Singlet Exciton Fission for Solar Cell Applications: Energy Aspects of Interchromophore Coupling[†]

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Singlet exciton fission, a process that converts one singlet exciton to a pair of triplet excitons, has the potential to enhance the efficiency of both bulk heterojunction and dye-sensitized solar cells and is understood in crystals but not well understood in molecules. Previous studies have identified promising building blocks for singlet fission in molecular systems, but little work has investigated how these individual chromophores should be combined to maximize triplet yield. We consider the effects of chemically connecting two chromophores to create a coupled chromophore pair and compute how various structural choices alter the thermodynamic and kinetic parameters likely to control singlet fission yield. We use density functional theory to compute the electron transfer matrix element and the thermodynamics of fission for several promising chromophore pairs and find a trade-off between the desire to maximize this element and the desire to keep the singlet fission process exoergic. We identify promising molecular systems for singlet fission and suggest future experiments.

Introduction

Singlet exciton fission, a process in which a singlet exciton splits into two triplet excitons, was first discovered in crystalline anthracene in 1965.[1] Early work examined singlet fission (SF) in a few solid polyacenes[2–10] and analyzed its unique magnetic field dependence.[11–17] More recently, SF has been observed in additional neat solids such as benzophenone[18] and *p*-sexiphenyl.[19] In most materials studied in the past, the excitation energy of the vibrationally relaxed first excited singlet S_1 is somewhat less than twice the excitation energy of the first excited triplet T_1, $E(S_1) \leq 2E(T_1)$, making the SF process in the vibrationally relaxed S_1 state endoergic and too slow to compete with fluorescence.[20–22] In this situation, only excitation above the $2E(T_1)$ threshold, which produces a vibrationally excited S_1 state, or thermal excitation of a vibrationally relaxed S_1 state permits SF to be observed. When the SF process needs to compete with rapid vibrational deactivation, its triplet yield is low.

In addition to crystalline solids, SF has also been observed in polymers such as polydiacetylene, poly(*p*-phenylenevinylene), and a ladder-type poly(*p*-phenylene).[23–30] Recent studies have revealed SF in carotenoids[31–33] and covalent dimers of tetracene[34,35] and of 1,3-diphenylisobenzofuran.[36]

The SF process is spin-allowed since the two triplets that it produces are coupled into an overall singlet state. If the individual triplets interact only weakly, the other two sublevels that result from their interaction, a triplet and a quintet, are not far in energy and can be populated as well, thanks to interactions

introduced by the spin dipole–dipole interaction operator.[37] In a crystal, the triplets can diffuse apart.

Singlet fission could provide a pathway to enhance energy efficiency in dye-sensitized solar cells, assuming that it is possible for each of the generated triplet states to inject an electron independently.[38,39] In a cell with a single light-absorbing dye, the maximum theoretical efficiency is ∼31%,[40] and best actual yields are close to 11%.[41] By adding a second dye capable of undergoing SF on the high frequency fraction of solar radiation, it would be possible to gather up to ∼46% of the incoming light energy, if each photon with sufficient energy produces two triplet excitations and, ultimately, two electron–hole pairs.[42]

To avoid the need for SF to compete with vibrational deactivation (to be exoergic), it would be best to select sensitizers that meet the condition $E(S_1) \geq 2E(T_1)$. To make all channels of undesired triplet–triplet annihilation endoergic, it would be best to also satisfy the condition $E(T_2) \geq 2E(T_1)$. A recent paper addressed the issue and proposed general structural criteria to be met in the search for chromophores that meet these conditions. It found that among other structures certain *p*-benzoquinodimethanes, isobenzofurans, and polyacenes meet these conditions and are thus good molecular candidates for efficient SF.[43] Another set of chromophores that holds promise comprises conjugated polyenes, in which the free energy of SF is quite favorable. However, the condition $E(T_2) \geq 2E(T_1)$ is generally not fulfilled, suggesting that the initially formed pair of triplets may be readily destroyed by annihilation. We have therefore not included these chromophores here.

The next issue that needs to be addressed is the mode of coupling of these selected chromophores into dimers, oligomers, polymers, or crystals, which is required for SF to take place. Such coupling can occur directly through the two-electron part

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of the Hamiltonian or indirectly by the intermediacy of charge-transfer or related states.[44] In crystals, SF appears to be fast even though the intermolecular coupling consists of mere physical contact between molecules. Little is known about the degree of interchromophore coupling that is needed in molecular systems. Here, three main factors deserve attention.

(i) First, weak interchromophore coupling may permit the SF process from the initially excited singlet state to occur but only at a rate that is too slow to compete with other deactivation channels, such as fluorescence. One can expect some minimal coupling strength to be required for SF to be competitive. The results of recent experiments that examined several choices of covalent coupling of two 1,3-diphenylisobenzofuran chromophores provide an illustration.[36,45] The S_1 state of this chromophore has a relatively small fluorescence rate constant and no additional deactivation channels (lifetime of ~5 ns and quantum yield close to unity). Yet, no SF and only fluorescence was observed from nonpolar solutions of dimers in which two such chromophores are connected either through a methylene group or directly through an orthogonally twisted single bond. Triplet formation was observed only in polar solvents in which a dipolar charge transfer intermediate is formed, and in a strongly coupled dimer in which the two chromophores were in direct conjugation, connected through a slightly twisted single bond.

(ii) Second, one suspects that interchromophore coupling that is too strong may cause the singlet sublevel of the double-triplet excited state of the sensitizer to be well separated from the triplet and quintet sublevels that result from the same coupling. The dimer molecule is then in effect a single chromophore. The singlet sublevel will act as just another molecular excited singlet state, capable of injecting an electron into the conduction band of a semiconductor, but not two electrons. "Doubly excited" singlet states that carry triplet excitation on two tightly coupled halves of a molecule have been long known. An example is the $2A_g$ state in 1,3-butadiene, which can be viewed as carrying a triplet excitation at each of the two double bonds, coupled into an overall singlet.[46-48] A double electron injection from a single molecule has never been observed, and more work is needed to determine how strong an interchromophore coupling can be tolerated.

(iii) A third factor to consider is that the interchromophore coupling will inevitably affect the relative positions of the lowest energy levels to some degree. If it stabilizes the S_1 state much more than the T_1 state, it may make SF from the vibrationally relaxed S_1 state endoergic in a covalent dimer, even if the condition $E(S_1) \geq 2E(T_1)$ was satisfied in the isolated chromophore. An illustration is again provided by the results obtained for the directly coupled (conjugated) covalent dimer of 1,3-diphenylisobenzofuran (**D5**).[45] As was mentioned above, the interchromophore coupling in this dimer is strong enough for SF to be observed. However, it is also strong enough to displace the S_1 level of the dimer below its double triplet level, and significant SF was only observed for excitation with photons whose energies lie above this threshold. The triplet yield attributed to SF was low, presumably since it now had to compete with vibrational deactivation.

Of course, if strong interchromophore coupling is necessary for sufficiently fast SF, a significant decrease in $E(S_1)$ upon coupling may be unavoidable. If the coupling does not reduce the energy of the double triplet state similarly, it will be necessary to select chromophores in which $E(T_1)$ lies significantly below $E(S_1)/2$. This will limit the choices of chromophore structure, which are relatively few to start with.

It is clear that finding an ideal degree of interchromophore coupling requires a balancing act between the need for a strong and a weak coupling simultaneously. In summary, a compromise is needed between (i) the desire to enhance the kinetic rate of SF by choosing strong coupling and the need to ensure (ii) an independent electron injection from each chromophore and (iii) unperturbed energy relationships between the S_1, T_1, and T_2 levels, by choosing weak coupling.

As a quantitative measure of the interchromophore electronic coupling, we choose the electronic coupling matrix element t, variously known as the electron transfer integral, the hopping integral, or the resonance integral. It is an important factor in short-range energy transfer[49] and in electron transfer,[50] and it is likely to be an important factor for SF as well. It is clearly not the only factor that determines the rate at which SF occurs, and additional work will be needed to evaluate factors such as the splitting of the singlet, triplet, and quintet levels that result from the combination of two triplet chromophores, and the addition of the two spin dipole—dipole interaction tensors.

For SF to be feasible, individual chromophores need to be coupled into dimers, oligomers, polymers, or crystals. Depending on the choice made, the initial excitation can then be localized on a single chromophore, as is common in covalent dimers and oligomers, or delocalized over two or more chromophores, as is common in certain types of aggregates and in crystals. This may have an effect on the rate of SF and is perhaps responsible for the generally higher triplet yields in crystals than in dimers. In the present paper we focus on molecular dimers. We design and examine numerous covalently coupled 1,3-diphenylisobenzofuran (**D**), 3-dicyanovinylidene-6-(2′-imidazolidinylene)-1,4-cyclohexadiene (**B**), and tetracene (**T**) chromophores (Figure 1); later, we will also include related structures and denote them as **F** and **F1**. We investigate how various types of connections affect the electronic structure of the system, focusing on parameters important for SF. In particular, we examine the electron transfer integral t and the energy balance for singlet fission. Finally, we use the results of these computations to predict specific structures that appear promising for SF.

The three chromophores that we consider are derived from large alternant[51] and/or biradicaloid hydrocarbons, structural motifs that are expected to lead to a favorable relation of singlet and triplet excitation energies.[43] We used the frontier molecular orbitals of the individual chromophores to guide our study, as they provide a simple tool for predicting how strongly perturbed a coupled chromophore pair will be relative to two noninteracting chromophores. The perturbation is roughly proportional to the amount of overlap between the frontier orbitals of the two monomers. In some cases, the chromophore structure was altered slightly to create a larger variety of coupled structures and parameter values.

Methods

We focus on two important parameters for singlet fission, the electron transfer integral t and the free energy of singlet fission ΔG^0, which is approximated (ignoring entropy changes) as the potential energy of the final state minus that of the initial state, ΔE^0. We derive both parameters from electronic structure computations for individual chromophores and coupled chromophore pairs, done using Density Functional Theory (DFT) with the B3LYP functional and the 6-31G** basis set, with time-dependent DFT (TDDFT) calculations for the excited states. Pariser—Parr—Pople (PPP) calculations[52,53] were used to confirm DFT and TDDFT results; the parameter choice is taken from ref 54 and references therein.

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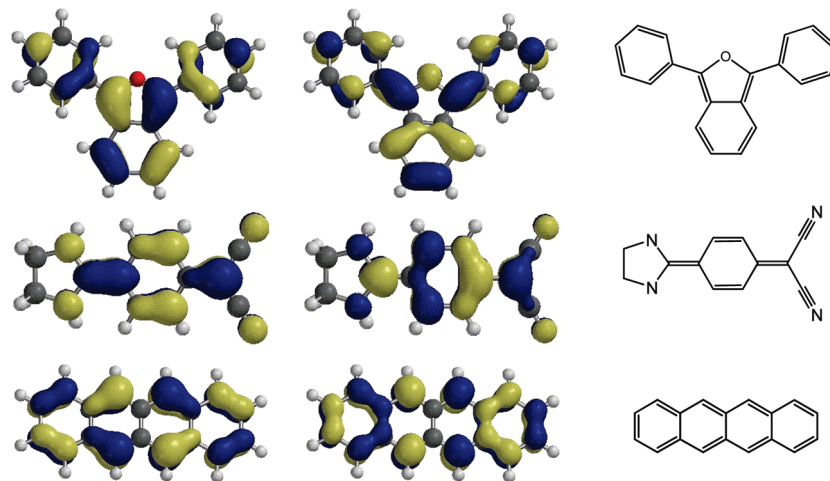
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Figure 1. Left to Right: HOMO, LUMO, and chemical structure of 1,3-diphenylisobenzofuran (top) **D**, 3-dicyanovinylidene-6-(2′-imidazolidinylene)-1,4-cyclohexadiene (center) **B**, and tetracene (bottom) **T**.
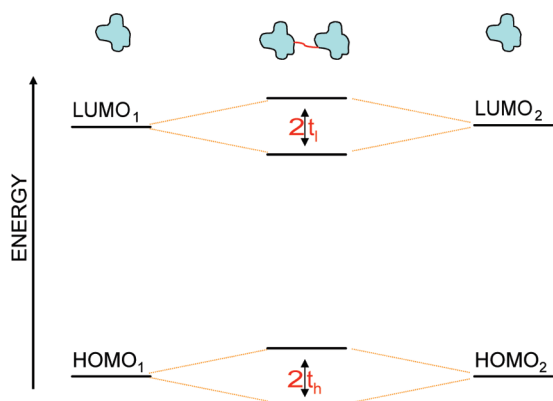

Figure 2. Electron transfer integrals t for the HOMO and LUMO approximated as half the splitting of the coupled chromophore pair orbitals in a homodimer.

The ground and first excited singlet states were evaluated at the optimized geometry of the ground state singlet; additionally, we found the energy-minimized S_1 system geometry and energy, to quantify the role of vibrational relaxation, that generally would be expected to compete well with SF. The first excited triplet state was evaluated at its own minimum energy geometry. We also calculated the optimized geometry and energy of the lowest quintet state Q_1 that includes the coupled $^1(TT)$ structure. All calculations were performed with QChem 3.0,[55] Turbomole 5.10,[56] or NWChem 5.0.[57,58]

The electron transfer integrals were approximated by invoking Koopmans' theorem and assuming that only the two monomer LUMOs (HOMOs) mix to form the LUMO and LUMO+1 (HOMO and HOMO−1) of the coupled chromophore pair (Figure 2).[59] We believe this is a safe approximation because the energy gaps between the HOMO−1 and HOMO and LUMO and LUMO+1 are more than 1 eV for the three chromophores of Figure 1, where $\Delta e = e_1 - e_2$ is the difference in the HOMO (LUMO) energies of the two isolated chromophores and $2t_h$ ($2t_1$) the differences in the energy of the HOMO and HOMO−1 (LUMO, LUMO+1) of the coupled chromophore pair. The electronic coupling is normally dominated by through-space interactions, and the sign of the electron transfer integral t is negative.[60] When through-bond coupling dominates, t can be positive. Since only the magnitude of t^2 matters for our purposes,

we shall deal with $|t|$ throughout this paper. This does not affect any of the results.

When the two chromophores are identical, $e_1 = e_2$, and t is the energy by which the HOMO and HOMO−1 (LUMO, LUMO+1) of the dimer lie above and below the HOMO (LUMO) of the monomer.

$$e_{+/-} = e \pm t \qquad (1)$$

To evaluate the energy balance of singlet fission, ΔG^0, we assume entropy changes to be negligible. The initial state is the vibrationally relaxed lowest excited singlet state of the coupled chromophore pair, with energy given by $E(S_1)$ as calculated by TDDFT, minus the ground state energy $E(S_0)$, as computed by static DFT. The energy of the final state, a pair of singlet-coupled triplets in the interacting chromophore pair, is approximated by the energy of the lowest quintet state of the coupled pair, as computed by static DFT. This leads to the equation

$$\Delta E^0 = E(Q_1) - E(S_1) \qquad (2)$$

where $E(Q_1)$ and $E(S_1)$ are the energies of the lowest quintet and excited singlets of the coupled chromophore pair. Equation 2 is exact if the two chromophores do not interact and is ordinarily assumed in treatments of triplet exciton interactions in molecular crystals.[37] In the limit of very strong interaction, the energy differences between the singlet, triplet, and quintet states resulting from a pair of triplet excitations can be large and have been calculated to be 1−1.5 eV in butadiene, viewed as two strongly interacting ethylenes.[47,48] In the dimeric chromophores treated presently, the error introduced by the use of eq 2 is most likely less than 0.1 eV, judging by our TD-DFT (B3LYP/SVP) results for **D2**,[45] **D5**,[45] and **D10**,[45] for which the quintet excitation energies are within 0.1 eV of twice the triplet excitation energies.

Finally, we investigate the inherent trade-off between the desire for exoergic singlet fission and the desire for a large electronic mixing matrix element between the initial and final states. Qualitatively, the energy balance of the singlet fission process can be expressed in terms of properties of the monomeric chromophore and the charge transfer integrals, if we approximate the first singlet excitation by a one-electron HOMO to LUMO transition and the energy of the quintet excitation in the dimer by twice the energy of the triplet excitation in the

monomer. The energy of the first excited singlet of a coupled chromophore pair is then approximately related to the singlet excitation energy of the monomeric chromophore by subtraction of $(t_h + t_l)$, the sum of the amounts by which the HOMO is destabilized and the LUMO stabilized upon creation of the dimer

$$\Delta E^0 = 2[E(T_1) - E(S_0)] - [E(S_1) - E(S_0) - t_h - t_l] \quad (3)$$

where all energies now refer to the monomeric chromophore. Relation 3 shows clearly why the two desired features, exoergic fission and large electronic matrix elements, act at cross purposes.

Results

In this section, we present the calculated parameters and discuss their systematic variations. The values of interest are the matrix elements t_l and t_h and the energy differences ΔE^0. Table 1 presents the calculated matrix elements for the 47 dimers considered, shown in Charts 1−4. The discussion deals sequentially with the four families presented in the charts.

Covalent Dimers of 1,3-Diphenylisobenzofuran (D). The frontier molecular orbitals (HOMO and LUMO) of **D** are extended π systems with high amplitude on all carbons except the meta positions of the two phenyl rings. Because the two phenyl rings are twisted only ~30° out of the plane of the isobenzofuran core in both low-energy conformers (C_2 and C_s

symmetry), the whole molecule acts as one extended π system.[61] Most carbons have a similar electron density in the HOMO and in the LUMO, and most covalent dimers should have a similar degree of coupling between the two HOMOs (t_h) and between the two LUMOs (t_l). The energy of singlet fission ΔE^0 estimated first, from the first excited singlet energy and the first triplet energy of an isolated chromophore **D** and next, from the quintet and the singlet of the dimer, is listed in Table 2.

We examine covalent dimers of **D** bound through the meta and the para positions of the phenyl rings, as well as the two distinct positions on the carbocyclic ring of the isobenzofuran unit (Chart 1). The ortho position of the phenyl rings was not used, as attachment there would force the phenyl rings out of the plane of the isobenzofuran core, significantly changing its electronic structure. Most of the dimers contain a more or less strongly twisted direct π-conjugating link between the two chromophores, but three of them (**D4**, **D23**, **D24**) contain a π-stacking interaction. The results quoted here were calculated for the C_2 conformer, which is the one obtained experimentally in ref 61.

Effective conjugation between the chromophores, whether planar as in **D16** or nearly planar as in **D5**, leads to very strong coupling. Chromophores that are connected through a methylene bridge (**D2**) or directly bonded through the meta position of a phenyl ring (**D11**) all have much smaller coupling, owing to little orbital overlap. The three π-stack containing dimers (**D4**,

TABLE 1: Electronic Matrix Elements

compd.[a]	t_h (eV)	t_l (eV)	compd.[a]	t_h (eV)	t_l (eV)	compd.[a]	t_h (eV)	t_l (eV)
D1	0.027	0.014	D17	0.036	0.054	B8	0.122	0.041
D2	0.027	0.027	D18	0.035	0.025	B9	0.041	0.177
D3	0.203	0.133	D19	0.079	0.105	B10	0.172	0.122
D4	0.190	0.200	D20	0.118	0.155	B11	0.069	0.091
D5	0.122	0.136	D21	0.085	0.082	F1	0.041	0.074
D6	0.122	0.122	D22	0.027	0.013	T1	0.302	0.308
D7	0.041	0.054	D23	0.064	0.073	T2	0.014	0.014
D8	0.027	0.027	D24	0.094	0.082	T2@70°	0.068	0.082
D9	0.054	0.068	D25	0.032	0.049	T3	0.211	0.189
D10	0.004	0.009	D26	0.020	0.044	T4	0.041	0.014
D10@70°	0.068	0.068	B1	0.082	0.109	T5	0.012	0.010
D11	0.002	0.006	B2	0.014	0.027	T6	0.010	0.010
D12	0.014	0.014	B3	0.020	0.029	T7	0.034	0.026
D13	0.014	0.014	B4	0.054	0.104	T8	0.031	0.024
D14	0.019	0.006	B5	0.008	0.007	T9	0.190	0.159
D15	0.014	0.014	B6	0.054	0.041			
D16	0.176	0.216	B7	0.068	0.014			

[a] See Charts 1−4.

TABLE 2: TD-DFT (B3LYP/6-31G**) State Energies and Fission Energetics (eV) for Covalent Dimers of D

compd[a]	$E(S_1)_{adiab}$[b]	$E(S_1)_{vert}$[c]	$E(T_1)_{adiab}$[d]	$E(Q_1)_{adiab}$[e]	$\Delta E^0(T)$[f]	$\Delta E^0(Q)$[g]
D	2.70 (3.00)	2.92	1.43			
D5	2.23 (2.73)	2.44	1.37	2.87	0.51	0.64
D8	2.51 (2.79)	2.77	1.42	2.85	0.33	0.34
D9	2.40 (2.80)	2.69	1.42	2.85	0.44	0.45
D10	2.57 (2.80)	2.80	1.48	2.84	0.39	0.27
D11	2.55 (2.81)	2.81	1.44	2.87	0.33	0.32
D12	2.53 (2.80)	2.79	1.44	2.87	0.35	0.34
D17	2.47 (2.76)	2.71	1.40	2.81	0.33	0.34
D19	2.37 (2.80)	2.63	1.45	2.94	0.53	0.57
D22	2.50 (2.85)	2.73	1.43	2.87	0.36	0.37
D25	2.41	2.60	1.40	2.82	0.39	0.41
D26	2.57	2.63	1.49	2.99	0.41	0.42

[a] See Chart 1. [b] Adiabatic excitation energy of the first excited singlet (PPP numbers in parentheses). [c] Vertical excitation energy of the first excited singlet at ground state geometry. [d] Adiabatic excitation energy of the first excited triplet. [e] Adiabatic excitation energy of the first excited quintet. [f] Fission endothermicity calculated as $2E(T_1)_{adiab} - E(S_1)_{adiab}$. [g] Fission endothermicity calculated as $E(Q_1)_{adiab} - E(S_1)_{adiab}$.

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CHART 1: Chemical Structures of D and Covalent Dimers of D, with Coloring to Represent Compounds That Have Been Experimentally Tested
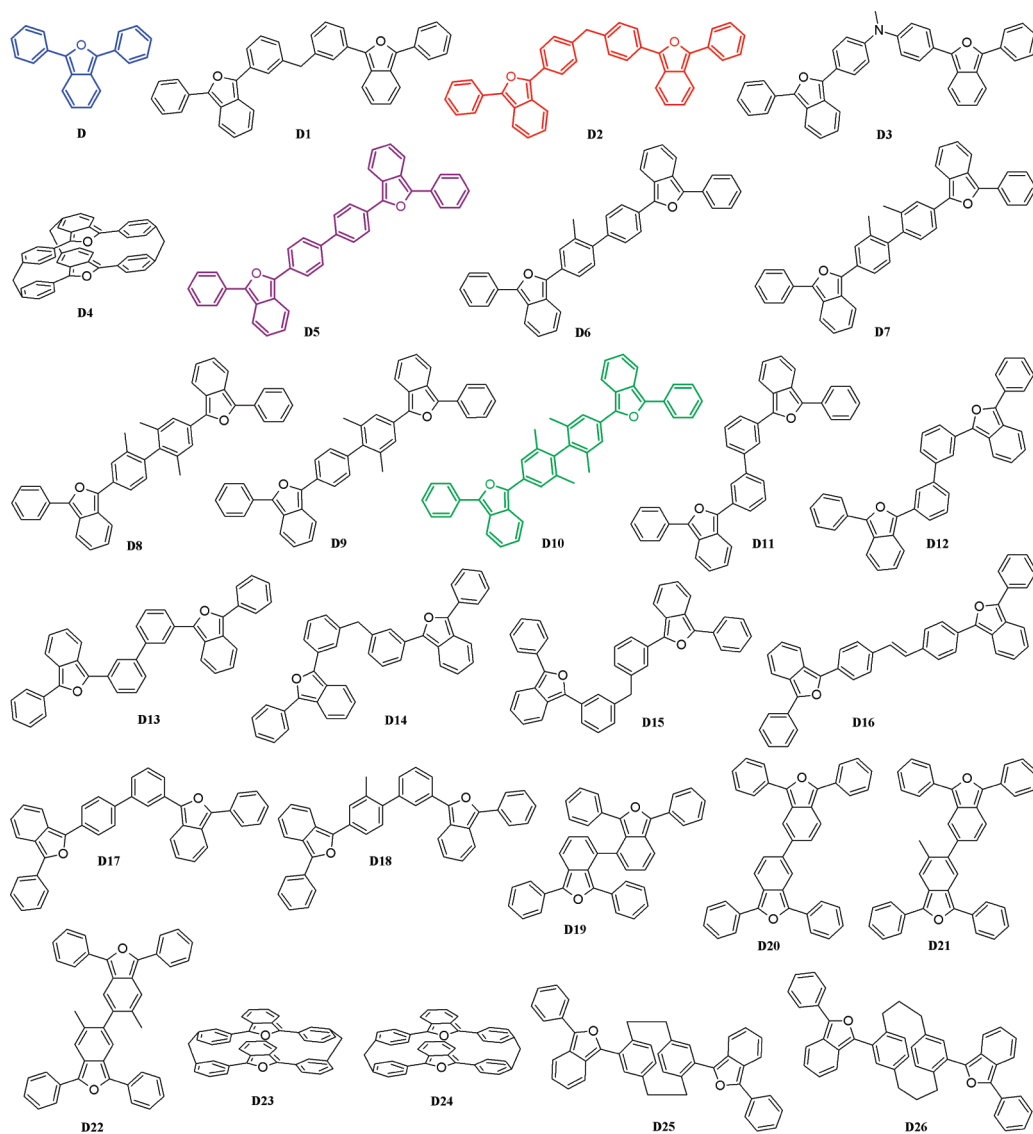

D23, **D24**) have electron transfer elements that are roughly proportional to the overlap of their π systems, which is altered by changing the location of the trimethylene tethers, from meta (**D23**) to para (**D24**), or by adding a third tether (**D4**).

The electron transfer elements t_h and t_l are of similar magnitude for almost all of the dimers, owing to the similar electron density in the HOMO and LUMO of **D**. By adding a heteroatom to the linker, as in **D3**, one can form covalent dimers of **D** that have different amounts of coupling between the HOMOs and LUMOs. One interesting series of dimers is **D5**−**D10**, all of which are directly connected through the para position of the phenyl rings but which differ in twist angles (from 31 to 89°) due to steric interference by methyl groups; as expected, greater twist gives weaker coupling (far weaker for the tetramethylated **D10**).

All computations were done at the optimized C_2 geometry with respect to the monomer units, and for many dimers a quick search of the potential energy surface reveals no geometries with significantly different coupling or energetics. This means that the electronic coupling is not likely to change significantly as a function of temperature owing to vibrations and geometry changes. The notable exceptions to this lack of temperature

dependence are molecules where the primary overlap is controlled by the torsion angle about a single bond, such as the **D5**−**D10** series. To illustrate the importance of finite temperature on dimers with torsion-dependent coupling, we performed a potential energy surface scan for **D10** and found that the central bond could twist from 89 degrees in the optimized structure to 70 degrees at room temperature. The coupling of this twisted **D10** (**D10@70°**) is roughly an order of magnitude above the coupling in the optimized geometry. Other dimers of **D** expected to behave similarly are **D19**−**D22**.

The frontier molecular orbitals of both strongly (**D20**) and weakly (**D2**) coupled dimers look exactly as expected, as a weakly perturbed sum and difference of the frontier orbitals of **D**. The HOMO−1 and LUMO of the dimer have an antinode, and the HOMO and LUMO+1 have a node at the joining bond. This supports our simple model in which each dimer is formed from two weakly coupled monomers, with the monomer HOMOs interacting to form the dimer HOMO−1 and HOMO and the monomer LUMOs interacting to form dimer LUMO and LUMO+1.

CHART 2: Chemical Structures of Covalent Dimers of B
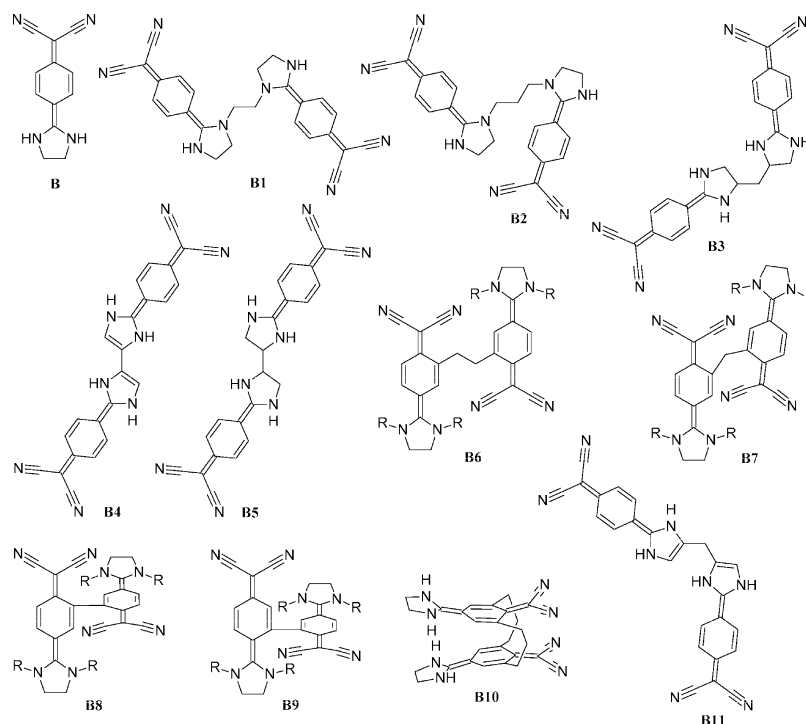
CHART 3: Chemical Structures of Covalent Dimers of F
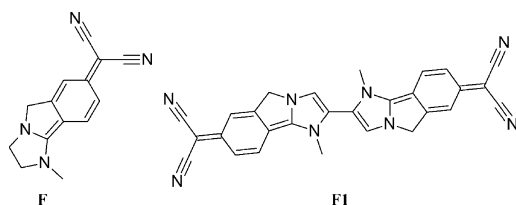
Covalent Dimers of 3-Dicyanovinylidene-6-(2′-imidazolidinylene)-1,4-cyclohexadiene (B and F). The isolated chromophore is approximately planar, and the frontier orbitals form an extended π-electron system. Unlike the chromophore **D**, chromophore **B** consists of a strongly interacting donor and an acceptor part, and its HOMO and LUMO do not have similar amplitudes in all regions of the molecule and differ particularly in their distribution over the central six-membered ring. The HOMO is concentrated on positions that are ipso or meta to the imidazolidinylene moiety and the LUMO on those that are ipso or meta to the dicyanovinylidene moiety. We have formed covalent dimers by connecting two **B** chromophores through both distinct positions on the six-membered ring and also through the nitrogen and carbon positions on the heterocyclic ring (Table 3, Chart 2).

The donor−acceptor nature of **B** stabilizes a zwitterionic electron configuration. The TD-DFT method has difficulty properly evaluating energies for molecules of this kind.[62−66] Table 3 predicts that any dimer, regardless of coupling strength, has a significantly different first singlet excitation energy than the monomer. Even two unconnected molecules of **B** placed 20 Å apart are computed to have a very different S_1 excitation energy (2.4 eV) than a single molecule (3.2 eV). We correct for this problem by using the HF-CIS method, which ordinarily does not predict the absolute magnitude of excitation energies as well as TD-DFT but does not suffer from the same problem with charge-transfer states.

The last two columns of Table 3 present our best guess as to the actual values, which were found by using the S_1 energy of

an isolated chromophore **B** obtained from TD-DFT and adding the differences in HF-CIS energies for **B** and its various dimers. These tend to agree with the simple expectation that the first singlet excitation energy decreases proportionally to the increase in the electron transfer integrals. We believe these numbers illustrate the proper behavior of **B** and its dimers but note that a set of far more computationally intensive multireference calculations could be done to confirm these figures.

The donor−acceptor structure of **B** permits the construction of dimers that have very different t_h and t_l values, such as **B8** and **B9**, because of the disparate amplitudes of HOMO and LUMO in the two positions of the quinone ring used in the coupling. **B8** has a large t_h because of the large HOMO amplitude at the coupling position, while **B9** has a larger t_l owing to the larger LUMO amplitude at its coupling position.

Dimers connected through the carbon of the heterocyclic ring (**B3**, **B5**) have a small coupling because the π system does not extend onto those carbon atoms. We also consider dimers of a variant of **B** in which the heterocyclic ring is unsaturated (**B4**, **B11**). This results in a monomer predicted to have approximately the same energetics as **B**.[41] The dimer **B4** is an example of a pair of coupled chromophores that has a reasonable coupling owing to the presence of a direct bond, and **B11** maintains this reasonable coupling despite the methylene spacer because the two chromophores are closer to planar than in the twisted **B4**. Dimers of **B** that are connected through the nitrogen of the imidazole ring (**B1**, **B2**) have smaller coupling for a longer alkyl spacer, as expected. As was the case with **D**, all frontier orbitals of dimers of **B** are a weakly perturbed sum or difference of frontier orbitals for two constituent chromophores. The largest transfer integrals are seen in the π-stacked structure **B10**, which is reminiscent of stacked π-conducting solids.

In species **F** and **F1** (Chart 3), rigid ring fusion prevents torsion about the inter-ring double bond in **B**. Despite the formally conjugated structure of **F1** at the interdimer C−C bond, the t_l and t_h are of the same size as for most of the species in Chart 2.

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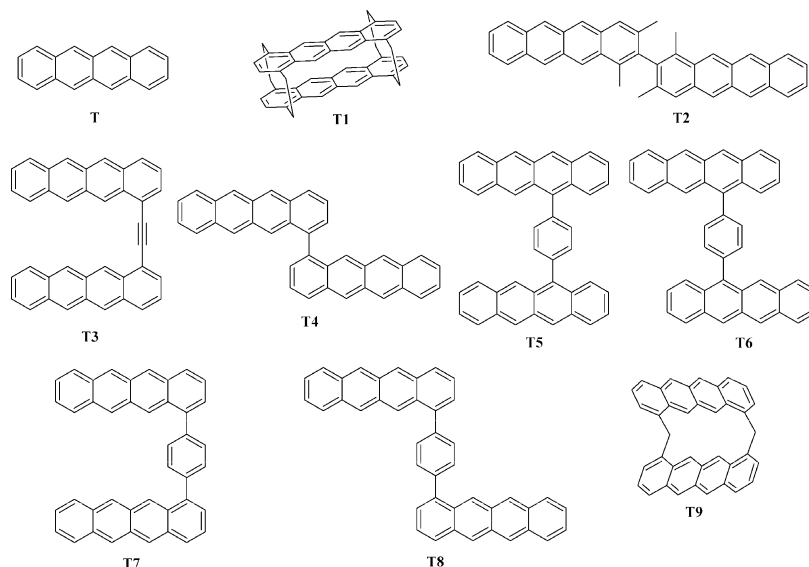**CHART 4: Chemical Structures of Dimers of T**

TABLE 3: TD-DFT (B3LYP/6-31G) and HF-CIS (6-31G**) State Energies and Fission Energetics (eV) for Covalent Dimers of B and F**

compd[a]	$E(S_1)_{adiab}$[b]	$E(S_1)_{vert}$[c]	$E(S_1)_{HF-CIS}$	$E(S_1)_{corr}$[d]	$E(T_1)_{adiab}$[e]	$E(Q_1)_{adiab}$[f]	$\Delta E^0(T)$[g]	$\Delta E^0(Q)$[h]
B	3.06 (2.50)	3.16	3.76	3.06	1.63			
B4	1.74 (2.00)	2.25	3.39	2.69	1.40	2.94	0.11	0.25
B5	1.73	2.54	3.59	2.88	1.40	2.85	−0.08	−0.03
F	2.72 (2.36)	3.05	3.72	2.72	1.75			
F1	1.76 (2.00)	2.26	3.63	2.63	1.59	3.27	0.55	0.64

[a] See Charts 2 and 3. [b] Adiabatic excitation energy of the first excited singlet (PPP numbers in parentheses). [c] Vertical excitation energy of the first excited singlet at ground state geometry. [d] Corrected adiabatic excitation energy of the first excited singlet for dimer molecules calculated as $E(S_1)_{HF-CIS\{Dimer\}} - [E(S_1)_{HF-CIS\{Monomer\}} - E(S_1)_{adiab\{Monomer\}}]$. [e] Adiabatic excitation energy of the first excited triplet. [f] Adiabatic excitation energy of the first excited quintet. [g] Fission endothermicity calculated as $2E(T_1)_{adiab} - E(S_1)_{corr}$. [h] Fission endothermicity calculated as $E(Q_1)_{adiab} - E(S_1)_{corr}$.

TABLE 4: Free Energies for Dimers of T

compd[a]	$E(S_1)_{adiab}$[b]	$E(S_1)_{vert}$[c]	$E(T_1)_{adiab}$[d]	$E(Q_1)_{adiab}$[e]	$\Delta E^0(T)$[f]	$\Delta E^0(Q)$[g]
T	2.32 (2.80)	2.49	1.20			
T2	2.32 (2.79)	2.50	1.25	2.44	0.18	0.12
T4	2.16 (2.75)	2.33	1.19	2.39	0.22	0.23
T6	2.22 (2.73)	2.43	1.18	2.34	0.14	0.12
T8	2.25 (2.74)	2.39	1.19	2.39	0.13	0.14
T9	1.88	2.03	1.28	2.38	0.68	0.50

[a] See Chart 4. [b] Adiabatic excitation energy of the first excited singlet (PPP numbers in parentheses). [c] Vertical excitation energy of the first excited singlet at ground state geometry. [d] Adiabatic excitation energy of the first excited triplet. [e] Adiabatic excitation energy of the first excited quintet. [f] Fission endothermicity calculated as $2E(T_1)_{adiab} - E(S_1)_{adiab}$. [g] Fission endothermicity calculated as $E(Q_1)_{adiab} - E(S_1)_{adiab}$.

Overall, there are fewer viable dimers of **B** than of **D**, owing to the existence of fewer attractive connection points, and a less favorable set of energy levels in the monomer. The chromophore **B**, however, provides more options for creating dimers with disparate t_h and t_l values. If the mechanism of singlet fission is found to be dominated by either hole or electron transfer, for example, maximizing one electronic matrix element while keeping the other small could result in both good kinetics and a good free energy of fission.

Covalent Dimers of Tetracene (T). Polyacenes are promising chromophores for SF because they have low triplet levels, leading to a good ΔE^0 (Table 4, Chart 4), and because there already is ample experimental evidence for efficient SF in polyacene crystals. We examine tetracene because of the recent experimental work on this chromophore[35] but emphasize that these results should generalize well to pentacene, which we believe is more promising because it actually meets the condition

$E(S_1)$, $E(T_2) \geq 2E(T_1)$.[22,67] It would be possible to make all of these dimers with pentacene instead of tetracene. The electronic matrix elements would be nearly the same, and the free energy of fission would be close to 0.5 eV more exoergic for each dimer listed.

Like the other chromophores we have studied, tetracene is a planar molecule with frontier orbitals dominated by a large π-electron system. Because of the alternant pairing theorem, the HOMO and the LUMO are distributed similarly over the molecular framework. There are only three distinct locations at which **T** can be coupled to a dimer. We examine all of them, as well as one π-stacked dimer (Chart 4).

When tetracene molecules are π-stacked, as in **T1**, both the HOMOs and the LUMOs of the two chromophores overlap strongly, leading to large electronic matrix elements. This large coupling also makes singlet fission significantly endothermic. A more moderate degree of coupling can be obtained by using
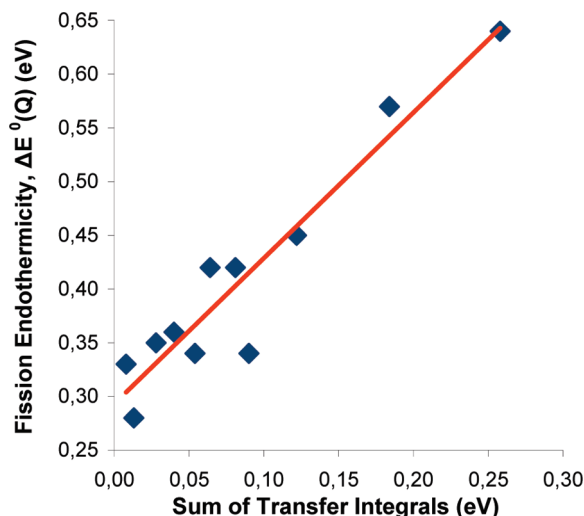
Figure 3. Fission endothermicity (eq 3, Table 2) and the coupling between two chromophores **D**.

methylene linkers to align the two chromophores in the herringbone structure **T9**, similar to the interaction in a tetracene single crystal. Despite the methylene spacers, the two chromophores maintain a very large orbital overlap between the bottom lobes of their π systems. Inserting a phenylene bridge between the chromophores, as in **T5–T8**, results in very small coupling because the hydrogen atoms on the bridge and the chromophores repel, forcing the phenylene group to be perpendicular to both tetracene planes. An ethynylene bridge between the chromophores (**T3**) leads to a large coupling, but similarly as in **T1**, singlet fission becomes less thermodynamically favorable. Two options for pairing tetracene chromophores to a more moderate degree are illustrated by the V-shaped dimer **T4** and by **T2**, where the two tetracene planes are nearly orthogonal. These connections are very similar to those for the dimers of **1** (**D5–D10**), and methyl groups can be added or removed to tune the interaction. Room temperature thermal vibrations allow **T2** and **T4** to achieve higher coupling (up to 70° for **T2**) by rotating about the linking bond, similar to **D5–D10**. The steric interactions in **T5–T8** provide a dramatically sharper well in the potential energy surface, however, and the coupling will not increase appreciably at room temperature.

As is the case for the previous two sets of dimers, the frontier orbitals of tetracene dimers, such as **T4**, look very much like the sum and difference of frontier orbitals from two isolated chromophores.

Discussion

Trade-Off between Kinetics and Thermodynamics. Equation 3, which uses a one-electron picture of the ground and excited states, illustrates this trade-off. In this approximation, the driving force decreases linearly with the sum of the transfer elements. This is similar to what we find in the TD-DFT total energy results, as shown in Figure 3. For a series of dimers of **D**, there is a reasonable linear correlation ($R^2 = 0.91$) between increased transfer integrals and unfavorable thermodynamic driving force. The slope of this line is 1.36, meaning that the driving force ΔE^0 derived from the actual singlet excitation is even more strongly affected by coupling than this simple approximation predicts. The error in the simple model arises from the assumption that orbital energy differences are the same as state energy differences—this is often qualitatively, but rarely quantitatively, true.

Overall, the data show that the simple one-electron picture can be used to predict the singlet excitation energy and hence the free energy of fission, approximately (without the need for an explicit TD-DFT calculation).

It is notable that the S_1 and Q_1 energies for the different dimers made from a given monomer pair are quite similar. This reflects the relative weakness of the charge transfer integrals (most t values are of the order of 0.1 eV or less). If the single chromophore has $2E(T_1) < E(S_1)$, the dimers will be strong candidates for fission; if this energy difference is both favorable and large, strong mixing will facilitate fission, and the resulting reduction in the (S_1) to $^1(TT)$ exoergicity will not render the fission endoergic.

Tables 2–4 show that the calculated energy for the quintet is very close to twice that for the triplet. This is sensible, given the relatively weak mixing integrals t_l and t_h.

Geometry relaxation in the excited S_1 state clearly will reduce the overall exoergicity, while relaxation in the T_1T_1 pair will increase it. On balance (Tables 2 and 4), chromophores in the **D** and **T** series show such relaxation energies around 0.25 and 0.20 eV, respectively, in S_1. In (T_1T_1), the comparable values are near 0.20 eV, so the effects of geometry relaxation in the (T_1T_1) and S_1 states nearly cancel.

Comparison with Experimental Data. As mentioned briefly in the Introduction, triplet yields have been measured for three covalent dimers of **D** (**D2**, **D5**, and **D10**) in solution.[36,45] Unlike crystalline **D** (blue), none of them showed SF from the vibrationally relaxed S_1 state. At higher excitation energies, **D5** (purple) showed triplet formation attributed to SF with a yield of a few %, but the more weakly coupled dimers **D2** (red) and **D10** (green) still showed none. This was interpreted as meaning that the interchromophore coupling in **D2** and **D10** is too weak to provide an SF rate that would be competitive with fluorescence. In **D5**, it is strong enough to induce an adequate SF rate but also strong enough to make the SF process endothermic. Upon higher excitation, when SF is thermodynamically feasible, it then needs to compete with vibrational deactivation and has a low yield. The relative coupling strengths in **D2**, **D5**, and **D10** deduced from the experiments thus agree with the results shown in Table 1. The tentative conclusion is that t_h and t_l in a covalent dimer need to reach values close to 0.1 eV before SF can compete with fluorescence. This is a much larger value than we guessed at the outset of our investigations, given that in solutions and crystals exoergic triplet–triplet annihilation is often believed to be close to diffusion controlled, except for the limitations imposed by spin statistics.[68] The rate of the actual exoergic triplet–triplet annihilation step would then have to be faster than or at least comparable with the diffusive encounter rate, and it seems likely that exoergic singlet fission into two triplets would be similarly fast.

For chromophore **D**, the first one designed with SF in mind, there may well be no choice of coupling that would be strong enough for the rate of SF to be competitive with fluorescence yet weak enough to keep SF from becoming thermodynamically unfavorable. The obvious alternative is to look for a chromophore whose triplet excitation energy is less than half that of the singlet.

Benzoquinodimethane-based chromophores of type **B** have not yet been examined experimentally for SF in a dimer. They were initially considered promising because PPP calculations suggested that their energy levels are positioned suitably and because their donor–acceptor structure appeared to offer good electron injection properties. However, we are now more pessimistic. The present presumably more reliable TD-DFT

calculations suggest an SF exoergicity no better than that for **D**, and a preliminary examination of one of the monomers revealed a relatively low fluorescence quantum yield (unpublished results). This indicates that a radiationless deactivation process occurs at a competitive rate, such that the synthesis of dimers is hardly worthwhile. If the deactivation is due to twisting about one of the exocyclic double bonds, it could be suppressed by an appropriate structural modification, and Table 3 suggests that covalent dimers of such chromophores would be only about as suitable for SF as the dimers of **D**. For the fused structure **F1**, however, this negative conclusion is even stronger.

The efficient production of triplets by SF in tetracene (**T**) crystals[37] has encouraged work on covalent tetracene dimers.[34,35] However, SF in a dimer consisting of the conformers **T5** and **T6**, as well as two others coupled by phenyl rings, produced only low triplet yields of 3% at best.[45] The coupling strengths of most of the covalent dimers listed in Table 4 appear too low, presumably due to the severe twisting imposed by steric hindrance and to the small amplitude that the frontier orbitals have in any one position in this large chromophore. In the strongly coupled dimers **T1**, **T3**, and **T9**, SF is strongly endoergic. This suggests that the analogous covalent dimers of pentacene should be examined, as this chromophore has an ΔE^0 almost 0.5 eV more favorable than tetracene.

The TD-DFT estimates for $E(T_1)$ and $E(Q_1)$ are more reliable than simpler approaches such as configuration interaction singles (CIS) or time-dependent Hartree−Fock schemes.[69,70] Nevertheless, TD-DFT typically gives errors in the 0.1−0.4 eV range for such state energies in typical π-type chromophores.[71,72] Therefore, our computed ΔE^0 could well be inaccurate at the 0.1−0.6 eV range. This could easily bring the ΔE^0 into the exoergic range. That this might be true is suggested by experimental data showing fission in some of the species in Figure 2, particularly **D5**.[45]

Summary and Conclusion

We have examined how covalent coupling of individual chromophores into dimers affects the transfer integrals t_h and t_1, which is one of the factors that affect the rate of singlet fission. We have found that for several promising cases it is easy to achieve values ranging from almost zero to nearly half an electronvolt. Comparison with experimental results suggests that in dimers values close to 0.1 eV are needed for SF to be competitive with fluorescence. It has been shown that a simple analysis of the HOMO and LUMO of a monomeric chromophore can provide a very good preliminary guess as to how strong a given chemical coupling will be, based on orbital overlap. We have also discussed how coupling chromophores can modify their energy levels and make SF less thermodynamically favorable. The free energy of fission has been studied using TD-DFT, and we have shown how a simple one-electron HOMO to LUMO model can produce reasonable estimates of this quantity. In every covalent chromophore dimer, there is a trade-off between the electron transfer integral and the free energy of fission, which has to be balanced to optimize triplet yield. Moderately coupled pentacene dimers are considered the most promising candidates for further experiments.

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