National Renewable Energy Laboratory
Office of Energy Efficiency & Renewable Energy
Innovation for Our Energy Future

Singlet-Fission Sensitizers for Ultra-High Efficiency Excitonic Solar Cells

15 August 2005 – 14 October 2008

J. Michl
University of Colorado
Boulder, Colorado

Subcontract Report
NREL/SR-520-44685
December 2008

NREL is operated for DOE by the Alliance for Sustainable Energy, LLC Contract No. DE-AC36-08-GO28308

Singlet-Fission Sensitizers for Ultra-High Efficiency Excitonic Solar Cells

15 August 2005 – 14 October 2008

J. Michl
University of Colorado
Boulder, Colorado

NREL Technical Monitor: Lori Greene/Kaitlyn VanSant
Prepared under Subcontract No. XAT-5-33636-01

Subcontract Report
NREL/SR-520-44685
December 2008

National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
303-275-3000 • www.nrel.gov

NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency and Renewable Energy
Operated by the Alliance for Sustainable Energy, LLC

Contract No. DE-AC36-08-GO28308

NOTICE

Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: mailto:reports@adonis.osti.gov

Available for sale to the public, in paper, from:
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

Table of Contents

List of Figures

List of Tables

Abstract

Sensitizer dyes capable of producing two triplet excited states from a singlet excited state produced by the absorption of a single photon would allow an increase of the efficiency of photovoltaic cells by up to a factor of 1.5, provided that each triplet injects an electron into a semiconductor such as TiO_2. Although singlet fission in certain crystals and polymers was reported long ago, little is known about its efficiency in dyes suitable for use as sensitizers of photoinduced charge separation on semiconductors surfaces. In the present project, we have accomplished the following, in collaboration with Prof. A. J. Nozik at NREL and with a subcontractor, Prof. M. A. Ratner at Northwestern University:

(a) A theoretical analysis and a series of computations established that biradicaloids and alternant hydrocarbons are likely parent structures for meeting the exothermicity requirement $E(T_2)$, $E(S_1) > 2E(T_1)$ for the excitation energies of the lowest excited singlet (S_1) and the two triplet (T_1, T_2) states.

(b) 1,3-Diphenylisobenzofuran (**1**) has been chosen as a model compound of the biradicaloid type, and a complete spectroscopic and photophysical characterization has been obtained. In the neat solid state, **1** forms triplets by singlet fission in a yield of at least 10% and possibly as high as 50%. This appears to be the first compound displaying singlet fission by design.

(c) We have performed calculations of the degree of coupling to be anticipated in a large number of possible covalent dimers and pointed out the existence of contradictory requirements: the two halves of the dimer need to be coupled strongly enough for fast singlet fission kinetics and weakly enough for favorable singlet fission exothermicity (the coupling should not stabilize the excited singlet excessively to keep its excitation energy above twice the triplet excitation energy, as they are in the monomer).

(d) We have begun to explore ways in which the two conditions can be met simultaneously. We have synthesized dimers of **1** in which these chromophores were attached covalently to each other in three different ways differing in the nature of coupling of the two halves.

(e) Upon examining their photophysics we found that in non-polar solvents the two more weakly coupled dimers **2** and **3** have singlet excitation energies very similar to those of the monomer **1** but produce no triplets and only fluoresce. The rate of singlet fission is clearly too slow to be competitive, and we conclude that the coupling of the two halves is too weak. In polar solvents both form triplets in yields of up to 9% by converting into a intramolecular charge-transfer intermediate, which then undergoes intersystem crossing, but this process is not useful for our purposes.

(f) The third dimer (**4**) is much more strongly coupled and its excited singlet is clearly stabilized significantly. This dimer provides an illustration of the above mentioned contradiction: the coupling is strong enough to secure fast singlet fission, but also strong enough to make singlet fission endoergic. Singlet fission is observed, but it does not proceed from the relaxed excited singlet state and proceeds only upon excitation to a higher state. Then, it proceeds fast enough to be somewhat competitive with internal conversion and vibrational deactivation, but because of this competition it affords a triplet yield of only ~3%. Details of the process, which appears to yield the first observed quintet state of an aromatic molecule, are currently under investigation funded by a different contract.

(g) In summary, we have produced the first designed crystalline material for singlet fission, and we have made the first determinations of the coupling strength in a covalent dimer that is required for efficient singlet fission. We have suggested paths for overcoming a problem that has been identified and have already started to develop them in a follow-up project.

Introduction

This project has been done with a subcontractor, Prof. Mark A. Ratner of the Northwestern University. The work has been performed in close collaboration with the research group of Prof. Arthur J. Nozik at National Renewable Energy Laboratory. In particular, time-resolved spectroscopy and steady-illumination triplet spectral measurements on the samples prepared in our laboratory were done at NREL.

Single-stage photovoltaic cells can be inexpensive but suffer from low efficiency, in part because they only utilize that part of the energy of an absorbed photon that corresponds to a semiconductor band gap or to the lowest energy transition of a dye sensitizer, and convert the rest to heat. Singlet fission (SF) is being considered as one possibility for improving the situation.[1] In this process, a singlet excitation S_1 of a molecular chromophore is converted into triplet excitations T_1 on two molecular chromophores, both of which can then in principle generate electron-hole pairs. The SF process is the inverse of the long known and much studied triplet-triplet annihilation. It has been recognized for decades from studies of more or less randomly chosen organic molecular crystals, and also of certain polymers and oligomers, but it has not been widely studied or put to practical use. The literature on SF has been recently collected.

A quantitative analysis of the possible contribution of SF to excitonic solar cell efficiency[2] has shown that an improvement by as much as a factor of 1.5 is possible theoretically in a cell in which light first passes through a layer of semiconductor containing an adsorbed SF sensitizer with an absorption edge at ~2 eV and then through a layer of the same semiconductor carrying an ordinary sensitizer with an absorption edge at ~1 eV. It is assumed that the photons absorbed in the SF layer each generate two electron-hole pairs, and those absorbed in the second layer each generate a single electron-hole pair. For suitable sensitizer choices, all of the electrons generated are at the same potential and can be injected into the conduction band of the semiconductor and then transported to an electrode. All of the holes generated are at the same potential and can be transported to the other electrode. For efficient operation of the SF sensitizer one has to make sure that electron injection from the originally excited singlet state S_1 is slower than SF, while electron injection from the triplet state T_1 is faster than the decay of the T_1 into the ground state S_0. This appears feasible, given the huge difference between the usual lifetimes of the S_1 and T_1 states. At the same time, it needs to be recognized that the long T_1 lifetime provides opportunities for triplet-triplet recombination, which would defeat the purpose of the whole exercise.

General Considerations for a Singlet Fission Sensitizer

The adsorbed sensitizer could be in the form of nanocrystals or another type of non-covalent aggregate, or it could be in the form of a covalent polymer, oligomer, or dimer. There are advantages and disadvantages to all these choices. Most of the instances of rapid and presumably efficient SF that have been reported occurred in crystals, and they might be a natural choice. The crystallites could be prepared separately and then applied to the semiconductor surface, as long as they are small enough to penetrate into the pores in the semiconductor particles. They could also be grown directly on the surface from solution. The lifetime of the triplet exciton is limited and if the time required for it to diffuse to the crystal wall and to be injected into the semiconductor is excessive, the injection efficiency will be low. Similarly, the hole that results from the injection needs to diffuse to the opposite surface of the crystal, where it is to be transferred to a shuttle such as the iodide anion, or to a hole-conducting polymer. This diffusion also needs to be fast in order to minimize electron-hole recombination. Control of crystal or aggregate size therefore becomes critical.

Covalent polymers have been observed to undergo SF, and their structure and size might be easier to control. Also the adsorption process, which would occur from solution, seems simpler. The observation of SF in carotenoids, which can be viewed as covalent oligomers of ethylene, capable of decoupling into two smaller oligomers by twisting about an internal bond, suggests that other covalent oligomers might be suitable as well. In the extreme of smallness, one could use a covalent dimer. This would appear to be the simplest approach, but the one case reported in the literature is discouraging. Although crystalline tetracene seems to undergo SF quite efficiently, a covalent dimer of tetracene exhibited only an extremely low yield of SF.[3]

The next issue to address is the nature of the coupling between the individual chromophores that is optimal for the SF process to proceed fast. Very little if anything was known about this from theory. We thought at first that the coupling apparently does not have to be very strong, since SF proceeds well in crystals, where the chromophores merely touch, and our initial guess was that almost any degree of coupling will be sufficient. As we shall see below, this does not appear to be the case, and we now believe that the coupling actually needs to be quite strong when the initial excitation is localized. This complicates matters, since strong coupling will also reduce the energy of the relaxed singlet state and this will need to be taken into account in the design of the optimal chromophore.

In the simplest case only one potential energy surface describing the lowest excited singlet state of the chromophore pair needs to be invoked, although other states necessarily lie nearby. In a vibrationally relaxed system, SF is represented by a transition from an initially populated excimer-like (S_0S_1, S_1S_0) minimum in the lowest singlet surface to a minimum best described as doubly excited in the same surface (T_1,T_1; two triplets coupled into an overall singlet), usually over a barrier separating the two minima. This final minimum is located at a geometry in which both halves of the system are at equilibrium T_1 geometries, and their interaction is minimized. For efficient SF, it needs to lie below or at most only a little above the starting "excimer-like" minimum. It is likely that an energy barrier separating the two minima, or two barriers if a third intermediate minimum intervenes as discussed below, will be minimized when the difference in the S_1 and T_1 equilibrium geometries is small, and this may be one of the criteria for the selection of SF chromophores.

The states and electron configurations involved in the description of SF in a dimer are already familiar from earlier analyses of the photophysics of excimers and of photochemical dimerization, since the "double triplet" state correlates with the ground state of the photodimer,[4] but they may be worth a closer description. In addition to providing the starting minimum in the lowest excited singlet surface, the S_0S_1, S_1S_0 combination also gives rise to another excimer-like state, expected to lie only a little above the lowest excited singlet surface at the initial geometry, and both excimer-like states may have smaller or larger contributions from charge-transfer configurations in which an electron is transferred from one chromophore to the other (I^+I^-, I^-I^+). We first ignore these complications and only consider the lowest singlet surface.

At the geometry of the final "double triplet" singlet state, composed of two only weakly interacting triplet excited halves, the minimum in the lowest singlet surface is nearly degenerate with two additional states. One is a triplet and the other a quintet, and they result from the other possible couplings of local triplet excitations. After transition from the "excimer-like" into the "double triplet" minimum in the excited singlet state, the system can undergo rapid dephasing of the two only weakly coupled local triplet excitations from an initial overall singlet into an overall triplet or quintet, induced by minor perturbations such as the magnetic fields of protons or other magnetic nuclei present in the system.

Two cases of initial singlet excitation need to be distinguished. If this excitation is localized, as would usually be the case in covalent molecular dimers, SF starts from one of two isoenergetic minima that correspond to a combination of one chromophore in its S_1 state and the other chromophore in its S_0 state, both at their relaxed equilibrium geometries. These minima are usually separated by a very low energy barrier and both are normally populated in a rapid equilibrium, which corresponds to an electronic excitation transfer between the two halves of the molecule, accompanied by appropriate adjustment in nuclear positions. If the initial singlet excitation is delocalized, as would often be the case in molecular crystals where the singlet exciton can extend over many molecules (but not if it is trapped on a pair of molecules), there is no barrier between the S_0S_1 and S_1S_0 excitations and the lowest excited singlet surface contains only one "excimer-like" minimum. Which of the two situations prevails depends on the strength of the coupling between the two halves of the chromophore pair and on the site distortion energy, related to the difference in the equilibrium geometries in the S_0 and the S_1 states.

The difference between a localized and a delocalized starting singlet excitation may appear unimportant, as after all, the latter is just a limiting case of the former. However, this difference may actually have important consequences for SF. If we assume that the primary effect of the geometry change upon travel from the initial minimum to the final minimum on the lowest singlet surface is to act as a one-electron perturbation, and consider that the initial and the final electronic configurations differ in the occupancies of two spinorbitals as illustrated schematically in Figure 1, it is apparent that the perturbation operator needs to be applied twice and that there is a virtual or real intermediate state, represented by a configuration in which only one electron has been moved (only one choice is shown in Figure 1). Now, if the excitation is delocalized, the MOs whose energies and occupancies are shown in Figure 1 are delocalized equally over both halves of the system, and the creation of the intermediate configuration involves no charge separation. In contrast, if the excitation is localized, the MOs whose energies and occupancies are shown in Figure 1 are localized on one or the other half of the system, and the intermediate configuration involves an electron transfer from one to the other half (I^+I^-, I^-I^+). It is strongly dipolar and its energy will be greatly affected by the polarity of the medium. One might therefore suspect that SF in delocalized systems will proceed well in non-polar environments, but that SF in localized systems will be promoted by polar environments, which will lower the energy of the virtual or real intermediate charge-transfer state. If the intermediate state is stabilized sufficiently to become real and represent a third minimum on the lowest excited singlet state surface, located between the initially considered starting ("excimer-like") and final ("double triplet") minima, SF becomes a two-step process. The intervention of a real intermediate is not likely to be a welcome phenomenon, since it will most likely offer opportunities for various deactivation channels, such as intersystem crossing from the singlet to the triplet state, or back electron transfer to form the S_1 or S_0 state. These processes would result in a decreased triplet yield.

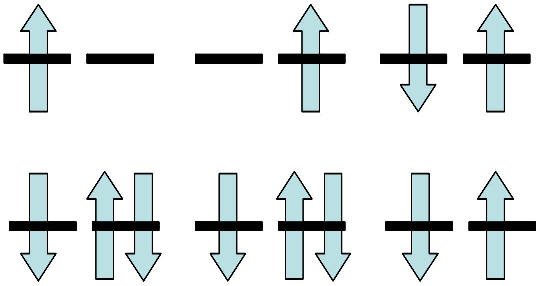


Figure 1. A symbolic representation of MO occupancies in the initial excited singlet state (left) and the final singlet state (right) in SF. Occupancy in one of the possible intermediate singlets is shown in the center.

Theoretical Requirements for the Molecular Structure of a Singlet Fission Sensitizer

We consider next the molecular structure of the SF chromophore that underlies the sensitizer, whether it is used in the form of a dimer, oligomer, polymer, aggregate, or crystal, and the results have been published. Because of the requirement of large absorption cross-sections, π-electron systems are most likely candidates and we shall focus on them. The compounds that have been observed to produce SF so far have been extremely limited structurally and have essentially all been alternant hydrocarbons, i.e. π-electron systems without odd-membered rings. In almost all of them, the excitation energy from S_0 into S_1 is less than twice the excitation energy from S_0 into T_1, and as a result SF is endothermic and only possible when the missing amount of energy is delivered by the thermal bath, or by an initial excitation into a higher vibrational level of S_1 or into a higher excited singlet state S_n. This is a clear disadvantage. The need for thermal excitation will slow down SF, and vibrational deactivation will compete with SF from an initially vibrationally hot sensitizer. Also, the undesirable T_1 - T_1 annihilation to produce S_1 and S_0 will be exothermic and will occur at a rate that is close to diffusion-controlled.

A search for suitable SF chromophores should therefore probably impose the level energy condition $E(S_1) > 2\,E(T_1)$ as one of the requirements. This highly unusual ordering immediately excludes most standard dyes. To make matters worse, it does not in itself guarantee that triplet - triplet annihilation will be slow. Although the $T_1 + T_1 \rightarrow S_1 + S_0$ channel will be suppressed, the $T_1 + T_1 \rightarrow T_2 + S_0$ channel may still be open, and in order to close it, the condition $E(T_2) > 2\,E(T_1)$ should be imposed as well. We probably do not need to worry about the third obvious channel, $T_1 + T_1 \rightarrow Q_1 + S_0$, since the energy of the lowest quintet state Q_1 is likely to be always too high. The channels $T_1 + T_1 \rightarrow S_0 + S_0$ and $T_1 + T_1 \rightarrow T_1 + S_0$ are likely to be too exothermic to compete and will not cause trouble.

There are two obvious classes of candidate structures, which are not mutually exclusive. One of these are systems derived from molecules with an ordinary closed shell ground state, and the other, systems derived from molecules with an open shell ground state (biradicals). Once a suitable fundamental structure is identified, it will undoubtedly be necessary to modify it by the attachment of heteroatoms or substitutents that will fine-tune the absorption wavelength and assure other desired properties.

Among π-electron parent systems with closed shell ground states, alternant hydrocarbons are the most likely to have a large S_1-T_1 splitting, and therefore to satisfy the condition $E(S_1) > 2\,E(T_1)$. This follows from the alternant pairing theorem long known from simple molecular orbital (MO) theory of π-electron systems,[5,6] according to which the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) have large absolute amplitudes on the same set of atoms. As a result, the exchange integral $K_{\mathrm{HOMO,LUMO}}$ between these two MOs is large, and so is the S_1-T_1 splitting, which is approximately equal to $2K_{\mathrm{HOMO,LUMO}}$.

In order to actually satisfy the condition $E(S_1) > 2\,E(T_1)$, the alternant hydrocarbon has to have a small S_0 to S_1 excitation energy. Since a singlet excitation energy of only about 2 eV is desired in any event, this requirement is not bothersome, but it means that the hydrocarbon has to be quite large. For instance, in the polyacene series, which has been investigated most thoroughly, the first hydrocarbon that meets the requirement is pentacene. Tetracene is not quite large enough, and the energy of its S_1 lies a little above twice the energy of T_1. Fortunately, the misfit is small and the difference can be made up easily by thermal excitation at room temperature. Nonalternant systems, such as azulene, can have similarly low S_0 to S_1 excitation energies already at much smaller molecular size. However, their HOMO and LUMO are typically predominantly located on different sets of atoms. This results in a small $K_{\mathrm{HOMO,LUMO}}$ value and a small S_1-T_1 gap, which does not permit them to meet the condition $E(S_1) > 2\,E(T_1)$.

There seems to be no particular reason to expect T_2 to lie at or above S_1 in large alternant hydrocarbons, but in pentacene it does. This chromophore therefore looks promising for a possible use in SF, and it is unfortunate that it is highly reactive and difficult to handle. In this regard, the rylenes, the higher analogues of perylene, may offer advantages.

The other class of likely π-electron hydrocarbon parent structures are those with an open-shell ground state, biradicals. In these, T_1 may actually be the ground state, and in any event, it is not far in energy from the lowest singlet S_0. Two additional singlet states result from intra-shell excitation. The upper one, S_2, is usually significantly above S_0 and T_1 in energy. The S_1 state is degenerate with S_0 in axial biradicals, such as charged $4N$-electron annulenes, and nearly degenerate with S_2 in pair biradicals, such as uncharged $4N$-electron annulenes.[7] Inter-shell excitation is needed to produce additional states, including T_2, and usually requires higher energies. As a result, in the parent π-electron biradicals, both conditions $E(S_1)$, $E(T_2) > 2\,E(T_1)$ are generally satisfied effortlessly. However, the S_0 to T_1 excitation energy is usually far too low, and possibly even negative, and the compounds are much too reactive to be useful. Both of these detrimental characteristics are removed simultaneously when the parent biradical is modified by a polar or a covalent perturbation[8] to produce a biradicaloid. Such perturbations stabilize the S_0 state relative to the T_1 state and give the former a more or less ordinary closed shell structure, often endowed with fairly normal chemical stability. For instance, the parent antiaromatic dication biradical $C_6H_6^{2+}$ can be formally converted into quinone, $C_6H_4O_2$, by the attachment of two phenolate oxygen substituents -O^-. One can hope that when the extent of the perturbation is just right, the S_0 - T_1 energy gap will be only a little smaller than the T_1 - S_1 energy gap, T_2 will lie above S_1, and the compound will be perfectly stable.

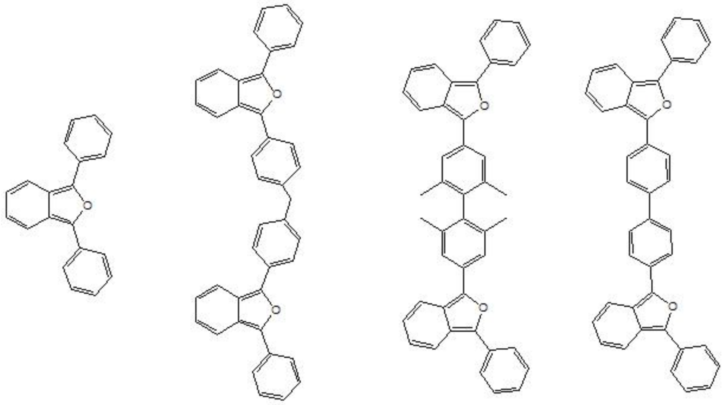
In addition to the conditions $E(S_1)$, $E(T_2) > 2\,E(T_1)$, the requirement that intersystem crossing (ISC) from S_1 to T_1 be negligibly slow, and possibly the requirement that the equilibrium S_1 and T_1 geometries be as close as possible, the SF chromophore needs to meet the same series of criteria as ordinary sensitizers. The redox properties have to be matched to the semiconductor and the shuttle used, the electron injection kinetics from T_1 have to be fast and back electron transfer insignificant, the material needs to adhere well to the semiconductor, its photostability needs to be outstanding, etc. We shall be concerned with these matters only if it turns out that an SF sensitizer with a T_1 quantum yield close to 200% can actually be produced.

We then performed the next logical step in the search for a suitable SF sensitizer, a series of calculations for a many candidate chromophore structures, and found which ones satisfy the conditions $E(S_1), E(T_2) > 2\,E(T_1)$. We used a semiempirical method that ordinarily provides an accuracy of about 0.2 - 0.3 eV. We have selected a few chromophores that appeared promising for proof of principle studies and verified that their energy levels behave as calculated.

Results for a Model Chromophore 1

We have selected one of these chromophores, 1,3-diphenylisobenzofuran (structure **1** in Figure 2), for a detailed study.[9] The chromophore **1** can be formally derived from a biradical in which two CH_2 groups are attached in the ortho positions of a benzene ring, and twisted by 90° out of conjugation with its π system. This biradical is then converted into a biradicaloid by twisting the CH_2 groups into conjugation to make a planar π-electron system. The resulting molecule, *o*-quinodimethane,[10] is still extremely reactive. It is stabilized further by formation of a five-membered heterocyclic ring with oxygen and addition of two phenyl substituents to yield **1**, a stable commercially available compound, albeit sensitive to oxygen under irradiation and therefore ultimately impractical.

We have obtained the single-crystal X-ray structure of **1** (Figure 3) and found that bond lengths and angles agree well with calculations. A comparison of results calculated for various electronic states of the monomer **1** as well as the various dimers **2** - **4**, using DFT procedures, is given in Table 1. There is nothing surprising about the molecular structure of the ground state of **1**. The molecules are packed in parallel stacks that appear quite favorable for providing a weak coupling between neighbors. In accordance with this notion, the absorption spectrum of the polycrystalline layer is ~20 nm red shifted relative to the solution spectrum. The two computed conformers have virtually identical energies and differ by the sense of the angle of rotation of the phenyl substituents out of the heterocyclic plane; one has C_2 and the other has C_s symmetry. Only the former is observed in the crystal, but both are undoubtedly present in solutions. Their spectral properties are calculated to be nearly identical.



1 **2** **3** **4**

Figure 2. Molecular structures **1** - **4**.

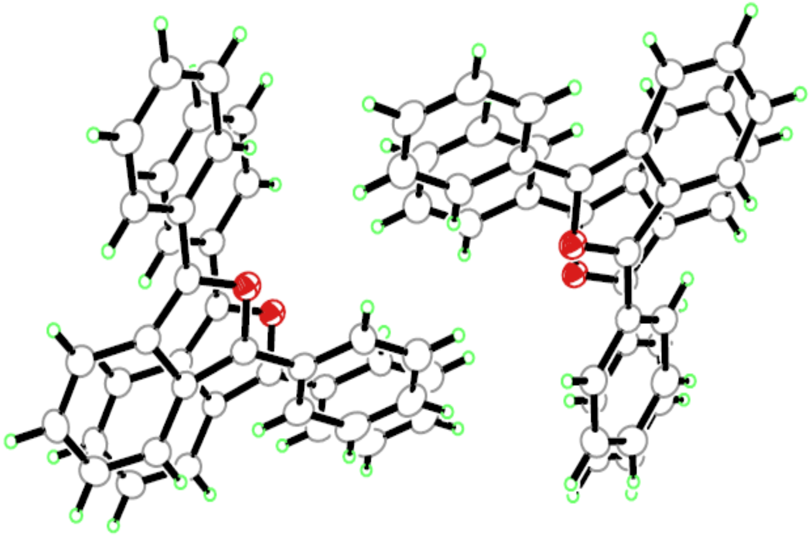


Figure 3. The crystal structure of **1**. Oxygen is shown in red.

In the singlet and triplet excited states, the phenyl substituents are essentially coplanar with the heterocyclic ring, and bond lengths in the heterocycle alternate much less. The results given in Table 1 for S_1 are only preliminary and unreliable because of convergence difficulties.

Table 1. Calculated Geometries of 1 - 4 in Various Electronic States (TD-DFT, B3LYP/6-31G*, bond lengths, Å; angles; degrees)

	1(S_0)	**1**(S_1)	**1**(T_1)	**2**(S_0)	**2**(S_1)^{v}	**2**(T_1)	**2**(Q_1)	**3**(S_0)	**3**(S_1)^{v}	**3**(T_1)	**3**(Q_1)	**4**(S_0)	**4**(S_1)	**4**(T_1)	**4**(Q_1)
$\Delta E^{w,x}$	0.00	61.79	33.07	0.00		32.82	65.67	0.00		32.77	65.48	0.00	68.35	31.68	66.22
a ^{y}	1.456	1.429	1.423	1.456		1.423	1.423	1.456		1.456	1.423	1.456	1.442	1.455	1.423
b	1.399	1.423	1.444	1.399		1.444	1.444	1.399		1.399	1.444	1.399	1.411	1.400	1.444
c	1.428	1.412	1.399	1.428		1.399	1.399	1.428		1.428	1.399	1.428	1.421	1.427	1.399
d	1.374	1.411	1.411	1.374		1.411	1.411	1.374		1.374	1.411	1.374	1.385	1.375	1.412
e	1.432	1.396	1.390	1.432		1.391	1.391	1.432		1.432	1.391	1.432	1.417	1.431	1.391
f	1.374	1.411	1.411	1.374		1.411	1.411	1.374		1.374	1.411	1.375	1.389	1.375	1.411
g	1.428	1.412	1.399	1.428		1.399	1.399	1.428		1.428	1.399	1.427	1.415	1.426	1.399
h	1.399	1.424	1.444	1.399		1.444	1.444	1.399		1.399	1.444	1.401	1.421	1.403	1.442
i	1.358	1.380	1.386	1.358		1.387	1.387	1.358		1.358	1.387	1.359	1.369	1.360	1.385
j	1.358	1.380	1.386	1.359		1.386	1.386	1.359		1.359	1.385	1.358	1.365	1.358	1.387
k	1.452	1.443	1.436	1.452		1.436	1.436	1.452		1.452	1.436	1.451	1.446	1.451	1.437
l	1.456	1.429	1.423	1.455		1.421	1.421	1.456		1.456	1.422	1.453	1.426	1.449	1.423
a′				1.456		1.456	1.423	1.456		1.423	1.423	1.456	1.442	1.425	1.423
b′				1.399		1.399	1.444	1.399		1.444	1.444	1.399	1.411	1.442	1.444

	1(S_0)	**1**(S_1)	**1**(T_1)	**2**(S_0)	**2**(S_1)[v]	**2**(T_1)	**2**(Q_1)	**3**(S_0)	**3**(S_1)[v]	**3**(T_1)	**3**(Q_1)	**4**(S_0)	**4**(S_1)	**4**(T_1)	**4**(Q_1)
c′				1.428		1.428	1.399	1.428		1.399	1.399	1.428	1.421	1.401	1.399
d′				1.374		1.374	1.411	1.374		1.411	1.411	1.374	1.385	1.408	1.412
e′				1.432		1.432	1.391	1.432		1.391	1.391	1.432	1.417	1.393	1.391
f′				1.374		1.374	1.411	1.374		1.411	1.411	1.375	1.388	1.409	1.411
g′				1.428		1.428	1.399	1.428		1.399	1.399	1.427	1.415	1.398	1.399
h′				1.399		1.399	1.444	1.399		1.444	1.444	1.400	1.421	1.446	1.442
i′				1.358		1.358	1.387	1.358		1.387	1.387	1.359	1.369	1.385	1.385
j′				1.358		1.359	1.386	1.359		1.385	1.385	1.358	1.365	1.384	1.387
k′				1.452		1.452	1.436	1.452		1.436	1.436	1.451	1.446	1.435	1.437
l′				1.455		1.455	1.421	1.456		1.421	1.422	1.453	1.427	1.412	1.423
A[z]	18.0	5.1	2.1	-17.9		-3.7	-2.7	-17.5		-18.4	-3.9	-18.6	-9.8	-18.1	-3.9
B	18.0	5.1	2.1	-19.2		-4.9	-1.9	17.8		18.9	5.1	-16.4	-4.6	-14.3	-6.0
C				-56.2		-54.6	-54.9	-89.3		-88.7	-88.9	31.1	14.9	23.6	30.3
D				-19.2		-19.2	-2.9	17.8		5.1	5.1	-16.4	-5.1	-4.2	-5.9
E				-17.9		-17.8	-0.6	-17.5		-4.6	-3.9	-18.6	-10.1	-5.2	-3.9

[v] Calculations are still in course. [w] The absolute energies for the ground state of **1**, **2**, **3**, and **4** are *-844.653483*, *-1727.374540*, *-1845.151430*, and *-1688.123380* respectively. [x] Relative energies are kcal/mol. [y] Bond lengths are in Å . [z] Dihedral angles are in degrees.

Table 1 (cont.)

Cmpd.	ΔE (kcal/mol)	A	B	C	D	E
1(S_0)[a]	0.00	18.0	18.0			
1(S_1)	61.79	5.1	5.1			
1(T_1)	33.07	2.1	2.1			
2(S_0)[a]	0.00	-17.9	-19.2	-56.2	-19.2	-17.9
2(S_1)[b]						
2(T_1)	32.82	-3.7	-4.9	-54.6	-19.2	-17.8
2(Q_1)	65.67	-2.7	-1.9	-54.9	-2.9	-0.6
3(S_0)[a]	0.00	-17.5	17.8	-89.3	17.8	-17.5
3(S_1)[b]						

Cmpd.	ΔE (kcal/mol)	A	B	C	D	E
3(T_1)	32.77	-18.4	18.9	-88.7	5.1	-4.6
3(Q_1)	65.48	-3.9	5.1	-88.9	5.1	-3.9
4(S_0)[a]	0.00	-18.6	-16.4	31.1	-16.4	-18.6
4(S_1)[b]						
4(T_1)	31.68	-18.1	-14.3	23.6	-4.2	-5.2
4(S_0)	66.22	-3.9	-6.0	30.3	-5.9	-3.9

---

[a] The total ground state energies of **1**, **2**, **3**, and **4** are -844.653483, -1727.374540, -1845.151430, and -1688.123380 a. u., respectively.
[b] Calculations are still in course.

We have performed a thorough experimental characterization of the electronic and vibrational excited states of **1** and accompanied it with semiempirical, DFT, and ab initio calculations. The following spectra were measured (mostly at room temperature and 77 K): absorption, fluorescence, fluorescence anisotropy, fluorescence excitation, fluorescence excitation anisotropy, magnetic circular dichroism, and electron energy loss (EELS) in the ground state. We have also measured the linear dichroism in stretched polyethylene and deduced the purely polarized spectra from it. We have further obtained the absorption spectra of the first excited singlet and triplet states, including absolute intensities. The $T_1 \rightarrow T_n$ absorption spectrum was obtained both from laser flash photolysis and from a steady-state absorption experiment. In these measurements, a mixture of **1** and anthracene sensitizer in cyclohexane solution was irradiated at a wavelength absorbed nearly exclusively by anthracene, and absorbance in the visible was measured. In the absence of the anthracene sensitizer, the absorption was not detectable. We concluded that intersystem crossing in **1** is negligible, at least in solution. The absorption spectra of the radical cation and the radical anion of **1** were measured for us by Dr. John Miller at Brookhaven National Laboratory. A selection of these results is displayed in Figures 4 - 8.

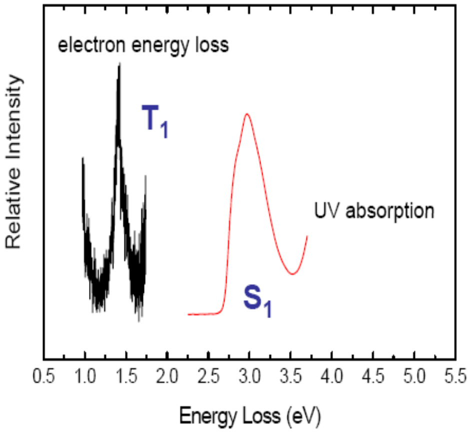


Figure 4. T_1 and S_1 states of **1** from EELS and UV absorption spectroscopy.

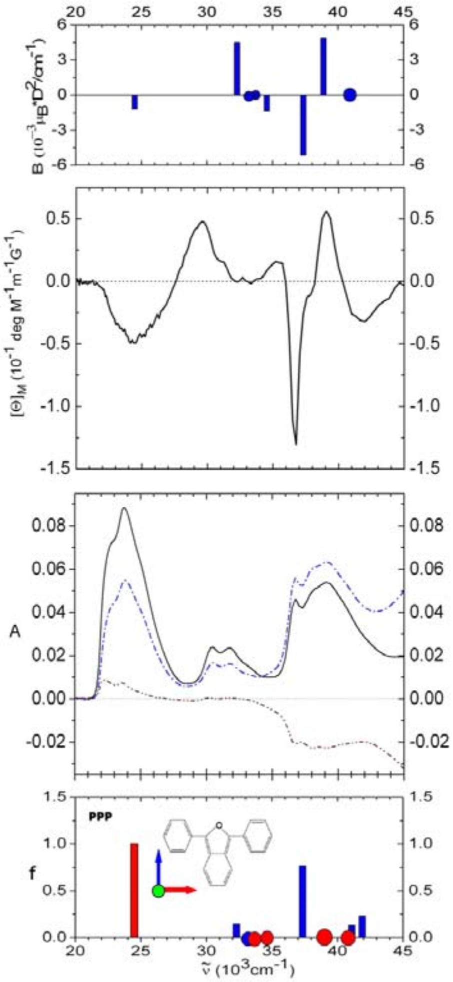


Figure 5. Magnetic circular dichroism of **1** (top) and its polarized absorption in stretched polyethylene (bottom) along with results of PPP calculations.

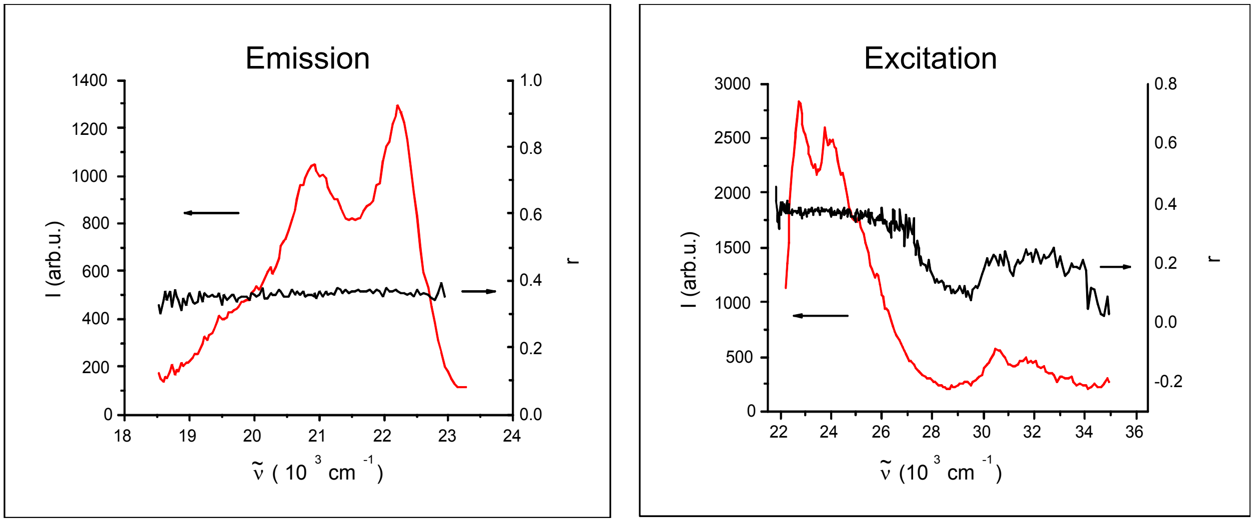


Figure 6. Anisotropy of fluorescence and fluorescence excitation of **1** (3-methylpentane glass at 77 K).

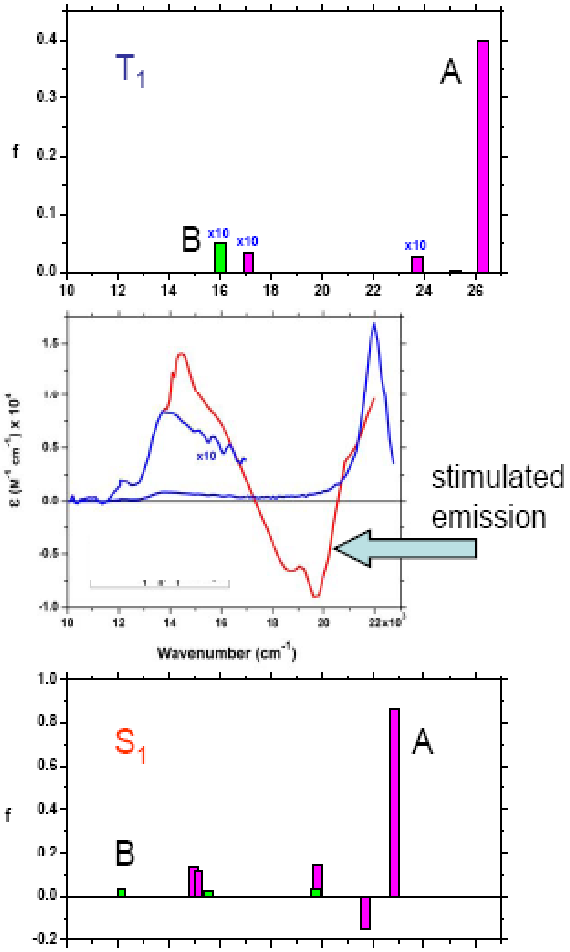


Figure 7. Absorption spectra of the S$_1$ (red) and T$_1$ (blue, sensitized with anthracene) states of **1** and results of CASPT2 calculations.

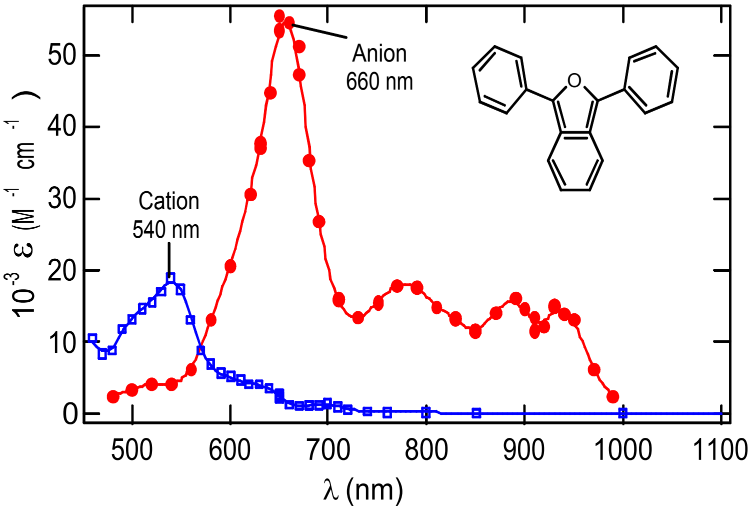


Figure 8. Absorption spectra of the radical cation (blue) and radical anion (red) of **1** from pulse radiolysis (courtesy of J. Miller, Brookhaven National Laboratory).

We have also measured the IR spectra of **1** in stretched polyethylene at room and low temperature and calculated the frequencies and polarizations of the transitions. These results were used to analyze the dichroism observed in the UV region. The detailed interpretation of all the spectra is being published. Here we merely note the presence of an unusual discrepancy between the conclusion that seems obvious from the fluorescence polarization and magnetic circular dichroism spectra, as well as the PPP, TD-DFT, and CASPT2 computational results, namely that the first excited singlet state is quite isolated, and the clear conclusion from the linear dichroism in stretched polyethylene, supported by the results of SORCI computations, namely that two oppositely polarized nearly degenerate states are present in the region of the lowest singlet excitation. Our best interpretation is that the first singlet excitation is indeed isolated and that the linear dichroism results are distorted by the simultaneous presence of the C_2 and C_s conformers, which happen to have mutually perpendicular principal orientation axes in stretched polyethylene.

The calculated and experimental excitation energies of **1** are listed in Table 2. The S_1 excitation energy was determined from absorption and fluorescence spectra and the T_1 excitation energy was known from a study[11] of solution sensitization with donors of different triplet energies. We have added a value for the polycrystalline solid using EELS, and are presently attempting to use the same method to ascertain the energy of the T_2 state as well. Within the experimental uncertainty of about 0.1 eV the singlet excitation energy is twice the triplet excitation energy, both in an isolated molecule in solution and in a polycrystalline solid, and singlet fission should be roughly thermoneutral as long as the chromophore coupling is small. The same should be true in covalent dimers of **1**, again provided that chromophore coupling does not change the state energies much.

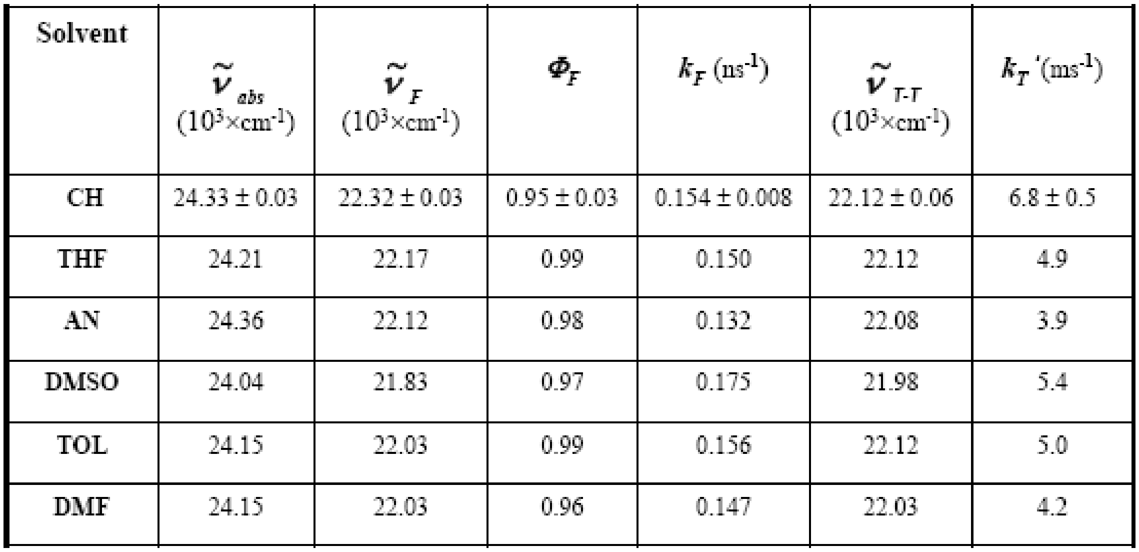
The photophysical data for **1** are collected in Table 3 and it is seen that they are also highly favorable for a hoped-for singlet fission chromophore. In particular, the fluorescence yield is very high, suggesting that there are no active channels likely to compete with singlet fission in crystals or dimers, such as intersystem crossing, internal conversion, or photoproduct formation. The fluorescence lifetime is quite long, giving singlet fission a good chance to compete successfully with emission. The results are in good agreement with the absence of any detectable triplet-triplet absorption upon excitation of solutions of **1**, in which singlet fission cannot take place.

Table 2. Excited State Energies for 1,3-Diphenylisobenzofuran (1) in eV

	Calcd.	Obsd. (solution)	Obsd. (solid)
S_1	3.0	~2.8	~2.7
T_1	1.7	~1.5[a]	~1.4[b]
T_2	3.3		

[a] From bracketing with sensitizers. [b] From electron energy loss.

Table 3. Photophysical Characteristics of 1 in Solution.[a]



Solvent	$\tilde{\nu}_{abs}$ (10^3×cm^{-1})	$\tilde{\nu}_F$ (10^3×cm^{-1})	Φ_F	k_F (ns^{-1})	$\tilde{\nu}_{T\text{-}T}$ (10^3×cm^{-1})	k_T' (ms^{-1})
CH	24.33 ± 0.03	22.32 ± 0.03	0.95 ± 0.03	0.154 ± 0.008	22.12 ± 0.06	6.8 ± 0.5
THF	24.21	22.17	0.99	0.150	22.12	4.9
AN	24.36	22.12	0.98	0.132	22.08	3.9
DMSO	24.04	21.83	0.97	0.175	21.98	5.4
TOL	24.15	22.03	0.99	0.156	22.12	5.0
DMF	24.15	22.03	0.96	0.147	22.03	4.2

---

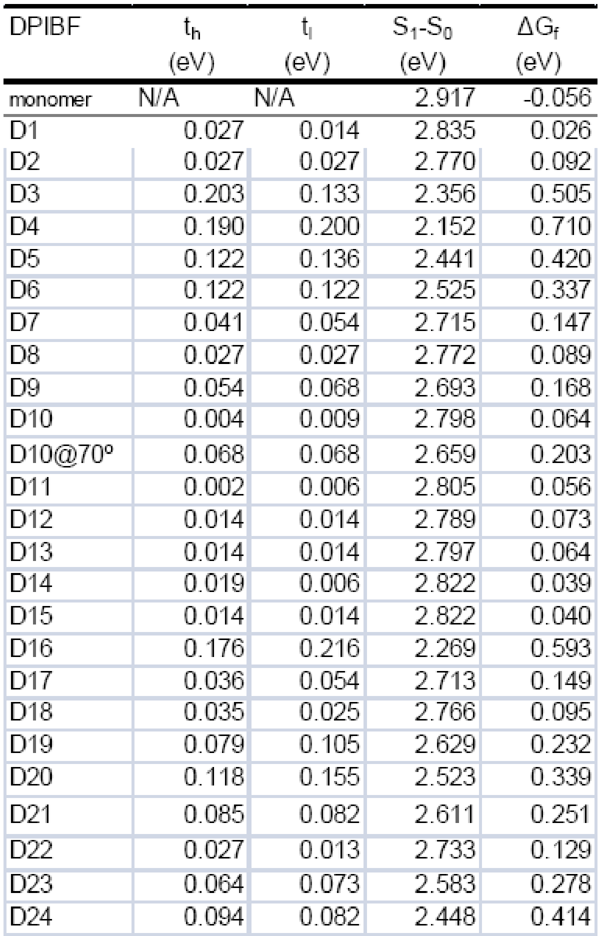
[a] The position of the first absorption and fluorescence peaks, the fluorescence quantum yield, the fluorescence rate constant, the position of the intense triplet-triplet absorption peak, and the triplet decay rate constant, respectively. CH: cyclohexane, THF: tetrahydrofuran, AN: acetonitrile, DMSO: dimethylsulfoxide, TOL: toluene, DMF: dimethylformamide

Since most of the reported successful observations of singlet fission were performed on crystalline material, we have attempted the same type of experiment on a polycrystalline film of **1**. We found that unlike an unsensitized solution, the polycrystalline sample shows an intense triplet-triplet absorption spectrum upon UV irradiation. It turned out to be relatively difficult to obtain an accurate value of the triplet yield but the data we have obtained so far leave little doubt that it is at least 10% and possibly as high as 50%. The triplet formation action spectrum (efficiency of triplet formation as a function of energy of the exciting photon) follows accurately the absorption spectrum. This is exactly the behavior anticipated for exothermic or thermoneutral singlet fission, which we attempted to achieve by choosing **1** as the chromophore. We cannot strictly rule out the possibility that intersystem crossing from S_1 to T_1, which is negligible in the isolated molecule, is for some unanticipated reason efficient in the crystalline material and generates the triplet state that we observe, but it appears highly improbable. Definitive evidence will be obtained if the triplet quantum yield is found to exceed 100%, or from future measurements in magnetic field. For the moment, we consider it virtually certain that **1** is the first crystalline material in which singlet fission has been observed by design. The next question is, will it also occur in covalent dimers of **1**?

Calculations of Coupling in Covalent Dimers

The next task was the covalent coupling of two molecules of the chromophore **1** into a dimer. Nothing was known about the strength of coupling that is required for singlet fission to be fast relative to fluorescence, which has a natural lifetime of about 5 ns in the monomer and could be somewhat faster in the dimer. A subcontractor on the project, Prof. M. Ratner, and his student have performed a series of calculations for a variety of dimers and evaluated the coupling constant. Selected results are shown in Table 4. In themselves, these numbers have no absolute significance, but they do provide a feeling for the relative strength of coupling between the two chromophores present in the molecules. They need to be calibrated by measurement of absolute singlet fission rates in several dimers.

Table 4. Electronic Matrix Elements and Free Energies for Various Covalent Dimers of 1[a]



DPIBF	t_h (eV)	t_l (eV)	S_1-S_0 (eV)	ΔG_f (eV)
monomer	N/A	N/A	2.917	-0.056
D1	0.027	0.014	2.835	0.026
D2	0.027	0.027	2.770	0.092
D3	0.203	0.133	2.356	0.505
D4	0.190	0.200	2.152	0.710
D5	0.122	0.136	2.441	0.420
D6	0.122	0.122	2.525	0.337
D7	0.041	0.054	2.715	0.147
D8	0.027	0.027	2.772	0.089
D9	0.054	0.068	2.693	0.168
D10	0.004	0.009	2.798	0.064
D10@70º	0.068	0.068	2.659	0.203
D11	0.002	0.006	2.805	0.056
D12	0.014	0.014	2.789	0.073
D13	0.014	0.014	2.797	0.064
D14	0.019	0.006	2.822	0.039
D15	0.014	0.014	2.822	0.040
D16	0.176	0.216	2.269	0.593
D17	0.036	0.054	2.713	0.149
D18	0.035	0.025	2.766	0.095
D19	0.079	0.105	2.629	0.232
D20	0.118	0.155	2.523	0.339
D21	0.085	0.082	2.611	0.251
D22	0.027	0.013	2.733	0.129
D23	0.064	0.073	2.583	0.278
D24	0.094	0.082	2.448	0.414

---

[a] Matrix element for HOMO-HOMO (t_h) and for LUMO-LUMO (t_l) interaction, free energy of S_0 to S_1 excitation, and of singlet fission. Structural formulas of the dimers are shown in Figure 9.

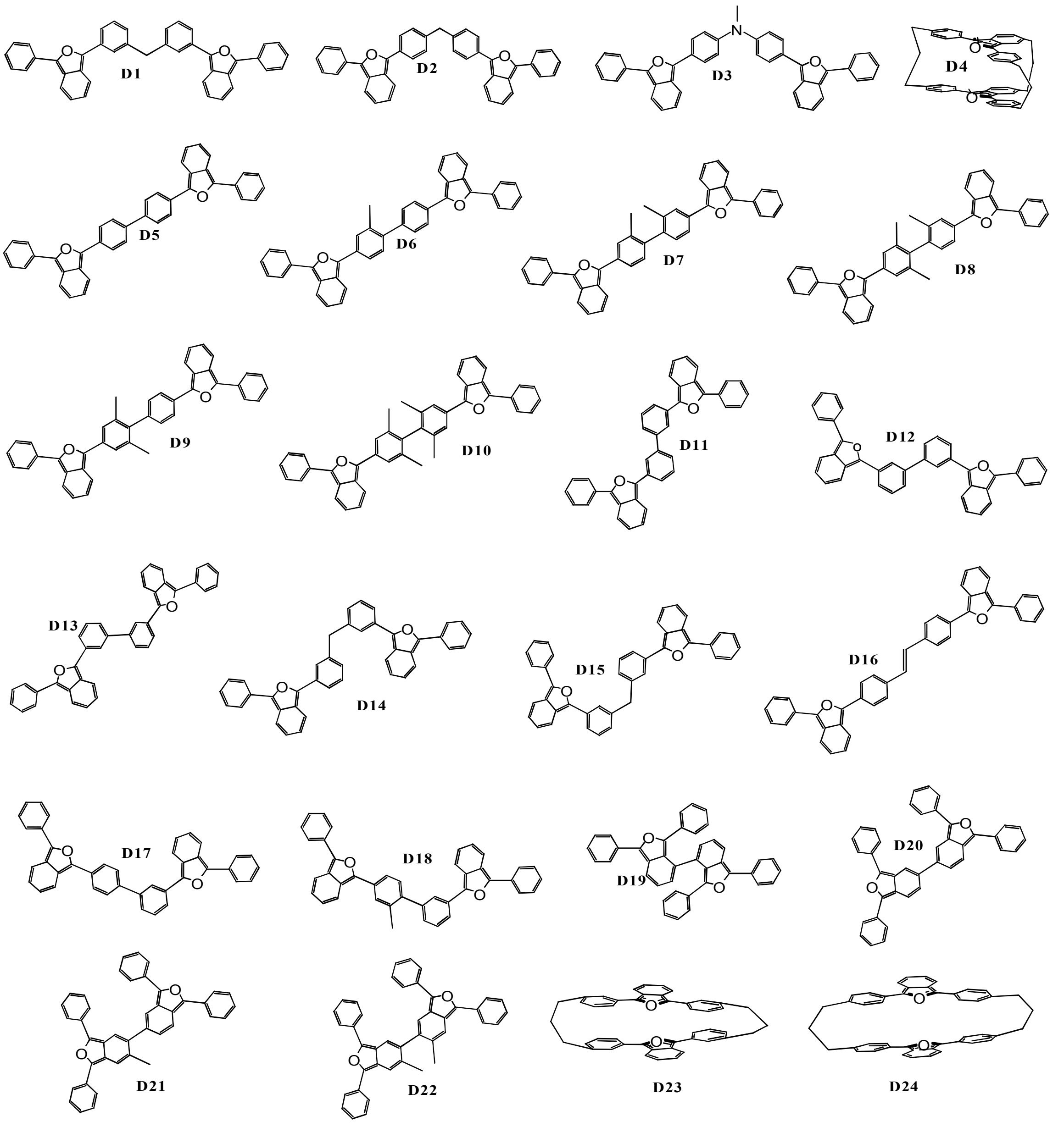


Figure 9. Structures of dimers of **1** for which DFT computations have been performed.

Synthesis of Covalent Dimers

Figure 2 presents the chemical structures of the dimers **2** - **4** that were synthesized for the purpose. The synthetic paths to **2** - **4** are shown in Figures 10, 11, and 12, respectively. The routes shown for **3** and **4** are particularly simple and efficient, and the same procedure was subsequently also employed for **2**. We will not discuss the details of the synthetic procedures and their pros and cons here, and merely note that the purification of the products is quite demanding, especially due to their sensitivity to the simultaneous action of light and atmospheric oxygen. It was done very carefully, and we believe that the disagreement between the absorption and fluorescence excitation spectra of **4** that will be noted below is genuine and not due to a minor impurity.

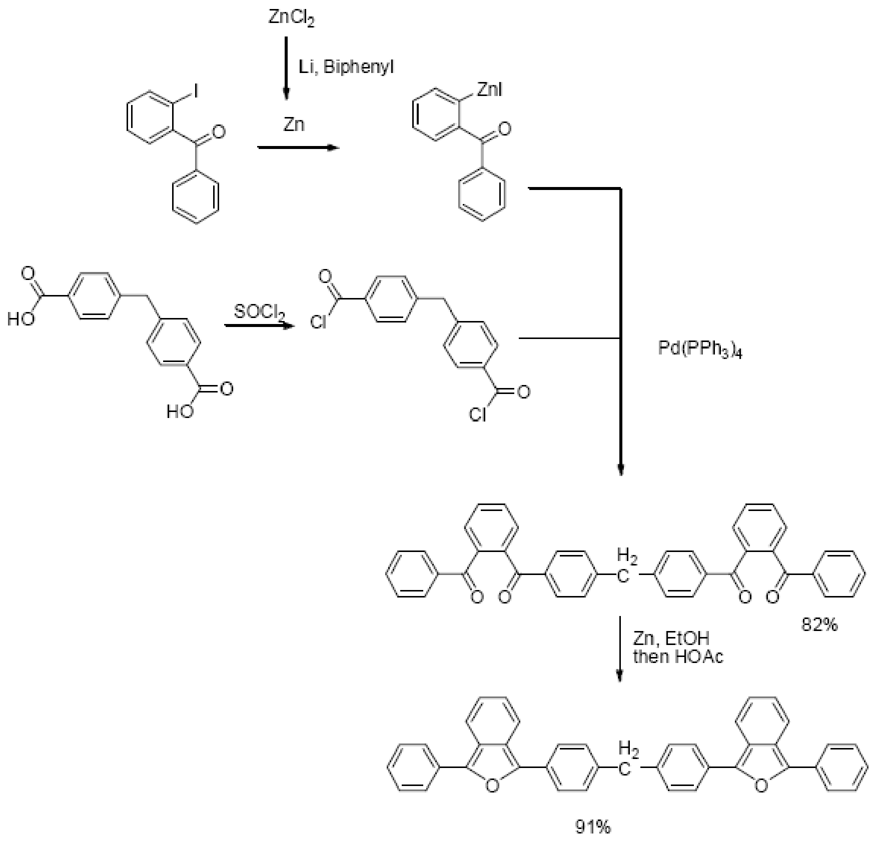


Figure 10. Synthetic route to **2.**

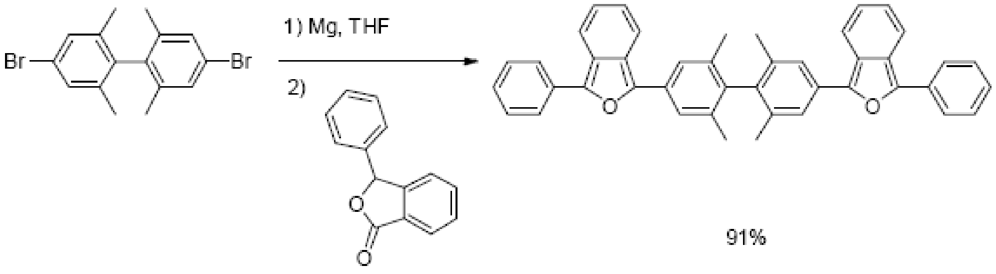


Figure 11. Synthetic route to **3**.

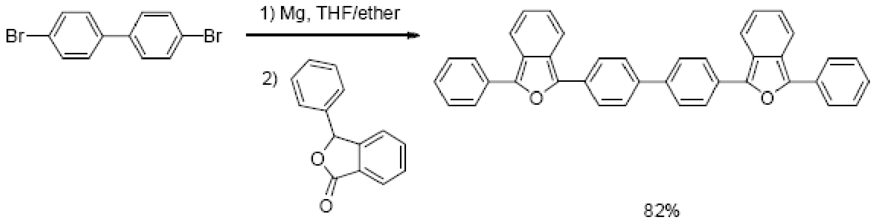


Figure 12. Synthetic route to **4**.

Solution Photophysics of the Weakly Coupled Dimers 2 and 3

We start this section by commenting on the behavior of **2** and **3** as polycrystalline solids. Since we noted above that irradiation of polycrystalline **1** produces triplets fairly efficiently, almost certainly by singlet fission, it is not surprising that solid **2** and **3** do so as well. From the point of view of application in a solar cell, they however offer no obvious advantage, and are harder to make. The interesting question in their case is whether their dimeric nature permits efficient singlet fission within a single molecule, and this section therefore focuses on their photophysics in solution.

The issues to be addressed are (i) is singlet or triplet excitation in these dimers localized in one of the constituent chromophores, or delocalized as it undoubtedly is in a crystal, (ii) is the coupling between the two chromophores contained within **2** and **3** strong enough for singlet fission to compete with fluorescence and other possibly present channels that depopulate the S_1 state, (iii) is the coupling of the chromophores weak enough not to perturb the state energies excessively, or does it shift the excitation energy of the S_1 state below twice that of T_1, making the formation of a pair of triplets from the excited singlet endothermic, hence singlet fission too slow.

We have examined the spectral properties of **2** and **3** similarly as those of **1**. Figure 13 compares the absorption and fluorescence spectra of **1** - **4** and Figure 14 compares their triplet-triplet absorption spectra obtained by anthracene sensitization in DMSO. The spectra of **2** and **3** are only about 20 nm red shifted relative to **1**, similarly as in crystalline **1**, leaving no doubt that the coupling between the two chromophores in the dimeric molecules is only weak, as anticipated. This is reasonable, considering that there is only hyperconjugative interaction between the two halves of the dimer in **2**, and that there is very limited conjugation between them when the ortho methyl groups force them to be nearly perpendicular to each other in **3**.

The spectra are compatible with the localization of excitation on one of the chromophores, presumably rapidly jumping from one to the other. TD-DFT calculations of optimized S_1 and T_1 geometries (Table 1) support this interpretation.

The photophysical properties of **2** and **3** are collected in Tables 5 and 6. In cyclohexane solution, there is no indication that the dimers **2** and **3** undergo singlet fission as isolated species. Their photophysical properties are nearly identical with those of **1** in the same solvent. The quantum yield of fluorescence is still very close to unity and its lifetime is 5 - 6 ns as before. No triplet-triplet absorption is detectable after direct irradiation of the solution without a sensitizer, nor is any other transient absorption other than that due to the $S_1 \rightarrow S_n$ process. This absorption decays with the same lifetime as fluorescence, and the decay follows a single exponential.

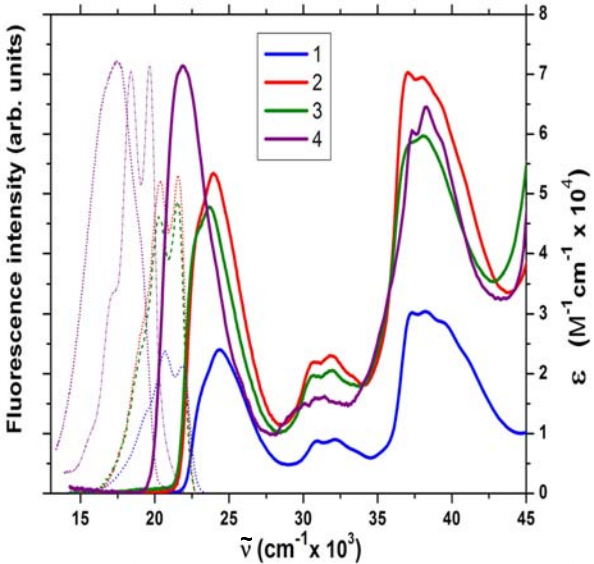


Figure 13. Absorption (solid line) and fluorescence (broken line) spectra of the ground state of **1** (blue), **2** (red), **3** (green) and **4** (purple) in acetonitrile. The fluorescence spectrum of **4** in toluene is also shown.

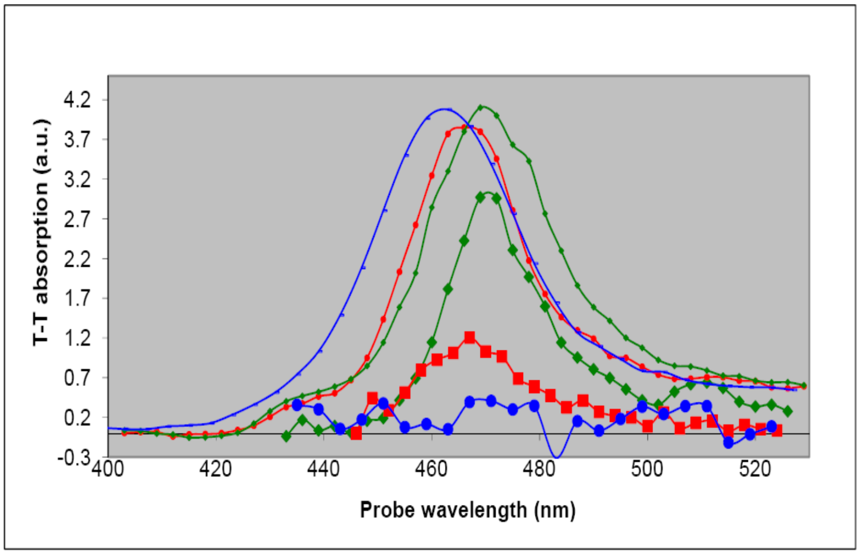
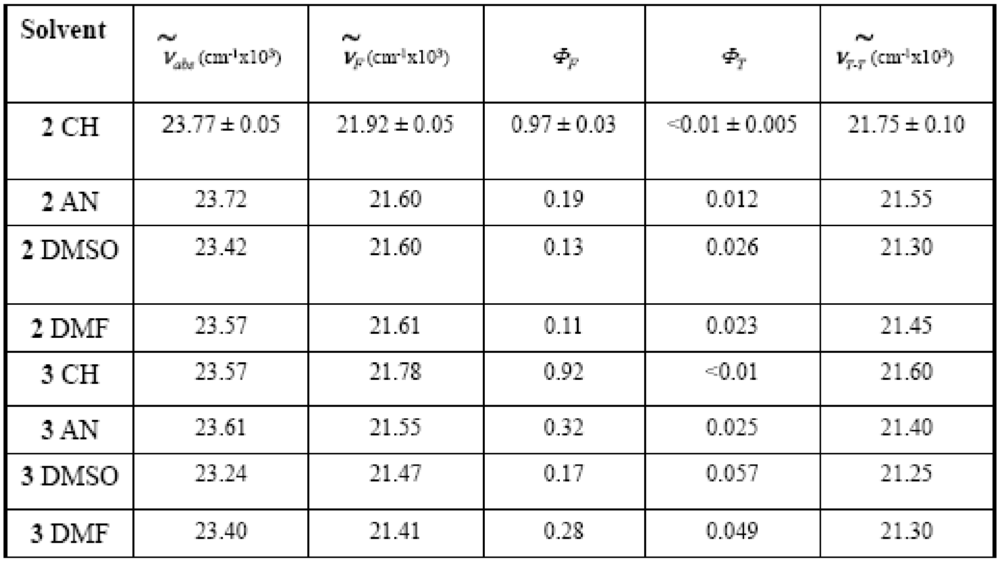


Figure 14. Triplet-triplet absorption of **1** (blue), **2** (red), **3** (green) sensitized with anthracene (small dots) and obtained upon direct excitation (large dots, intensity multiplied by ten) in DMSO.

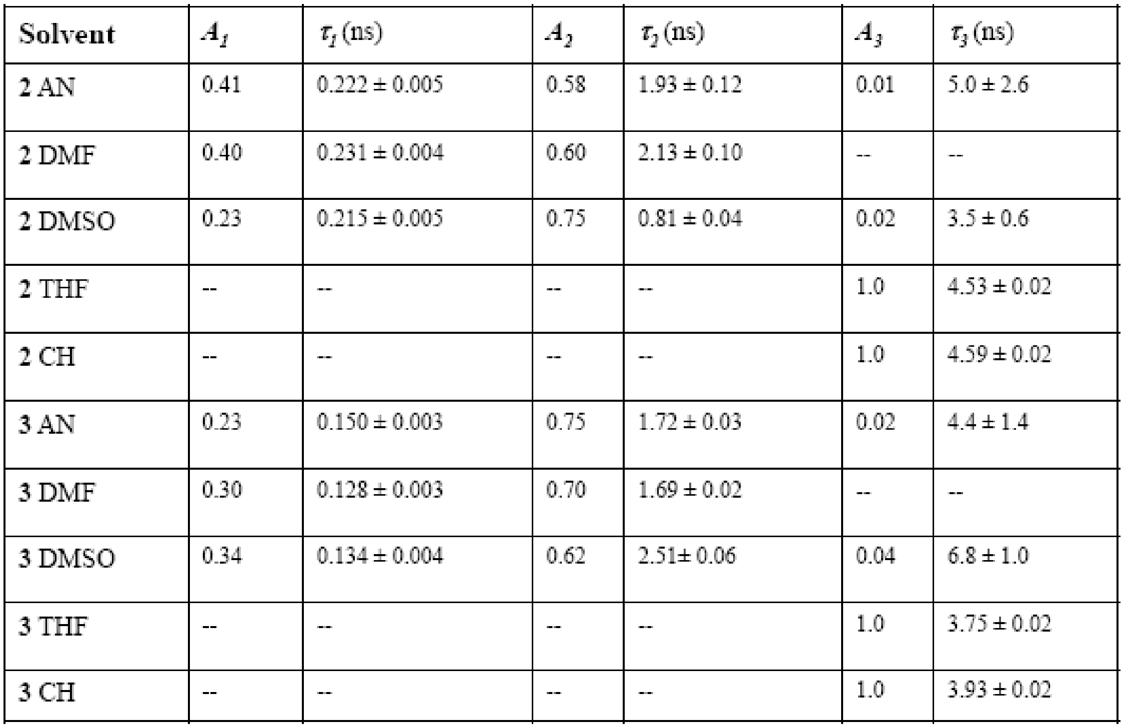
Table 5. Photophysical Characteristics of 2 and 3.[a]



Solvent	$\tilde{\nu}_{abs}$ (cm^{-1}x10^3)	$\tilde{\nu}_F$ (cm^{-1}x10^3)	Φ_F	Φ_T	$\tilde{\nu}_{T-T}$ (cm^{-1}x10^3)
2 CH	23.77 ± 0.05	21.92 ± 0.05	0.97 ± 0.03	<0.01 ± 0.005	21.75 ± 0.10
2 AN	23.72	21.60	0.19	0.012	21.55
2 DMSO	23.42	21.60	0.13	0.026	21.30
2 DMF	23.57	21.61	0.11	0.023	21.45
3 CH	23.57	21.78	0.92	<0.01	21.60
3 AN	23.61	21.55	0.32	0.025	21.40
3 DMSO	23.24	21.47	0.17	0.057	21.25
3 DMF	23.40	21.41	0.28	0.049	21.30

[a] For symbol definition see Table 3. Φ_T is the triplet quantum yield. CH: cyclohexane, AN: acetonitrile, DMSO: dimethylsulfoxide, DMF: dimethylformamide

Table 6. Multiexponential Fluorescence Decay of **2** and **3** in Solution.[a]



Solvent	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)
2 AN	0.41	0.222 ± 0.005	0.58	1.93 ± 0.12	0.01	5.0 ± 2.6
2 DMF	0.40	0.231 ± 0.004	0.60	2.13 ± 0.10	--	--
2 DMSO	0.23	0.215 ± 0.005	0.75	0.81 ± 0.04	0.02	3.5 ± 0.6
2 THF	--	--	--	--	1.0	4.53 ± 0.02
2 CH	--	--	--	--	1.0	4.59 ± 0.02
3 AN	0.23	0.150 ± 0.003	0.75	1.72 ± 0.03	0.02	4.4 ± 1.4
3 DMF	0.30	0.128 ± 0.003	0.70	1.69 ± 0.02	--	--
3 DMSO	0.34	0.134 ± 0.004	0.62	2.51± 0.06	0.04	6.8 ± 1.0
3 THF	--	--	--	--	1.0	3.75 ± 0.02
3 CH	--	--	--	--	1.0	3.93 ± 0.02

[a] A_i are the amplitudes associated with the lifetimes τ_i shown. CH: cyclohexane, THF: tetrahydrofuran, AN: acetonitrile, DMSO: dimethylsulfoxide, DMF: dimethylformamide

The situation changes when the solvent is highly polar. In DMF or DMSO, and to a lesser degree in acetonitrile, the fluorescence quantum yield is considerably reduced (Table 5) and fluorescence lifetime is shorter and multiexponential (Table 6). Triplet-triplet absorption after direct excitation without a sensitizer becomes quite pronounced and the quantum yield of T_1 is 0.01 - 0.06. These measurements were repeated at various temperatures and the highest observed quantum yield of T_1 was about 0.09. However, time-resolved absorption measurements show that the faster decay of the S_1 species is not due to its conversion into T_1. Instead, in a few hudred ps this decay produces a new species S* with a broad absorption peak from 500 to 600 nm and another broad peak near 670 nm. Our search for a fluorescence from this species has been fruitless. The species S* decays to form the triplet on a time scale of a few ns (Figure 15). The lifetime for the decay of S_1 is equal to the rise time of S* and the decay time of S* is equal to the rise time of T_1. Global analysis of transient absorption in the 450 to 700 nm region at times up to 8 ns yielded the absorption spectra of S_1, S*, and T_1, evidence for stimulated emission from S_1, and a set of rate constants for the transformation of S_1 to S* and back and for the transformation of S* to T_1 in **2** and **3** (Figure 16 and Table 7). The inefficiency of T_1 formation is attributed to the conversion of S* and probably also T* to S_0. The overall reaction scheme is shown in Figure 17 (for simplicity we do not show explicitly the direct path from T* to S_0).

The structural assignment of S*, which is only formed in polar solvents, to a dipolar species in which a radical cation of **1** is covalently attached to the radical cation of **1** is secured by comparison of its absorption spectrum with those of the radical cation and radical anion of **1** (Figure 8). A good precedent for this type of intramolecular charge transfer in a polar solution is provided by 9,9'-bianthryl.[12] The existence of T*, the triplet state of the dipolar species S*, is postulated to account for the temperature dependence of the triplet yield. Its absorption spectrum is expected to be essentially identical with that of S* and it is believed to be only slightly more stable than S*, because the two unpaired electrons are well separated in space.

At room temperature the vertically excited state S_1 is rapidly converted by electron transfer into an equilibrium mixture with the dipolar species S*, which can undergo back electron transfer to yield S_1. From temperature dependence of the equilibrium constant we find that S* is more stable than S_1 by 1.8 kcal/mol. At low temperatures, the electron transfer in S_1 to yield S* becomes rate limiting and has an activation energy of 3 kcal/mol. At the same time, the quantum yield of T_1 formation increases, and this is attributed to a shift of the equilibrium between S* and T* in favor of the lower energy species T*. The available data are not good enough to permit a quantitative evaluation of their energy difference.

Upon the disappearance of one molecule of S*, 1.2 ± 0.4 molecules of T_1 are formed. Within the error margin, this can be attributed fully to intersystem crossing, and singlet fission need not be invoked, although we cannot exclude that it makes a minor contribution to the formation of T_1.

The nature of the inter-chromophore coupling in **2** and **3** is distinctly different than the stacking π-face - π-face interaction in crystalline **1**, but the effects on absorption spectra are similar, a red shift of about 20 nm. This suggests that the contrast between the efficient singlet fission in polycrystalline **1** and non-existent singlet fission in the isolated dimers **2** and **3** is not due to a vastly different strength of the inter-chromophore coupling. Instead, we believe that it is related to the delocalized nature of the S_1 excitation in the crystal and localized nature of S_1 excitation in the dimers, along the lines discussed above in connection with Figure 1. It is of interest to direct future efforts in the direction of covalent structures in which the excitation would also be delocalized, perhaps stacked dimers or oligomers and polymers instead of dimers.

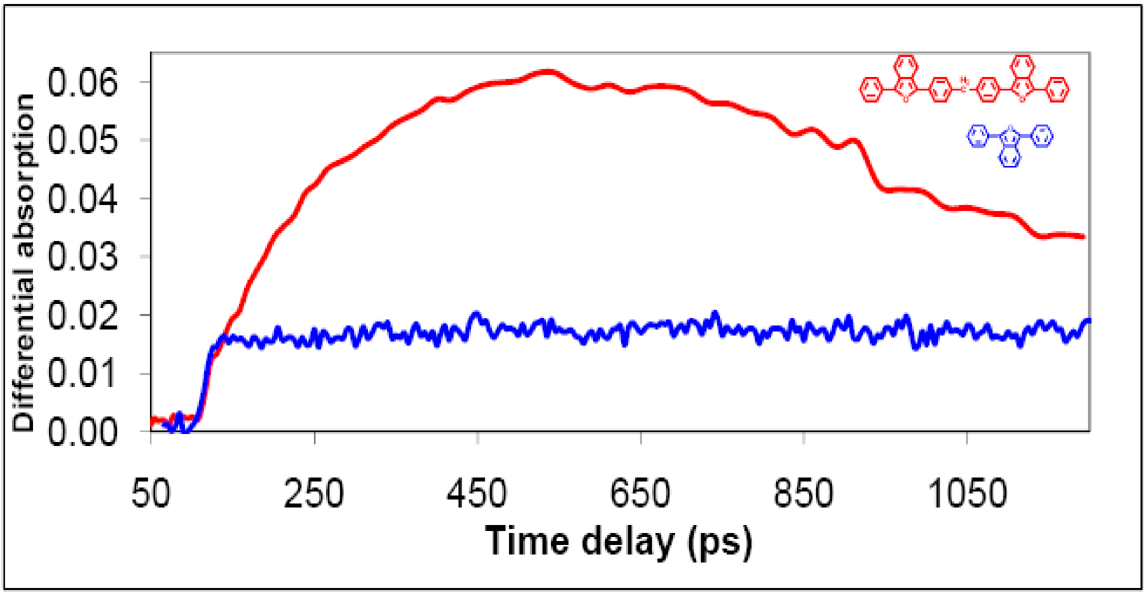


Figure 15. Transient absorption at 575 nm of **1** (blue) and **2** (red) obtained upon direct excitation at 400 nm in DMSO.

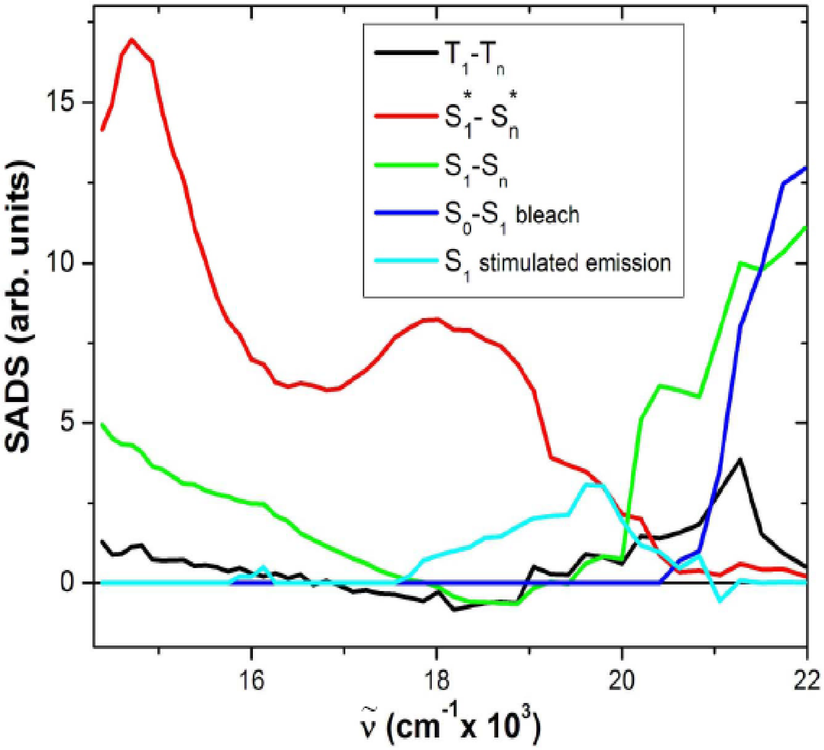


Figure 16. Absorption spectra of the S_1, S*, and T_1 states of **2**, transient bleach of S_0, and stimulated emission from S_1 obtained from global analysis of

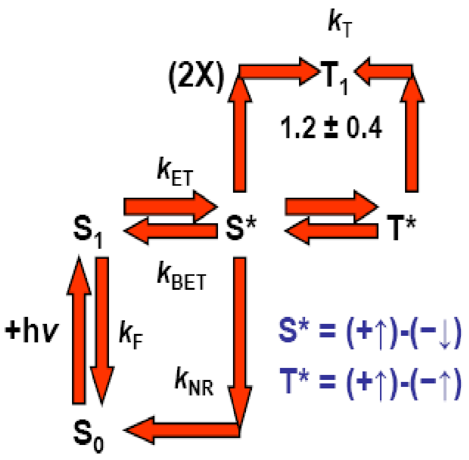


Figure 17. Reaction Scheme for the Photophysics of **2** and **3** in DMSO.

Table 7. Rate Constants[a] for the Photophysics of **2** and **3** in DMSO solution.

RT rate contants (1/ns)	k_F	k_{ET}	k_{BET}	k_{NR}	k_T
2 DMSO	0.23	1.8	2.8	~1.0	~0.1
3 DMSO	0.25	3.8	4.9	~0.8	~0.09

---

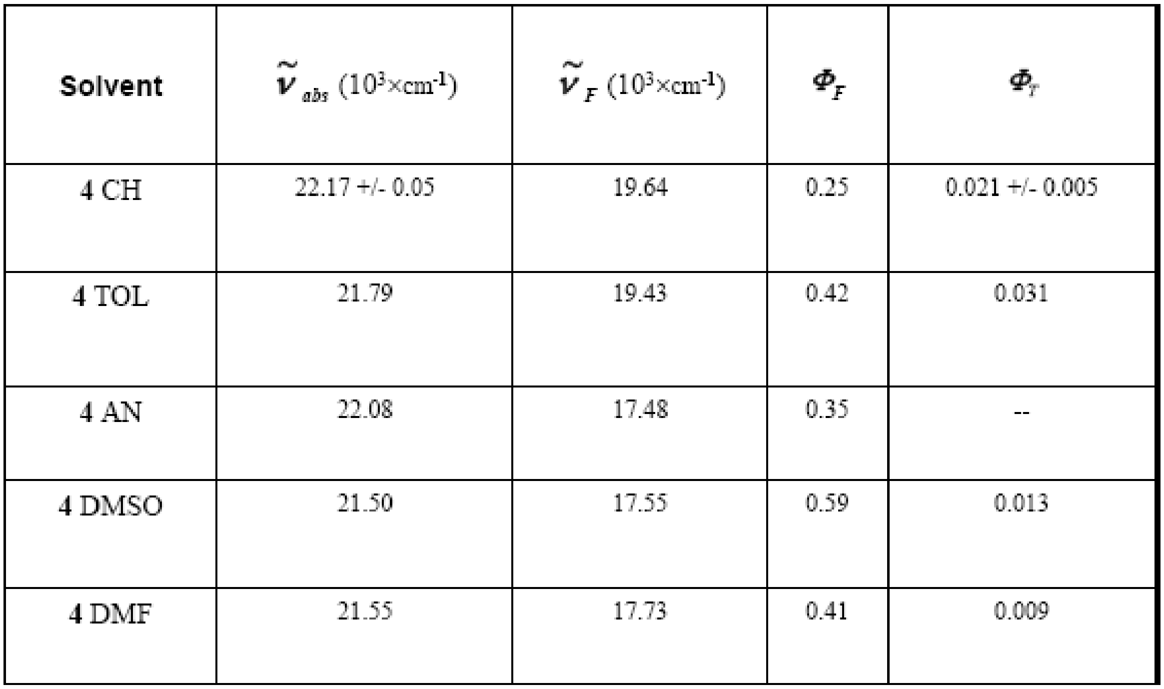
[a] See Figure 17 for the meaning of symbols.

Solution Photophysics of the Strongly Coupled Dimer 4

It is clear in Fig. 13 that the first transition in **4** is not just doubled in intensity relative to that of **1** and otherwise nearly unchanged, like those of **2** and **3**. Instead, it is significantly red shifted and intensified. This is true for the solid spectrum as well and is not surprising, given the quite strong direct conjugation when the two halves of the molecule are nearly coplanar. This structure is best viewed as a single chromophore conjugated throughout, even though it still has the capability to accommodate two triplet excitations after the two halves are uncoupled by twisting around the central bond. Our investigations of this dimer are just now in course as a part of the follow-up contract, but some photophysical results can already be stated here (Table 8).

In the solid state, and also in solution, T_1 formation is easily detectable, but only at higher excitation energies. The triplet formation action spectrum does not follow the absorption spectrum, as it did in solid **1** - **3**. Instead, in solution and in the solid, it shows a clear threshold at about twice the triplet energy of **1**. Clearly, in **4**, the coupling of the two halves is too strong for the condition $E(S_1) \geq 2\,E(T_1)$ to be satisfied. Even above the threshold, the triplet formation efficiency is low, only 3%, undoubtedly because singlet fission has to compete with fast vibrational deactivation and/or internal conversion. It appears that in **4** the coupling is strong enough to undergo singlet fission in solution and in neat crystalline material, but that it also is strong enough to lower the singlet excitation energy below twice the triplet excitation energy.

Table 8. Photophysical Characteristics of 4 in Solution.[a]



Solvent	$\tilde{\nu}_{abs}$ ($10^3\times$cm^{-1})	$\tilde{\nu}_F$ ($10^3\times$cm^{-1})	Φ_F	Φ_T
4 CH	22.17 +/- 0.05	19.64	0.25	0.021 +/- 0.005
4 TOL	21.79	19.43	0.42	0.031
4 AN	22.08	17.48	0.35	--
4 DMSO	21.50	17.55	0.59	0.013
4 DMF	21.55	17.73	0.41	0.009

[a] For symbol definition see Tables 3 and 5. CH: cyclohexane, TOL: toluene; AN: acetonitrile, DMSO: dimethylsulfoxide, DMF: dimethylformamide

Summary

We have considered the potential benefits offered by using singlet fission sensitizers in photovoltaic cells and identified two key issues involved in the search for such sensitizers. One of these is thermodynamic and deals with the arrangement of the electronic levels of the chromophore, and the other is kinetic and deals with the strength of coupling between the two or more chromophores that need to be present in a singlet fission sensitizer. Considerable theoretical and experimental progress in both has been described, and it has been pointed out that the two criteria impose contradictory demands.

A set of guidelines for the search for an optimal singlet fission chromophore has been elaborated, and has led to the first observation of what we believe to be singlet fission in a rationally designed polycrystalline neat solid sensitizer, **1**, and its covalent dimers **2** - **4**. The triplet yield has not yet been measured accurately, but in **1** itself it appears to be at least 10%. The behavior of the covalent dimers **2** - **4** in solution is different. In nonpolar solvents, the weakly coupled dimers **2** and **3** form no triplets, and the coupling between the constituents is clearly too weak. The thermodynamic criterion is met, but the kinetic one is not. In strongly polar environments, 2 and 3 form triplets in yields that range up to ~9%, but this occurs primarily or exclusively by intersystem crossing in a dipolar intermediate. Although this is interesting photophysics, it does not lie on the path to more efficient singlet fission. In dimer **4**, the coupling is strong enough for singlet fission to take place with a triplet yield of ~3%, and the kinetic criterion is satisfied. However, the coupling is so strong that the thermodynamic criterion is no longer satisfied and the singlet fission takes place only upon excitation above a threshold that lies considerably above the 0-0 transition into the lowest excited singlet state. Competition with vibrational deactivation and/or internal conversion is then inevitable and is responsible for the low triplet yield.

The paths to further progress are clear: (i) work with nanocrystals of the monomer, (ii) find a mode of covalent coupling that causes the initial singlet excitation to be delocalized (this may involve stacking interactions or perhaps going to oligomers and polymers), (iii) identify a different chromophore in which the excitation energy of the lowest triplet T_1 is significantly smaller than half the excitation energy of the lowest excited singlet S_1, such that even after the required strong coupling in a dimer the S_1 excitation energy remains larger than twice the T_1 excitation energy. These routes are being pursued in a current follow-up project.

References

---

1. I. Paci, J. C. Johnson, X. Chen, G. Rana, D. Popović, D. E. David, A. J. Nozik, M. A. Ratner, and J. Michl, "Singlet Fission for Dye-Sensitized Solar Cells: Can a Suitable Sensitizer Be Found?," *J. Am. Chem. Soc.* **128**, 16546-16553, 2006.

2. M. Hanna and A. J. Nozik, "Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers," *J. Appl. Phys.* **100**, 074510/1-074510/8, 2006.

3. A. M. Müller, Y. S. Avlasevich, K. Müllen, and C. J. Bardeen, "Evidence for exciton fission and fusion in a covalently linked tetracene dimer," *Chem. Phys. Lett.* 421, 518-522, 2006.

4. J. Michl and V. Bonačić-Koutecký, *Electronic Aspects of Organic Photochemistry*, John Wiley and Sons, Inc., New York, 1990.

5. R. Pariser, "Theory of the electronic spectra and structure of the polyacenes and of alternant hydrocarbons," *J. Chem. Phys.* **24**, 250-268, 1956.

6. J. Koutecky, "Contribution to the theory of alternant systems," J. Chem. Phys. 44, 3702-3706, 1966; "Some properties of semiempirical Hamiltonians," *J. Chem. Phys.* **47**, 1501-1511, 1967.

7. V. Bonačić-Koutecký, J. Koutecký, and J. Michl, "Neutral and Charged Biradicals, Zwitterions, Funnels in S_1, and Proton Translocation: Their Role in Photochemistry, Photophysics, and Vision," Angew. Chem. Internat. Ed. Engl. **26**, 170-189, 1987.

8. J. Michl, "Singlet and Triplet States of an Electron Pair in a Molecule--A Simple Model," J. *Mol. Struct.* (THEOCHEM.) **260**, 299-311, 1992.

9. Michl, J.; Nozik, A. J.; Chen, X.; Johnson, J. C.; Rana, G.; Akdag, A.; Schwerin, A. F. "Toward singlet fission for excitonic solar cells," in Organic Photovoltaics VIII, Kafafi, Z. H. and Lane, P. A., Eds., Proc. of SPIE Vol. 6656, 66560E1-66560E1, 2007.

---

10. C. R. Flynn and J. Michl, "π,π-Biradicaloid Hydrocarbons: *o*-Xylylene. Photochemical Preparation from 1,4-Dihydrophthalazine in Rigid Glass, Electronic Spectroscopy, and Calculations," *J. Am. Chem. Soc*. **96**, 3280-3288, 1974.

11. W. G. Herkstroeter and P. B. Merkel, "The triplet state energies of rubrene and diphenylisobenzofuran," *J. Photochem.* **16**, 331-342, 1981.

12. M. Schütz and R. R. Schmidt, "Deactivation of 9,9'-Bianthryl in Solution Studied by Photoacoustic Calorimetry and Fluorescence," *J. Phys. Chem.* **100**, 2012-2018, 1996.

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* December 2008	**2. REPORT TYPE** Final Subcontract Report	**3. DATES COVERED** *(From - To)* 15 August 2005 - 14 October 2008

4. TITLE AND SUBTITLE Singlet-Fission Sensitizers for Ultra-High Efficiency Excitonic Solar Cells	**5a. CONTRACT NUMBER** DE-AC36-08-GO28308
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) J. Michl	**5d. PROJECT NUMBER** NREL/SR-520-44685
	5e. TASK NUMBER PVA72401
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Dept. of Chemistry and Biochemistry CB 215 Boulder, Colorado 80309-0214	**8. PERFORMING ORGANIZATION REPORT NUMBER** XAT-5-33636-01
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393	**10. SPONSOR/MONITOR'S ACRONYM(S)** NREL
	11. SPONSORING/MONITORING AGENCY REPORT NUMBER NREL/SR-520-44685

12. DISTRIBUTION AVAILABILITY STATEMENT

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

13. SUPPLEMENTARY NOTES

NREL Technical Monitor: Lori Green/Kaitlyn VanSant

14. ABSTRACT *(Maximum 200 Words)*

Sensitizer dyes capable of producing two triplet excited states from a singlet excited state produced by the absorption of a single photon would allow an increase of the efficiency of photovoltaic cells by up to a factor of 1.5, provided that each triplet injects an electron into a semiconductor such as TiO2. Although singlet fission in certain crystals and polymers was reported long ago, little is known about its efficiency in dyes suitable for use as sensitizers of photoinduced charge separation on semiconductors surfaces. In summary, we have produced the first designed crystalline material for singlet fission, and we have made the first determinations of the coupling strength in a covalent dimer that is required for efficient singlet fission. We have suggested paths for overcoming a problem that has been identified and have already started to develop them in a follow-up project.

15. SUBJECT TERMS

PV; singlet fission; sensitizer; ultra-high efficiency; excitonic; solar cells; photoinduced charge; semiconductor; nanocrystals;

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			
Unclassified	Unclassified	Unclassified	UL		**19b. TELEPHONE NUMBER** (*Include area code*)

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18