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Singlet Fission: Toward More Efficient Solar Cells

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Abstract. A survey is provided of the current status of singlet fission as a tool for bypassing the Shockley-Queisser limit on the efficiency of single-junction solar cells.

Keywords. Solar cells, Shockley-Queisser limit, singlet fission, photophysics, solid state packing.

INTRODUCTION

The human mind is remarkable in many ways. One of them is its ability to disregard reality in order to induce pleasant feelings. I know for sure that my wife of 50 years, who recently unexpectedly passed away, will never return. Yet, several times a day, I catch myself expecting her to open the door and smile at me. Twice a year, I tell my students that there will be a final examination at the end of the semester. They ignore this repugnant thought blissfully, since the distant future is of no concern. A few days before the exam, when disaster is at the door, they start coming and asking what they are expected to know. I doubt that as a student I was any better. No wonder that much of the general public and numerous influential politicians deny that the incipient climate change has anything to do with human activities, least of all with the burning of fossil fuels, although in sober moments they must surely realize that thousands of climate scientists actually know their business. After all, the most serious consequences of climate change are not yet at the door, unlike many immediate and apparently more important issues of the day that are.

I suspect that the tendency to deny inconvenient reality and cherish immediate gain at the expense of distant troubles are in our genes and must have offered evolutionary advantages in some distant past. They surely do not offer long-term advantages now and our generation will be cursed by all that follow. Past generations did not know what effects a drastic rapid increase in the concentration of carbon dioxide in the atmosphere will have. We do and yet on the whole we act as if it did not matter.

Given the nature of the human mind, it seems to me that the best gift that science and engineering could presently offer to mankind is to make sustainable energy economically preferable. This is not an easy task. However, if solar, wind, and other forms of energy generation that do not contribute to climate change were cheaper than the burning of fossil fuels, hardly anybody would burn fossil fuels and the already inevitable damage would be limited.

SOLAR CELLS AND THE SHOCKLEY-QUEISSER LIMIT

The largest potentially available source of safe renewable energy is solar radiation, and an increase of the efficiency or reduction of the cost of solar cells would go a long way toward reducing the currently huge release of greenhouse effect gases. Many scientists and engineers are working on this task all over the world and great strides have been made in recent decades. In many parts of the world, the goal appears to be realistic, although well recognized and very formidable technical obstacles stand in the way, such as the need for large-scale energy storage and for transportation fuels.

Unfortunately, the energy efficiency of inexpensive solar cells is limited to about 1/3 (the Shockley-Queisser limit[1]). These cells contain only a single junction (interface) at which negative and positive charges separate to proceed to their respective electrodes, The primary cause of the limitation is the broadband nature of solar radiation, whose photon energies range from the infrared to the ultraviolet. No matter how small or large we choose the bandgap of a solar cell material, which determines the maximum voltage produced, there always are some solar photons with less energy than the bandgap that are not absorbed and utilized, and others that have more energy than the bandgap. The latter are absorbed but their excess energy is almost immediately converted into vibrational energy and ultimately wasted as heat.

The current produced by a solar cell is limited by the number of photons absorbed and the voltage is limited by the size of the bandgap. A smaller bandgap permits the collection of a bigger fraction of the incident photons and hence leads to a larger current at the cost of generating a smaller voltage. A larger bandgap will produce a higher voltage but will cause a smaller fraction of the photons to be absorbed and therefore will generate a smaller current. The power generated is the product of the current and the voltage, and the best compromise is to choose a bandgap of about 1.1 electronvolt (eV), which provides a theoretical efficiency of about 1/3 (Figure 1), a limit that has been approached but not quite reached by modern silicon cells. Little further improvement of the efficiency of single junction cells is possible.

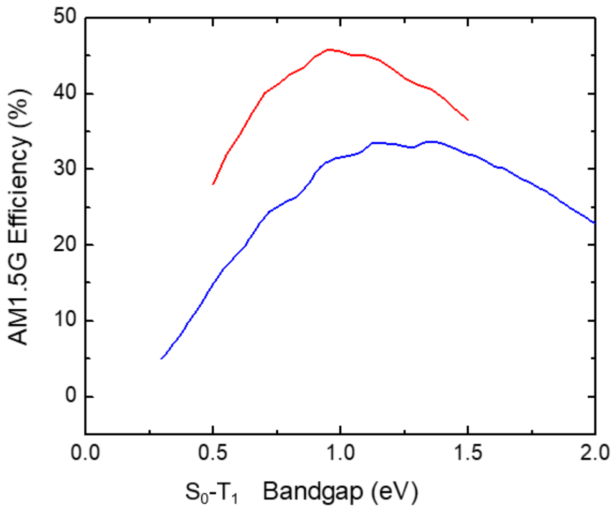

Figure 1. Maximum theoretical efficiency of a single-junction solar cell, assuming 1 sun illumination, full absorption of incident solar light above 1.1 eV, detailed balance, 200% triplet yield in the singlet fission layer, and production of an electron-hole pair from each triplet. Bottom curve (blue): ordinary; top curve (red): top layer, singlet fission and bottom layer, ordinary. Reproduced by permission from Hanna and Nozik.[2]

All this has been known for over half a century, ever since Shockley and Queisser, his postdoc at the time, published their pivotal paper.[1] Once I asked Prof. Queisser about the correct pronunciation of his name (it is German, kwi-ser) and he told me about the hard time they had when they tried to get the article accepted for publication. The reviewers did not see anything wrong in the derivations, but they felt that the results were of no theoretical or practical interest and publishing them would waste precious journal pages. Half a century later, this may well be one of the most quoted paper ever published in the journal. I mention this story to remind myself and others not to get discouraged when our papers are not immediately accepted for publication and proposals for funding.

BEYOND THE SHOCKLEY-QUEISSER LIMIT

Overcoming the Shockley-Queisser limit at low cost is a stimulating challenge. True, the use of cells containing multiple junctions with different bandgaps already has led to efficiencies approaching 1/2. However, since the currents flowing through each junction need to be matched, the fabrication is very demanding and so expensive that such cells are suitable only for special uses, for instance on space vehicles. They are valuable, but using them does not have much chance to be cheaper than burning coal.

Several other schemes have been proposed for going beyond the Shockley-Queisser limit, promise to be inexpensive, and are the subject of intense research. One of them is multiple exciton generation (MEG), which relies on solids in which each high-energy electronic excitation can be converted into two or more lower energy electronic excitations faster than it is converted into vibrational excitation and thus ultimately into heat. Then, each absorbed low-energy photon is used to produce a single electron-hole pair as in ordinary solar cells, while absorbed high-energy photons act as if they were two or more low-energy photons. As a result, a smaller fraction of their high energy is converted into heat and efficiency rises.

Materials known to behave in this manner are of two types: (i) semiconductor nanoparticles and (ii) organic molecular solids. The most obvious difference between the photophysics in the two is the absence of a clear distinction between singlet an triplet excitations in semiconductors and its presence in organic molecular solids. The latter are the subject of the present article.

The conversion of a singlet exciton into two triplet excitons, known as singlet fission (Figure 2),[3,4,5,6] was first observed over half a century ago.[7] Since the two triplets are coupled into an overall singlet when they are first born, the process is spin-allowed. It can be very fast and can outcompete all other decay modes, providing an up to 200% triplet yield. The fundamental nature of the phenomenon was elucidated in half a dozen years after the initial discovery and thereafter interest in it died off. It revived early in this century when Hanna and Nozik pointed out that a combination of a top layer of singlet fission capable material followed by a bottom layer of an ordinary solar cell material would increase the maximum theoretical efficiency of a solar cell to almost 1/2 (Figure 1).[2] No current matching would be required and the cost would remain low. A similar suggestion in this direction was made even earlier by Dexter but did not elicit much attention until very recently. By now, singlet fission has been shown in two laboratories to provide an external quantum efficiency over 100%.[9,10,11,12,13]

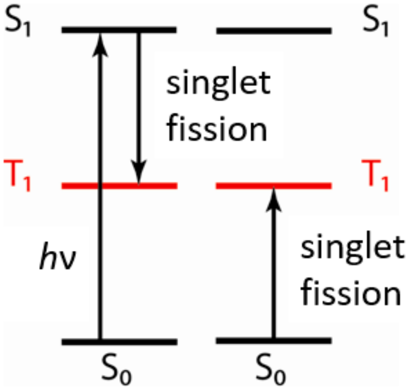

Figure 2. Schematic representation of singlet fission.

SINGLET FISSION SOLAR CELLS

Why, then, if the theory is understood and the principle proven in the laboratory, are singlet fission solar panels not commercially available after a decade of intense effort in many laboratories? The problem has to do with finding a practical singlet fission material and with moving charges out of it into a useful electrical circuit. A truly practical material must produce two triplets upon absorption of nearly every photon of sufficient energy. This will occur if singlet fission outcompetes all other modes of excited state decay, which is only possible when the process is exothermic or only slightly endothermic. It should not be too exothermic, since that would incur a loss of efficiency by converting electronic excitation energy into vibrational and subsequently into heat. For the maximum efficiency to approach 1/2, the singlet excitation energy should be about 2.2 eV and the triplet excitation energy, about 1.1 eV. The two triplets must separate easily, must be long-lived, and must move readily through the material in order to reach an interface where the negative and positive charges are to separate. During their travel to this junction, the triplets should not encounter any of the separated charges, because these quench triplet excitation efficiently to generate the ground state and heat.[3]

There is another reason for insisting that singlet fission must occur very fast, even if there are no competing decay processes other than the relatively slow fluorescence, which occurs on a nanosecond time scale. Ordinarily, singlet excitation moves through a molecular solid much faster than triplet excitation. Although singlet excitation is much shorter lived, nanoseconds instead of microseconds, it still may reach the interface where excitation separates into charges before singlet fission has had a chance to occur, especially if the initial excitation occurred very close to or right at the interface. If this happens, only one electron-hole pair will result and efficiency suffers.

The requirement of approximate thermoneutrality of the singlet fission process imposes a demanding condition on the energies of the lowest excited singlet and triplet levels in the solid, $\Delta E(S_1)$ and $\Delta E(T_1)$, respectively:

$$\Delta E(S_1) \geq 2\ \Delta E(T_1) \quad (1)$$

Only a handful of compounds, mostly tetracene, pentacene, and their derivatives, are known to meet the condition and to perform singlet fission with full efficiency. Unfortunately, structures of this type are notorious for their inability to withstand the combination of light and air. Yet, a practical singlet fission material must continue to function after a long time of exposure to sunlight under ambient conditions. It is possible to protect it from the atmosphere with a suitable coating, but the more perfect the insulation against traces of oxygen, the higher the cost.

In addition to meeting the conditions imposed by the requirements of singlet fission, the material must meet many others that are common to all solar cell materials: for instance, it should have a high absorption coefficient for all visible and ultraviolet photons with energies above the absorption threshold, and its redox properties must be appropriate for the intended separation of charges at the junction.

Assuming that all these potential pitfalls are avoided, all the necessary conditions met, and the charges generated at the junction are successfully brought to electrodes, the question remains, how do we identify an optimal practically useful singlet fission material? The search can be subdivided into two tasks: (i) What molecular structure do we choose? (ii) How do we pack the molecules in the solid? Before addressing these issues, the singlet fission mechanism needs to be described in more detail.

SINGLET FISSION MECHANISM

The process is rather complex and provides many opportunities for decay to the ground state, all of which need to be bypassed if triplet yield is to be 200%. In Figure 3, the desirable path is indicated by narrow blue arrows and the decay paths by stubby red arrows. The introductory event is the absorption of a photon, which generates a singlet exciton. This contains a single excitation, which is however typically shared among half a dozen or perhaps a dozen adjacent molecules in the solid. Note that in contrast, a triplet exciton would be usually localized on a single molecule.

Singlet fission consists of two main events. First, the singlet exciton is converted into a singlet biexciton, a molecular pair in which each partner is in its triplet state and the two triplets are coupled into an overall singlet. Second, the spin state of the biexciton transforms from singlet to a mixture with quintet and triplet, and the two triplet excitations separate as two free and independent triplet excitons whose spins usually remain coherent ("entangled") for tens of nanoseconds. We shall consider the two main events separately.

(i) Formation of a biexciton

The singlet exciton may meet one of several fates. It can undergo singlet fission to produce two triplet excitations as desired, but it can also undergo intersystem crossing to produce a single triplet, it can form an excimer, it can form a charge-transfer state, in which one molecule has transferred an electron to a neighbor, and it can perform a photochemical reaction. If all of these processes are too slow, it will ultimately fluoresce. The formation of a biexciton typically occurs without any intermediates and its rate can be approximately divided into a dominant "superexchange" contribution mediated by virtual singlet charge-transfer configurations and a usually negligible "direct" contribution provided by the two-electron part of the interaction Hamiltonian.

In rare cases, the relative energy of the charge-transfer configurations is so low that they describe real states that correspond to minima in the potential energy surface of the first excited singlet S_1. They then have a finite lifetime and are actually observable. They still have an opportunity to generate a triplet biexciton and sometimes they do,[14] but mostly they take one of two other undesirable options. One is internal conversion to the singlet ground state by back electron transfer, with a complete loss of all the excitation energy as heat. The other option is intersystem crossing to the nearly isoenergetic triplet charge-transfer state. In that instance only half of the original excitation energy is lost, and one triplet exciton is generated. It may be difficult to tell whether the origin of observed triplets is singlet fission or this type of intersystem crossing.[15]

In certain solids limited molecular motion is relatively facile.The crystal structure may permit two of the molecules that share the initial singlet excitation to approach each other and form a stabilized stacked pair, known as an excimer. Its wave function typically contains comparable amounts of the initial locally excited configurations and charge-transfer configurations, whose energy has been lowered by the approach of the two partners. The excimer is often considerably stabilized relative to the original exciton and its conversion to a biexciton is usually too endothermic to compete with radiative and non-radiative decay to the ground state.

It is likely that the formation of charge-transfer states, which also can compete with singlet fission from the singlet exciton, is merely a more extreme version of the process of excimer formation. If the approach of the two molecules stabilizes the charge-transfer configurations so much that they dominate in the excimer wave function, even a small dissymmetry that favors electron transfer from one partner to the other over electron transfer in the opposite direction will collapse the wave function in the more favorable direction and form a radical ion pair, known in solution as an exciplex, and in the solid as a charge-transfer state. The facility of the collapse is due to the very small value of the interaction element between the two charge-transfer configurations, which only contains contributions from the two-electron part of the Hamiltonian. Once again, the exciplex is usually stabilized too much relative to the original exciton to permit its conversion to a biexciton. As noted above, such states usually decay to the singlet ground state by back electron transfer, or to a triplet exciton by intersystem crossing to the nearly isoenergetic triplet charge-transfer state.

(ii) Formation of free triplet excitons

Once the singlet biexciton is formed, the path to its dissociation into two independent triplet excitons

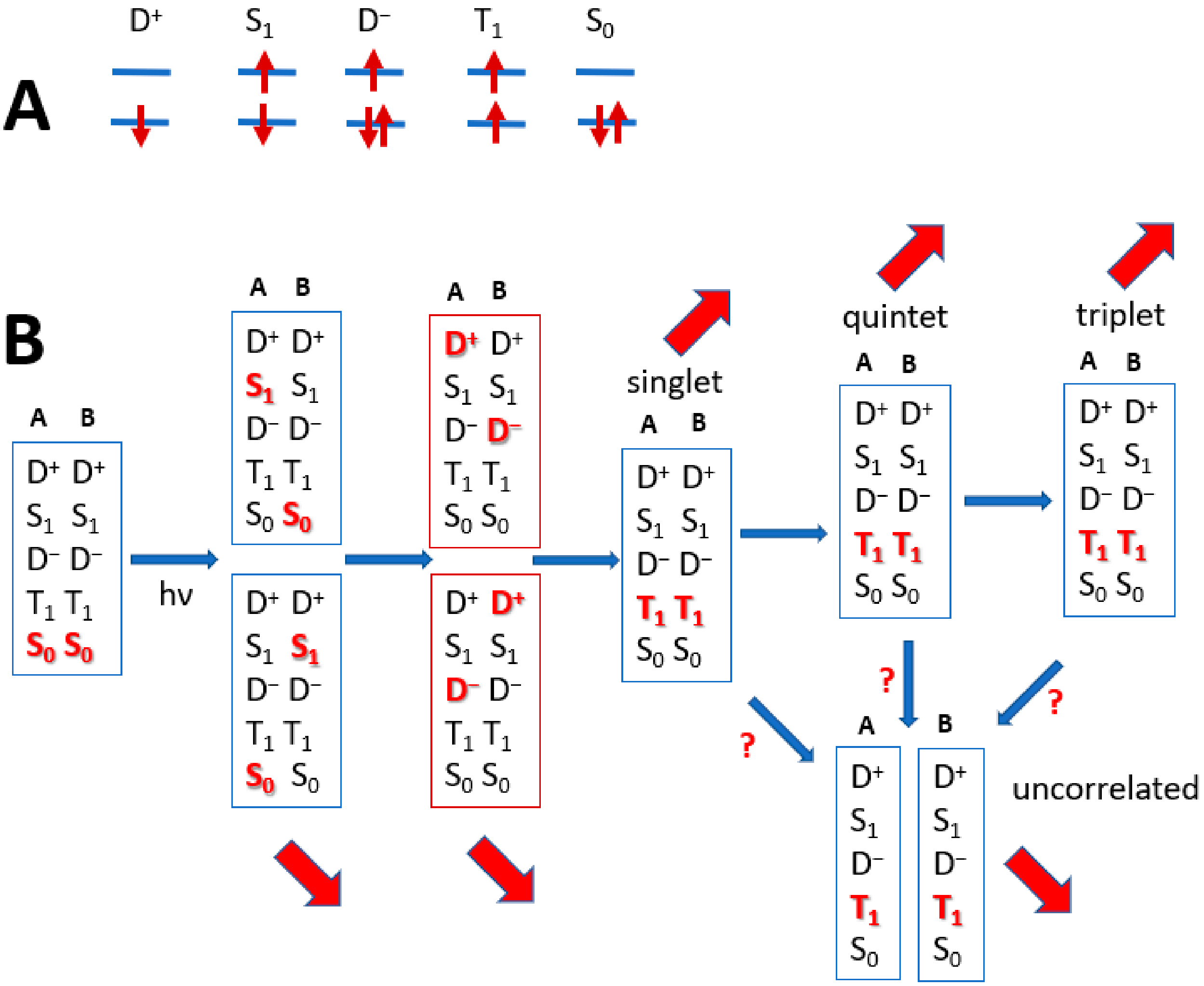

Figure 3. A: Symbolic representation of states available to molecules A and B. B: The general mechanism of singlet fission. The possible electronic configurations of partners A and B are listed in black and the actually occupied configuration is shown in red. Frames located above each other indicate the sets of configurations that need to be mixed to form a state. Black frames indicate real states and red frames show states that usually are only virtual. Thin blue arrows indicate the path for singlet fission and fat red arrows indicate undesirable decay channels. See text.

may appear to be smooth. In reality it is anything but smooth, and the yield of free triplet excitons is often disappointingly low. Although the calculated biexciton binding energies are usually quite small and the dissociation should be fast, the decay of the biexciton to two ground state molecules, or possibly to one ground state and one triplet molecule, tends to compete successfully. Unfortunately, relatively little is known about the mechanisms involved.

First of all, we need to note that the conversion of a singlet exciton into a singlet biexciton is reversible.[16] The reverse process is known as triplet-triplet annihilation. An exact reversal yields the singlet exciton back and delayed fluorescence may be observed. Two free triplet excitons can still be formed, but it will take longer and this is not helpful. Conversion of the singlet biexciton into the singlet ground state of both molecules might be expected to be slow because of the large energy gap, but often it is fast and competitive with the desired dissociation into two free triplet excitons. The mechanism that makes it so is not understood, and conceivably the process goes through the intermediacy of the quintet or triplet states of the biexciton. If it goes solely through the singlet manifold, it might possibly be related to events that occur during photochemical pericyclic reactions, specifically photocycloadditions.[17,18] In these reactions, the ground state of the starting material correlates with a doubly excited state of the product and vice versa. This correlation produces a conical intersection ("pericyclic funnel") half-way along the reaction path, through which the excited molecule or molecular pair returns to the ground state surface and then partitions between starting material and photocycloadduct. Since the doubly excited state has a singlet biexciton (double triplet) character, it is conceivable that the decay of the biexciton formed in the first step of singlet fission involves an approach toward the same conical intersection. The lowest energy point of the intersection would not have to be reached before decay to the ground state potential energy surface becomes rapid. At this point, however, this is pure speculation.

If the biexciton has time to modify its spin function, the reverse process might produce a triplet excited molecular state. Formation of the lowest triplet state would be strongly exoergic and probably quite slow, but if the excitation energy of one of the next higher molecular triplet states lies only a little below the energy of the biexciton, it might be formed fast. Subsequent internal conversion would afford the lowest triplet and this decay process would then represent the conversion of the singlet biexciton to one triplet exciton, a significant loss. Although such a process has apparently not yet been observed with certainty, in order to minimize its likelihood it is desirable although probably not essential to complement the condition expressed in equation (1) with the condition $\Delta E_{T2} > 2\ \Delta E_T$.

In principle, the biexciton might also convert to a molecular quintet excited state, but this will hardly ever be energetically possible. After all, even the lowest molecular quintet state is a doubly excited state and the condition $\Delta E_Q > 2\ \Delta E_T$ is fulfilled more or less automatically.

Why should the wave function of the singlet biexciton change its spin part into triplet or quintet so easily when it is an eigenfunction of the electrostatic Hamiltonian and only some very minor additional terms in the full Hamiltonian can be responsible? The relatively facile intersystem crossing is enabled by the nearly exact degeneracy of the singlet, triplet, and quintet states of the biexciton. Then, even the very weak magnetic dipole - magnetic dipole interactions, familiar from electron paramagnetic resonance spectroscopy of triplets (zero-field or D, E tensor), are able to induce intersystem crossing. The levels can also be mixed by Zeeman terms due to an external magnetic field and indeed, the sensitivity of singlet fission to external magnetic fields was one of its early recognized hallmarks.[19]

According to theory, the initial conversion should be from the singlet biexciton to the quintet biexciton, which has already been observed,[20,21]and then to triplet.[3,19] These pathways, and the paths from the three spin states of the biexciton to free excitons and to the ground state, are currently under intense scrutiny. The separation into two independent triplet excitons that are spatially separated seems to occur by a hop of excitation in one of the triplet partners in the biexciton to a neighboring ground-state molecule, similar to the hopping motion of triplet excitons through the solid.[22]

MOLECULAR STRUCTURE

Some of the structural requirements on the molecules to be used in singlet fission materials are dictated by common knowledge. The need for high absorption coefficients and absorption onset near 2.2 eV is generally satisfied by the use of extended π-electron systems. The redox properties can normally be controlled by a choice of substituents. The need for slow intersystem crossing is usually met by avoiding heavy atoms and low-lying $n\pi^*$ states. Suppression of fast internal conversion calls for structural rigidity and absence of structural elements with low-frequency vibrations. Inspiration for light fastness is provided by industrial dyes.

The condition that is the most difficult to meet is the location of the lowest triplet level (T_1) approximately half-way between the ground (S_0) and first excited (S_1) singlet levels.[23] In most ordinary molecules, T_1 and S_1 result from the same promotion from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and are separated by approximately twice the exchange integral between these two orbitals. This integral is very small for $n\pi^*$ excitations and excitations with strong charge-transfer character, in which the HOMO and the LUMO avoid each other in space. It is also small in most non-alternant hydrocarbons and in contrast, tends to be large for alternant hydrocarbons (no odd-membered cycles). Thus, large alternant hydrocarbons tend to be good choices. Tetracene and pentacene were recognized as suitable a long time ago, and a derivative of a large alternant hydrocarbon, terrylene, has also been recently shown to perform well.[23] A more general group of compounds that was recognized early on as providing suitable candidates are biradicaloids, compounds that are part way between perfect biradicals and ordinary molecules. In the former, the S_0-T_1 gap is typically much smaller than half the S_0-S_1 gap, and in the latter, much bigger. In between, there is a range of biradicaloid structures where the two are comparable. Considerations of this type led to a set of guidelines for the choice of two partially overlapping sets of chromophores that meet the energy criterion, large alternant hydrocarbons and biradicaloids.[22] Theoretical requirements for the use of biradicaloids have subsequently been elaborated[24,25,26,27] and several biradicaloid structures have been identified as suitable candidates computationally.[22,27,28,29,30] So far, only one of these proposals has been tested. The compound in question is 1,3-diphenylisobenzofuran, which was indeed found to be highly efficient.[31] However, the triplet yield was up to 200% in only one of its two very similar known crystal modifications, and was a mere ~15% in the other.[32]

PACKING IN THE SOLID PHASE

The above observation leads us to the second variable in singlet fission materials, and that is the packing of the selected molecule in the solid phase. There is ample evidence that it plays a critical role in determining the suitability of a compound as singlet fission material.[34] We leave aside the difficult question of methods for enforcing a particular packing, whether by crystal engineering or synthesis of non-conjugated covalent dimers, and focus on the need to know what packing to aim for. This was not clear in the past, but recently theory has provided some advice. This is available in the form of a publicly available computer program Simple,[34] which finds the local maxima of the rate constant for the formation of a singlet biexciton from a singlet exciton by singlet fission as a function of all physically possible geometrical arrangements of a pair of rigid π-electron chromophores (six degrees of freedom). Geometries in which the molecules interpenetrate are excluded. The output consists of the best geometries, drawn in the order of decreasing relative rate constant, and an example[35] is provided in Figure 4.

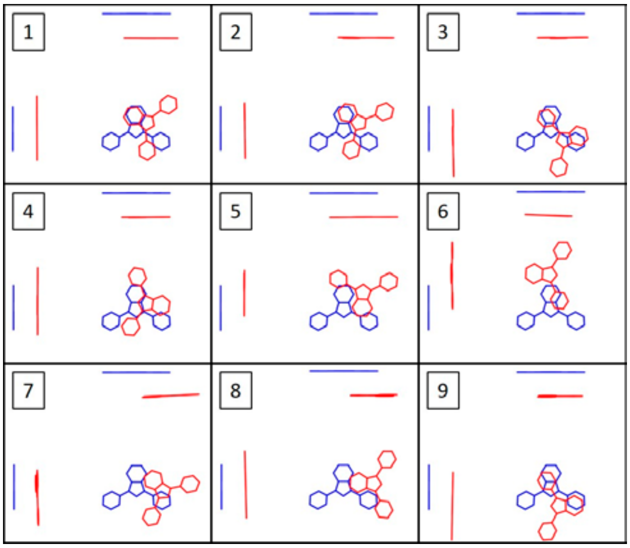

Figure 4. Multi-view projections of the nine best pairs of the C_2 rotamer of 1,3-diphenylisobenzofuran optimized for the rate of singlet fission. The computed rate constants for biexciton formation relative to the rate computed for the structure actually found in the crystal, in the order 1-9, are 4306, 2944, 2261, 896, 892, 806, 717, 546, and 536.

The calculation is based on the Fermi golden rule, according to which the rate is proportional to the square of the electronic matrix element for singlet exciton into biexciton conversion and the density of states at the energy of the biexciton. It involves the evaluation of the electronic matrix element at billions of geometries but is still quite fast, because it uses a series of physically motivated and tested[34,36] approximations. The relative rate constants are evaluated using Marcus theory, and the program has been used without problems for molecules as large as cibalackrot, with 36 atoms in the conjugated π-electron system of each member of the pair.[36]

A simplified version of the theory was used to develop pictorial rules for evaluating the suitability of a pair geometry, which require only the knowledge of the approximate shapes of the frontier orbitals of the molecule, HOMO and LUMO.[37,38]

Inspection of the results for several chromophore choices suggests that two dominant factors determine the relative rate of singlet fission at the optimized geometries. They are, first, the size of the squared electronic matrix element, and second, the energy balance of the process. The former enters directly into the Fermi golden rule and the latter, along with the reorganization energy, enters the Marcus equation. The energy balance is not determined solely by molecular properties. It depends strongly on the size of the Davydov splitting, the separation of the two levels into which an exciton pair is split by intermolecular interactions. After vibrational equilibration, the exciton level that is energetically lower will carry the bulk of the initial population. If it is stabilized excessively, it will not have enough energy to produce a biexciton, even if in the isolated molecule the T_1 level was positioned ideally half-way between the S_0 and S_1 levels. Instead, the exciton will decay to the ground state, radiatively or radiationlessly.

The magnitude of the Davydov splitting can be approximated as four times the electrostatic interaction between the S_0-S_1 transition charge densities on the two molecules, which in turn can be roughly estimated from the interaction of their transition dipoles. It vanishes when the dipoles are perpendicular to each other and this goes a long way toward an explanation of the twists seen in the optimal pair structures shown in Figure 4. These geometries reflect a compromise between the tendency of the electronic matrix element to favor strong overlap of the two molecules and the proclivity of the dipole-dipole interaction to minimize their interaction and vanish at orthogonally twisted geometries.

INTRAMOLECULAR SINGLET FISSION

This survey would not be complete if we did not mention singlet fission in which the two generated triplet excitons reside in different parts of the same molecule, known as intramolecular singlet fission. When the interaction between the two covalently connected chromophores is strong, especially when the bridging unit or units are capable of π conjugation, it becomes difficult and ultimately even impossible to distinguish the now intramolecular singlet biexciton state from other intramolecular singlet excited states and the use of the term singlet fission could then be questioned. It would be unusual to refer to the internal conversion of the optically allowed B_u state of 1,3-butadiene into its “double triplet” A_g state as singlet fission, although their wave functions suggest it. It is not obvious just where to draw the line.

A case of particular interest are conjugated polymers, but only a few recent references can be provided here.[39,40,41,42,43] In such polymers, the two triplet excitations can move quite far apart on the same chain, and also jump to separate chains. It is then certainly appropriate to talk about singlet fission. As long as the two excitons stay on the same chain and only undergo a one-dimensional diffusion, they have a high probability of re-encountering each other, and it is then important that they do not mutually annihilate. As discussed above, such a reverse of singlet fission would often provide ample opportunities for ultimate decay to the ground state with a release of heat.

SUMMARY

In conclusion, it is fair to say that singlet fission is now known to be a much more complicated process than it appeared to be before the recent spurt of activity in the field, and that there are many ways in which it can go astray. It is possible that a practical material for singlet-fission solar cells will be recognized tomorrow, but it is also possible that it will take many years. I believe that the ultimate goal, making sustainable energy less expensive than the burning of fossil fuels, is important enough to make it worth turning over every stone on the beach.

It should also be recognized that by their very nature, scientific discoveries build on each other in unpredictable ways. The fundamental understanding of the photophysics of organic molecular systems that is generated in the studies of singlet fission may end up being the largest gain from the enterprise, and may turn out to be valuable in very unexpected contexts. For example, perhaps the initial spin coherence (“entanglement”) of the two triplet excitons generated by singlet fission might be utilized in quantum information science? After all, when Bunsen and Kirchhof discovered that the sodium D line is a doublet, their discovery must have appeared to have no practical consequences. They could not have foreseen that they have launched a process that will lead to the concepts of electron spin, nuclear spin, magnetic resonance spectroscopy, and a century and a half later, imaging of brain tumors!

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