The Role of Chromophore Coupling in Singlet Fission

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RECEIVED ON JULY 1, 2012

CONSPECTUS

Certain organic materials can generate more than one electron-hole pair per absorbed photon, a property that could revolutionize the prospects for solar energy. This process, called singlet fission, is one possible "exciton multiplication" scheme that could be useful in a variety of photovoltaic device designs from dye-sensitized solar cells to solar cell bilayers to bulk heterojunctions. For such applications to be possible, however, singlet fission must occur with near perfect efficiency in compounds that also have other requisite properties such as strong visible light absorption and photo-stability. Many recent investigations of singlet fission have focused on crystalline polyacenes, which have been known for some time to undergo singlet fission. While these materials have promise, limitations in stability, cost, and performance may hinder practical application of polyacene solar cells, while their complex photophysics may limit our fundamental understanding of singlet fission in crystalline polyacenes.

In this Account, we describe rationally designed singlet fission chromophores whose excited state dynamics should be fairly simple and whose coupling can be well controlled through the formation of covalent dimers, aggregates, or polycrystalline films. In principle, investigations of these chromophores should provide the clearest connection to theoretical concepts explaining how an excited state evolves from a singlet (S_1) into two triplets (TT). Realizing the promise of efficient singlet fission rests with two tasks: (i) producing an ideal molecular energy level structure and (ii) inducing the correct type and strength of chromophore coupling. In this Account, we offer theoretical guidance for achieving (i) and consider more extensively recent results aimed at (ii).

For (i), theoretical guidance suggests that, in addition to alternant hydrocarbons like tetracene and pentacene, biradicals (i.e., molecules with two independent radical centers) may also be used as the basis for designing chromophores with low-lying triplet states such that the energy relationship $2E(T_1) \leq E(S_1)$ is satisfied. Although molecules that do not fulfill this condition can also exhibit singlet fission from a higher lying or vibrationally excited singlet state, fast relaxation processes will likely reduce the singlet fission yield and complicate determination of the singlet fission mechanism.

For (ii), once an appropriate chromophore has been chosen, the task of coupling two or more of them together must be done carefully. We discuss three pathways by which a dimer could undergo singlet fission: (1) A direct route in which slipped cofacial stacking is favorable under certain conditions. Cofacial stacking is common in molecular crystals, and it is likely not a coincidence that recent reports of efficient singlet fission involve slipped-stacked molecules in polycrystalline thin films. (2) A mediated route in which S_1 interacts with (TT) through a virtual radical cation/anion state, which may be important in some situations. (3) A two-step route (i.e., through a real charge transfer intermediate) which others have suggested theoretically. We present data on 1,3-diphenylisobenzofuran (DPIBF) dimers that are consistent with this pathway.

Finally, we review potential solar photoconversion efficiency gains utilizing singlet fission in several contexts.
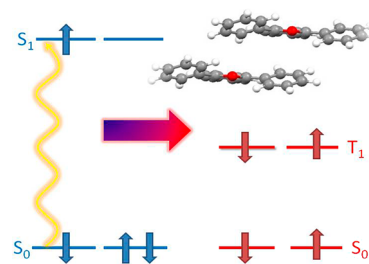
1. Introduction

Singlet fission is the formation of two triplet excitons in a set of coupled organic chromophores after photoexcitation of a singlet state.[1] The process mirrors multiple exciton generation (MEG), which has received considerable attention as a scheme for improving solar cell efficiencies employing semiconductor nanocrystals.[2] In the limit of very small $E(S_1)-E(T_1)$ splitting, the two processes are essentially
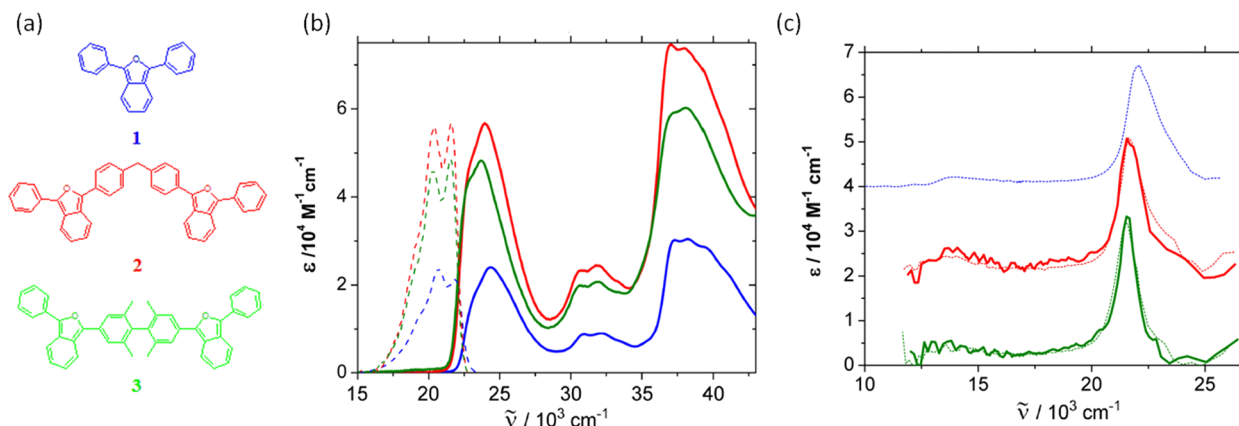
FIGURE 1. (a) "Hot" and (b) relaxed singlet fission. (c) Typical MEG scheme in a semiconductor QD.

identical (Figure 1a,c), and each must compete with relaxation within the excited state manifold. However, unlike in semiconductor quantum dots (QDs) whose lowest excitons are "bright" and "dark" states that are not pure eigenstates of spin and are typically split by 0.1 eV or less, in molecules it is possible to tune $E(S_1)-E(T_1)$ by 1 eV or more through molecular structure. As this difference increases (Figure 1b), the $2E(T_1)$ threshold falls at or below the $E(S_1)$ level, allowing singlet fission to occur from a state that otherwise would have a lifetime of ns or longer. The reverse process of triplet−triplet annihilation is also inhibited in this scheme if $E(T_2) > 2E(T_1)$. There is no direct analogy for this situation in pure inorganic QDs, since the initial and final states of MEG are connected by fast cooling routes via a large density of states (Figure 1c). Although in most cases the two or more excitons formed by MEG initially reside in the same QD, recent work on electronically coupled Si QDs embedded in a SiO_2 matrix has suggested that two excitons can be created separately and instantaneously on adjacent QDs.[3] If confirmed, this would be in close analogy with singlet fission into adjacent molecular chromophores and may allow further flexibility in controlling the MEG process.

Since most molecules possess one true chromophore and cannot usually sustain multiple independent electronic excitations, two or more molecules must be coupled together for singlet fission to be efficient. Much work from the past half century on exciton coupling in crystals,[4−6] covalent dimers,[7] and aggregates[8] can be consulted for guidance toward addressing the problem of singlet fission. The processes of charge transfer and energy transfer in such systems are well understood, and the formalism that describes them is likely to be important in singlet fission as well. For example, triplet−triplet energy transfer in some molecular systems is thought to occur via a concerted electron−hole mechanism (Dexter-type) with a virtual charge-transfer state intermediate.[9] Singlet fission can also be conceived as an energy transfer process in which the energy lost in one

molecule and gained in the other is approximately equal to $E(T_1 - S_0)$. Recent ab initio investigations have described a nonpolar "dark" multiexciton state in a pentacene dimer that facilitates singlet fission,[10] and future studies employing such methods will undoubtedly provide further detail on the excited state pathways through which the photoexcited state evolves into two independent triplets.

In this Account, we will consider the direct, mediated, and two-step routes of singlet fission, in which we expect the intermolecular geometry will play a critical role. We investigate several covalently bound dimers of 1,3-diphenyliso-benzofuran (**1**, Figure 2) as model systems for exploring how the strength of linear coupling of chromophores and the polarity of the environment can lead to changes in the excited state dynamics.[11,12] We then explore cofacial intermolecular coupling in several types of crystals of **1**, finding a strikingly large dependence of the triplet yield on the exact morphology of the polycrystalline thin film.[13] Although we limit ourselves to the compound **1** and its known intermolecular coupling geometries here, recent reviews provide more extensive detail on the field of singlet fission as a whole.[1,14]

2. Desirable Monomer Properties

The most important features of a suitable monomer are the absence of fast deactivation processes such as intersystem crossing and chemical reactions, and a favorable alignment of energy levels that makes singlet fission isoergic or somewhat exoergic and makes triplet−triplet annihilation endoergic or at least isoergic. The first of these conditions is most easily satisfied by choosing chromophores with a high quantum yield and relatively long lifetime of fluorescence. The second condition is met when $E(S_1)$, $E(T_2) \geq 2E(T_1)$. Two classes of parent structures have been identified as likely to satisfy this state energy criterion.[15] One are alternant hydrocarbons that are sufficiently large to have a S_0-T_1 splitting small enough to be equal to the T_1-S_1 splitting, which is

FIGURE 2. (a) Molecular structures of the monomer and two weakly coupled dimers. (b) Absorption and fluorescence spectra of **1**−**3**. T_1-T_n absorption spectra for **1**−**3** observed directly (solid curves) or via sensitization (dashed curves). Adapted from ref 11. Copyright 2012 American Chemical Society.

unusually large in these hydrocarbons due to alternant orbital pairing, nearly independently of molecular size. Until recently, all known efficient singlet fission chromophores were of this type. The other class of favorable parent structures are biradicaloids, systems derived by a stabilizing perturbation of a perfect biradical that removes the degeneracy of the nonbonding orbitals and makes the electronic structure of the ground state closer to ordinary closed shell. In a perfect biradical, S_0 and T_1 are close in energy, with S_1 and S_2 significantly higher. The perturbation stabilizes S_0 and destabilizes T_1, S_1, and S_2, and if pursued to just the right extent, it equalizes the S_0 - T_1 and T_1 - S_1 gaps. This principle was first illustrated on 1,3-diphenylisobenzofuran,[16] which indeed displayed a 200% triplet yield at 77 K,[13] while other biradicaloid heterocycles have recently been investigated computationally.[17] The two classes are not mutually exclusive and it has been shown recently[18,19] that alternant hydrocarbons with a high diradicaloid character are particularly likely to meet the state energy criterion.

3. Weakly Coupled Covalently Bound Dimers of Singlet Fission Chromophores

Although physical binding via ionic, dipole, or van der Waals forces can be used to engender aggregation and chromophore coupling between organic molecules, covalent coupling would seem to be preferred for fundamental studies because the geometry and strength of intermolecular interactions can be carefully tuned through chemical synthesis. Many aspects of the coupling of organic chromophores in crystals and covalently bound dimers have been extensively studied, but for our work on linearly coupled dimers discussed below, J-type excitonic coupling and charge transfer effects are the most relevant. Coupling of the parallel transition dipoles of the two chromophores in a perfectly linear

dimer causes a splitting of the lowest singlet transition, with the lower of the split transitions receiving all of the oscillator strength. Since perfectly linear coupling is rarely found in covalently linked dimers, the nonzero angle between transition dipoles results in both transitions being partially allowed. Charge transfer states, if not too high in energy, may also influence singlet fission. For the two-step mechanism of singlet fission, the role of the surrounding dielectric on the charge transfer state energy and the kinetics of its formation are of particular relevance. Solvents with high dielectric constants typically stabilize the charge transfer state, which may lie well above the lowest locally excited singlet state in the gas-phase dimer. The kinetics of charge transfer are then controlled by inner and/or outer sphere reorganization as the dipolar solvent and the molecules respond to the separation of charge.

For molecules like **1**, linear coupling via covalent bridges is fairly easy to produce and tune synthetically. A series of linear dimers has been synthesized in Boulder, and most have been investigated spectroscopically at NREL. For purposes of this Account, a subset of this series is worth considering in detail. The structures of these dimers are shown in Figure 2. Calculations of the transfer integral[20] suggest that the trade-off of stronger coupling in linear dimers is a smaller exoergicity, or an increase in endoergicity, for the transformation $S_1 \rightarrow (TT)$ due to the tendency of the singlet state to be stabilized by conjugation more than the triplet. The S_1 energy for a strongly coupled dimer can thus fall below $E(2T_1)$, even if a positive $E(S_1) - 2 E(T_1)$ offset exists in the monomer. Indeed, a directly coupled dimer of **1** with no methylene bridge that can sustain conjugation through its two halves exhibits a > 1500 cm^{-1} red shift in the absorption onset. Although singlet fission can still occur under these circumstances, it is no longer of the type shown
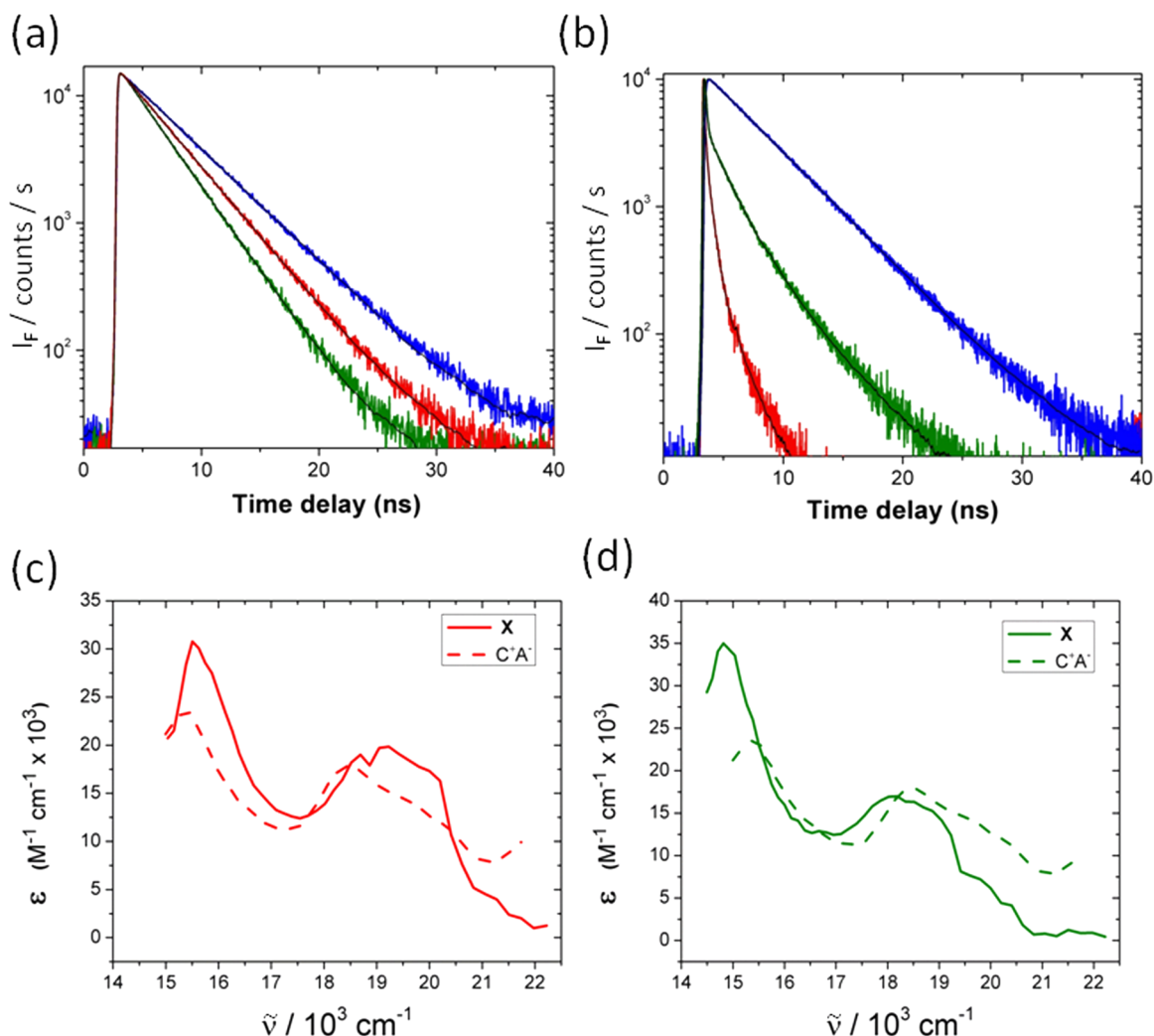
FIGURE 3. Fluorescence decays of **1**−**3** in (a) nonpolar and (b) polar solution. C^+A^- absorption (dashed) compared with decay associated spectra for intermediate state **X** (solid) for **2** and **3** (c and d, respectively). Adapted from ref 11. Copyright 2012 American Chemical Society.

in Figure 1b, and we will not discuss it further in this Account. Instead, we focus on dimers for which the red shift of absorption is reasonably small ($<300\ cm^{-1}$), and exoergic singlet fission from relaxed S_1 remains possible.

The absorption spectra of two weakly coupled dimers displayed in Figure 2a, **2** (red) and **3** (green), are shown in Figure 2b. A small red shift of the absorption onset from that of **1** (blue) occurs in all solvents, indicative of weak excitonic coupling. In addition, the peak molar absorption coefficients are roughly double that of **1**, indicating both halves of the dimer absorb light as independent chromophores. The radiative efficiency and lifetime of these dimers in nonpolar solution are essentially identical to that of **1** (Figure 3a), indicating that the rate constant of singlet fission is no higher than about $3 \times 10^6\ s^{-1}$. Work on weakly coupled side-by-side tetracene dimers in solution has also revealed a singlet fission rate constant no higher than $10^7\ s^{-1}$.[21]

However, in a polar solvent, the fluorescence decay of **2** and **3** becomes nonexponential, and the fluorescence efficiency drops (Figure 3b). For both dimers transient absorption spectroscopy and subsequent global fitting reveal two strong bands (**X**, solid lines in Figure 3c,d) that rise in concert on a time scale that matches the fast component of the fluorescence decay. The species associated with this spectrum has been identified as the radical cation and anion (C^+A^-) of **1** by comparison with the sum of absorption spectra of charged species of **1** obtained by pulsed radiolysis measurements.[15] The signature of T_1-T_n absorption (Figure 2c), absent in all monomer solutions, rises in concert with the C^+A^- band decay, suggesting triplet formation proceeds through this charge transfer state. The triplet quantum yield at room temperature, as determined by direct comparison with the intensity of T_1-T_n bands of **1** in anthracene-sensitized solution, is found to be about 3% and

$$2\ T_1 \qquad\qquad T_1$$
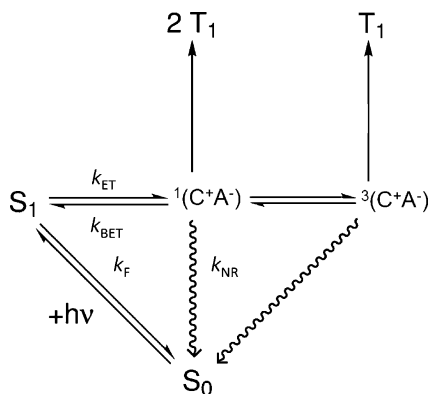
FIGURE 4. Kinetic scheme describing pathways for triplet formation in **2** and **3** in polar solution at room temperature.

6% for **2** and **3**, respectively. The triplet photoproduction action spectrum matches the absorption spectrum nearly exactly, suggesting that the weak intermolecular coupling has not significantly altered the preferred energy level alignment.

The temperature dependence of the fluorescence and triplet quantum yields imply the formation of an excited state equilibrium, $S_1 \rightleftharpoons C^+A^-$ (Figure 4) via forward (k_{ET}) and back (k_{BET}) electron transfer between halves of the dimer. The low triplet quantum yield, never rising above 10%, suggests relatively fast nonradiative decay routes (k_{NR} in Figure 4) for the C^+A^- state and precludes a definitive "state-to-state" analysis of the triplet formation process. However, there is no doubt that the C^+A^- state is used as an intermediate for triplet formation, possibly leading to two triplets by singlet fission.[22] An alternative pathway to forming triplets via the $^1(C^+A^-)$ state is intersystem crossing to $^3(C^+A^-)$ followed by back electron transfer to T_1, as has been suggested for 9,9'-bianthryl,[23] which also forms a twisted charge-transfer state in polar solution. In 9,9'-bianthryl, emission is observed from both the S_1 and the dipolar state, and thus the excited state kinetics can be followed easily.[24] The C^+A^- state in **2** and **3** is nonemissive, and the exact nature of its decay has not been directly determined. Solvent polarity dependent intersystem crossing may play a role in **2** and **3**.

4. Chromophore Coupling in a Molecular solid

Molecular solids provide the opportunity to simultaneously encompass several unique geometries for chromophore coupling and a network of neighboring molecules to share and transfer excitations. Cofacial interactions, often difficult to produce in covalent dimers, are prevalent in most crystals, leading to significant intermolecular $\pi-\pi$ interactions. These interactions are tunable through the natural polymorphs of a particular compound, or by substitution at specific positions to produce steric hindrance that modulates the

intermolecular distance and geometry. A priori, it is not obvious what geometry of interaction is ideal for producing fast singlet fission, nor how the type of singlet fission that occurs will depend on these interactions. These issues will be discussed below. Regardless of the pairwise interaction geometry, however, the network itself may help to separate the nascent triplet pairs formed after singlet fission by providing a pathway for quick decoherence and diffusion. However, if coupling is strong enough to induce ultrafast charge separation or excimer formation, it may instead hinder singlet fission. In this sense, a balance must be struck that allows singlet fission to compete for the photoexcited singlet exciton more effectively than other intermolecular processes.

Our initial investigations of singlet fission in a polycrystalline network were for **1**, the bulk crystal structure of which was recently determined.[16] It possesses monoclinic symmetry and is of the $P2/c$ space group with all molecules adopting the C_2 conformation. The molecules in the crystal form an array of slip-stacked columns, one of which is shown in Figure 5a. Although only one bulk crystalline form of **1** was found, two polymorphs of **1** were produced in thermally evaporated or drop-cast thin films. The two film types (hereafter referred to as A and B) are both oriented with the (002) plane parallel to the substrate but yield slightly different d spacings in powder X-ray diffraction: (A) 9.681 Å and (B) 9.626 Å, with 9.605 Å found in bulk (Figure 5a). The film of type B was found to form under a larger set of deposition conditions, suggesting it is a lower energy polymorph. Somewhat surprisingly, the two types of films exhibit very different triplet quantum yields. Film A produces triplet yields of 200% at 77 K (125% at 300 K), whereas film B exhibits a yield no higher than 10% at room temperature and <5% at 15 K (Figure 5b).

Further structural characterization of thin films of **1** is necessary to fully understand these dramatic differences in excited state dynamics, but some clues are provided by other photophysical measurements, displayed in Figure 6a. Examination of the UV−vis spectrum compared with that of **1** in a frozen matrix reveals a red shift of about 1900 cm^{-1} for film B, compared with a red shift of only about 280 cm^{-1} for film A. The Franck−Condon envelope of the first transition of film A matches that of **1** in frozen solution very closely, while the envelope of film B exhibits a more intense first peak. Film A was found to be less susceptible to oxidation and showed less light scattering, suggesting lower porosity and larger grains.

The bulk crystal structure contains only the conformer of **1** with disrotated phenyl group (C_2 symmetry, Figure 6a,
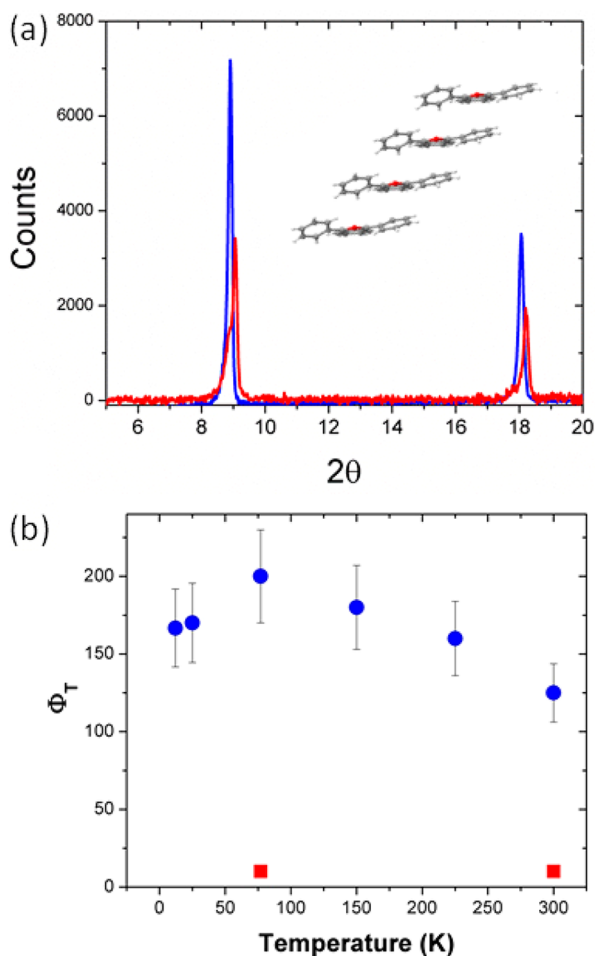
FIGURE 5. (a) X-ray diffraction of two film types of **1**. (b) Triplet quantum yield in film A (blue) and B (red).
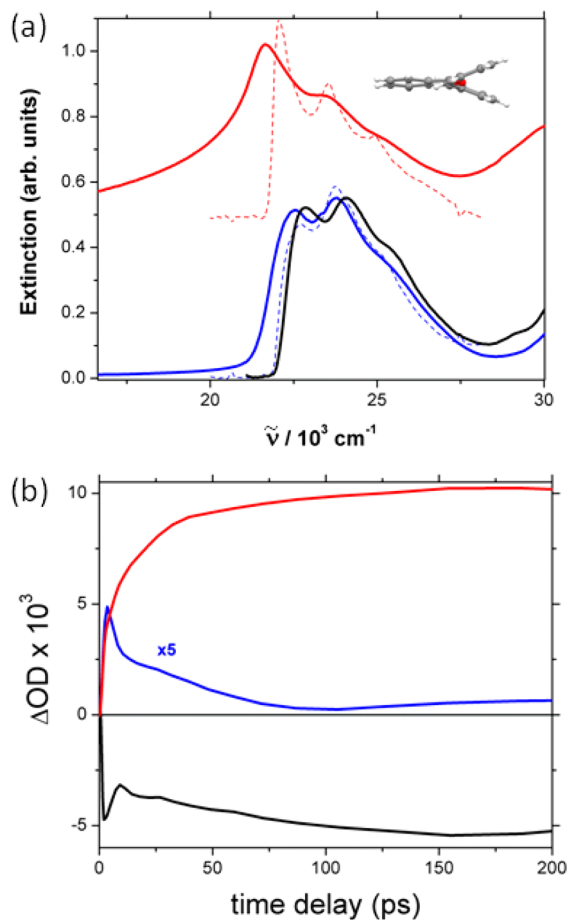

FIGURE 6. (a) Absorption of two conformers of **1** deduced from linear dichroism (dashed curves), overlaid with absorption of thin films (solid curves) of type A (blue) and B (red). Data for **1** in frozen 3-methylpentane (black) is shown for reference. (b) Biexponential rise in triplet absorption (red) and concomitant increase in bleach (black) and decay in singlet excited state absorption (blue). Adapted from ref 13. Copyright 2010 American Chemical Society.

inset). From studies of the isolated monomer,[16] it is known that an additional conformer with conrotated phenyl groups (C_s symmetry) also exists. The spectra of these conformers (Figure 6b, dashed lines) qualitatively match those of the two types of thin films, suggesting that the films are composed purely of one type of conformer or the other. There is not enough information to definitively assign the spectra to particular conformers, nor do we know exactly whether film A or B corresponds to the bulk crystal structure. The conformer with conrotated phenyl groups may hinder tight packing between molecules, weakening $\pi-\pi$ interactions. The conformer with disrotated phenyl group may lead to tighter packing and a red-shifted absorption onset. The conformers have nearly equal energy and undoubtedly interconvert quickly at room temperature in solution or vapor, explaining the sensitivity of the film type to deposition conditions.

All of these features suggest that, despite the relatively similar overall crystal structure of the two films of **1**, subtle differences in intermolecular geometry significantly affect the photophysical properties. There are two possible explanations for the lower triplet quantum yield in film B compared with film A: (i) due to the red shift of the absorption onset, $E(S_1)$ lies significantly below the singlet fission threshold; or (ii) the electronic coupling that gives rise to singlet fission is weaker. Prior work on **1** has shown[16] that for the isolated monomer 2 $E(T_1)$ is equal to or slightly higher than $E(S_1)$. A decrease of 1900 cm^{-1} in S_1 in films of type B may make the singlet fission channel energetically inaccessible at room temperature. The <300 cm^{-1} shift of S_1 for films of type A may not significantly disrupt the S_1-T_1 alignment. It is more difficult to conjecture about possibility (ii) without more detailed knowledge of the intermolecular coupling in the two types of films. Recent work on diphenyltetracene thin films[25] and diphenyl substituted derivatives of indigo[26]

has suggested that the intermolecular spacing provided by the pendant phenyl groups in molecules with appropriate S_1-T_1 splitting may be nearly ideal for efficient singlet fission. As in **1**, the relative sense of twisting of the phenyl groups leads to different molecular crystal packing densities and slightly different intermolecular geometries, which can potentially have a large impact on the singlet fission rate. Further control over crystal properties can be attained with more systematically designed substitution. One such example is bis(6,13-triisopropylsilylethynyl ("TIPS")) pentacene,[27] in which singlet fission was recently discovered in a thin film.[28] While pure pentacene thin films possess a tight herringbone packing and exhibit complex ultrafast photophysics that have led to varying estimates of the triplet yield,[29,30] the bulky TIPS side groups enforce a packing more similar to diphenyltetracene or **1**. The TIPS-pentacene photophysics appear simpler, and the triplet quantum yield approaches 150% at room temperature. The high triplet yield in TIPS-pentacene despite ostensibly weaker intermolecular coupling than herringbone-packed pentacene could result from two effects: face-to-face interactions present at equilibrium enhance the singlet fission rate or competing processes such as ultrafast charge separation or excimer formation occur less rapidly. It has been suggested that fast intermolecular motion toward cofacial stacking participates in singlet fission in pentacene,[10] which may also explain modulation of triplet yields in tetracene films by selective excitation of intermolecular modes.[31]

The kinetics of triplet formation in film A of **1** are multiexponential, occurring with time constants of roughly 2 and 25 ps. Similar biexponential rise times for triplets have been measured in tetracene[32] and diphenyltetracene.[25] Multiple rates for singlet fission in polycrystalline films could result from: (i) different rates from higher-lying and lower lying singlet states; (ii) different degrees of electronic coupling at different "dimer" sites undergoing singlet fission; (iii) diffusion limited energy transfer from sites with negligibly small singlet fission rate to sites with a large singlet fission rate. The first effect was proposed to explain the biexponential rise in tetracene thin films,[32] in which the singlet fission process is known to be endoergic,[1] assigned to a fast component due to $S_n{\rightarrow}2T_1$ and a slower activated component from $S_1{\rightarrow}2T_1$. Effect (iii) has been proposed to account for the secondary rise in triplet absorption in quasi-amorphous diphenyltetracene thin films.[25] In that case, most excitations in the film may not initially form at a site with appropriate intermolecular coupling for fast singlet fission; however, relatively fast energy transfer may allow those excitations to find appropriate sites before they decay by other means. Effect (ii) is more difficult to evaluate directly, and future theoretical efforts that treat both direct and mediated routes of singlet fission and accurately mimic the crystalline environment will be necessary to arrive at a more detailed microscopic picture.

5. Direct and Mediated Singlet Fission Rates versus Interchromophore Geometry

It is clear that in a nonpolar solution the weak linear covalent coupling of **1** into a dimer does not induce fast singlet fission, consistent with expectations for both the direct and mediated paths,[1] even though in a neat solid film, mere physical contact among the molecules of **1** does. In polar solvents, the weak covalent coupling enables reasonably fast charge transfer to form a stable dipolar intermediate, which represents the first event in the two-step mechanism of fission.[22] However, other decay pathways available to this intermediate appear to be too fast for the second step of the singlet fission process to dominate.

It is not known whether the direct mechanism or the mediated mechanism is dominant when singlet fission proceeds in neat solid **1**. There is no indication that a real charge-transfer state is formed, and the two-step mechanism can be excluded. The slip-stacked cofacial arrangement of molecular pairs is favorable for the one-step mechanisms,[1,14] and singlet fission in covalent dimers might also benefit from mimicking this geometry. Intuitive understanding of why the singlet fission rate depends on the pairwise geometry in this way can be gained through qualitative examination of the matrix elements that determine this rate.

Using a model Hamiltonian that includes all relevant dimer states and focusing exclusively on the direct route of singlet fission, the matrix element $\langle S_0S_1|V_{el}|T_1T_1\rangle$ was analyzed for the core isobenzofuran unit of **1** as a function of a relative translation of the molecules in a stacked dimer.[1] According to the Fermi golden rule, the rate constant of singlet fission is proportional to the square of this element. Qualitative considerations revealed that the matrix element is zero at perfect stacking and increases upon slippage along the axis of the S_0-S_1 transition dipole moment. Crude calculations with a small basis set suggested that it is maximized when the slippage reaches $\sim$0.6 Å. Similar considerations suggested that the linear covalent attachment of two chromophores of **1**, found in **2** and **3**, produces particularly small values of the matrix element, accounting for negligible singlet fission in nonpolar solutions of these compounds.

It is most likely not desirable to focus strictly on the direct mechanism of singlet fission as we did above. The matrix element between the S_1 and $^1(TT)$ states is dominated by terms originating in the two-electron part of the Hamiltonian, which are often small relative to those provided by the one-electron part. The latter connect the S_1 and $^1(TT)$ states indirectly, via virtual charge-transfer states, and unless the energies of these states are truly excessive, can provide as much interaction, if not more (the mediated mechanism). Qualitative considerations similar to those above allow estimates of the effects of changes in dimer geometry on the efficacy of the mediated mechanism. Now, the dominant factors are not electrostatic interactions of charge densities provided by products of the frontier orbitals on the two partners, but the resonance (transfer) integrals between these orbitals. Specifically, in eqs 7 - 9 of ref 1 the one-electron part of the matrix element connecting the initial S_1S_0 state with one or the other CT state is $\langle h_A|F|h_B\rangle$ or $\langle l_A|F|l_B\rangle$ (F is the Fock operator), which are maximized when the stacking is perfect. In contrast, the one-electron part of the matrix element connecting the CT state with the double triplet state TT is $\langle l_A|F|h_B\rangle$ or $\langle h_A|F|l_B\rangle$ and is therefore zero when the stacking is perfect. To make it nonzero, a slip along the direction of the electric dipole of the l_Ah_B or h_Al_B density is needed (hence along the direction of the transition moment of the HOMO−LUMO excitation in each single chromophore). The two-electron parts of the matrix elements are small in comparison and do not need to be considered, but simple symmetry arguments apply to them as well and it is seen that they vanish by symmetry for perfect stacking. Overall, among stacked geometries, slip stack seems to be the winner on all counts. Again, linear attachment as in **2** and **3** is not favorable.[1]

6. Singlet Fission in Solar Photoconversion Processes

As mentioned above, MEG in semiconductor QDs is analogous to singlet fission in that in both systems it is possible to create two excitons from a single photon of appropriate energy, separate the charges, and extract two electrons and two positive holes into external contacts to a solar conversion device to generate an enhanced efficiency for the conversion of solar photons into either solar electricity or solar fuels (e.g., H_2 from H_2O splitting). The thermodynamics of such solar photon conversion processes have been analyzed;[33] these calculations show that the maximum possible conversion efficiency can be increased between about 40% to 50% relative to present solar cells operating
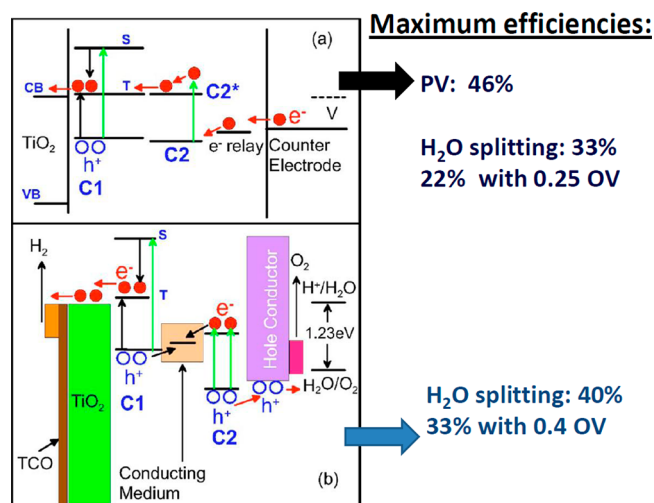

FIGURE 7. Parallel (upper) and series (lower) connected tandem PV or water splitting schemes involving singlet fission.

with one charge separating junction and wherein only one electron−hole pair is created per absorbed photon.

The details of the cell architecture vary between the use of MEG and singlet fission processes and also within the same multiple charge carrier generation process. For devices based on singlet fission of the type shown in Figure 1b, two separate layers of absorbing chromophores must always be used for high efficiency since the $S_0 \rightarrow T_1$ optical transition is forbidden, and a second chromophore having a HOMO−LUMO energy equal to $T_1 - S_0$ must be placed in tandem behind the chromophore undergoing singlet fission in order to absorb the lower energy solar photons. A unique property of these singlet fission cell types is that the two chromophores of different HOMO−LUMO energies, while both in optical series, can be placed electrically in either series or parallel connections. The latter has the advantage that the photocurrents generated from each chromophore add and do not have to be equal in order to avoid charge imbalance. However, in the former cell configuration, the photocurrents must match in both chromophores to maintain charge neutrality in the device. Also, in the former case, an electron generated in one chromophore must recombine with a hole from the other chromophore to produce current continuity and charge neutrality in the cell. This is analogous to the mechanism of the Z scheme in biological photosynthesis.[34] The optimum values of the band gap or HOMO−LUMO transition energies for the two chromophores depend upon the cell architecture shown in Figure 7. For PV cells they are 1.6 eV (top cell) and 0.65 eV (bottom cell), yielding an efficiency of about 46%. For H_2O splitting cells, they depend upon the overvoltage; for zero overvoltage, they are about

1.8 eV (top cell) and 0.9 eV bottom cell, yielding an efficiency of about 43%. With an overvoltage of 0.4 eV, the optimum values are about 2.0 eV (top cell) and 1.0 eV (bottom cell), yielding an efficiency of about 33%. For cells using single chromophores, the PV and H_2O splitting efficiencies decrease by about 40% and 50%, respectively.

7. Future Prospects

Since the number of compounds in which singlet fission has been definitively observed is very small, at this point there is little incentive to construct practical solar harvesting systems that take advantage of singlet fission, such as those proposed in Figure 7. Some effort has been made to observe enhanced photocurrent from singlet fission in tetracene[35] and pentacene,[36] but long-term stability, low-cost and large scale production, and high performance remain questionable with these materials. In order to have a significant impact on applications in photovoltaics, a larger library of molecules and a low-cost and scalable strategy for assembling them together with the correct coupling must be developed. Although one of the reasons for the relatively slow pace of singlet fission chromophore discovery in the past may have been too narrow of a focus (primarily on polyacenes), another is the dearth of simple experimental methods for quantifying triplet yields that would expedite screening. Spectroscopic methods are clearly hampered by the lack of quantifiable emission from and absorption into the T_1 state, necessitating time-resolved spectroscopies that can be difficult to implement and interpret. Pump−probe transient spectroscopy for observation of the triplet state absorption has found the most use, but methods such as time-resolved resonance Raman spectroscopy[37] may often be more definitive. Other methods, including photoacoustic calorimetry or the detection of free carriers electrically or spectroscopically after singlet fission into a planar acceptor like TiO_2,[38] may provide a more expedient route to quantifying triplet yields. Magnetic field effects, which can offer proof of the influence of singlet fission, should also find broader utilization. Exciting recent results discussed here will undoubtedly serve to catalyze efforts to discover and characterize a broader range of practical molecular systems in which singlet fission can find utility.

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