.90		0.061	-1.81	2.00
	1	4	14.75 <sup>c</sup>	239	0.19	-1.58	2.00
	3	1	15.21	224	0.23	-1.12	2.00
	4	1	4.91		0.059	-1.86	2.00
$R = 5.6 \text{ \AA}^d$	1	4	23.20	96	0.22	-1.49	1.99
$R = 5.0 \text{ \AA}^e$	1	4	37.30	37	0.37	-1.09	1.96

<sup>a</sup>Singlet fission starts with the donor (D) in the  $\text{S}_1$  state and acceptor (A) in the ground state. <sup>b</sup>The charges on the  $\text{T}_1\text{T}_1$  donor are all less than 0.02. <sup>c</sup>The slight variation in the coupling as compared to  $V_{31}$  is due to a small structural difference in the X-ray structure. <sup>d</sup>A MM3 force-field-optimized structure,<sup>5</sup> with  $R$  being the distance between the two pentacenes in the nearest C–C distance. <sup>e</sup>A transition-state structure.<sup>5</sup>



**Figure 3.** Leading pairs of NTOs for the pentacene 1–4 dimer, relative to the  $|\text{T}_1\text{S}_0\rangle$  reference state in the calculation. In the upper panel are the results for molecule 1 excited initially, and in the lower panel is the case when molecule 4 is excited initially. The corresponding coupling values (in meV) are listed in the parentheses.

the  $\Delta s$  values range from nearly ideal  $-1.96$  to  $-1.09$ . The cases with large coupling have a larger deviation from ideal  $\Delta s$  values, indicating that the  $\text{S}_1\text{S}_0$  states are mixed with other components that do not contribute to spin population change, such as the CT components. FSD yields diabatic states with CT components without manually including CT states in the perturbation.

Singlet fission for several polyacenes have been theoretically and experimentally studied recently.<sup>7</sup> Molecules studied include 6,13-bis(triisopropylsilyl)ethynyl pentacene (TIPS-P), 6,13-di(2'-thienyl)pentacene (DTP), 6,13-dibenzothiophene pentacene (DBTP), 6,13-dibiphenyl-4-yl-pentacene (DBP), 6,13-diphenylpentacene (DPP), tetracene, rubrene, and 6,13-di(2'-thienyl)tetracene (DTT). In Table 2, the largest FSD coupling values derived from molecular pairs in their crystal structures

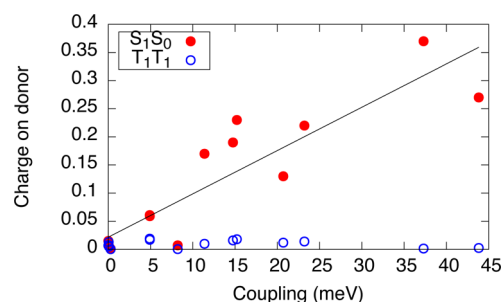
Table 2. Largest Singlet Fission Couplings (meV) Derived from Molecular Pairs in Their Crystal Structure

molecule	$V_{\text{FSD}}$	$V_{\text{CDFT}}^a$	$q_{\text{D}}(\text{S}_1)^b$
pentacene	14.75	84	0.19
TIPS-P	43.83	72	0.27
DTP	8.21	16	0.0072
DBTP	0.054	5.4	0.013
DBP	0.023	2.0	0.0075
DPP	0.087	0.82	0.0057
tetracene	11.38	83	0.17
rubrene	0.012	5.9	0.015
DTT	20.70	6.2	0.13

<sup>a</sup>Data from ref 7 with CT corrected, from a QM/MM sampling. <sup>b</sup>The charges on the  $\text{T}_1\text{T}_1$  donor are less than 0.013.

are listed. The charges on the donor in the  $\text{S}_1\text{S}_0$  diabatic state ( $q_{\text{D}}(\text{S}_1)$ ) are also listed in Table 2. It is seen that charge in the diabatic state is closely correlated with the singlet fission coupling. In ref 7, the couplings reported are the largest values calculated using constraint density functional theory (CDFT) from QM/MM samplings. A small movement along the intermolecular distance would lead to a big change in the size of coupling. Therefore, the coupling values cannot be compared directly. For small coupling cases, a structural difference may contribute significantly, but it is still seen that the set of small-coupling molecules are rather similar. For the large coupling cases (pentacene, TIPS-P, DTP, tetracene), the values are large from both sides as well. We note that the discrepancy is large for DTT, and it would be interesting to see whether the differences are due to the different Hamiltonians or the structures. Despite the many differences in our approaches, we still see a general agreement with these results.

The charge on the donor in both  $\text{S}_1\text{S}_0$  and  $\text{T}_1\text{T}_1$  FSD diabatic states, versus the corresponding coupling strength, is plotted in Figure 4. It is seen that the charge on the donor in the  $\text{S}_1\text{S}_0$

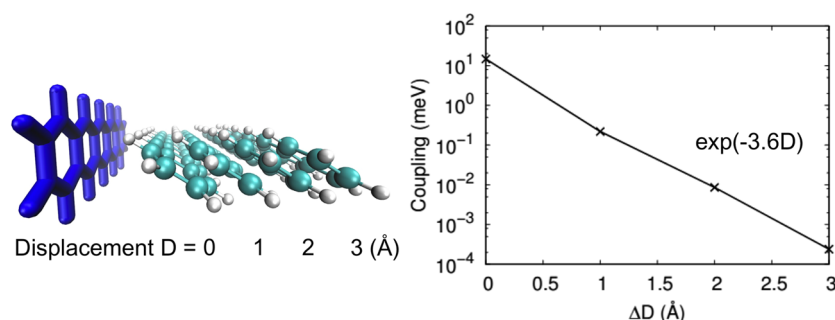


**Figure 4.** Charge on the donor in  $\text{S}_1\text{S}_0$  (red dots) or  $\text{T}_1\text{T}_1$  (blue circles) FSD diabatic states versus the corresponding FSD coupling strengths. Shown are data derived from all pentacene and polyacene pairs reported above. A linear regression is added for the  $\text{S}_1\text{S}_0$  data.

state is highly correlated with the coupling strength. However, the charges on the  $\text{T}_1\text{T}_1$  donor are small ( $<0.02$  for all cases studied), and there is no obvious correlation with the coupling value. This result further confirms that the size of the CT component plays an important role on the singlet fission coupling.<sup>3,4,7,15–18,34</sup>

Seeing singlet fission coupling as an exchange-like interaction, we further tested FSD couplings for the expected exponential decay. The distance dependence for singlet fission was calculated with the case with a CT component, the 1–4 pentacene coupling. As seen in Figure 5, an exponential decay rate of  $3.6 \text{ \AA}^{-1}$  is observed for FSD. The electronic configuration in a singlet fission involves a change of two





**Figure 5.** Distance dependence for pentacene 1–4 coupling. Shown in the left panel is our model for displacing one of the two pentacene molecules, and in the right panel is the distance dependence of the singlet fission coupling.

electrons, which leads to a two-electron integral in its coupling, and the corresponding distance dependence is typically  $2-3 \text{ \AA}^{-1}$ .<sup>22,35</sup> In a perturbative treatment, the CT component contributes a product of two one-electron electron-transfer couplings,<sup>3,16</sup> and therefore, a decay slope that is twice the electron-transfer decay rate ( $1.2-1.4 \text{ \AA}^{-1}$ ) is expected. Therefore, we confirm that the calculated coupling has the desired property in distance dependence. Together with earlier reports on the importance of intermolecular configurations in singlet fission couplings,<sup>15,20,34</sup> in the search for systems with high singlet fission efficiency, a generally applicable computational scheme, such as the currently proposed FSD, would be very important.

In general, SF-CIS states are not proper eigenstates of the spin operator. A spin-complete  $T_1T_1$  singlet configuration contains six spin configurations. When coupled to an  $S_1S_0$  state, there are only a few nonzero terms. Comparing the couplings from ideal states versus those from SF-CIS states, we found that all of the nonzero contributions are accounted for in SF-CIS (details are given in the Supporting Information accompanying this work). The spin contamination that we observed is modest; for the 1–4 pentacene case, the  $\langle S^2 \rangle$  is 2.0 for the reference  $T_1S_0$  state and 2.3 for the  $T_1T_1$  state.<sup>36</sup> However, for  $S_1S_0$ , the  $\langle S^2 \rangle$  is 1.3, which indicates that the quality of the  $S_1S_0$  state may be limited. It would be important to test the FSD coupling with a better Hamiltonian that yields spin-complete states with less or no spin contamination. Nevertheless, in the present work, we show that FSD offers a simple, quick, and first-principle-based way to estimate singlet fission coupling and the corresponding rates with little empirical input.

In this work, we generalized the FSD scheme to account for singlet fission coupling. For pairs of pentacenes in a thin-film crystal structure, we found that the rate estimated from the FSD coupling value is close to the experimental result. The diabatic states obtained through FSD contain CT components, and the amount of CT in the initial  $S_1S_0$  state is highly correlated with the coupling value. The exponential distance dependence of singlet fission coupling follows its two-electron nature. The FSD scheme developed in this work provides a general, first-principle approach to predict singlet fission rates without manually including CT configurations in a further treatment.

## ■ ASSOCIATED CONTENT

### Supporting Information

Full NTO analyses, molecular structures, and detailed computational results are included. The Supporting Informa-

tion is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b00437.

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### Notes

The authors declare no competing financial interest.

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