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Singlet Fission for Dye-Sensitized Solar Cells: Can a Suitable Sensitizer Be Found?

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Abstract: We discuss possible improvements in the efficiency of dye-sensitized photovoltaic cells using dyes capable of singlet fission into two triplets, thus producing two electron−hole pairs from a single photon. It is pointed out that, in addition to derivatives of large alternant hydrocarbons, those of biradicals are also likely candidates for a favorable ordering of excited-state energy levels, $E(T_2)$, $E(S_1) > 2E(T_1)$. A large number of potentially favorable structures has been examined by the semiempirical Pariser−Parr−Pople method and some also by the time-dependent density functional theory method. Several likely candidates have been identified for experimental examination.

Introduction

Singlet Fission for Dye-Sensitized Solar Cells. Dye-sensitized photochemical solar cells, also known as Grätzel cells,[1−3] have been investigated for many years. Their operation is based on photoexcitation of dye molecules bonded to the surface of nanocrystalline TiO_2, present as a porous thin film (10−20 μm) on a transparent electrode in a photoelectrochemical cell containing a nonaqueous I_3^-/I^- redox electrolyte. The dyes have an excited-state redox potential more negative than the potential of the TiO_2 conduction band, allowing for energetically favorable electron injection from the excited dye into the TiO_2 nanoparticles. The injected electrons move freely in the TiO_2 conduction band, percolate through the TiO_2 particle network, and exhibit very high efficiency for collection at the transparent electrode. These electrons can then traverse the external circuit to deliver electrical power to an external load and return to the cell at a metal cathode. The electrons injected into the electrolyte at the cathode reduce I_3^- to I^- , and I^- ions then diffuse toward the anode and reduce the oxidized dye back to its original dark oxidation state, thus completing the circuit.

Power conversion efficiency is a critical parameter to maximize in any photovoltaic (PV) cell. This is because the cost of electrical power ($/kWh) is inversely proportional to conversion efficiency. Thus, for example, to produce PV electric power at a cost comparable to that of current electric power generated from fossil-fueled power plants (about $ 0.05/kWh) would require PV module panels with 30% efficiency if the current PV systems costs of the photoactive modules plus all other components ("balance of systems") could be reduced to half of the present cost, which is $ 600/m^2. Since module efficiencies are only about two-thirds that of the individual cells, the cell efficiency has to be about 45% to meet the above power cost goal.

Present Grätzel cells have efficiencies of 10−11%,[1−3] and this value has not changed significantly for many years. There are several factors that limit the conversion efficiency; these include incomplete absorption of solar photons, loss of some of their energy as heat, voltage loss due to the much more negative redox potential of the I^-/I_3^- relay compared to that of the ground-state dye, and electron−hole recombination at various stages of the cell operation.

A possibly useful approach[4,5] to improving the efficiency of dye-sensitized photochemical solar cells would be to design the molecular dye sensitizer to undergo efficient singlet fission upon absorption of a photon of sufficient energy, such that two triplets are created from one excited singlet and these triplets each inject an electron into the TiO_2 nanoparticle film. This process would be the molecular analogue of multiple exciton generation in semiconductor quantum dots (QDs),[6−8] where multiple electron−hole pairs (excitons) can be efficiently created from single photons absorbed in PbS, PbSe, and PbTe QDs. Quantum yields

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of 300% (three electrons per photon) for excitation at 4 times the QD band gap (HOMO−LUMO transition) in PbSe,[9,10] PbS,[10] and PbTe[11] and 700% (seven electrons per photon) at 8 times the PbSe QD band gap have recently been reported.[12]

An analysis of the increase in the theoretical thermodynamic solar power conversion efficiency[13] indicates that the maximum upper limit for an ideal Grätzel cell can be increased from 32% for an ordinary sensitizer that provides the usual one electron per photon to ∼46% for a singlet fission sensitizer combined in optical series with an ordinary one. In that case, the optimal values are ∼1.8−2.2 eV for $E(S_1)$ and ∼0.9−1.1 eV for $E(T_1)$ in the singlet fission sensitizer and ∼0.9−1.1 eV for $E(S_1)$ in the ordinary one.

In addition to an electron-injecting dye capable of singlet fission (C1), one could imagine a hole-injecting one (C2), and in a broader context, singlet fission could be useful more generally in all kinds of solar cells based on organic chromophores. The temporary storage of energy in the form of triplets promises advantages relative to the multiple singlets generated in inorganic quantum dots, such as greatly reduced rate of radiative decay and absence of spatial confinement, which reduces the likelihood of annihilation events. However, it would appear premature to speculate further about the possible advantages of using singlet fission in solar cells based on organic chromophores until it has been demonstrated in practice.

Prior Observations of Singlet Fission. Singlet fission was first observed by Siebrand, Schneider, and collaborators[14] in crystalline anthracene. It was subsequently invoked to account for the thermally induced fluorescence quenching in crystalline tetracene[15] and confirmed beyond doubt by several studies of tetracene and pentacene crystals in rapid succession.[16−25] This early work has been reviewed with particular emphasis on magnetic field effects.[26] More detailed studies of polyacene crystals followed.[27−35] More recently, singlet fission has been observed in crystalline benzophenone[36] and *p*-sexiphenyl.[37] Other crystals in which it was observed were those of charge-transfer complexes of aromatics with tetracyano-*p*-quinodimethane (TCNQ) and its tetrafluoro derivative.[38,39]

In addition to crystals, singlet fission has been observed in polymers: polydiacetylene,[40−44] a ladder-type poly(*p*-phenylene),[44,45] and poly(*p*-phenylenevinylene).[44,46,47] Observations on single molecules capable of acting as a pair of weakly interacting chromophores are particularly relevant to the present study. They have been reported only more recently, first on carotenoids[48−50] and then on 1,4-bis(tetracen-5-yl)benzene.[51]

This prior work firmly established the singlet fission phenomenon and clearly recognized that it is favored in materials in which $E(S_1)$ is approximately equal to $2E(T_1)$, such as the higher polyacenes. It did not involve any attempts to design and then synthesize chromophores that could be paired in a sensitizer optimized for singlet fission, let alone for photovoltaic applications. The present paper represents an effort to develop initial guidelines for the structure of chromophores designed to be paired or grouped into molecular sensitizers suited for efficient singlet fission with solar photons.

Results and Discussion

Requirements for a Singlet-Fission Sensitizer. The usual primary requirements for a sensitizer to be used with a semiconductor such as TiO_2 are good adsorption on the surface, high absorption coefficient for light at all wavelengths of the solar spectrum shorter than the absorption onset, appropriate onset wavelength, fast electron injection from the excited sensitizer into the semiconductor, slow electron back transfer from the semiconductor, and fast kinetics for the reduction of the oxidized sensitizer with a relay such as I^-, which dictate suitable ground- and excited-state redox potentials. For practicality, one needs to add photostability and low cost. It is not surprising that years of searching produced only a small number of suitable candidates for ordinary one-electron-injecting sensitizers.

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In addition to these usual requirements, the ideal singlet fission sensitizer will also exhibit excited singlet (S_1) fission into two triplets (T_1) at a rate faster than all competing processes, above all, electron injection into the semiconductor, but also fluorescence, intersystem crossing into the triplet manifold, and internal conversion to the S_0 ground state. At the same time, its T_1 will inject electrons into the semiconductor at a rate faster than all competing processes, in particular triplet−triplet annihilation, but also phosphorescence and intersystem crossing into the S_0 ground state. Although these clearly are demanding additional requirements, they might perhaps be possible to meet. After all, in polyacene crystals, singlet fission rates are of the order of 10^{13} s^{-1},[35] and one could engineer the distance of the sensitizer from the TiO_2 surface so as to suppress electron injection from the shorter-lived excited singlet yet keep it efficient from the longer-lived triplet.

Since the intended goal of the fission process is the production of two more or less independent triplet species, the sensitizer needs to be composed of two or more chromophores capable of supporting triplet excitation. It is not yet clear whether the very high singlet fission rates observed in crystals can be duplicated in dimers or small oligomers. The information obtained so far is limited and only moderately encouraging, in that the singlet fission yield reported[51] for 1,4-bis(tetracen-5-yl)benzene is less than 1%. However, the chromophores for which singlet fission has been observed so far were all chosen essentially at random, and a targeted search is only just beginning. In the first chromophores designed for the purpose, the various dimers of 1,3-diphenylisobenzofuran, the triplet yield is a few percent,[4,5,52] which is better but still far from the theoretical limit of 200%.

The list of requirements is formidable, and it is intrinsically harder to design a function than a structure. The search for an optimal singlet fission chromophore thus faces uncertain prospects, especially when one considers that the structural factors that determine properties such as the rate of electron injection into the semiconductor, the rate of electron back transfer, the rate of singlet fission, and the rate of triplet−triplet annihilation are understood either poorly or not at all. Yet, the fundamental scientific challenge and the potential practical impact are hard to ignore.

Initial Design Criteria. Presently, we address the issue about which the least is known, namely the rates of singlet fission and its reverse, triplet−triplet annihilation, as a function of sensitizer structure. The separation of the sensitizer into chromophoric subunits could be static, with the two or more weakly interacting substructures well defined already in the ground state, as is the case in the recently studied 1,4-bis(tetracen-5-yl)-benzene[51] and dimers of 1,3-diphenylisobenzofuran.[4,5,52] It could also be dynamic, generated by a molecular distortion in the excited state, as is presumably the case in carotenoids.[48,50] Given that the sensitizer must function while adsorbed on the surface of titania particles, under conditions of limited mobility, it may be better not to rely on its internal motion.

This problem in fundamental molecular photophysics can be formulated as a search for answers to two questions: (i) What are the desirable properties of the individual subunit chromophores, and (ii) what is the optimal structure for their coupling? The present paper addresses the first of these issues.

We start with the assumption that it is desirable for the generation of the two T_1 states to be slightly exoergic starting from the vibrationally relaxed excited state. Although in most of the examples quoted above singlet fission only occurred from a vibrationally hot state and still was competitive, the need to compete against the normally very fast vibrational relaxation was clearly detrimental. Our first requirement thus will be $E(S_1) > 2E(T_1)$ for the vibrationally relaxed state (zero−zero excitation energy). This requirement, meant to ensure a high yield of singlet fission, is not easy to meet, since in most common chromophores the $E(S_1)-E(T_1)$ gap is considerably smaller than the $E(T_1)-E(S_0)$ gap.

The same requirement also assures a low room-temperature rate of T_1-T_1 annihilation to yield S_1 and S_0, since this process is now endoergic. Annihilation could be a very serious problem in dimers and oligomers, in which the triplet excitons cannot diffuse apart as they can in crystals. The annihilation to yield $S_0 + S_0$ is likely to be slow in any event, because it is very exoergic and occurs in the "inverted region" (energy gap law). However, this is not sufficient to guarantee a low yield for T_1-T_1 annihilation, since dephasing of the two triplets formed in the fission process could be fast, and the annihilation of two uncorrelated triplets can also yield an overall triplet or quintet (Q). The annihilation to yield $Q_1 + S_0$ is likely to be strongly endoergic and not much of a concern. T_1-T_1 annihilation to yield $T_1 + S_0$ is again very exoergic and probably slow. However, T_1-T_1 annihilation to yield the next higher triplet, T_2, and S_0 could well be nearly isoergic and very fast. We therefore assume that it is desirable to impose the condition $E(T_2) > 2E(T_1)$, which will guarantee that this annihilation process is endoergic and slow. If T_2 lies above S_1, undesired intersystem crossing from S_1 into the triplet manifold is less likely to be fast, too.

In summary, then, we believe that optimal chromophores should satisfy the highly unusual condition $E(S_1)$, $E(T_2) > 2E(T_1)$. Among chromophores in which singlet fission has been studied in the past, only pentacene crystal satisfies the condition $E(S_1) > 2E(T_1)$. According to our TD DFT/DFT (B3LYP/6-311G**) calculation of excitation energies of an isolated molecule at optimized T_1 geometry, $E(T_1,B_{1u}) = 0.78$ eV and $E(T_2,B_{2g}) = 2.24$ eV, it also satisfies the condition $E(T_2) > 2E(T_1)$. Can other such structures be found at all, even if we leave aside all the other requirements listed above, and how should one go about it?

Theoretical Considerations for Classes of Candidate Structures. The requirement of intense absorption at all wavelengths shorter than a threshold prompts us to focus our search on conjugated systems of π electrons. The simplest quantum chemical description of molecular structure that distinguishes singlet and triplet energies is likely to provide a useful guide, and Figure 1 indicates how one can think of the S_1 and T_1 levels of an actual dye (figure center) expected to inject electrons (C1) or holes (C2) into a semiconductor, in relation to those of some parent structure (figure edge) that does not yet contain all the relevant substituents and/or heteroatoms. The key is to select a parent structure that in itself offers a favorable disposition of the S_1 and T_1 levels, which will then be modified only moderately upon going to the actual dye. The

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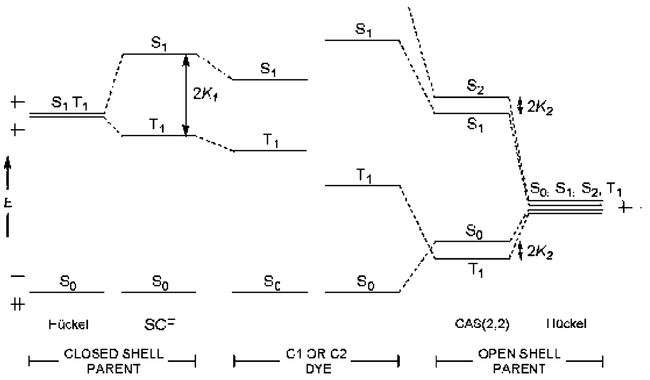

Figure 1. Design of energy levels for singlet fission sensitizers.

relative location of these levels can be estimated starting with the simplest (Hückel) description of electronic excitation (the very edge of the figure) and then introducing the effects of electron repulsion (proceeding toward the center of the figure). Additional modifications may be needed before one arrives at the actual dye (figure center), in order to secure the desired redox potential, adhesion to TiO_2 surface, etc.

Ordinarily, we tend to think of stable closed-shell molecules (e.g., pentacene) as parents of classes of potential dyes, and this case is shown on the left-hand side of Figure 1. We assume that the S_1 and T_1 states of such ordinary molecules can be approximated by excitations from the highest doubly occupied (HOMO) to the lowest unoccupied (LUMO) molecular orbital, even though in the case of S_1 and even some T_1 states exceptions due to strong configuration mixing are known. Even in these exceptional cases, the HOMO−LUMO excited singlet state is usually not very high above S_1. In the Hückel approximation, the S_1-T_1 splitting vanishes, and in the simplest self-consistent field approximation, it is given by $2K_1$ (twice the exchange integral between the HOMO and LUMO). This will be maximized when these two orbitals have large amplitudes at the same atoms in the conjugated system, i.e., in alternant hydrocarbons, such as naphthalene, anthracene, and tetracene (S_1-T_1 differences of 1.3, 1.3, and 1.2 eV, respectively).

In order for $2K_1$ to exceed one-half of the S_0-S_1 energy gap, it is necessary to reduce the S_0-S_1 separation, and the alternant π-electron system needs to be quite large. As noted above, in the polyacene series, this occurs only starting with pentacene, where the S_1-T_1 and S_1-S_0 differences are 1.0 and 1.8 eV, respectively. The requirement of a large size is not detrimental, in that the alternant π system in any event needs to be large before the S_0-S_1 energy gap is reduced to the desired small value of ~2 eV. However, in both the excited singlet and excited triplet manifolds, states may then be spaced fairly closely, and T_2 may not lie above S_1 as desired. As noted above, this is not a problem in pentacene.

The requirement for an alternant structure (no odd-membered rings) for the parent system is then the main outcome of a consideration of the left-hand side of Figure 1. However, it would be desirable to identify additional classes of structures in which there would be a reason to expect not only the S_1-T_1 gap to be large but also the T_2-T_1 gap to be large. One such class suggests itself when one considers a perfect biradical rather than a closed-shell molecule as a point of departure (right-hand side of Figure 1). The highest occupied MO shell of a perfect biradical consists of a degenerate pair of orbitals carrying a total of only two electrons.[53−55] This occupancy produces a triplet and three singlet states, all degenerate in the Hückel approximation, but split as soon as electron repulsion is considered explicitly (the self-consistent two-electrons-in-two-orbitals approximation). Transitions among these four states correspond to intrashell electron promotions and therefore lie at fairly low energies. Typically, T_1 and S_0 are separated by much less than 1 eV, and one or the other is the ground state.

In approximate theory, T_1 lies below S_0 by $2K_2$, twice the exchange integral between the two degenerate orthogonal frontier MOs A and B, selected as the most localized choice. The T_1 and S_0 states are followed at somewhat higher energies by S_1 and S_2. The T_1-S_1 splitting is $2K_{a,b}$, where a,b is the most delocalized choice of real orthogonal orbitals, $a = 2^{-1/2}(A + B)$ and $b = 2^{-1/2}(A - B)$. Other states, including T_2, involve inter-shell excitation and lie at higher energies. As shown in Figure 1, the state order is then exactly as desired, except that T_1 lies too low relative to S_0. Also, perfect organic biradicals are extremely unstable and reactive, and their practical use as chromophores for solar cell sensitizers is unlikely.

However, one could remedy both deficiencies by starting the design of a suitable chromophore with a perfect biradical structure as a point of departure and converting it into a homosymmetric biradicaloid[54] by a structural perturbation that removes the perfect degeneracy of the half-occupied MOs by introducing a resonance integral between the orbitals A and B, and stabilizes S_0 relative to the other states. One can reasonably hope that a strong enough perturbation will position T_1 at just the right distance above S_0 and simultaneously will endow the chromophore with adequate chemical stability. Instead of trying to introduce structural modifications that maximize the S_1-T_1 gap, as was the case starting on the left-hand side of Figure 1, one will now be faced with the presumably easier task of increasing the S_0-T_1 energy gap.

We have thus identified two classes of likely structures: (i) large alternant hydrocarbons, for which the order of S_1 and T_2 might however pose a problem, and (ii) biradicaloids. We note that the first of the proposed candidate classes is not really new, in that it comprises nearly all of the chromophores listed in the Introduction as having exhibited singlet fission in low-lying vibronic levels so far. Although these compounds were originally chosen for study more or less randomly, the resulting "natural" structural selection is clearly not accidental. The absence of any biradicaloid compounds in the list is most likely the result of their very limited commercial availability. We further note that the two classes are not mutually exclusive, as polyacenes have an increasingly biradicaloid character when they get longer.

Computational Search for Groups of Candidate Structures. Once the general range of the search for suitable chromophores has been constrained to some degree, it becomes sensible to evaluate the S_0, T_1, S_1, and T_2 energies of a large number of likely candidate structures very approximately by a computationally simple semiempirical procedure in the hope of finding a group of a few dozen that represent serious candidates for a more thorough evaluation. A suitable choice is the Pariser−Parr−Pople (PPP) method,[56,57] which has pro-

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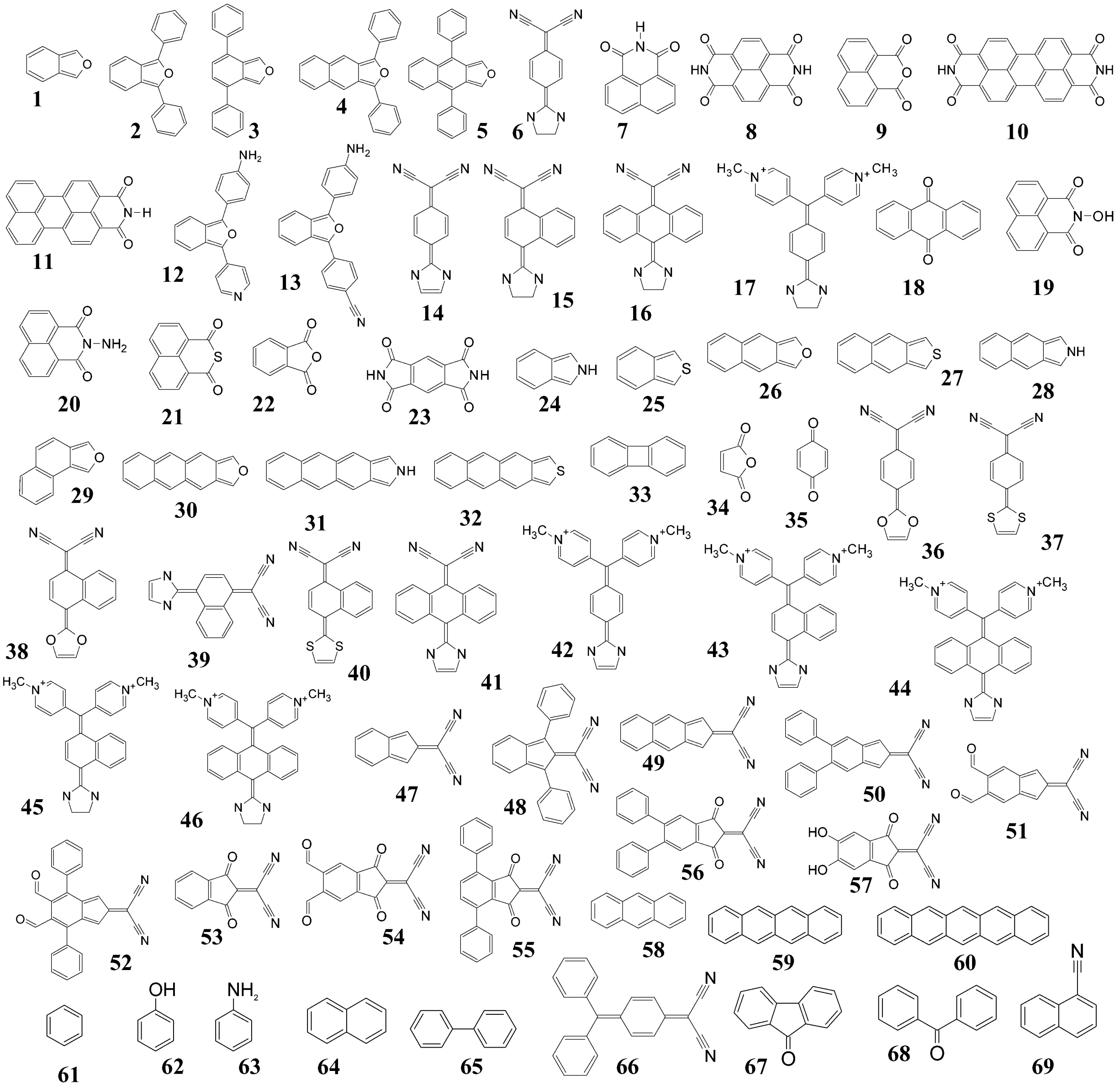
Chart 1. Molecular Structures of Singlet Splitting Chromophore Candidates



duced a vast number of remarkably accurate results over a period of decades and often reproduces excitation energies with errors of the order of 0.1−0.2 eV. In this initial paper, we describe the results obtained from an examination of the first 60 candidate structures (Chart 1).

In addition to a few derivatives of ordinary alternant π-electron systems such as **7**−**11** and the polyacenes, already known to undergo singlet fission, the list contains two groups of compounds derived from biradicals. There are two easily envisaged types of parent perfect π-electron biradicals: [4*N*]-electron annulenes such as the cyclopentadienyl cation (axial biradicals[54]) and systems obtained by a union of an aromatic hydrocarbon with two methyl radicals whose p orbital axes are twisted into the aromatic plane (point biradicals[54]). The former can be converted into biradicaloids by symmetry-lowering distortion and introduction of substituents and heteroatoms (e.g., two $-O^-$ subsituents and a $CH^- \rightarrow O$ replacement convert $C_5H_5^+$ to maleic anhydride, **34**), and this suggests structures such as **35**. The latter can be converted into biradicaloids by twisting the methyl groups to make their p orbitals parallel to the others (in non-Kekulé hydrocarbons such as *m*-xylylene, this is insufficient by itself) and further substitution. This leads to structures of the *o*-xylylene (e.g., **1**−**5**) and *p*-xylylene (e.g., **14**−**17**) types. A more detailed description of the ways in which parent π structures relate to actual molecules can be found elsewhere.[58] Finally, we have included some substituted isobenzofulvenes such as **47**, for which low-lying triplet states are expected on the basis of the work of Ottosson and collaborators,[59] and some structures used for method calibration, such as **61**−**69**.

PPP Calculations. Our application of the PPP method is somewhat more demanding than most, in that we need to consider simultaneously the singlet and triplet manifolds of excited states, and in that we are interested in energies of

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Table 1. Electron Affinity (A_μ) and Ionization Potential (I_μ) of the p-Symmetry Valence AOs Used in PPP Calculations (eV)[64]

element and bonding type	I_μ	A_μ
C	11.42	0.58
N (in C═N)	14.10	1.80
N (in $-\overline{\mathrm{N}}<$)	23.13	9.10
O (in $-\underline{\overline{\mathrm{O}}}-$)	27.17	11.54
O (in C═O)	17.70	2.47
S (in $-\underline{\overline{\mathrm{S}}}-$)	20.00	9.16

Table 2. PPP Adiabatic Excitation Energies from S_0 (eV, Cf. Chart 1)[a]

compd	$E(S_1)$	$E(T_1)$	$E(T_2)$	compd	$E(S_1)$	$E(T_1)$	$E(T_2)$	compd	$E(S_1)$	$E(T_1)$	$E(T_2)$
1	3.8	1.8	3.0	**21**	3.7	2.1	2.3	**41**	2.3	1.3	2.2
2	3.0	1.7	3.3	**22**	4.0	2.3	3.0	**42**	2.3	0.6	2.3
3	3.3	1.8	3.2	**23**	3.6	1.8	2.0	**43**	2.6	1.1	2.5
4	2.6	1.2	2.3	**24**	3.9	2.1	3.2	**44**	2.7	1.4	2.6
5	2.8	1.3	2.8	**25**	3.9	2.3	3.3	**45**	2.6	1.3	2.6
6	2.5	0.8	3.1	**26**	2.9	1.0	2.5	**46**	2.8	1.7	2.7
7	3.6	2.1	3.1	**27**	2.9	1.4	2.8	**47**	0.8	0.2	2.2
8	3.3	1.8	2.9	**28**	2.9	1.2	2.6	**48**	0.7	0.2	1.7
9	3.7	2.2	3.1	**29**	3.7	2.0	2.8	**49**	0.3	−0.4	2.0
10	2.4	1.3	2.6	**30**	2.4	0.6	1.8	**50**	1.1	0.5	1.7
11	2.3	1.4	2.9	**31**	2.4	0.9	2.1	**51**	0.8	0.2	2.0
12	2.9	1.6	2.8	**32**	2.4	0.7	2.0	**52**	0.9	0.3	1.8
13	2.5	1.4	2.8	**33**	2.8	1.8	3.2	**53**	3.7	1.6	3.0
14	2.4	0.7	2.5	**34**	4.2	1.7	2.8	**54**	3.5	1.5	2.3
15	2.5	1.1	2.6	**35**	2.9	1.2	2.1	**55**	3.5	1.9	3.5
16	2.8	2.0	2.6	**36**	2.4	0.5	2.6	**56**	3.2	1.9	2.8
17	1.7	0.3	2.8	**37**	2.2	0.9	2.7	**57**	0.6	−0.9	0.0
18	3.6	2.1	2.9	**38**	2.4	0.8	2.3	**58**	3.4	1.7	3.3
19	3.4	2.1	2.8	**39**	2.3	0.9	2.4	**59**	2.8	1.0	2.3
20	2.4	1.6	2.9	**40**	2.2	1.1	2.5	**60**	2.4	0.7	1.7

Table 3. Observed Energies of Band Maxima[a] and Calculated Vertical Excitation Energies (eV)

	PPP		TD DFT		expt		
compd	$E(S_1)$	$E(T_1)$	$E(S_1)$	$E(T_1)$	$E(S_1)$	$E(T_1)$	solvent
61	4.8	3.1	5.5	3.7	4.8	3.7	nonpolar
62	4.5	2.9	5.1	3.7	4.5	3.5	polar
63	4.2	2.4	4.7	3.6	4.1	3.1	nonpolar
64	3.9	2.3	4.0	2.7	4.0	2.6	gas phase
65	4.6	3.0	5.0	3.3	4.3	2.8	nonpolar
66	2.1	0.1	2.7	0.8	2.5[b]		polar
67	2.8	2.1	3.1	2.5	2.8	2.2	nonpolar
68	4.4	2.7	3.6	2.9	3.3	3.0	nonpolar
69	3.8	2.0	4.1	2.5	4.1	2.5	polar

[a] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Dekker: New York, 1993. [b] Naya, S.; Yoda, K.; Nitta, M. *Tetrahedron* **2004**, *60*, 4953.

geometrically relaxed excited states. We have relied on the procedures and parameters of Pancíř and Zahradník.[60,61] After some experimentation, we have adopted the following procedure.

Molecular orbitals are calculated for the single-determinant closed-shell ground state S_0 by the self-consistent-field method, and the energy of this state is adopted as the energy zero. Interaction of all configurations singly excited with respect to S_0 is considered in the calculation of the S_1 and T_1 energies. Interaction of all triplet configurations singly excited with respect to the HOMO−LUMO excited triplet configuration is considered in the calculation of T_2 energy.

Geometries calculated by molecular mechanics minimization with the Universal Force Field[62] in the Maestro program[63] were used in the evaluation of electron repulsion integrals. The core integrals β_{rs} were taken all equal to −2.318 eV in the initial SCF calculation of the S_0 state, with the exception of the C≡N bond, $\beta_{rs} = -3.0$ eV.[64] In order to crudely mimic the effect of bond length variation, core integrals were made a function of the bond order β_{rs} in the particular state that is being calculated, S_0, S_1, T_1, or T_2: $\beta_{rs} = -2.318 \exp[0.335(p_{rs} - 2/3)]$. The bond order p_{rs} was obtained from a calculation with the initial set of core integrals (no iteration). In addition, core integrals for all exocyclic C−C bonds similar to that in biphenyl were reduced according to their twisting angle, θ, by multiplication with cos θ.

The electron affinity and ionization potential needed for the evaluation of one-center repulsion integrals are listed in Table 1. Two-center electron repulsion integrals were calculated from one-center integrals using the Mataga−Nishimoto formula[65] in singlet calculations and the Dewar−Ohno−Klopman formula[66−68] in triplet calculations.

Adiabatic (zero−zero) excitation energies between S_0 and another state are obtained as averages of vertical excitation energies calculated with the core integrals appropriate for the S_0 state and those calculated with the core integrals appropriate for the excited state. This is equivalent to assuming that the destabilization of the ground state and the stabilization of the excited state that occur upon going from the equilibrium geometry of the ground state to that of the excited state are equal. This would be the case if their minima in the potential energy surfaces were displaced but their shapes were the same. Clearly, one could improve the PPP procedure further, but we felt that this was not necessary for the intended fast survey.

Excitation energies obtained with the PPP method for compounds **1**−**60** are presented in Table 2. For most of the chromophores investigated here, the relationships between the singlet and triplet excitation energies we calculated follow the behavior anticipated from qualitative arguments quite well. Derivatives close to fulfilling the energy level requirements desired for singlet fission, $E(T_2) \geq E(S_1) > 2E(T_1)$, are those of isobenzofuran (**2**−**5**, **12**, **13**) and *p*-xylylene (**6**, **14**−**17**) but also some derived from perylene (**10**, **11**). Also promising, but apparently requiring further tuning, are the derivatives of isobenzofulvene (**47**−**57**). The T_1 values for many of these compounds are close to the desired value of ∼1 eV. While the crude nature of the method of calculation does not guarantee the desired level order for any of the compounds chosen, the results in Table 2 provide many useful hints for experimental work.

TD DFT Calculations. Evaluated on a fairly random set of π-electron systems, the performance of the DFT/TD DFT method is comparable to that of the PPP in calculating excitation energies of π-electron systems (Table 3). The experimental excitation energies listed correspond to band maxima, and the

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Table 4. TD DFT and PPP Excitation Energies for **1**−**11** (eV)

	TD DFT			PPP		
compd	$E(S_1)$	$E(T_1)$	$E(T_2)$	$E(S_1)$	$E(T_1)$	$E(T_2)$
1	3.6	2.0	3.8	3.8	1.8	3.0
2	2.7	1.4	3.1	3.0	1.7	3.3
3	3.0	1.8	3.4	3.3	1.8	3.2
4	2.0	0.9	2.6	2.6	1.2	2.3
5	2.3	1.1	3.1	2.8	1.3	2.8
6	3.0	1.5	3.3	2.5	0.8	3.1
7	3.4	2.3	3.2	3.6	2.1	3.1
8	3.0	2.0	2.8	3.3	1.8	2.9
9	3.6	2.3	3.3	3.7	2.2	3.1
10	2.3	1.2	2.7	2.4	1.3	2.6
11	2.5	1.4	2.9	2.3	1.4	2.9

comparison therefore is with single-point excitation energies obtained without any geometry relaxation.

The search at the PPP level identified four groups of structures whose T_1, S_1, and T_2 levels appeared at suitable energies relative to S_0 (Table 2). We felt that using two approximate methods would be better than using a single one, and for structures **1**−**11** we have optimized the S_0 and T_1 state energy and geometry with the DFT method (all Hessian matrix eigenvalues were positive). Optimized excited-state energies for S_1 and T_2 states were calculated using time-dependent density functional theory (TD DFT).[69] These calculations were performed at the B3LYP[70] level, with the SV(P) basis set,[71] using version 5.6 of the Turbomole[72] program.

The results are presented in Table 4. For most compounds, the values obtained using TD DFT are within 0.3 eV of those obtained with the PPP calculations, and we conclude that the much faster PPP method is appropriate for a search over a very large number of compounds.

One of the few structures for which the PPP and TD DFT results are significantly different is the benzoquinodimethane derivative **6**, for which the T_1 values differ by 0.7 eV. In the optimization of the singlet excited state, TD DFT performed poorly for this compound in that it consistently predicted double bond twisting and immediate return to the ground state, whereas in reality the compound is known to fluoresce in room-temperature solution, although with a small yield.[73] In order to obtain a TD DFT result for **6**, we constrained the dihedral angle between the five-membered and the six-membered rings to zero.

Consideration of Selected Structures. The PPP excitation energies of two of the promising groups of structures, the *o*-xylylene derivatives **1**−**5** and the *p*-xylylene derivatives **6**, **15**, and **16**, are compared with the target intervals for singlet fission chromophores in Figure 2.

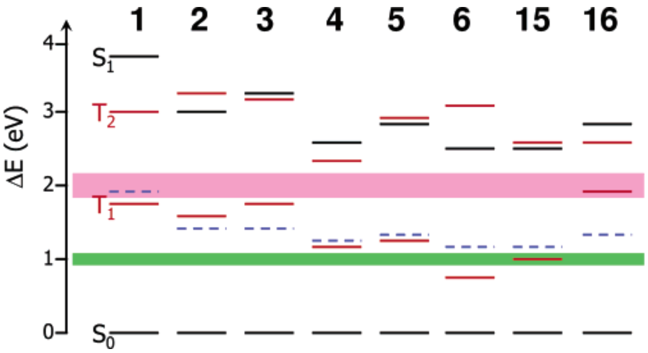

Figure 2. Excitation energies for isobenzofurans **1**−**5** and *p*-quinodimethanes **6**, **15**, and **16**. Solid black lines, S_0 and S_1; solid red lines, T_1 and T_2; dashed blue lines, $E(S_1)/2$; pink and green bands, target S_1 and T_1 ranges, respectively.

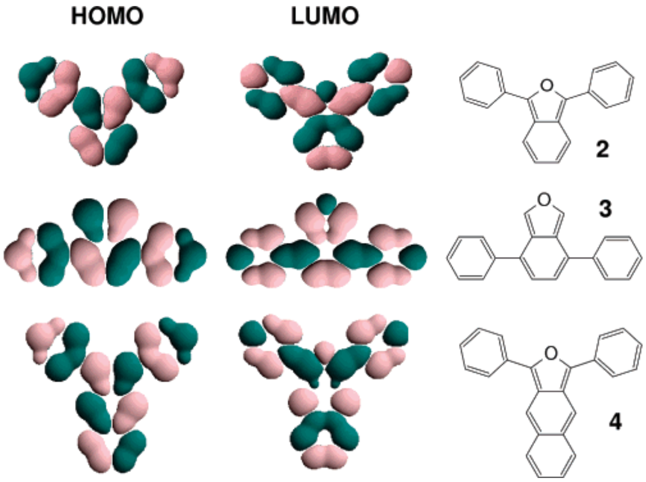

Figure 3. PPP HOMO (left) and LUMO (center) of structures **2**−**4** (right).[74]

***o*-Xylylene Derivatives.** Isobenzofuran (**1**) has $E(T_1)$ close to $E(S_1)/2$, but the values are significantly higher than the range desired and $E(T_2)$ is lower than $2E(T_1)$. Adding two phenyl rings in the 1,3 positions to produce the derivative **2** reverses the order of S_1 and T_1 and reduces the S_1 and T_1 energies somewhat. In the isomer **3**, the effect of the added phenyl substituents is smaller, at least in part because increased steric repulsion causes the phenyl substituents to be more strongly twisted. In the ground state, the twist angles are 23° in **2** and 45° in **3**. The frontier orbitals for the chromophores **2**, **3**, and **4** are shown in Figure 3. We also have examined many related structures (**12**, **13**, **24**−**32**).

In the PPP approximation, the S_1 state in the chromophores **1**−**5** is well described as the HOMO-to-LUMO transition, but in the T_1 state this configuration contributes only about 65%. Introduction of another condensed ring (**4**) moves the singlet and triplet excitation energies into the desired range. In general, the *o*-xylylene derivatives appear to be about as suitable for singlet fission studies as the already well examined tetracene and pentacene. The degree of perturbation of the parent biradical is apparently just a little too high, and as a result $E(S_1)$ is very close to $2E(T_1)$. These structures are of interest to fundamental studies of singlet fission but are probably too fragile to be of eventual practical utility. We have already prepared a few dimers of **2** and will report their photophysics elsewhere.[5,52]

Isobenzofulvene Derivatives. These structures are a special type of *o*-xylylene derivatives. The rationale for expecting them to have low T_1 energies has been discussed recently[59] and will not be repeated here. In the PPP approximation, a structure such as **47** has a HOMO localized on the six-membered ring and has a fully delocalized LUMO. The S_1 state is described essentially exclusively, and the T_1 state to the extent of ∼70%, by the HOMO−LUMO excitation. They have considerable charge-transfer character.

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(74) Density cutoff at 10^{-4}. Plotted with the Orbital Viewer program [http://www.orbitals.com/orb/ov.htm].

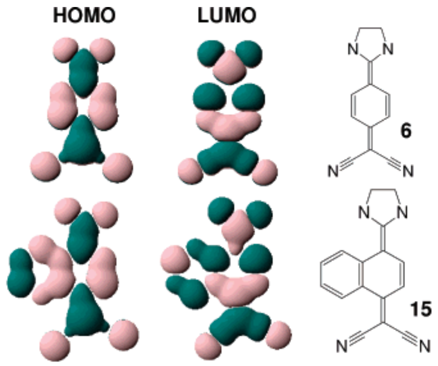

Figure 4. PPP HOMO (left) and LUMO (center) of structures **6** and **15**.[74]

***p*-Xylylene Derivatives.** In **6**, **15**, and **16** (Figure 2), we have chosen a donor/acceptor substituent combination to stabilize the parent biradical and simultaneously provide the T_1 state with some charge-transfer character, likely to be helpful for electron injection into TiO_2. Compounds **36**−**46** are similar, and the cations **42**−**46** are designed for absorption on TiO_2.

The energy levels computed for the simplest compound chosen, **6**, are positioned nearly perfectly. Condensation of additional rings raises the calculated T_1 energy to an optimal value in **15** and far too much in **16**, while S_1 is not greatly affected. The increased excitation energies in **16** are in part due to steric repulsion by the hydrogen atoms on the aromatic ring, which push the substituents on the central ring out of plane. Ring annelation lowers the energy of the second excited triplet state in an undesirable fashion.

Frontier orbitals for the structures **6** and **15** are shown in Figure 4. In the PPP approximation, the S_1 state of **6**, **15**, and **16** is represented by nearly pure HOMO-to-LUMO excitation, whereas T_1 is only 50−70% due to the HOMO → LUMO configuration.

A potential source of trouble with these molecules is double bond twisting in the excited state, which is suggested by the DFT results for **6**, and which could provide an efficient path for radiationless decay. We are currently examining a few of these *p*-xylylene derivatives experimentally.[5,73]

Perylene Derivatives. The cyclic imides **10** and **11** come close to meeting our requirements and have the advantage of great thermal and photochemical stability. In the PPP approximation, the S_1 state is of HOMO−LUMO character essentially exclusively, whereas the T_1 state has that character only to the extent of ∼60%. This class of compounds also appears worth experimental attention.

Conclusion

The purpose of the present study was to introduce the notion of a singlet-fission sensitizer into the discussion of Grätzel cell efficiency and to identify a few chromophores that would be suitable for an experimental testing of the concept and a practical demonstration of the notion that chromophore structures for singlet fission sensitizers can be designed in a rational fashion. We did not address the issue of optimal coupling of pairs or larger aggregates of such chromophores into actual sensitizers, nor the subsequent issues of redox level tuning, electron-transfer kinetics optimization, etc. The next obvious immediate theoretical task is a search for optimal coupling structures.

Simple concepts of quantum theory have proven useful as a guide for the identification of likely classes of structures in our search for the highly unusual arrangement of the lowest two singlet and lowest two triplet energies that is believed to be conducive to singlet fission in a dimer or an aggregate. Perhaps surprisingly, quite a few candidate structures have been identified in addition to the one already known (pentacene), and this suggests that the presently proposed use of perfect biradicals as parent structures has merit. A definitive verification of our claim that biradicaloids represent suitable starting points cannot be provided by the approximate PPP and DFT calculations presented here but has to await the synthesis of these compounds and an experimental determination of their T_1, S_1, and T_2 excitation energies.[5,52,73] A final proof of the utility of the present concepts will require the synthesis of dimers or oligomers in which these chromophores are suitably coupled, and actual detection of singlet fission. Then, there will still be a long way to practical systems, considering for instance the sensitivity of many of the presently considered systems to the combination of light and oxygen (pentacene, diphenylisobenzofuran).

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Supporting Information Available: Energies and optimized geometries of DFT-calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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