

Recent Advances in Singlet Fission

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Abstract

A survey is provided of recent progress in the understanding of singlet fission, a spin-allowed process in which a singlet excited molecule shares its energy with a ground-state neighbor to produce two triplet excited molecules. It has been observed to occur in single-crystal, polycrystalline, and amorphous solids, on timescales from 80 fs to 25 ps, producing triplet yields as high as 200%. Photovoltaic devices using the effect have shown external quantum efficiencies in excess of 100%. Almost all the efficient materials are alternant hydrocarbons of the acene series or their simple derivatives, and it is argued that a wider structural variety would be desirable. The current state of the development of molecular structure design rules, based on first-principles theoretical considerations, is described along with initial examples of implementation.

Singlet fission (SF):

a process in which a singlet-excited and a ground-state molecule ($S_1 + S_0$) share energy to produce a correlated pair of triplet excited molecules ($T_1 T_1$)

1. RATIONALE AND HISTORY

Solar energy is an attractive option for meeting the world's energy needs while avoiding the worst consequences of climate change induced by continuing massive combustion of fossil fuels. As immediate economic needs will always trump any desire to avoid likely future disasters, it appears inevitable that the promise of solar energy will only be fulfilled if it becomes economically competitive. This could be achieved by reducing the cost and/or increasing the efficiency of solar panels.

The Shockley-Queisser (1) theoretical limit to the efficiency of a single junction solar cell is only 32% because some of the photons remain unabsorbed and because the absorbed ones convert to heat the part of their energy that is in excess of the absorber band gap. Several ways of avoiding the latter loss have been proposed. A process that increases the limit to 45% (2) is to split the energy of high-energy photons in two, producing two excitons that are both capable of charge separation, while using lower-energy photons in the usual fashion.

With molecular chromophores, such excitation splitting is known as singlet fission (SF). In this process, some of the energy of a singlet excitation in a chromophore is transferred to a neighboring ground-state chromophore to produce a triplet excitation on each. SF was first invoked in 1965 to explain observations made on crystalline anthracene (compound 1 in **Figure 1**) (3) and then was firmly established in crystalline tetracene (compound 2 in **Figure 1**) (4–6). Its theory was worked out (7, 8) and comprehensive reviews appeared (9, 10). Although SF was later also found in carotenoids (11) and conjugated polymers (12), interest gradually abated. It was clear that in solid tetracene and probably also solid pentacene (compound 3 in **Figure 1**), SF is very fast. However, triplet yields were measured for very few compounds, all values obtained were far below 50%, and SF acquired the reputation of an obscure and inefficient phenomenon.

Interest in SF was revived when Nozik et al. (13) pointed out its potential utility for increasing the efficiency of solar cells. Theoretical guidelines for the design of chromophores offering isoergic or slightly exoergic SF appeared (14), and by 2010, four compounds were found to produce triplet yields well over 100% and mostly close to 200%: tetracene (15), pentacene (16, 17), 1,3-diphenylisobenzofuran (DPIBF; compound 4 in **Figure 1**) (18), and zeaxanthin (compound 5 in **Figure 1**) (19). A comprehensive review (20) provided an initial version of guidelines for packing chromophores for optimal coupling for SF. Since 2010, the number of compounds known to exhibit efficient SF has increased, but most have similar structures. An SF workshop held in June 2011 in Golden, Colorado, was attended by about a dozen researchers. A similar workshop held in June 2012 in Lyons, Colorado, had 50 participants. This rapid development justifies another review of the subject merely 1-1/2 years after the previous one. We focus on developments reported in the past two years but do not attempt an exhaustive survey.

2. BACKGROUND

2.1. The SF Process

The simplest description of SF that provides insight into the process is embodied in Equation 1, where S_0 is the ground and S_1 the first excited singlet state of a chromophore, and T_1 is its lowest triplet state (7, 21). It needs to be recognized (8) that in solids in which exciton diffusion is possible the rate constants k_{-1} [for the dissociation of the initially formed triplet pair $^1(TT)$] and k_2 [for the return of $^1(TT)$ to an $S_1 + S_0$ pair] do not have independent significance and only the branching ratio ε is meaningful [defined variously as $\varepsilon = k_2/k_{-1}$ or $\varepsilon = 2k_2/(2k_2 + k_{-1})$]. The process starts with a noninteracting combination of an S_0 molecule and an S_1 molecule. SF is induced by the interaction Hamiltonian operator $H_{\text{int}} = H_{\text{el}} + H_{\text{sp}}$, where H_{el} is a spin-free electrostatic part

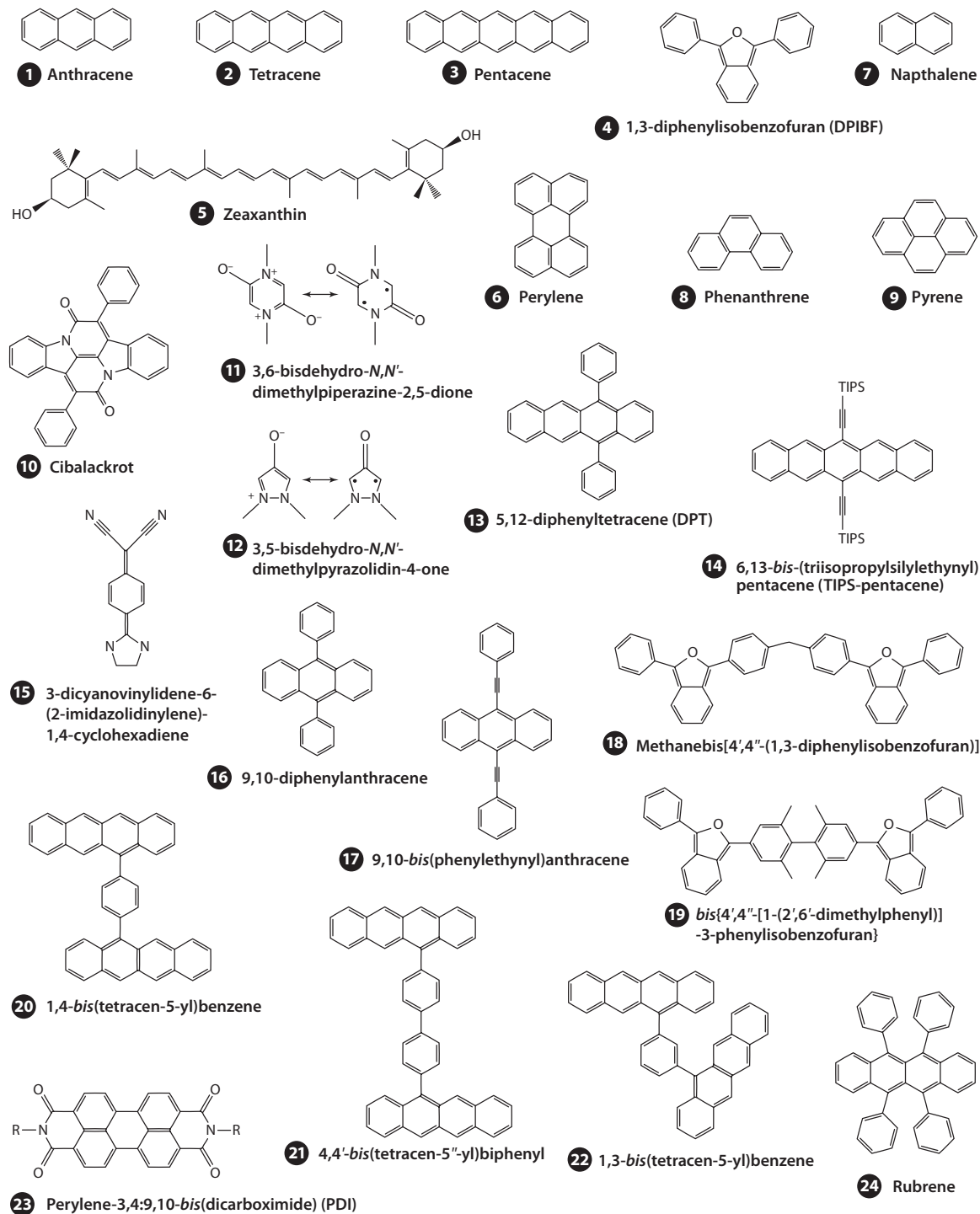


Figure 1

Structures of compounds discussed in the review.

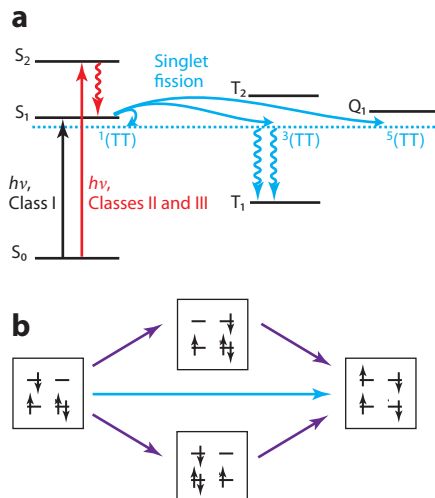
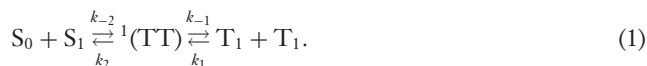


Figure 2

(a) An expanded Jablonski diagram illustrating singlet fission (SF) from S_1 following ground-state excitation. An initially formed coherent $^1(TT)$ state dissociates to form two independent triplets. (b) Direct (blue) and mediated (purple) interactions in SF.

and H_{sp} is a spin-dependent part familiar from electron paramagnetic resonance spectroscopy, whose main constituents are the spin dipole-dipole interaction and the Zeeman interaction with an outside magnetic field. In the simplest description, the action of H_{el} first converts the initial $S_0 + S_1$ state into $^1(TT)$, a pair of local triplet states coherently coupled into a pure overall singlet. This process is spin allowed and represents the internal conversion aspect of SF. The resulting pair of correlated triplet excitations $^1(TT)$ is variously referred to as a multiexciton state, a doubly excited state, a dark state D (a label we do not use to avoid confusion with a doubly excited state of a single partner in the pair), or a correlated triplet pair, the expression we adopt.



In the second of the two artificially separated steps, H_{sp} is allowed to act. If the interaction between the two chromophores is very weak, e.g., if they merely touch, the singlet $^1(TT)$ state is nearly degenerate with the triplet $^3(TT)$ and quintet $^5(TT)$ states that also result from the coupling of two triplets. If they lie within $\sim 1 \text{ cm}^{-1}$, H_{sp} can mix them significantly, and an outside magnetic field can then have observable effects on the SF process. Spin coherence is gradually lost and the triplets can diffuse apart (and back together). These processes represent the intersystem crossing (ISC) aspects of SF. As shown in an expanded Jablonski diagram (**Figure 2**), they can result in the formation of free intramolecular excited triplet and potentially also quintet states (in organic molecules, the latter usually are energetically inaccessible and have never been observed). The SF process and formation of $^1(TT)$ can occur on a subpicosecond scale (22, 23).

If the interaction between the two partners is stronger and the $^1(TT)$, $^3(TT)$, and $^5(TT)$ states are not nearly degenerate, the effects of H_{sp} can be safely ignored, and a pure spin state $^1(TT)$ is produced in the SF event. If it is sufficiently more stable than $^3(TT)$ and $^5(TT)$, it will be energetically uphill for the two triplets to diffuse apart. Thus, there is an optimal range of strength of interaction between the two partners if free triplet excitons are the desired outcome. Coupling

Correlated triplet

pair: a pair of triplet chromophores with coherent electron spins

ISC: intersystem crossing

that is too weak is insufficient to permit the formation of a correlated triplet-pair state fast enough to compete with other events such as fluorescence, and coupling that is substantially stronger than kT keeps $^1(\text{TT})$ bound such that the triplets cannot separate on the timescale available. An extreme example of intramolecularly strongly coupled chromophores is 1,3-butadiene viewed as two coupled double bonds. Here the $^1(\text{TT})$ state is identical to the molecular $2A_g$ state, and the $^3(\text{TT})$ and $^5(\text{TT})$ states are separated by 1–2 eV (24).

There is an ambiguity in the use of the term SF. It is tempting to apply it to the production of the correlated triplet pair alone and to view the subsequent dissociation into free triplets as a distinct event, but the two cannot be separated (8), and the term SF is commonly applied to the whole process. Although the correlated triplet pair could be viewed as an observable intermediate in SF, we follow the common usage and, for the purposes of nomenclature, call SF described by Equation 1 a one-step process.

Equation 1 represents the standard simplified depiction of SF and is probably quite adequate for cases in which SF is relatively slow. An excellent example would be SF in solution, which would have to wait for diffusion to bring S_1 and S_0 together. The initial excitation event and SF are then well separated in time. There are increasing indications that Equation 1 does not apply to cases in which SF is faster than vibrational relaxation, e.g., in solid tetracene (22) and pentacene (23). In such cases, the initial excitation appears to produce a coherent superposition of the $S_0 + S_1$ and the $^1(\text{TT})$, $^5(\text{TT})$, and perhaps also $^3(\text{TT})$ states, and nuclear motion is not required (see Section 7).

There is little doubt that nuclear motion accompanies the SF process on a longer timescale, even in tetracene and pentacene. The first calculations that attempted to follow the reaction path have appeared (25, 26). These studies provided the first explicit and relatively difficult *ab initio* quantum mechanical description of the long postulated $^1(\text{TT})$ state of pentacene (26) and tetracene (25). Results for 2-methylhexa-1,5-diene, which was used as a simple model (25) showed that the energy and optimized geometry of the $^1(\text{TT})$ state can be very closely simulated by the $^5(\text{TT})$ state, which is much easier to calculate and for which standard density functional theory (DFT) methods can be used. In solid pentacene, initial delocalized excitation apparently first localizes on a pair of molecules (excimer) (26–28). Nuclear motion-driven SF results from intermolecular motion through a narrowly avoided state crossing that induces $(S_1 + S_0)/^1(\text{TT})$ nondiabatic coupling. Given the size of these molecules, a calculation of true molecular dynamics was not attempted, and an optimized one-dimensional reaction path was assumed and followed.

It is not clear whether the $^1(\text{TT})$ state of solids such as pentacene is bound or whether the two triplets are free to diffuse apart. Earlier computational work (29) suggested the former, newer computations (26) suggested the latter, and a very recent interpretation of ultrafast experimental data for tetracene (22) suggests the former again. In the standard interpretation of the slightly endothermic SF in tetracene, vibrational excitation is believed to be required to reach a nondiabatic coupling region. Shaped laser pulse-induced transient absorption spectroscopy has begun to identify the required vibrational modes (30).

We shall see below that the spatial arrangement of neighbors in the crystal lattice of acenes (tilted slip-stacked, with slip in the direction of the short axis, i.e., of the S_0 – S_1 transition moment) and also of DPIBF (slip-stacked, with slip in the direction of the long axis, i.e., of the S_0 – S_1 transition moment) happens to be nearly optimal for efficient SF coupling.

A new model (31) for fast SF considered the broadening of the density of initial and final states by environment-induced fluctuations and derived a time-dependent non-Markovian transition rate expression that did not match the golden rule transition rate in the first 600 fs. The golden rule transition rate was highest for an energy gap between initial and final states that matched the

magnitude of the fluctuations. Excessive fluctuations stabilized the two states and decreased the transition rate.

2.2. Detecting SF

One of the experimental challenges posed by SF is differentiation between triplet formation by SF, in which one singlet excitation produces two triplets, and by ordinary ISC, in which spin-orbit coupling induces a conversion of a singlet into a triplet excitation plus vibrational energy. A triplet yield higher than 100% is a sure signature of SF, and a time-resolved observation of ground-state bleaching kinetically concurrent with excited singlet state disappearance and with triplet formation (18) is also unambiguous. Other safe ways of differentiating triplet formation by SF and by ordinary ISC are the detection of quantum beats in delayed fluorescence (32–34) and the observation of the anticipated spin polarization of the triplet levels by electron paramagnetic resonance (35–38).

The observation of magnetic field effects on yields of prompt and delayed fluorescence, photoconductivity (39), and photocurrent (16, 40, 41) is less direct but was the most common way to detect SF in the early days (20). Their absence does not rule out SF. As explained in detail elsewhere (10, 20), the coupling between the $S_0 + S_1$ state and a triplet-pair state depends on the content of $^1(TT)$ in the eigenstates of the latter. In these eigenstates, $^1(TT)$, $^5(TT)$, and possibly also $^3(TT)$ are mixed as dictated by H_{sp} (6) and thus by the strength and direction of the magnetic field through the Zeeman term, most simply in single crystals. The SF rate grows as states with significant $^1(TT)$ character become more numerous. With increasing magnetic field strength, the number of pair states with $^1(TT)$ character briefly increases and then decreases (21). In the high-field limit, certain crystal orientations bring about a degeneracy between two sublevels with partial $^1(TT)$ character, which mix to form a pure $^1(TT)$ singlet and a pure $^5(TT)$ quintet (level-crossing resonances), reducing the number of states with significant $^1(TT)$ character (6, 9). Then, the SF rate and therefore also the intensity of delayed fluorescence drop, and the intensity of prompt fluorescence grows. The Johnson-Merrifield model (7) uses a density matrix treatment and correctly predicts the positions of level-crossing resonances but not the lineshapes. The much more complicated Suna model (8) includes exciton diffusion and reproduces the lineshapes too. Magnetic field effects on electroluminescence have also been observed and have been attributed to fission of charge-transfer states (42).

Often the attribution of triplet formation to SF is based on its ultrafast rate alone, usually deduced from femtosecond transient absorption measurements (15, 17, 23, 27, 28, 43–57). This is relatively safe as long as heavy atoms are absent, as triplet appearance times from ordinary ISC would rarely be shorter than ~ 10 ps and ordinarily are much longer. However, triplet appearance times from SF can be as long as 25 ps (18).

The correct assignment of transient absorption peaks can be quite difficult, and the use of excessive fluences produces artifacts, such as discrepancies in fluorescence decay times (58, 59). In tetracene, increased emission quantum yield at high illumination intensities (6, 60) has been attributed to increased triplet-triplet annihilation (61). What was proposed to be T-T absorption in pentacene has been recently identified as an artifact due to heating (50), and a previous discrepancy (15) between a decay time of 100 ps for fluorescence and 10 ps for stimulated emission disappeared at excitation densities below $2 \times 10^{17} \text{ cm}^{-3}$, at which exciton-exciton annihilation no longer interferes (57).

When SF is endoergic, triplet formation depends on temperature and/or excitation energy. A thermally induced decrease in fluorescence yield (6, 60, 62) or singlet lifetime (63), the onset of delayed fluorescence (3, 64) and magnetic field response (6, 65–70), and the appearance of

triplet-triplet absorption (48) result but are not uniquely associated with SF because ordinary ISC can be thermally activated as well.

3. EXCITED STATES OF SF CHROMOPHORES

It is useful to divide the parent hydrocarbons from which SF chromophores are normally derived into three classes according to the nature of their S_0 to S_1 excitation. Different expressions are obtained for the matrix elements involving S_1 in each of these classes, and different rules for the design of optimal interchromophore coupling for SF result. In the following, we focus on rules for chromophores derived from hydrocarbons of class I, which have been most commonly studied.

In class I hydrocarbons, S_0 to S_1 excitation corresponds to the highest occupied molecular orbital [HOMO (b)] to lowest unoccupied molecular orbital [LUMO (l)] transition $b \rightarrow l$. Examples are compounds 1–4 and 6 in **Figure 1**. In class II hydrocarbons, the $S_0 \rightarrow S_1$ transition corresponds to a linear combination of two promotions [$(b - 1 \rightarrow l) - (b \rightarrow l + 1)$]. The $b \rightarrow l$ transition usually produces S_2 . In hydrocarbons derived from $(4N + 2)$ -electron perimeters, the $b \rightarrow l$ transition is strongly allowed and is often responsible for most light absorption. After excitation, these chromophores undergo fast internal conversion from S_2 to S_1 . Examples are compounds 7–9 in **Figure 1**. In class III hydrocarbons, S_1 contains a large contribution from the doubly excited configuration $b, b \rightarrow l, l$, usually along with contributions from the singly excited configurations $b - 1 \rightarrow l$ and $b \rightarrow l + 1$. As in class II chromophores, an intense $b \rightarrow l$ transition to S_2 or possibly a higher state is usually responsible for most absorption and is followed by internal conversion to S_1 . Examples of this class include primarily polyenes such as zeaxanthin (compound 5 in **Figure 1**). A recent computational result suggesting that an isolated molecule of pentacene also belongs to this class (71) contradicts experimental observations (summarized in Reference 20) and cannot be correct.

4. DESIGNING SF CHROMOPHORES

To be practically useful, an SF sensitizer needs to meet many conditions. The most important are a 200% triplet yield, long triplet lifetime, strong visible absorption starting at ~ 2.2 eV (2), redox potentials and other properties conducive to efficient charge separation, and long-term stability in light. An SF sensitizer is defined by the nature of its chromophores and by the way in which they are coupled. In this section we consider the nature of SF chromophores, and in the next section we consider their coupling. The limited number and structural similarity of chromophores currently known to undergo SF efficiently are unlikely to offer a sufficiently wide choice for SF solar-cell design, and we consider it essential that additional classes of efficient SF chromophores be discovered. Here we consider only factors that favor a 200% yield of long-lived triplets (14, 20) and ignore other requirements, which are not trivial but appear less difficult to meet. First, SF needs to be faster than any competing processes. It will be best if it is slightly exoergic or at least isoergic, $E(S_1) \geq 2E(T_1)$. Excessive exoergicity would cause a loss of efficiency by heat generation, and it would also make SF nonresonant and slower. Slight endothermicity is tolerable because a small energy deficit can be made up by thermal energy or by coherent excitation. As mentioned below, the price that must then be paid is an increased rate of triplet-triplet annihilation, which is then slightly exothermic. In the widely studied tetracene, SF has been traditionally believed to be endothermic and absent at temperatures below ~ 160 K (6, 63, 66, 72, 73), but the latest results disagree with this view (see Section 7.2). Excess energy can also be provided using optical excitation into higher states or vibrational levels (20), in which case SF must compete with vibrational relaxation and internal conversion and is rarely efficient.

HOMO: highest occupied molecular orbital

LUMO: lowest unoccupied molecular orbital

Chromophore coupling:

interaction of two chromophores via H_{int} , the part of the total Hamiltonian that is absent in isolated chromophores

Alternant hydrocarbon:

a conjugated hydrocarbon with no odd-membered rings

Biradicaloid:

a molecule derived from a perfect biradical by a perturbation that splits the energies of the orbitals that are singly occupied in the T_1 state

SF can occur in systems of mixed chromophores in a process known as heterofission (74, 75). For a mixture of chromophores A and B, the $E(S_1)$ energy of at least one of the chromophores must equal or exceed the sum $E(T_{1A}) + E(T_{1B})$.

Second, triplets have the potential to annihilate each other to form singlets, triplets, or quintets, and in order to make the triplets long-lived, such processes should be slow. Because we already demand that SF be somewhat exoergic, annihilation to yield $S_0 + S_1$ will be endoergic (or at best isoergic). The formation of $S_0 + T_1$ or $S_0 + S_0$ is likely to be too exoergic to be fast, and the formation of $S_0 + Q$ is normally excluded as too endoergic. (Q is an intramolecular excited quintet state.) The remaining concern is the formation of $S_0 + T_2$, where T_2 is the next higher molecular triplet state, and we therefore also impose the condition $E(T_2) \geq 2E(T_1)$ to make it endoergic and slow.

Third, SF ordinarily occurs on the picosecond timescale or faster and can outcompete fluorescence. A fluorescence yield close to unity in the isolated chromophore will thus guarantee that no faster unimolecular pathways are available. However, in dimers, aggregates, and solids, additional competing channels may open that are intermolecular in nature (such as excimer and charge-transfer state formation), and this will need to be considered when dealing with chromophore coupling.

There are some common-sense guidelines for choosing molecular structures that are likely to have high fluorescence yields, such as skeletal rigidity and the absence of atoms of heavy elements. It is more challenging to come up with general rules for parent structures that will fulfill the demanding conditions $E(T_2), E(S_1) \geq 2E(T_1)$. Simple molecular orbital theory identified two classes of structures as promising (14): among those derived from a closed-shell S_0 state, alternant hydrocarbons, and among those derived from an open-shell (biradical) S_0 state, biradicaloids. The two classes are not mutually exclusive, and it has been demonstrated recently that those alternant hydrocarbons that have high biradicaloid character, as judged by occupancies of frontier natural orbitals, are especially suitable (76).

The S_1 and T_1 states of a closed-shell ground-state structure are split by approximately $2K_{hl}$, where the exchange integral K_{hl} is the repulsion of two identical charge distributions defined by the product of the orbitals h (HOMO) and l (LUMO) multiplied by electron charge e (Figure 3). In uncharged alternant hydrocarbons, K_{hl} is unusually large because sizeable amplitudes of h and

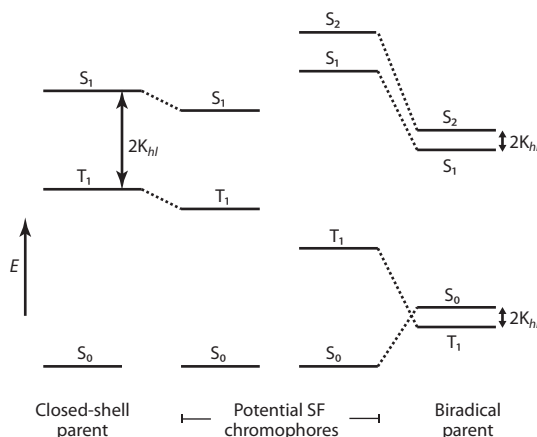


Figure 3

Potential singlet fission (SF) chromophores derived from closed-shell (*left*) and biradical (*right*) parent structures.

l occur on the same carbon atoms, as dictated by the alternant pairing theorem, which is strictly valid in certain semiempirical theories (77, 78) and almost exactly valid in *ab initio* theory too. In the product of *ehl*, large charges occur at these centers and produce large one-center contributions to K_{hl} . Because K_{hl} does not change much with system size, all that remains is to choose an alternant hydrocarbon large enough to reduce the S_1 excitation energy below twice the S_1 - T_1 splitting. In the polyacene series, this point is almost reached in tetracene and exceeded in pentacene. Indeed, all systems for which SF was reported up to 2010 were alternant hydrocarbons or their simple derivatives. We note that this argument says nothing about the energy $E(T_2)$.

Systems with a biradical ground state offer a wider variety of starting points and have the additional advantage that the condition $E(T_2) \geq 2E(T_1)$ is likely to be met, making T_1 longer-lived. Biradicals contain two approximately nonbonding orbitals singly occupied in the S_0 and T_1 states when chosen in the most localized form. The splitting between S_0 and T_1 is small, and either state can be lower in energy. S_1 and S_2 are usually significantly higher. Removing the degeneracy of the two nonbonding orbitals to just the right degree by a suitable structural perturbation leads to a biradicaloid in which the S_0 state has been stabilized and the T_1 , S_1 , and S_2 states destabilized (Figure 3). This was the argument that led to the biradicaloid structure DPIBF (compound 4 in Figure 1), which has indeed been found to meet the conditions $E(T_2)$, $E(S_1) \geq 2E(T_1)$ and to give a 200% triplet yield by SF (18). Cibalackrot (compound 10 in Figure 1), an industrial dye related to indigo, is another biradicaloid that exhibits significant SF (J.C. Johnson, B.R. Stepp, J.L. Ryerson, M.B. Smith, A. Akdag, et al., unpublished results), and Figure 1 also shows two small biradicaloid heterocycles (compounds 11 and 12) that have been recently calculated (79) to approximately fulfill the conditions $E(T_2)$, $E(S_1) \geq 2E(T_1)$. With only 10 nonhydrogen atoms, high-quality calculations for their dimers should be much easier than for tetracene or pentacene.

Pairing theorem:

paired bonding and antibonding molecular orbitals of an alternant hydrocarbon, such as the HOMO and LUMO of uncharged even-carbon π systems, have identical amplitudes on each carbon site, except possibly for sign

One-step SF

mechanism: SF

proceeding from $S_1 + S_0$ to the correlated triplet pair (1T) without an observable intermediate

5. CHROMOPHORE COUPLING: THE ONE-STEP SF MECHANISM

In an SF sensitizer, chromophores need to be coupled by physical contact and/or weak noncovalent bonding in a crystal or an aggregate, or by covalent bonding in a dimer, oligomer, or polymer. Crystalline materials have given the highest triplet yields (15, 16, 18). The coupling must meet many requirements and has been the subject of a recent brief review (80). For SF to compete with fluorescence, it needs to occur on a picosecond or subpicosecond timescale; hence the coupling cannot be too weak. We have already noted that the $^{1,3,5}(TT)$ states need to be nearly degenerate for triplets to diffuse apart easily; hence the coupling must not be too strong either. Strong coupling might also wreak havoc with the relative state energies of a carefully selected chromophore, as noted below in the case of cibalackrot, and it might interfere with the subsequent charge-separation step (spin one-half particles quench triplets). It would probably be best if the coupling does not open channels that do not exist in an isolated chromophore, such as charge-transfer state or excimer formation, because they may cause decay to S_0 . Excimer formation has been suggested (26–28) and disputed (29) as an intermediate step in fission in pentacene.

Although meeting all these conditions for coupling is difficult, it is not impossible, as shown by the high SF yields that have been observed for solid tetracene (15), pentacene (16), DPIBF (18), cibalackrot (J.C. Johnson, B.R. Stepp, J.L. Ryerson, M.B. Smith, A. Akdag, et al., unpublished results), 5,12-diphenyltetracene (DPT; compound 13 in Figure 1) (43), 6,13-bis-(triisopropylsilyl)ethynylpentacene (TIPS-pentacene; compound 14 in Figure 1) (44), and aggregated zeaxanthin (45). Only for TIPS-pentacene was there a conscious effort to engineer the crystal structure, and the other structures merely happened to meet the requirements. The importance of the details of the coupling is illustrated by the observation (80) that different polymorphs of a thin polycrystalline film of DPIBF give very different yields of triplets. The same is true of

ZINDO: Zerner's intermediate neglect of differential overlap method

Direct interaction: interaction of a strictly intramolecularly excited initial state with a strictly intramolecularly excited final state due to a matrix element of H_{el} between them

cibalackrot (compound 10 in **Figure 1**). In this compound, strong intermolecular interactions in the crystal make SF endoergic, although it is isoergic in a pair of isolated molecules, and the highest observed triplet yield is only 70%. Also, the presence of active sites in amorphous neat DPT (see below) strongly suggests that some spatial arrangements of neighbors are more effective than others. High SF yields have so far not been achieved in covalent dimers, oligomers, and polymers.

In two numerical studies, the degree of coupling was estimated from calculated interaction energies. One DFT study computed the coupling strength in dimers of tetracene, of DPIBF, and of 3-dicyanovinylidene-6-(2-imidazolidinylene)-1,4-cyclohexadiene (compound 15 in **Figure 1**), covalently connected in various ways (81). The coupling strength was qualitatively consistent with the SF rates in these systems (46, 47, 82). In a second study, time-dependent DFT and ZINDO (Zerner's intermediate neglect of differential overlap) methods were used to evaluate the energy of interaction for each unique chromophore pair that occurs within a crystal of anthracene, tetracene, or 9,10-diphenylanthracene (compound 16 in **Figure 1**), in which the conclusion was that exciton diffusion should be directional, and in 9,10-*bis*(phenylethynyl)anthracene (compound 17 in **Figure 1**) in which it should be isotropic and which the authors recommend for a study of SF (83). It is, however, not clear to us why there should be any simple relation between the rate of exciton diffusion and the rate of SF, as implied by these authors.

A full ab initio numerical evaluation of the matrix element $\langle {}^1(TT) | H_{el} | S_1 S_0 \rangle$ was performed for pentacene (26). The authors did not attempt to separate it into contributions from the direct and mediated interactions discussed below but felt that charge-transfer states played no significant role because they mixed only weakly with the locally excited states. A more recent ab initio study of tetracene, in which the direct and indirect contributions were evaluated separately, reached the opposite conclusion (25), which we believe is correct.

General coupling design rules follow from a qualitative consideration of a simple model (20), and we work them out in more detail below only for chromophores derived from parent structures of class I. Using mutually Löwdin-orthogonalized Hartree-Fock frontier molecular orbitals HOMO (b_A , b_B) and LUMO (l_A , l_B) on two identical weakly interacting class I chromophores A and B, singlet electronic states were approximated as follows: the ground state $S_0^A S_0^B = (|b_A \alpha b_A \beta b_B \alpha b_B \beta|)$, the singly excited states $S_1^A S_0^B = (2^{-1/2}[|b_A \alpha l_A \beta b_B \alpha b_B \beta| - |b_A \beta l_A \alpha b_B \alpha b_B \beta|])$ and $S_0^A S_1^B = (2^{-1/2}[|b_A \alpha b_A \beta b_B \alpha l_B \beta| - |b_A \alpha b_A \beta b_B \beta l_B \alpha|])$, the double triplet state ${}^1(T_1^A T_1^B) = (3^{-1/2}[|b_A \alpha l_A \alpha b_B \beta l_B \beta| + |b_A \beta l_A \beta b_B \alpha l_B \alpha| - \{ |b_A \alpha l_A \beta b_B \alpha l_B \beta| + |b_A \alpha l_A \beta b_B \beta l_B \alpha| + |b_A \beta l_A \alpha b_B \alpha l_B \beta| + |b_A \beta l_A \alpha b_B \beta l_B \alpha| \} / 2])$, and two charge-transfer states ${}^1(C^A B) = (2^{-1/2}[|b_A \alpha l_B \beta b_B \alpha b_B \beta| - |b_A \beta l_B \alpha b_B \alpha b_B \beta|])$ and ${}^1(A^B C) = (2^{-1/2}[|b_A \alpha b_A \beta l_A \alpha b_B \beta| - |b_A \alpha b_A \beta l_A \beta b_B \alpha|])$. Excitation was assumed initially localized on one member of the chromophore pair, but similar results for the rate constant were obtained for delocalized initial excitation.

To first order, the isoergic SF rate $w(\text{SF})$ is given by the Fermi golden rule with the wave functions of the initial and final states approximated simply by the $S_0 S_1$ and ${}^1(TT)$ configurations defined above,

$$w(\text{SF}) = (2\pi/\hbar) | \langle {}^1(TT) | H_{el} | S_0 S_1 \rangle |^2 \rho[E], \quad (2)$$

where $\rho[E]$ is the Franck-Condon weighted density of states at energy $E = E(S_0 S_1) = E({}^1(TT))$. The matrix element contains only contributions from the two-electron part of the Hamiltonian and tends to be small (see Section 5.1). It is therefore important to consider in the description of the initial and final states the possible effect of mixing with other configurations of the system by H_{el} , even if this mixing is only weak. Using the next order of perturbation theory, this has the effect of allowing the $S_0 S_1$ and ${}^1(TT)$ configurations to interact also indirectly through the intermediacy of these additional virtual configurations (**Figure 2b**). Two matrix elements

connecting each virtual electronic configuration to the initial and the final configuration now need to be considered, as well as its energy. The lowest-energy relevant virtual configurations are of charge-transfer nature, $^1(\text{C}^{\text{A}}\text{A}^{\text{B}})$ and $^1(\text{A}^{\text{A}}\text{C}^{\text{B}})$, and the matrix elements that connect them to the initial and final configurations contain contributions from both the one-electron and the two-electron parts of H_{el} . In this better approximation, Equation 2 is converted into the more complicated Equation 3 given in Section 5.2. As shown below, the situation remains simple enough to still permit qualitative considerations.

The contributions that result from the first-order approximation are said to be due to the direct interaction (Equation 2), and the additional ones that originate in higher orders to the mediated interaction (Equation 3 contains terms from both interactions). On the basis of numerical estimates for several cases, we have become convinced that the mediated interaction dominates the direct one even when the energies of the charge-transfer states are quite high, and in most if not all cases is the only one that needs to be considered.

Above we discuss only a one-step SF mechanism, which proceeds directly from S_0S_1 to $^1(\text{TT})$ without intermediates. If a charge-transfer state is sufficiently low in energy (perhaps in a polar environment), it may actually represent a minimum on the S_1 surface and may occur in the SF process as a real state rather than a virtual intermediate configuration (see Section 6). The two steps involved are both known independently. The formation of an intramolecular charge-transfer state from an excited singlet has been known for a long time (84), and the formation of two triplets from a charge-transfer state in solid anthracene (42) or from a tetracene radical ion pair in solution (85) has been reported as well. In solid anthracene, the formation of $^1(\text{TT})$ from the charge-transfer state initially formed by an encounter of a positive and a negative injected polaron must be direct, as it is energetically impossible to first produce a pair of neutral molecules, S_1 and S_0 , that would then proceed to $^1(\text{TT})$. In tetracene radical ion recombination in solution, this possibility cannot be excluded and is actually favored by the original authors. Observable intramolecular charge-transfer state formation and its subsequent conversion to triplet have been reported recently (86) for covalent dimers of DPIBF (compounds 18 and 19 in **Figure 1**). However, as discussed in Section 6, it was not clear whether two triplets were formed in a true two-step SF or whether only one triplet was formed because the second step was merely ISC.

5.1. Contribution from the Direct Interaction

According to Equation 2, the fission rate due to the direct mechanism alone is proportional to $|\langle ^1(\text{T}_1\text{T}_1) | H_{\text{el}} | \text{S}_1\text{S}_0 \rangle|^2$. Within the approximations adopted previously (20), especially the neglect of slight orbital delocalization over both chromophores resulting from Löwdin orthogonalization, $\langle ^1(\text{T}_1\text{T}_1) | H_{\text{el}} | \text{S}_1\text{S}_0 \rangle$ is equal to $(3/2)^{1/2} [\langle l_{\text{A}}l_{\text{B}} | e^2/r_{12} | b_{\text{B}}l_{\text{A}} \rangle - \langle b_{\text{A}}b_{\text{B}} | e^2/r_{12} | l_{\text{B}}b_{\text{A}} \rangle]$. The electron repulsion integrals $\langle l_{\text{A}}l_{\text{B}} | e^2/r_{12} | b_{\text{B}}l_{\text{A}} \rangle$ and $\langle b_{\text{A}}b_{\text{B}} | e^2/r_{12} | l_{\text{B}}b_{\text{A}} \rangle$ represent the electrostatic attraction or repulsion between two overlap densities and can be estimated by inspection. The four overlap densities $l_{\text{A}}l_{\text{B}}$, $b_{\text{B}}l_{\text{A}}$, $b_{\text{A}}b_{\text{B}}$, and $l_{\text{B}}b_{\text{A}}$ depend on the spatial overlap of orbitals located on different chromophores A and B and are small; they would be neglected in the zero differential overlap approximation. They are especially insignificant for linearly linked dimers (compounds 18–22 in **Figure 1**), the only ones that have been investigated experimentally so far (46, 47, 82, 86). Most of the overlap in compounds 20–22 in **Figure 1** is believed to result from through-bond interactions (47). The densities have a somewhat better opportunity to be large when the chromophores are stacked, but the repulsion integrals vanish by symmetry when the stacking is perfect. Among the mutual orientations examined (20), the optimal situation occurs when the chromophores are slip stacked, with the slip in the direction of the transition moment of the $b \rightarrow l$ transition. This arrangement is often found in crystals of aromatics, sometimes with an additional tilt along an axis perpendicular to the direction of the slip.

Mediated interaction:

interaction of a strictly intramolecularly excited initial state with a strictly intramolecularly excited final state due to matrix elements of H_{el} between one of them and other (“virtual”) states

Two-step SF mechanism:

SF proceeding from $\text{S}_1 + \text{S}_0$ to the correlated triplet pair (^1TT) through the intermediacy of an observable (charge-transfer) species

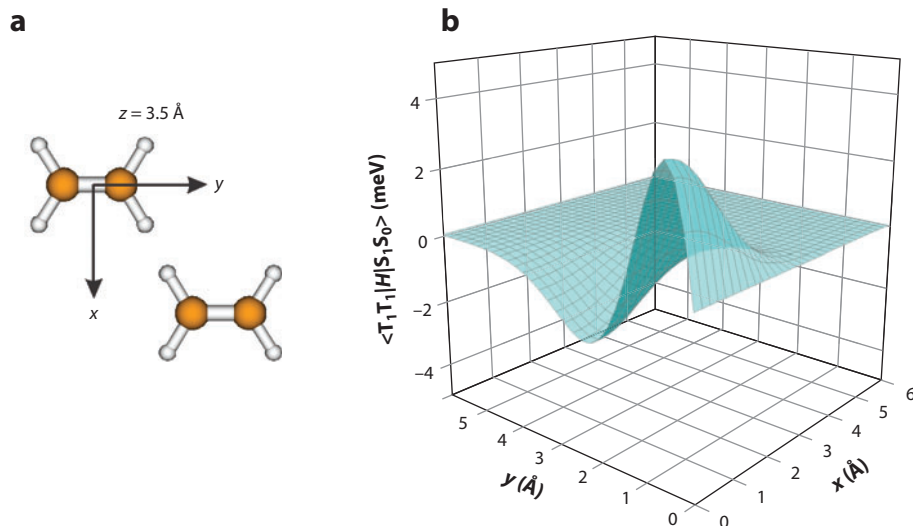


Figure 4

(a) Slip-stacked ethylene molecules and definition of axes. (b) The matrix element $\langle {}^1(T_1 T_1) | H_{el} | S_1 S_0 \rangle$ as a function of slip in directions x and y (6-311G basis set; M. Jovanovic, Z. Havlas & J. Michl, unpublished results).

Figure 4 illustrates the result by showing the value of the matrix element $\langle {}^1(T_1 T_1) | H_{el} | S_1 S_0 \rangle$ computed for two ethylene molecules stacked at a distance of $3.5 \text{ \AA}$ as a function of the degree of slip in the direction y of the $b \rightarrow l$ transition moment and in the direction x perpendicular to it.

5.2. Contribution from the Mediated Interaction

In a better approximation for the SF rate $w(\text{SF})$ for two identical chromophores A and B, it is recognized that charge-transfer states can mix into the initial and final states of the SF transformation, and the matrix element whose square enters the Fermi golden rule then contains not only the direct contribution but also the mediated contribution (20). The rate is now given by Equation 3:

$$w(\text{SF}) = (2\pi/\hbar) | \langle {}^1(T_1 T_1) | H_{el} | S_1 S_0 \rangle - \langle {}^1(T_1 T_1) | H_{el} | \text{CA} \rangle \langle {}^1\text{CA} + {}^1\text{AC} | H_{el} | S_1 S_0 \rangle / \Delta E_{\text{CT}} |^2 \rho[E], \quad (3)$$

where ΔE_{CT} , which occurs in the mediated term, is the difference between the energy of the charge-transfer states and the energy of the nearly degenerate $S_0 S_1$ and ${}^1(\text{TT})$ states. Both the one-electron and the two-electron parts of the Hamiltonian now contribute (20). Introducing the symbol F for the Fock operator of the ground state, one obtains

$$\langle {}^1\text{TT} | H_{el} | \text{CA} \rangle = (3/2)^{1/2} [\langle l_A | F | b_B \rangle + \langle l_A l_B | e^2 / r_{12} | b_B l_B \rangle - \langle l_A b_A | e^2 / r_{12} | b_B b_A \rangle], \quad (4)$$

$$\langle {}^1\text{CA} | H_{el} | S_1 S_0 \rangle = \langle l_A | F | l_B \rangle + 2 \langle b_A b_A | e^2 / r_{12} | l_A l_B \rangle - \langle b_A l_A | e^2 / r_{12} | b_B l_B \rangle, \quad (5)$$

$$\langle {}^1\text{AC} | H_{el} | S_1 S_0 \rangle = - \langle b_A | F | b_B \rangle + 2 \langle b_B b_A | e^2 / r_{12} | l_B l_B \rangle - \langle l_B b_A | e^2 / r_{12} | l_B l_B \rangle. \quad (6)$$

Figure 5 shows the magnitudes of the three matrix elements in Equations 4–6 for the case of two slip-stacked ethylene molecules. It is seen that they are two orders of magnitude larger than

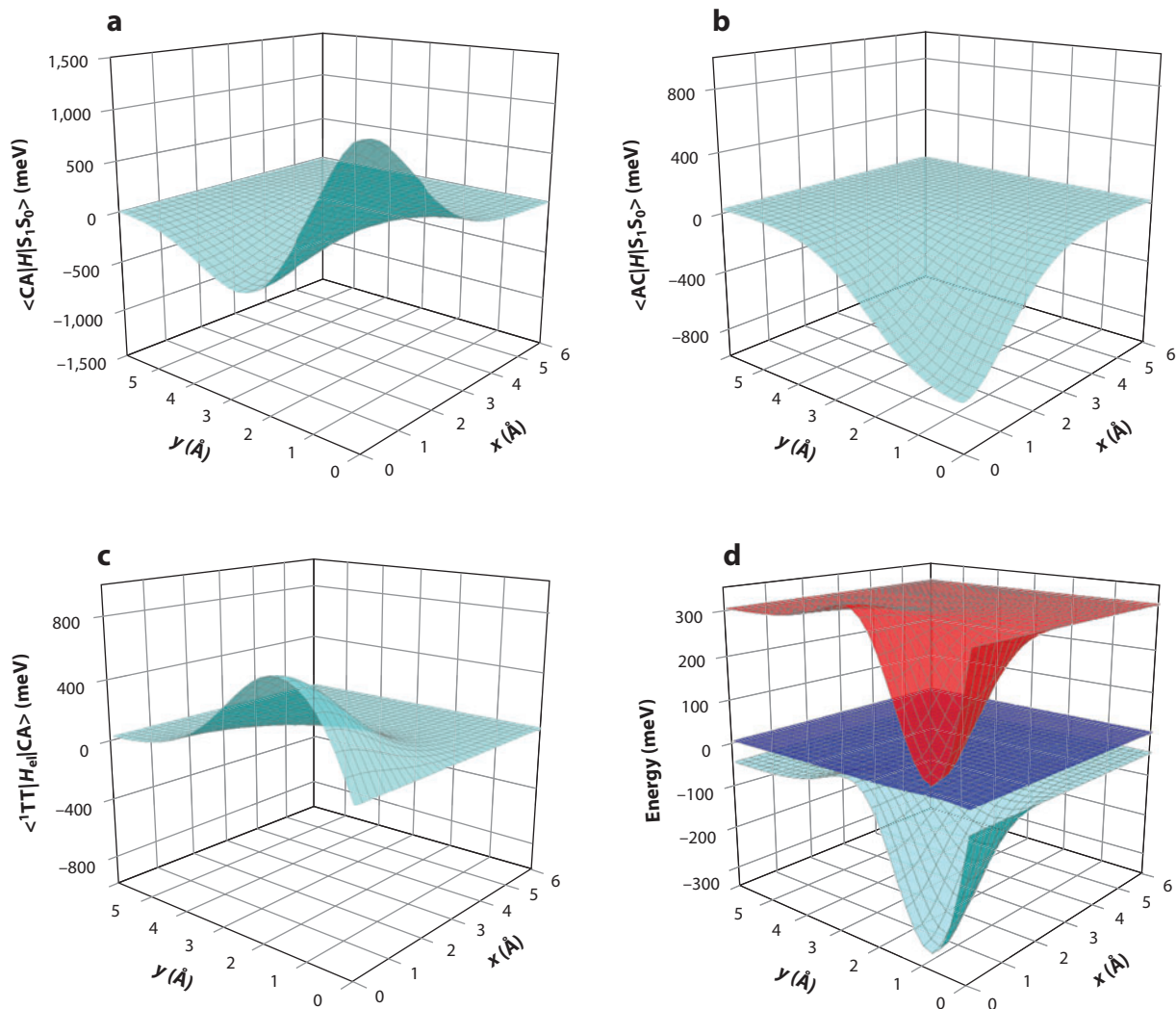


Figure 5

Singlet fission interaction matrix elements for slip-stacked ethylene molecules as a function of slip in directions x and y (see **Figure 4**): (a) $\langle \text{CA} | H_{\text{el}} | S_1 S_0 \rangle$, (b) $\langle \text{AC} | H_{\text{el}} | S_1 S_0 \rangle$, and (c) $\langle \text{1TT} | H_{\text{el}} | \text{CA} \rangle$. (d) The sum (light blue) of direct (dark blue) and mediated (red) contributions assuming a 50-kcal mol $^{-1}$ difference E between the energy of the initial and final states and the energy of the charge-transfer states (6-311G basis set; M. Jovanovic, Z. Havlas & J. Michl, unpublished results).

the matrix element of the direct contribution shown in **Figure 4**. Importantly, the matrix element $\langle \text{1TT} | H_{\text{el}} | \text{CA} \rangle$ that appears as a multiplicative factor in the mediated term in Equation 3 vanishes for perfect stacking. Moreover, the other two elements, which enter as a sum, have opposite signs in the region of nearly perfect stacking and tend to cancel. Once again, a slip in the direction of the $b \rightarrow l$ transition moment is necessary to produce a sizeable value. This is clear in **Figure 5d**, which shows the direct and the mediated terms separately along with their sum, assuming a relatively large value of 50 kcal mol $^{-1}$ for the energy difference E . Even with this unfavorable choice, the mediated term completely dominates the direct term. The results do not change significantly when one of the ethylene molecules is tilted along the CC axis.

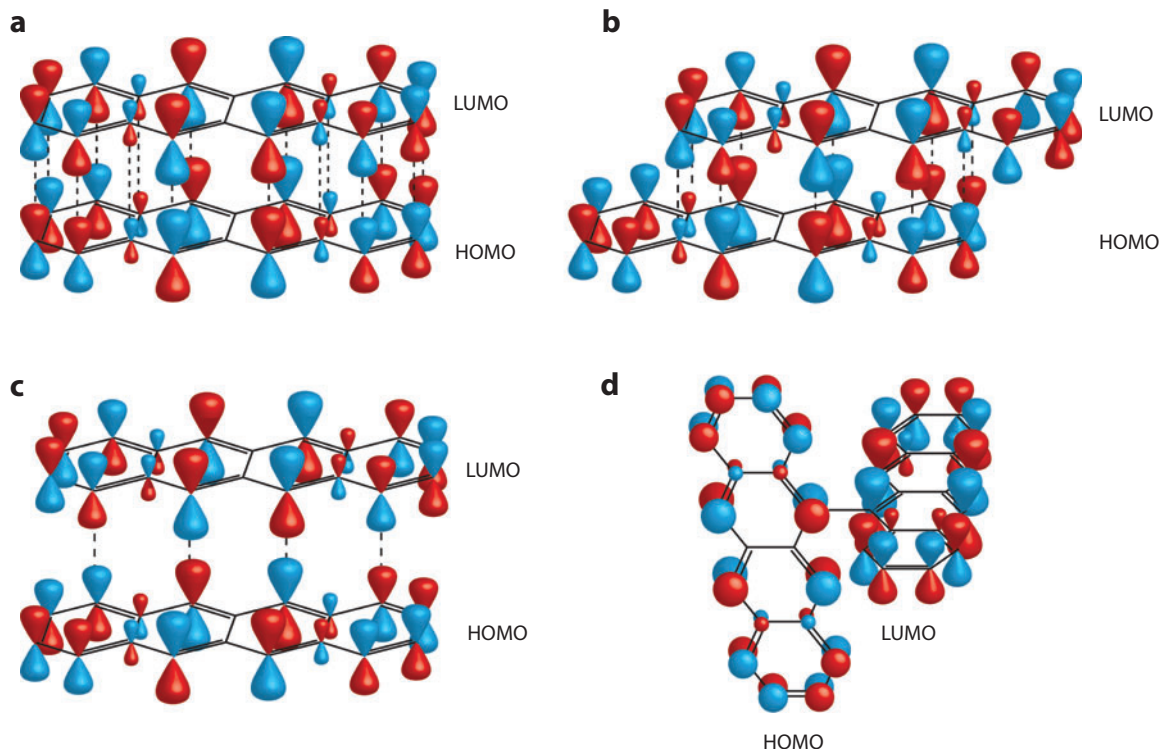


Figure 6

Singlet fission interaction of two tetracene chromophores: (a) stacked, (b) slip-stacked with slip perpendicular to the $b \rightarrow l$ transition moment, (c) slip-stacked with slip parallel to the $b \rightarrow l$ transition moment, and (d) covalently linked and twisted.

The two-electron integrals on the right-hand side of Equations 4–6 depend on overlap densities of orbitals located on different molecules and are small. If both the direct term $\langle {}^1(T_1 T_1) | H_{el} | S_1 S_0 \rangle$ and these integrals are neglected in the spirit of the zero differential overlap approximation, Equation 3 simplifies to Equation 7:

$$w(\text{SF}) = (3\pi/\hbar) | \langle l_A | F | b_B \rangle - [\langle l_A | F | l_B \rangle - \langle b_A | F | b_B \rangle] / \Delta E_{CT} |^2 \rho[E]. \quad (7)$$

Expansion of orbitals l and b in atomic orbitals μ on chromophore A and v on chromophore B and the introduction of the tight-binding approximation finally yield an approximate expression for the SF rate that is suitable for rapid qualitative estimates of the relative merits of various spatial arrangements of the chromophores, and thus represents a simple design rule for the coupling of a pair of SF chromophores:

$$w(\text{SF}) = (3\pi/\hbar) | [\sum_{(\mu\nu)} (c_{\mu l} c_{\nu b} + c_{\nu l} c_{\mu b}) \beta_{\mu\nu}] [2 \sum_{(\mu\nu)} (c_{\mu l} c_{\nu l} - c_{\mu b} c_{\nu b}) \beta_{\mu\nu}] / \Delta E_{CT} |^2 \rho[E], \quad (8)$$

where the sums are over pairs $(\mu\nu)$ of interacting (neighboring) atomic orbitals, μ on A and ν on B, and $\beta_{\mu\nu}$ is the resonance (hopping) integral between them. The coefficients $c_{\mu b}$, $c_{\nu b}$, $c_{\mu l}$, and $c_{\nu l}$ are the amplitudes of b and l at these atomic orbitals. We illustrate the use of Equation 8 for qualitative estimates of SF coupling of two molecules of tetracene (compound 2 in **Figure 1**) in two situations: slip stacking and linear covalent attachment. **Figure 6** shows the interaction of the b_A and l_B orbitals, which corresponds to the first bracket in Equation 8, and similar drawings could

be used to illustrate the h_A - h_B and l_A - l_B interactions, which correspond to the second bracket in this equation.

In the slip-stacked arrangement, the atomic orbitals μ on molecule A can be directed at atomic orbitals v on molecule B and overlap in a σ fashion. **Figure 6a** shows perfect stacking and illustrates how the presence of a symmetry plane cutting through the long axes of molecules A and B causes the expression in the first bracket to vanish: For every choice of atomic orbitals μ and v that contributes $c_{\mu l} c_{v b}$, there is a symmetry-related choice that contributes a similar product in which either $c_{\mu l}$ or $c_{v b}$ has changed sign. A slip along the long molecular axis does not change the situation (**Figure 6b**), but a slip along the short molecular axis does (**Figure 6c**), as the symmetry plane is now absent in the total assembly, although it is still present in each partner taken separately. The antisymmetry of h and symmetry of l in either partner with respect to this plane determine the direction of its $h \rightarrow l$ transition moment and make clear its identity with the productive slipping direction. The optimal amount of slip will be reached when the atoms of the two partners that carry large orbital amplitudes are eclipsed and their atomic orbitals point directly at each other, as shown in **Figure 6c**.

Next, considering the second bracket in Equation 8, we see that in the optimal slip-stacked orientation, the terms $c_{\mu l} c_{v l}$ and $c_{\mu b} c_{v b}$ will have opposite signs because moving from one long edge of tetracene to the other will change the signs in the antisymmetric molecular orbital h but not in the symmetric orbital l . The differences $c_{\mu l} c_{v l} - c_{\mu b} c_{v b}$ will therefore be maximized in the same slip-stacked orientation that maximized the sums $c_{\mu l} c_{v b} + c_{v l} c_{\mu b}$, and this is the optimal slip-stacking in a tetracene dimer for maximizing the SF rate given by Equation 8. Tilting one or both of the partners will make no qualitative difference to the argument but can affect the magnitude of the resonance integrals $\beta_{\mu\nu}$. The arrangement found in tetracene crystal is close to optimal, as are those found in the crystals of pentacene and DPIBF. We believe that this is important for the fast SF observed in these materials. No slip-stacked covalent dimers have been studied so far.

In covalently linked dimers, connected through the atom that carries orbital κ on partner A linked to the atom that carries orbital λ on partner B, only one choice of the pair μ, v contributes to the sums in Equation 8, namely $\mu = \kappa, v = \lambda$ (the orbitals κ and λ now interact in a π fashion). The term in the first bracket becomes $(c_{\kappa l} c_{\lambda b} + c_{\lambda l} c_{\kappa b}) \beta_{\kappa\lambda}$, while the term in the second bracket becomes $2(c_{\kappa l} c_{\lambda l} - c_{\kappa b} c_{\lambda b}) \beta_{\kappa\lambda}$. If the dimer is symmetric, such as that shown in **Figure 6d**, $c_{\kappa l} = c_{\lambda l}$ and $c_{\kappa b} = c_{\lambda b}$. Because tetracene is an alternant hydrocarbon, the resulting term in the second bracket, $2(c_{\kappa l}^2 - c_{\kappa b}^2)$, vanishes by the pairing theorem. In this approximation, the mediated contribution to SF is zero, and it is no surprise that an experimental study of symmetric covalent dimers of this general type revealed hardly any SF at all (46, 47). It can be expected that unsymmetrical dimers, in which $c_{\kappa l} = c_{\lambda l}$ and $c_{\kappa b} = c_{\lambda b}$ do not hold, would be a superior choice. DPIBF is a heterocycle to which the pairing theorem does not apply, and therefore its symmetric covalent dimers do not suffer from this problem. The two dimers examined so far, compounds 18 and 19 in **Figure 1**, exhibit no detectable SF in solution (82, 86), presumably because the resonance integral $\beta_{\kappa\lambda}$ is too small (in one case the linking bond $\kappa\lambda$ is twisted to orthogonality and in the other the linking is only hyperconjugative through a CH_2 group).

The conclusion that the two halves of a covalent dimer should not be related by symmetry is not new. It was first reached from the numerical results of a density-matrix-based treatment of SF in dimers based on the assumption that the mediated interaction is the only coupling mechanism (87).

6. CHROMOPHORE COUPLING: THE TWO-STEP SF MECHANISM

SF may also occur as a two-step process with a charge-transfer intermediate state ^1CA or ^1AC . In this case, the initial state S_0S_1 is first transformed into a charge-transfer state by electron transfer and then to $^1(\text{TT})$ by a back-electron transfer.

Some evidence for the two-step process has been obtained recently in compounds 18 and 19 in **Figure 1**, two linearly linked covalent dimers of DPIBF (80, 82, 86). They do not yield any observable triplets upon excitation in nonpolar solutions, and in this regard differ from compounds 20 and 21 in **Figure 1**, two covalent dimers of tetracene that yield $\sim 3\%$ triplet in solution with SF rate constants $\sim 10^6 \text{ s}^{-1}$ (for a third dimer, compound 22 in **Figure 1**, SF was not observable) (46, 47).

In solutions of compounds 18 and 19 in **Figure 1** in polar solvents such as DMSO, the triplet is formed in yields up to $\sim 10\%$ but not directly from the initially excited S_0S_1 singlet. Instead, the excited singlet first equilibrates with a somewhat more stable charge-transfer state ^1CA , which then more slowly yields the triplet. At low temperatures, the conversion of the initial excited singlet into the ^1CA state is irreversible.

The accuracy of the measurement is not sufficient to tell whether the disappearance of a single ^1CA molecule results in one or two triplet excitations. The former would correspond to ordinary ISC by spin-orbit coupling, whereas the latter would be the second step of SF. Such a process of charge transfer to triplet state conversion has been postulated in earlier studies of solids (42).

7. INDIVIDUAL CHROMOPHORES

7.1. Acenes

Acenes are pivotal in SF studies, and important advances for tetracene and pentacene have been made recently. As the molecular length increases, the production of two T_1 excitons from an S_1 exciton becomes less endoergic. In anthracene (3, 68–70, 88, 89), the energy deficit is 0.53 eV, as $E(S_1) = 3.13 \text{ eV}$ (90) and $2E(T_1) = 3.66 \text{ eV}$ (91), and it is usually provided optically. In tetracene (6, 15, 39, 57, 60, 62–67, 69, 92–95), it is only 0.18 eV, as $E(S_1) = 2.32 \text{ eV}$ and $2E(T_1) = 2.5 \text{ eV}$ (64), and it can be supplied thermally or optically. In pentacene (17, 23, 27, 28, 48, 49, 51–53), the process is exoergic by 0.11 eV, as $E(S_1) = 1.83 \text{ eV}$ (96) and $2E(T_1) = 1.72 \text{ eV}$ (97). As noted above, crystal packing of the acenes generally places neighbors into a slip-stacked and partially tilted mutual orientation, with the slip in the direction of the $b \rightarrow l$ transition moment, hence into an arrangement that is highly favorable for fast SF.

The nature of the S_1 exciton in acenes remains controversial. In a computational study based on fitting the polarized absorption spectra of single crystals of tetracene to spectra derived using a multiband Frenkel-Holstein Hamiltonian that included S_1 – S_5 , the Davydov splitting of the 0–0 band was reproduced only when strong coupling between Frenkel and charge-transfer excitons was included (98). The contribution of charge-transfer states to the 0–0 band Davydov splitting was 27% (for anthracene and pentacene, the contributions were 14% and 48%, respectively). In stark contrast, a nonempirical time-dependent DFT study (25) found that S_1 – S_4 had no charge-transfer character, whereas states above S_5 did. In this work, the authors found that the excited states of a cluster of 10 molecules of pentacene concentrate most of the S_1 excitation on two centrally located molecules. The excited states of a dimer of pentacene within a crystalline lattice were then examined by a restricted active space calculation. Unlike previous calculations on an isolated dimer of pentacene that predicted that the excimer structure for S_1 was favored by 0.3 eV (28), the inclusion of strain from the crystal lattice showed that the excimer is favored only by 0.03–0.04 eV. The energy of the $^1(\text{TT})$ state calculated by the same method was 0.06 eV below S_1 for the excimer geometry. The probability of a nonadiabatic transition between S_1 and the $^1(\text{TT})$ state in the region of their narrowly avoided crossing was calculated to be 16% (and 26% with the addition of a 0.016-eV vibrational quantum). Previous results of a quantum mechanics/molecular mechanics calculation that also included lattice effects indicated that an excimer structure is not favored (29).

It is not clear whether charge-transfer states play a role in SF in pentacene (we do not doubt that virtual charge-transfer states do). The nonempirical approach to the calculation is attractive, but given the size of pentacene, its accuracy can be questioned.

7.2. Tetracene

In thin films of tetracene, a fast initial fluorescence decay with a 100-ps time constant was observed recently, irrespective of measurement temperature (298 K, 77 K, and 4 K) and excitation energy (2.43, 2.58, and 3.10 eV for samples measured at 298 K and 77 K) (57). This result is surprising if the fast decay results from free triplet exciton formation by SF, because of the 0.18-eV energy deficit. The absence of change in the decay at 77 K as excitation energies exceed $E(S_1) = 2.32$ eV indicates that the missing energy is not being supplied by optical excitation, although it is known from studies with shaped pulses (30) that this is possible in principle. The authors (57) proposed that the fast decay results from the initial relaxation of S_1 with a 100-ps time constant to a lower-lying dark state, such as the triplet-pair or a charge-transfer state, which then forms free triplet excitons in a thermally activated process. The idea that the $^1(TT)$ state of tetracene can be reached from S_1 without activation energy is not supported by calculations (26), which, however, cannot be highly accurate for a system of the size of two molecules of tetracene. In an ultrafast photoelectron spectroscopy study (22), the initial formation of a coherent superposition $S_1S_0/{}^1(TT)$ state has been claimed, and its ability to dissociate endothermically into free triplets was attributed to the associated entropic gain.

Quantum beats in the delayed fluorescence of tetracene (32, 33) have been reexamined (34). They reflect the role of H_{sp} in determining the mixing of the sublevels in the ${}^{1,3,5}(TT)$ manifold and permit an evaluation of the spin dipole-dipole interaction parameters D and E .

7.3. Pentacene

In solid pentacene, the fluorescence quantum yield is close to zero. Because SF is exoergic, it has long been expected to be the primary fate of singlet excitations, but this has been difficult to prove (20). Recently, transient absorption measurements on films with sub-20-fs resolution over a range of 1.24–2.48 eV, using broad-band pump energies of 1.77–2.07 eV and 2.16–2.61 eV (51), clarified several assignments. Positive features observed at 1.82, 1.95, and 2.12 eV upon excitation in the region of the lowest-energy absorption peaks (1.77–2.07 eV) were identified as the ground-state bleach. Stimulated emission depends on excitation energy. In films excited at 1.77–2.07 eV and measured with 20-fs time resolution, a positive feature overlapping with the bleach at 1.82 eV was assigned to stimulated emission decaying with a time constant of 35 fs (51). When the excitation is at 2.16–2.61 eV, stimulated emission at 1.82 eV is greatly reduced and is replaced with broad features between 1.82 and 2.53 eV, assigned as stimulated emission from a vibrationally hot state (51). Stimulated emission decaying with a time constant of 70 fs was previously reported in this spectral region for films excited at 1.85 eV and measured with a 30-fs time resolution (27). Films of pentacene pumped at 2.53 eV and measured with 200-fs resolution exhibited no stimulated emission (50).

Upon excitation at 1.77–2.07 eV, spectral features assigned to a singlet photoinduced absorption from 1.91 to 2.25 eV appear with a rise time of 85 fs and decay time of 78 fs (51), giving rise to transient absorption centered at 1.4 eV (discussed below). The difference between the 35-fs decay of stimulated emission and the 78-fs decay of the singlet photoinduced absorption led the authors to suggest that SF might be taking place through a dark intermediate state, such as the correlated triplet-pair or a charge-transfer state (51).

The identification of T_1 - T_n absorption in solid pentacene has been controversial (20). Because the calculated low-energy T_1 - T_n absorptions are polarized along the long molecular axis, which tends to orient perpendicular to the surface in thin films of pentacene, it is not surprising that this absorption has been difficult to detect in films studied at normal incidence. The effect has been quantified for tetracene, which has a similar polarization dependence (15).

Several authors (17, 27, 28, 52, 53) observed a long-lived photoinduced absorption of pentacene with an ~ 80 -fs rise time and peaks at 1.88, 1.97, and 2.16 eV, and some assigned it as T_1 - T_n . This assignment never seemed likely as these transitions are shifted fully 0.58 eV to the red relative to the solution spectrum and, more importantly, exhibit an incorrect polarization (28, 29). In an important development, these thin-film absorption features have been convincingly attributed to temperature-induced changes in the transient absorption, which changes greatly upon cooling from 300 K to 4 K (50). The heating caused by a 2.33-eV pump pulse with a flux of $120 \mu\text{J cm}^{-2}$ was estimated for 150-nm-thick pentacene films deposited on Spectrosil fused silica. Although the flux is often not reported, at least two other studies have used fluxes this high or higher (17, 52). A linear combination of the estimated thermal effect and bleach accurately reproduces the features in the transient spectrum at 7 ns, previously assigned to triplet absorption (50). In a pentacene film deposited on sapphire, which has a higher thermal conductivity than fused silica does, the decay is nearly 10 times faster. Moreover, the observed short-axis polarization of this transition agrees with expectations (27, 28).

Two photoinduced absorptions in crystals and films, with similar angular dependence demonstrating long-axis polarization and with almost identical decay kinetics, were attributed to T_1 - T_n transitions. The assignment of the absorbing species as a triplet formed by SF is based on a subpicosecond rise time, 10–20-ns lifetime, and the temperature dependence of an analogous photoinduced absorption in tetracene. (a) The presumed T_1 - T_2 transition is a broad band between 1.24 and 1.77 eV centered at 1.4 eV (17, 48, 49). (b) The presumed T_1 - T_3 transition is located at 2.34 eV (27, 28, 50). We agree that the two transitions indeed are attributable to T_1 - T_n absorption but wonder (20) about the origin of the relatively high intensity of the T_1 - T_2 transition, given the vanishing T_1 - T_2 intensity in gas (99) and solution (100) T_1 - T_n spectra of the isolated molecule of pentacene, which is in agreement with calculations (101).

In a crucial advance, femtosecond time-resolved two-photon photoemission measurements identified the $^1(\text{TT})$ state as energetically resonant with S_1 (23). A 10-monolayer film of pentacene was excited at 2.15 eV, then ionized by a 4.65-eV probe laser pulse, and the energy of the photoelectrons was analyzed. A short-lived state with an energy of 1.83 eV (3.31 eV below the band gap) was assigned to S_1 . A feature with a lifetime of at least 300 ps located 0.96 ± 0.05 eV below S_1 was assigned to T_1 . A third state located 0.11 eV above T_1 was populated concurrently with S_1 within the 20-fs resolution of the measurement and was assigned to the $^1(\text{TT})$ state. The electronic coupling constant of the strongly coupled S_1 and $^1(\text{TT})$ states was calculated to be 330 meV using a density matrix formalism. The $^1(\text{TT})$ state may relax to form two T_1 states following decoupling from S_1 . In films of pentacene with thickness between 1 and 10 monolayers deposited on C_{60} , S_1 decayed with a lifetime of 110 ± 20 fs. Because this result was independent of the number of monolayers used, the transfer of the excitation to C_{60} is not thought to be competitive with the generation of the triplet-pair state. Modeling the total $^1(\text{TT})$ and T_1 populations for samples with 0.6 and 1 monolayers yielded a $^1(\text{TT})$ to T_1 relaxation time constant of 900 ± 300 fs. The time constant calculated for electron transfer from $^1(\text{TT})$ to C_{60} is 400 ± 100 fs, much faster than the 5 ± 1 -ps rate deduced for T_1 to C_{60} . The data are consistent with a simultaneous transfer of both electrons from $^1(\text{TT})$ to C_{60} . If such a process is indeed efficient, it would circumvent the anticipated possible difficulties with a stepwise transfer of the two electrons in cases when the two triplets cannot diffuse apart, due to the anticipated quenching of the

second triplet by the spin one-half radical cation left behind after the transfer of the first electron (20).

7.4. Substituted Acenes

Substitution offers better solution processability and permits the study of crystal structure effects. SF has been observed in disordered films of DPT (triplet yield, 122%) (43) and in thin films of TIPS-pentacene ($144 \pm 25\%$), also containing as acceptors variously substituted perylene-3,4:9,10-*bis*(dicarboximide) (PDI) derivatives (compound 23 in **Figure 1**) (44).

In DPT, the phenyl rings attached to tetracene cause the packing of vapor deposited films to be disordered, as evidenced by X-ray and electron diffraction (43), yet their out-of-plane orientation prevents them from perturbing the π system significantly. Whereas solid tetracene exhibits Davydov coupling, thin-film and solution absorption and emission spectra of DPT are similar. The isotropic nature of the amorphous films also eliminates the problem of unfavorable T_1 - T_n transition dipole orientation at normal incidence. Unlike the single-exponential emission decay for DPT in solution, the decay in thin films is nonexponential, with a long-lived (>150 ns) component that decays as $t^{-1.8}$, close to the t^{-2} dependence expected for control by triplet-triplet annihilation. A kinetic model yielded a fluence-dependent triplet yield of 82–125% and identified two triplet rise times. The proposed interpretation is that SF only occurs at a subset of sites, those at which the relative orientation of neighboring DPT molecules is particularly favorable. When one of these sites is excited, the fast triplet rise time results. The slow rise time results from singlet excitons needing time to diffuse to an SF-active site before producing triplets.

These results represent a significant advance by demonstrating that crystallinity is not needed for efficient SF and by highlighting the dependence of the SF rate on the relative chromophore orientation. The simple theory discussed above suggests that the favorable orientation is slip-stacked, with the slip along the short molecular axis, but the bulky phenyl substituents prohibit this and require considerable simultaneous slip along the long axis, perhaps combined with other distortions.

For rubrene (compound 24 in **Figure 1**), with four phenyl substituents on tetracene, convincing evidence now exists that in single crystals, long-lived triplet excitons are produced by SF, but some issues still remain unresolved (54–56, 102). With 10-ps resolution, photoluminescence decayed with lifetimes of 8 ps and >100 ns with relative amplitudes of 66% and 25%, respectively (56). An additional 1.8-ns lifetime component (9%) was assigned to oxidized rubrene impurity. Measurements between 10 ns and $300 \mu\text{s}$ identified an initial fast triplet decay within the 10-ns instrumental resolution and a slow decay with a lifetime of $100 \pm 20 \mu\text{s}$ (55). Here 95% of the photoluminescence was assigned to the long decay component, indicating very efficient SF. However, others have argued that initial decay components may have been missed in this experiment (56), and the situation is not clear.

Transient absorption measurements on single crystals of rubrene excited with 2.48-eV pulses have shown singlet lifetimes of 5.2 ps and 57 ps assigned to decay by SF and a third component of >10 ns assigned to delayed fluorescence (56). Triplet rise times were 2.3 ps and 23 ps. The kinetics were identical under 2.18-, 2.25-, and 2.48-eV excitations, but upon excitation at 4.97 eV, triplet rise times were 200 fs and 2 ps. The 200-fs component was assigned to SF from vibrationally excited states.

SF has been invoked to explain the two distinct types of photoluminescence that can be obtained from single crystals of rubrene: A ($\lambda_{\text{max}} = 615$ nm) and B ($\lambda_{\text{max}} = 650$ nm) (102). Both types of emission exhibited the same quenching behavior when an exciton splitting layer was applied to the surface; therefore, both were attributed to singlets produced by triplet-triplet annihilation. In support of this assignment, after initial fast decay within 10-ns instrumental resolution, time-resolved

photoluminescence showed a slow decay following t^{-2} , nearly identical at 1.94 eV, 2.07 eV, and 2.18 eV, indicating the same origin for each band (55). Type B photoluminescence is also observed for amorphous samples of rubrene. In single crystals with type B photoluminescence, annihilation may occur at amorphous defects that trap triplet excitons (102). Organic field-effect transistors made from both type A and B rubrene showed nearly identical electrical characteristics, confirming that the defect concentration is low. The trapping of triplets at structural defects and subsequent changes in photoluminescence may explain some spectral changes previously attributed to chemical defects in other types of organic crystals (102). In tetracene, the slow (nanosecond) component of fluorescence decay has a different spectral shape at room temperature, 77 K, and 4 K, which the authors suggest may result from emission following the direct excitation of structural defects (57).

In films of TIPS-pentacene, SF produces triplets with a rise time of 1.0 ± 0.2 ps by transient absorption spectroscopy (44). In contrast to the amorphous films of DPT, X-ray diffraction and UV-visible measurements indicate that films of TIPS-pentacene are polycrystalline. This material was also studied as the donor in donor/acceptor thin films containing PDI as the acceptor. Transient absorption measurements indicated that SF is increasingly competitive with charge separation in films that are segregated to a greater extent into crystalline domains of TIPS-pentacene.

7.5. Carotenoids

SF in carotenoids, representatives of compounds derived from class III hydrocarbons that have seen relatively few SF studies, was first detected by magnetic field effects on fluorescence and later by transient absorption and Raman spectroscopy (20). Because of the natural origin of carotenoids, many biological samples were studied. For zeaxanthin, an SF triplet yield of 90–200% has been determined (19). The generally short T_1 lifetimes in aggregates of class III chromophores are not surprising, given that several triplet states lie between T_1 and S_1 , permitting rapid triplet-triplet annihilation with the ultimate formation of the T_1 state.

SF has now been observed in zeaxanthin contained in the gel phase of phospholipid bilayers, in which it is aggregated, whereas in the fluid phase, it is monomeric (45). At ~1% concentration of zeaxanthin in room-temperature bilayers of two lipids, once in the gel phase and once in the fluid phase, time-resolved resonance Raman measurements indicated the formation of triplets within the 6-ps response time of the instrument in the former but not in the latter. The amounts of ground-state bleaching per photon absorbed were 1.3 and only 0.8, respectively.

There now seems to be little if any doubt that SF in carotenoids is intermolecular, similarly to in all other chromophores in which it has been observed, and that the earlier notion that a single polyene chromophore can twist to accommodate two triplets, thus performing SF intramolecularly (20), although interesting conceptually, should probably be abandoned.

7.6. Polymers

Polydiacetylenes, methyl-substituted ladder-type poly(*p*-phenylene), poly(*p*-phenylene vinylene), polythiophene, and poly(diethyl dipropargylmalonate) were investigated for SF in the past with generally very low triplet yields (20), but SF in conjugated polymers has not received much attention lately. One recent study (103) has urged caution in the interpretation of transient absorption measurements in previous work on ladder-type poly(*p*-phenylene) (104, 105), which concluded that SF occurs at excitation energies above 3.4 eV. Picosecond gated photoluminescence excitation spectroscopy was used to measure the fluorescence and phosphorescence yields from a film synthesized with the addition of one palladium atom per ten polymer chains to enhance phosphorescence

(103). Both one-photon (2.4–5.5 eV) and two-photon (1.15–1.82 eV) excitation conditions were used. The ratio of triplets to singlets obtained by the integration of fluorescence from –50 to 50 ps and phosphorescence from 3 to 5 ns was constant with an excitation energy of up to 5 eV at both 30 K and 300 K. The authors suggest that with a large (1.3 eV) activation energy to overcome and no evidence of increased triplet production with increased excitation energy, no SF is occurring. The previously reported increase in triplet photoinduced absorption at higher excitation energies probably is an artifact of the high excitation densities used.

8. APPLICATIONS IN PHOTOVOLTAICS

The first proof-of-principle applications of SF in photovoltaic devices have appeared, and some external quantum efficiencies (EQEs) over 100% have been reported (16). SF was competitive with charge transfer in a tetracene/ C_{60} solar cell with tetracene concentrations as low as 12% (41). Organic photovoltaic devices in which triplets were produced in DPT by sensitization with 5% platinum tetraphenylbenzoporphyrin dopant exhibited an increase in photocurrent with increasing layer thickness of DPT up to the maximum of 25 nm that was examined (43).

A layer of lead-sulfide (PbS) nanocrystals with a 0.7-eV band gap was used to absorb IR photons and to accept triplet energy from a layer of pentacene that undergoes SF (106). The EQE spectrum confirmed that pentacene contributes to the photocurrent, and the internal quantum efficiency was consistent with exciton multiplication by SF. With PbS nanocrystals with a 1.3-eV band gap, pentacene did not contribute to the photocurrent. When PbS was replaced with PbSe of higher monodispersity, EQE up to 80% was observed. The power efficiency of the photovoltaic cell reached 4.7%, and a variation of nanoparticle size permitted the bracketing of the triplet energy of pentacene as 0.85–1.0 eV (107).

A heterojunction solar cell comprising tetracene as an SF sensitizer, copper phthalocyanine as a long-wavelength absorber, and C_{60} as an electron acceptor exhibited a magnetic-field-dependent photocurrent, with the magnitude of the effect at various wavelengths proportional to the absorption spectrum of tetracene (41). Further evidence for the contribution of SF-produced excitons to the photocurrent comes from a tetracene/ C_{60} multijunction photodetector that exhibited higher EQEs with increasing temperature over the range 175–292 K, consistent with thermally activated SF. The change in the EQE spectrum with increasing temperature fitted a model with a constant contribution from C_{60} and a temperature-dependent contribution from tetracene. The SF triplet yield in this system was $142 \pm 36\%$ at 292 K and $46 \pm 14\%$ at 175 K.

The application of a 60-mT magnetic field decreased the drain current of a field-effect transistor made from a 77-nm-thick thin film of tetracene only under illumination (40), consistent with tetracene being a hole carrier and triplets being able to detrapp holes. The decrease in photocurrent was attributed to the combined effects of a decrease in SF and a decreased interaction between triplet excitons and holes due to the magnetic field.

9. CONCLUSIONS

Considerable progress has been made in the past two years in the theoretical understanding of SF and toward its practical utilization, including proof-of-principle solar cells. The old mysteries surrounding the ultrafast transients in tetracene and pentacene are gradually being elucidated, and new ones have appeared. Structures other than the acenes are beginning to emerge, based on biradicaloid design (DPIBF, cibalackrot). Above we attempt to organize the mechanisms of the SF process (one-step SF, with the normally weak direct and ordinarily dominant mediated interactions, and two-step SF) and note that two-step SF may now have been observed in solution. We

state explicit design rules for the efficient coupling of class I chromophores based on a simple model for SF and emphasize the superiority of the slip-stack arrangement, with slip in the direction of the HOMO-LUMO transition moment, among all mutual orientations examined so far. The covalent dimers examined so far have been chosen very unfortunately if highly efficient SF was the goal.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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