

Final Progress Report

Project Title: "Exciton Fission for an Ultra-high Efficiency, Low Cost Solar Cell"

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Project Objective: Our ultimate objective is the fabrication of a photovoltaic cell that is inexpensive and highly efficient. The immediate goal is to demonstrate that the conversion efficiency in a molecule-based photovoltaic cells can be increased by the use of sensitizers capable of singlet fission, a process in which the absorption of a single photon leads to the generation of two excited molecules and, in the end, creation of two electron-hole pairs under conditions that permit their collection in the form of a photocurrent.

Background. Power conversion efficiency is a critical parameter to maximize in any photovoltaic (PV) cell, because it is inversely proportional to the cost of electric power (\$/kWh). 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/m². Since module efficiencies are only about 2/3 that of the individual cells, the cell efficiency has to be about 45% to meet the above power cost goal.

Maximal thermodynamic efficiency for the conversion of unconcentrated solar irradiance into electrical free energy in the radiative limit, assuming detailed balance, a single threshold absorber, thermal electron-phonon equilibrium, and a maximum photocurrent quantum yield of one, is ~31% (the Shockley-Queisser limit). This applies also to the conversion to chemical free energy. This is attainable in semiconductors with bandgaps of ~1.25 to ~1.45 eV. In this analysis, a major factor limiting the efficiency is the loss of absorbed photon energy above the absorption threshold as heat through non-radiative decay (such as electron-phonon scattering) as the carriers relax to their respective band edges. The main present approach to reduce this loss and increase efficiency above 31% is to use a stack of cascaded multiple p-n junctions in the absorber with bandgaps better matched to the solar spectrum. This is effective, but expensive. In the limit of an infinite stack of bandgaps perfectly matched to the solar spectrum, the ultimate conversion efficiency at one-sun intensity increases to about 66%.

We proposed to develop cells of a type suggested by Nozik and collaborators, based on singlet fission (SF). This is the molecular analog of multiple exciton generation in semiconductor quantum dots (QDs). Other approaches to exceed the 31% limit include hot carrier solar cells, solar cells producing multiple electron-hole pairs per photon through impact ionization, multiband and impurity solar cells, and thermophotovoltaic/thermophotonic cells.

Theoretical analysis showed that SF cells could in principle achieve an improvement of efficiency by a factor of about 1.5 above the Shockley-Queisser limit by using the high energy photons of the solar spectrum to create two electron hole pairs per absorbed photon. This principle is applicable generally, e.g. to all-organic photovoltaic cells, but the cell proposed in this specific proposal is related to the dye-sensitized solar "Graetzel" cells, which have been investigated for many years, and whose efficiency is now ~10%. Their operation is based on photoexcitation of sensitizer molecules bonded to the surface of nanocrystalline TiO₂, present as a porous thin film (10 - 20 μm) on a transparent electrode in a photoelectrochemical cell containing a non-aqueous I₃⁻/I⁻ redox electrolyte. The sensitizers have an excited state redox potential more negative than the potential of the TiO₂ conduction band, allowing for energetically favorable electron injection from the excited dye into the TiO₂ nanoparticles. The injected electrons move freely in the TiO₂ conduction band, percolate through the TiO₂ 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 I₃⁻ 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.

The presently proposed cell (Figure 1) also contains a sensitized nanocrystalline TiO₂ electrode, but it incorporates two sensitizers, C₁ and C₂. Light first passes through a layer containing the sensitizer C₁, which absorbs the high energy photons of the solar spectrum (ideally, 2.2 – 3.8 eV) and generates two electrons per photon, and then through a layer containing the sensitizer C₂, which absorbs the lower energy photons (ideally, 1.1 – 2.2 eV) and produces one electron per photon, as in present Graetzel cells. The maximum thermodynamic efficiency of such a cell is ~46%.

A major reason to propose work with the Graetzel cell to demonstrate the SF advantage, rather than another cell type, is that it offers us an opportunity for a smooth

transition from the lab bench to an initial prototype, using the close informal connection between the University of Colorado and the National Renewable Energy Laboratory (NREL) in Golden, Colorado. At NREL, there is ample experience with the fabrication of Graetzel type cell prototypes and we will be able to take advantage of it once we have developed a suitable sensitizer.

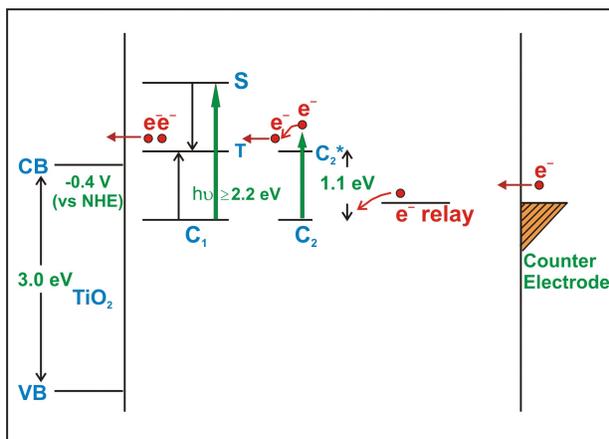


Figure 1. Working scheme of a cell operating with an SF sensitizer C_1 and an ordinary sensitizer C_2 .

Work Accomplished since Start of Current Project In the first quarterly report, we described progress on the development of experimental procedures for the preparation of thin layers and nanocrystals of 1,3-diphenylisobenzofuran (**1**) and of instrumentation for their characterization. We also described progress on the synthesis of oligomers of **1** and the results of a theoretical evaluation of the strength of inter-chromophore coupling in a large series of covalent dimers.

In the second quarterly report, we reported a successful completion of the effort to develop suitable protocols for the production of thin film samples, and a completion of the construction of a triplet-triplet absorption spectrometer in the Michl laboratory at CU Boulder, analogous to the one available in the Nozik laboratory at NREL. Further work with nanocrystals was postponed, awaiting the completion of this construction. The results of the study of the strength of inter-chromophore coupling were written up for publication. We also completed the remaining spectral characterization of the three dimers of **1** that was necessary for publication. Work on new types of chromophores continued. A previously identified chromophore of the *p*-benzoquinodimethane type turned out to have a low fluorescence quantum yield, presumably because of twisting around a double bond, and synthetic work started on the preparation of a rigidified derivative. A series of new types of chromophores was examined theoretically for suitability in SF. Two families, related to alizarin and indigo, respectively, showed sufficient promise for an experimental investigation; synthetic work on them was started. Finally, two theoretical studies of SF dynamics for a simplified model containing ten electronic states built by excitations involving only the HOMO and the LUMO on each chromophore in a dimer were completed. In the first one, coherent dynamics, and in the other, non-coherent dynamics in a dimer were considered, and general propensity rules for efficient SF were derived.

In the third quarterly report, we described how we managed to overcome reproducibility problems in studies of films of neat solid 1,3-diphenylisobenzofuran (**1**) when we discovered that on a particular face of a sapphire crystal high quality films can be deposited in a consistent manner. The singlet fission yield of 160% could then be produced at will. The new steady state photomodulation apparatus at Boulder was modified to permit measurements on samples immersed in liquid nitrogen. We measured the fluorescence quantum yield of aggregates of **1**. While micelles containing monomeric **1** have a fluorescence quantum yield of unity, which is comparable to **1** in solution, the nanosized aggregates have a fluorescence quantum yield of only ~10%, presumably because singlet fission now intervenes. The new long-lived suspected excited quintet state in the *p,p*-coupled covalent dimer of **1** was further characterized. A

TD-DFT calculation of the quintet-quintet absorption spectrum was performed and was found to be in excellent agreement with the spectrum observed for this intermediate, but additional control experiments remained to be done before publication of this highly unusual result. Also, in order to find the origin of the perturbations that permits spin decoherence on a ps time scale, we initiated the synthesis of suitable precursors for a fully deuterated form of this dimer. The [2,2]cyclophane-type dimer of **1** synthesized in the previous reporting period was found to be unstable with respect to a thermal interconversion between positional isomers, suggesting that the doubly benzylic bonds break easily. We decided that this made this dimer a poor candidate for an effective singlet fission material and stopped work with it. The inter-chromophore coupling in the *p,p*-coupled red dimer of **1** is clearly too strong and lowers the S_1 excitation energy below twice the T_1 excitation energy, thus reducing the triplet yield from singlet fission to only 3%. The two more weakly coupled yellow dimers also investigated earlier do not suffer from this problem, but the coupling in them is too weak to bring about any detectable singlet fission during S_1 lifetime. We previously performed DFT calculations needed for estimating intra-dimer coupling strength and now performed a synthesis of the *m,m*-coupled dimer, expected to display a coupling of intermediate strength. We synthesized three derivatives of indigo that are likely to be light-fast and for which calculations suggested a favorable energy level arrangement (indigo itself is non-fluorescent and unsuitable for our purposes since it clearly has a very efficient path for rapid electronic relaxation). All three dyes had their observed S_1 absorption edge in the optimal region (~ 2 eV) and the DFT calculated excitation energy near 1 eV for T_1 and above 2 eV for T_2 as desired. The measured fluorescence quantum yields were disappointing for two of them, only a few % at most, making their dimers unlikely to undergo singlet fission with a reasonable yield. We found that the third one (Cibalackrot) has a much higher fluorescence quantum yield, with the initial measurement indicating a value of at least 30%. It is worthy of continued investigation.. PPP calculations for a series of covalent dimers of Cibalackrot have produced very promising results. Finally, the Ratner group at Northwestern University, in close collaboration with the Michl group in Boulder, explored the nature of exciton fission in molecular chromophore pairs theoretically. It was assumed that the chromophores are weakly coupled by a tunneling matrix element, corresponding to the connecting covalent bond. A 2-electron/2-orbital representation on each of the molecules yielded 70 possible states for the 4-electron/4-orbital problem. Three sorts of analysis were done: the energetics and the tunneling matrix elements for three families of molecular chromophores were calculated: **1**, polyacenes, and *p*-xylylenes. We characterized the dependence of the mixing matrix elements on the nature of the bonding, on the length of the bond, and on the position of the bond within the delocalized chromophore. Formal analysis gave constraints on the efficiencies: the energetic constraints were the most severe, and if the coupling between the two sites was too strong, the resulting orbital splitting made the energetic criterion (triplet energy less than half of excited singlet energy) unapproachable. Dynamical studies were performed in two different limits: the fully coherent limit of electron tunneling without any dephasing or decoherence from the environment, and a pure Marcus rate limit, in which each independent occupation of the most significant of the 70 determinants was considered a state, and there was no coherence in the mixings.

In the subsequent quarter, the writing of two papers has been completed and they were submitted for publication. Much work on an invited comprehensive review article on the subject of singlet fission was also accomplished. The Boulder

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photomodulation apparatus was further improved by the addition of additional optical elements and elimination of a background signal in the electronics. Fluorescence quantum yield was remeasured for Cibalackrot and the final value is 98%, making this chromophore very promising for further work. DFT geometry optimizations on a series of dimers of **1** revealed singlet and triplet excitation localization in the weakly coupled dimers and delocalization in the strongly coupled *p,p*-coupled dimer. This may be related to the occurrence of singlet fission in the latter but not the former. Calculations were also performed on a series of quintet excited states as models for the double triplet states reached by singlet fission.

A lengthy synthesis of a perdeuterated analog of the red *p,p*-coupled dimer of **1** was attempted but failed and will have to be repeated. A new *m,p*-coupled dimer of **1** with an intermediate calculated coupling strength has been synthesized successfully, and both the *m,m*-coupled and the *m,p*-coupled dimers have been examined by our collaborators at NREL using steady-state and time-resolved spectroscopy. The fluorescence quantum yields in toluene were 0.83 and 0.85, respectively. In DMSO, the yields for both dimers were 0.15, and it is possible that charge-transfer takes place and dipolar species form, as they do in the weakly coupled dimers of **1** investigated earlier. The T_1 - T_n absorption spectra were determined by sensitization and found to be very similar to those of these earlier studied weakly coupled dimers, including triplet lifetimes on the order of 200 μ s. The yields of triplets were determined by comparison with sensitized solutions and found to be: 0.13 and 0.09 (*m,p* dimer in DMSO and toluene, respectively) and 0.08 and 0.02 (*m,m* dimer in DMSO and toluene, respectively). Investigation of the fs-ns excited state kinetics of these dimers has revealed the S_1 - S_n spectrum, the likely presence of a polar intermediate, and singlet excited state lifetimes. Global analysis of the data with an expanded data set is underway and is expected to reveal the charge transfer rates and yields and triplet formation times.

The spectroscopic properties of the red *p,p* dimer of **1** were investigated in further detail, with special attention to the characterization of the novel excited quintet state. In spite of considerable effort, we are not yet ready to claim this unusual result in public. Current efforts are focused on eliminating the trivial possibilities of aggregation or impurity being responsible for the unusual behavior. Careful studies of the temperature dependence of the decay of the suspected quintet into the by now well characterized triplet revealed that it is activated with $E_a = \sim 0.6$ kcal/mol, $\log A = 4.9$ (A in s^{-1}) while the triplet decay has $E_a = \sim 0.2$ kcal/mol, $\log A = 3.8$. Studies of the kinetics of decay of the suspected quintet as a function of concentration showed that rate depends approximately linearly on concentration of ground state molecules and approaches the decay rate of the triplet at the lowest concentrations ($< 5 \mu$ M), at which point the triplet no longer accumulates to a significant degree. The quenching of the putative quintet state of the dimer by the ground state dimer produces its triplet (only one triplet molecule per molecule of the quintet). Further development of a global analysis routine has produced a clearer picture of the excited state processes and has generated spectra associated with particular species (presumed quintet, triplet, and ground state singlet bleach). All of these spectra, including that of the presumed quintet, agree well with the results of TD-DFT calculations.

Finally, our collaborators at Northwestern University have further elaborated their dynamical simulations of fission within the 4-electron/4-orbital model. The nature of the phase correlations is surprising and important: under certain conditions, increasing the amplitude of mixing between the initially excited singlet and a charge transfer

intermediate can slow down the fission process and reduce the fission yield. Similarly, if the actual injection from a localized single molecule triplet into the semiconductor is too fast, that can actually decrease the relative fission yield. These and other observations can all be understood based on a steady-state analysis. We think this contribution is actually the first of its kind, and that it suggests important design criteria for the isolated molecular chromophores.

In the subsequent quarter, a second computational paper was completed and submitted. It dealt with the investigation of the effect of coupling strength on the energetics of singlet fission in a series of dimeric chromophores. Two of the three papers have now appeared in *J. Phys. Chem.* and we have just returned the proofs of the third one. Work on the invited review article on the subject of singlet fission has advanced further.

Another paper, dealing with the photophysics of two weakly coupled dimers prepared in our laboratory, advanced considerably. Our collaborators at NREL performed a refined analysis of spectroscopic data for extraction of rate constants, thermodynamic quantities, and spectra of the photoexcited species. We attempted to include a study of fluorescence polarization in an effort to obtain information on the degree of excitation delocalization in the dimer, but a simple interpretation has been thwarted by the existence of several spectrally overlapping conformers of the dimers, which greatly complicates the results.

Work on thin solid films of 1,3-diphenylisobenzofuran (**1**) was continued by our NREL collaborators. Various thermally evaporated film types have been characterized by X-ray diffraction patterns and UV-VIS absorption spectra, and the results suggest that the sensitivity of the results to deposition conditions is due to the existence of two conformers, present in the polycrystalline material in different proportions. The fluorescence quantum yield of the films was measured to be ~10% at room temperature, contrasting with the ~100% yield for the isolated molecules of **1** in solution, and compatible with efficient and highly competitive singlet fission. Thickness of films for spectroscopic analysis (roughly 75 nm) and thus molar absorption coefficients (similar to those of the monomer in solution, peaking near $25000 \text{ M}^{-1} \text{ cm}^{-1}$ at $22\,500 \text{ cm}^{-1}$) were measured. Kinetics of triplet, excited singlet, and ground state bleach formation and decay have been measured from 18 K to 295 K. Kinetics suggest that the formation of triplet on a 5 - 50 ps time scale is mirrored by an increase in ground state bleach, thus providing independent evidence for singlet fission. Triplet quantum yields in the highest quality films were measured to be near 120% at room temperature, and up to 160% at 18 K. Measurement of triplet quantum yield was found to be complicated by the discovery of a new excited state transition centered at $23\,300 \text{ cm}^{-1}$, which appears to be due to the triplet. This transition could be specific to the crystalline material or could be a transition to a higher lying triplet state that is only noticeable at low temperature. Such a state is actually predicted by our TD-DFT calculations. Accurate determination of the triplet quantum yield requires investigating this transition in more detail because it overlaps significantly with the ground state bleach, which is used to scale the triplet and singlet populations.

Another new strongly coupled dimer of **1** was synthesized (1,4-bis-(3-phenyl-1-benzisofuranyl)benzene).

A sample of Cibalackrot (**2**) was provided to our NREL collaborators for adsorption on TiO_2 and an investigation of possible sensitizing action. An attempted

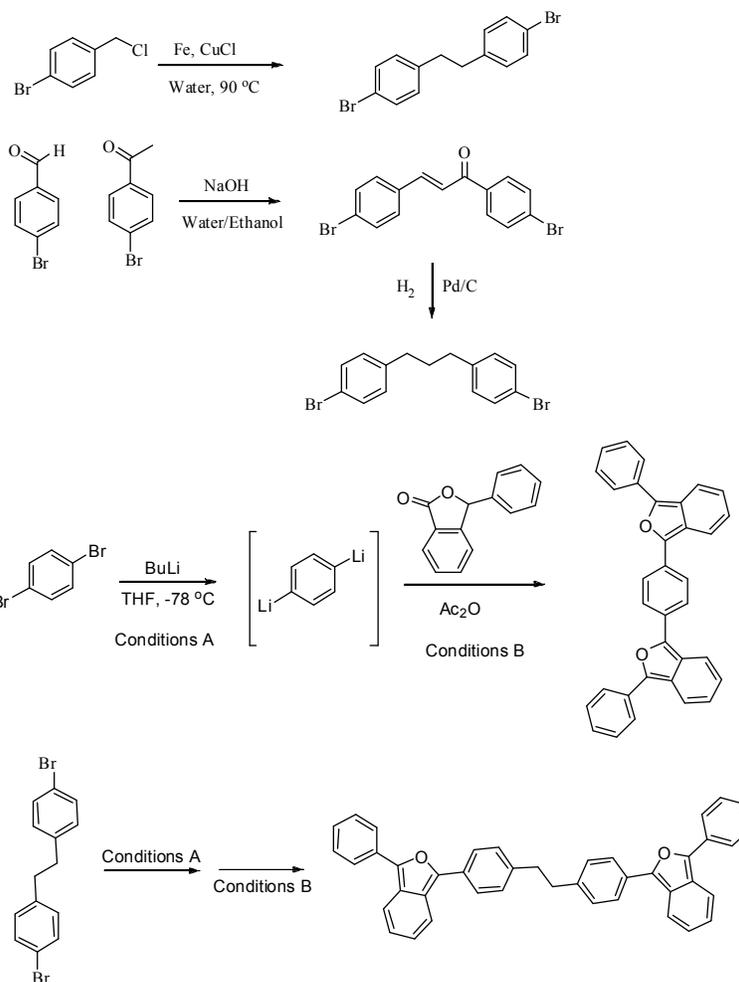
synthesis of the dimer of this chromophore failed. As noted previously, its absorption edge is located nearly perfectly for our purposes, but electrochemical studies revealed that its one-electron reduction and oxidation potentials (determined only approximately because of irreversibility) are not ideal for loss-free injection of electrons and holes into common semiconductors. We performed calculations of substituent effects and they suggested that in suitably donor-substituted derivatives the HOMO and LUMO energies could be adjusted to optimal values, thus providing a remedy for the situation.

The most tantalizing aspect of the continuing experimental work on the photophysics of the strongly coupled dimer of **1** is the possibility that the mysterious long-lived intermediate is its excited quintet state. We invested considerable effort into eliminating other possibilities. In particular, a minor impurity (< 1%) not detectable by NMR was detected by fluorescence and has properties expected for a product of partial air oxidation. We looked for ways to remove it in order to eliminate the possibility that it is responsible for the observed mystery signal, and are now nearly satisfied that it is not. A definitive proof that the signal is due to an excited quintet state would be provided by a measurement of its EPR spectrum. Ultimately, a characterization of zero-field splitting tensors of our chromophores will be needed in any event, and these results would be useful for the formulation of a separate research proposal.

In the theoretical arena, after the completion of two manuscripts on the topic of the simplified models for the dynamical analysis of SF, considerable progress has been accomplished on a third. In this study a more realistic mixture of quantum and classical dynamics is used. It starts from the Marcus approach, but uses coherence within the determinants, and rate constant decay away from the determinants.

In the following quarter, two isobenzofuran covalent dimers were designed and synthesized, as shown in Scheme 1. Further synthetic progress was however halted abruptly when our laboratory was closed down for nearly three months by a fire that damaged two of the hoods. It is only now that we have been able to resume synthetic work.

At the time when synthesis could not be done, we concentrated our efforts on the construction of an EPR



Scheme 1. Synthesis of covalent dimers.

setup that should allow us to detect the putative excited quintet state of a strongly coupled dimer of 1,3-diphenylisobenzofuran (**1**), the first of its kind in an organic molecule. This is now almost complete, but unfortunately, the EPR bridge went back to the manufacturer for repairs and no measurements could be made.

Further, we concentrated on the completion of a solicited review article on singlet fission that now has well over 100 references and will represent a comprehensive description of the state of the art in singlet fission. During work on this article, we performed a thorough theoretical analysis of singlet fission that has helped us to understand the contrast between the very high efficiency of singlet fission in crystals such as tetracene and **1** and the very low efficiency of singlet fission in covalent dimers of the same chromophores. There are two contributions to singlet fission, one based on the matrix element of the two-electron part of the Hamiltonian (in a crystal, a direct exchange interaction of a singlet excited state of a molecule with its neighbor), and the other, requiring two successive applications of the one-electron part of the Hamiltonian (in a crystal, mixing of the initial excited singlet state with the double triplet state via a charge-transfer exciton in which an electron has been transferred from a molecule to its neighbor). We have analyzed qualitatively the structural dependence of the exchange matrix elements involved and believe that it accounts for the dramatic difference between the singlet fission yields in crystals and the covalent dimers studied so far. We have used the resulting understanding to design covalent dimers of a new type that we expect to undergo efficient singlet fission, similar to that in crystals.

We have also applied the newly acquired understanding to the theoretical analysis of the behavior of those covalent dimers of **1** in which the exchange contribution is likely to be negligible but the charge-transfer contribution is facilitated by the use of a highly polar solvent. In such solvents, singlet fission could take place by the charge transfer mechanism in two separate kinetic steps, with a dipolar charge-transfer structure as a real intermediate. This advance provided insight into the otherwise puzzling results obtained by our NREL collaborator, Dr. Justin Johnson, for one of our covalent dimers in DMSO at elevated temperatures (400 K). Under these conditions, global fitting to ultrafast transient absorption data revealed that the initial excited singlet state is in fast equilibrium with a dipolar species, consisting of a radical cation in one and radical anion in the other half of the dimer. This equilibrium is established in about 0.2 ns. The dipolar intermediate is equilibrating on a slower time scale (2 ns) with a state whose absorption carries a T-T signature but whose energy is about twice that of the triplet. This presumably is the doubly excited quintet state of the weakly coupled dimer. If confirmed by further work, these results will represent the first direct observation of two-step singlet fission.

Dr. Johnson has also advanced the study of thin solid films of **1** over a large range of temperatures and established the conditions under which very high triplet yields are obtained (up to 160%).

Previous theoretical work with our collaborators at Northwestern used a simplified model in which singlet fission dynamics in the configuration space of a four-level, four-electron system occurs due only to the charge-transfer (tunneling, not exchange) mechanism. This model was analyzed both in the fully coherent limit (no interaction with the environment) and in the Marcus rate-constant limit (all electron hopping fully incoherent and following rate laws). This work is being generalized to the case in which the loss of phase within the electronic excitation manifold is neither total

nor absent, but rather occurs on reasonable time scales (from tens of fs to tenths of ns) depending on the systems and on their environments. The reanalysis of the fission process in dimers uses a relaxation model in which the loss of phase occurs due to an interaction with a bath described by colored noise. This allows a smooth transition between the limits previously analyzed, and more importantly, it will allow proper modeling of the full dynamics. The next theoretical challenge will involve simultaneous consideration of both singlet fission mechanisms, exchange and charge transfer.

Progress was also made in the investigation of Cibalackrot (**2**), whose calculated excited states are at 2.22 eV (S_1), 1.04 eV (T_1), and 2.39 eV (T_2). The value calculated for S_1 agrees with experiment but the triplets remain to be measured. Its electrochemical oxidation was found to be reversible in liquid SO_2 solvent (1.39 V vs. SCE). This should give its excited singlet state a driving force of 110 mV for injection of an electron into TiO_2 . In fact, an experiment at NREL revealed very a low but observable efficiency as a singlet sensitizer. The low efficiency is attributable to a very low concentration of material adsorbed on TiO_2 , which was barely pink. This could be remedied by installing carboxyls or similar groups on the dye molecule. However, from our point of view there is a more serious problem: if the calculated triplet energy is right, the triplet is too low in energy by about 1 eV for efficient injection of an electron into TiO_2 . According to our calculations, the placement of a dimethylamino substituent into the two para phenyl positions will reduce this deficiency by about 0.5 eV. Further structural modifications will be needed, or perhaps another semiconductor. The calculations suggest that SnO_2 would work.

In the next quarter, we reported advances on several fronts. In collaboration with Dr. Justin Johnson at NREL, all the polarization corrections for the analysis of triplet-triplet absorption and ground-state bleaching on thin films of **1** have been completed and this week we are submitting a short communication to *J. Am. Chem. Soc.*, announcing the highest triplet yield from singlet fission ever reported from a direct observation. While the previously reported highest yields were 20-30% (for natural aggregates of carotenoids in the light harvesting center), our yields for a thin film of **1** range up to ~150% (for a compound specifically designed for singlet fission; the exact number depends on temperature). This means that we have met the go/nogo milestone of the first phase of our project and provides a verification of the efficacy of the design principles that we have derived. It instills confidence that their future application will ultimately result in a practically useful material. A full paper on these results is under preparation. They include observations of polymorphism in the thin films of **1**, with different types of film giving very different triplet yields. This requires a more detailed structural study and promises to provide information on the role of the details of crystal structure on the rate of singlet fission.

Further, we have finally succeeded in purifying the directly coupled dimer of **1**, bis(*p,p'*-1,3-diphenylisobenzofuran), from traces of a tenacious fluorescent impurity present in such small amounts that it was not detectable by NMR. The impurity was observable as a shoulder in the fluorescence emission spectrum. As a result, the fluorescence excitation spectra differed when monitored at different wavelengths. Disappearance of the shoulder in the fluorescence emission spectrum as well as emission wavelength independence of fluorescence excitation spectra confirmed the purity of the sample. The previously observed long-lived species that we propose to assign to an excited quintet appears equally strongly in the fully purified sample and it is clearly not due to this impurity. After considerable trouble with instrumentation repairs,

first the EPR spectrometer and then the cryostat, we are now finally measuring EPR spectra of this sample in the hope of observing the characteristic spectral signature of a quintet state. If this is successful, we will be able to publish this remarkable result with confidence.

High temperature dynamics study in weakly coupled dimers of **1** has been completed and revealed indirectly that in this case a quintet state is being formed as well, in a two-step singlet fission process. These results are ready to be published.

Photophysical studies of Cibalackrot (**2**) were continued and we developed a procedure for producing continuous thin films of 35 nm thickness.

In the following quarter, we continued work with our collaborators at NREL. A thorough investigation of the temperature dependence of the triplet quantum yield in a thin film of 1,3-diphenylisobenzofuran on sapphire showed that it is well above 100% at all temperatures between 12 and 300 K and reaches a maximum of $200 \pm 30\%$ at 77 K. In the whole temperature range, the rate constant for triplet formation by singlet fission is constant and the variation of the quantum yield is due to the temperature dependence of various other competing processes. The directly observed time constants for the first-order disappearance of the initially excited singlet state S_1 , the appearance of the triplet state T_1 , and the concurrent reduction of the amount of ground state S_0 are all equal (25 ps), in perfect consonance with expectations for the singlet fission process, $S_1 + S_0 \rightarrow 2 T_1$. A short communication on these results has been submitted to *J. Am. Chem. Soc.* They represent a proof of principle for our concept that it is possible to use theoretical considerations to design both a chromophore structure (biradicaloid) and chromophore coupling (slip-stacked monomers) in a way that leads to completely efficient singlet fission. The next obvious tasks will be (i) elaborating and perfecting the structural design guidance principles and applying them to produce sensitizer dyes that are not only perfectly efficient in singlet fission, as our initial model compound is, but also have all the other necessary attributes for practical utility, such as high lightfastness, which is relatively rare for organic materials, and (ii) figuring out how to assure that each of the two triplets formed undergoes an efficient charge separation step. In the time that remains in the present contract, we plan to focus on item (i), whereas item (ii) will be the subject of a renewal proposal that we plan to submit in the next academic year if a proposal solicitation is issued by DOE.

Several new results have been obtained jointly with our partners at NREL as a part of continuing work on item (i). We have obtained steady-state photophysical data on the two new dimers whose synthesis is described and structures presented above in the lower part of Scheme 1.

One of these new dimers (bottom in Scheme 1) contains the two 1,3-diphenylisobenzofuran units linked with a $\text{CH}_2\text{-CH}_2$ unit and provides an opportunity for a dynamic behavior, with the two chromophores stretched apart in the ground state and stacked in an excimer-like geometry. In acetonitrile, the extinction coefficient of the first transition, located at $23\,980\text{ cm}^{-1}$, is $4.7 \times 10^4\text{ M}^{-1}\text{ cm}^{-1}$, about twice the value for the monomer, as expected for a very weakly coupled dimer, and the fluorescence quantum yield is ~ 0.50 . In chloroform, it rises to ~ 0.90 , suggesting the involvement of charge transfer similar to that in the already thoroughly studied dimer with a single CH_2 link. There is no strong indication of excimer emission, and we plan to synthesize a dimer linked with a $\text{CH}_2\text{-CH}_2\text{-CH}_2$ unit, known to be geometrically more favorable for excimer formation.

The other new dimer is actually not a dimer strictly speaking, since the two monomers share one of the phenyl substituents. In this structure, shown above the first new dimer in Scheme 1, the coupling between the chromophoric units is expected to be strong, and this is indeed reflected in its steady-state properties. In acetonitrile, the extinction coefficient of the lowest energy absorption peak, located at 24150 cm^{-1} , is $\sim 3.7 \times 10^4\text{ M}^{-1}\text{ cm}^{-1}$, and the fluorescence quantum yield is 0.95. Time-resolved experiments on both of these dimers are planned.

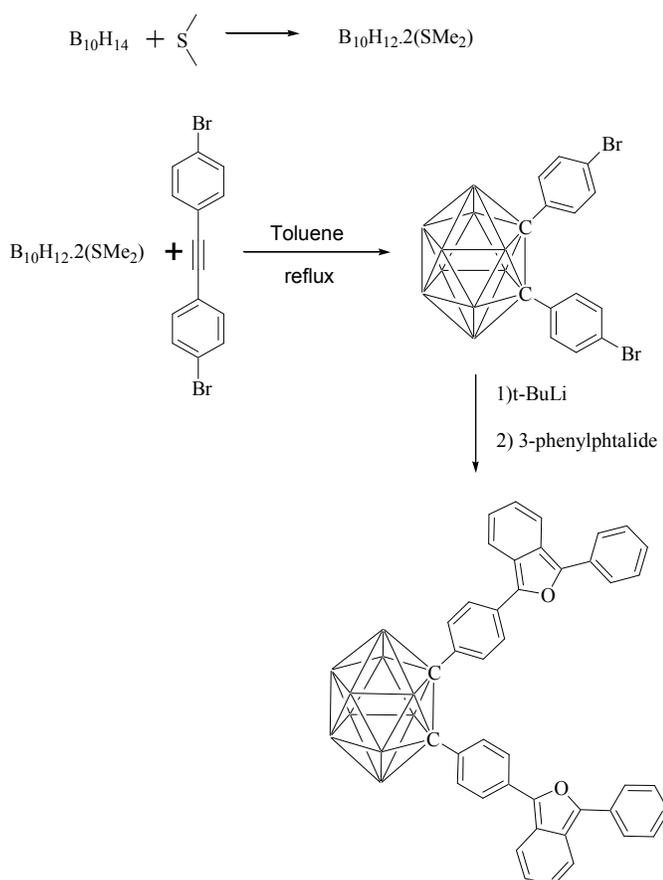
In order to explore further the structural space of dimers of our model chromophore, we have synthesized the dimer shown in Scheme 2, in which the chromophores are held stacked but not parallel, in a form reminiscent of a wedge. In addition to through-space interaction, in this dimer the two chromophores may also interact in a through-bond fashion via the carborane cage. The carborane itself does not absorb above 200 nm and is expected to represent a more or less inert linker.

We have also spent considerable effort on detecting EPR spectra of triplets of model aromatics in preparation of a serious search for the EPR signals of the suspected quintet state of the directly coupled dimer of 1,3-diphenylisobenzofuran. Details of the experimental procedures have been worked out.

We continued our work on polishing two manuscripts. One is a major review article on singlet fission for *Chemical Reviews*, in which the section on pentacene required a substantial revision in light of the

publications that appeared most recently in the literature. The other describes our results on weakly coupled dimers of 1,3-diphenylisobenzofuran, where we are not yet satisfied with the kinetic analysis of the high-temperature data and with the analysis of the density functional theory calculations of the excited states.

The next quarter was very exciting. The short communication in *J. Am. Chem. Soc.* in which our NREL collaborators and we describe a 200% triplet yield by singlet fission in a thin layer of 1,3-diphenylisobenzofuran, appeared, and was placed on the list of most significant papers by the journal (I have received requests to write an article for SPIE Newsletter and a Perspective for *J. Phys. Chem. Lett.*). The comprehensive review article in *Chemical Reviews* has also appeared. The positive response to its publication has prompted Dr. Justin Johnson of NREL and myself to organize a



Scheme 2. Synthesis of a wedge-stacked dimer of 1,3-diphenylisobenzofuran.

workshop on Singlet Fission, to take place at the Marriott hotel in Golden, CO, on May 9 and 10. All major groups in the world active in the area have signed up for participation.

Work on completing the analysis of experimental and computational data for a full article on singlet fission in weakly coupled dimers of 1,3-diphenylisobenzofuran continued and is nearly finished. Work on a similar article dealing with singlet fission in strongly coupled dimers is not far behind, but some experimental data are still missing. In particular, the issue of two long-lived states, presumably one triplet and one quintet, has not yet been settled to our satisfaction. We have tried very hard to find emission from one or both of these states in a 2-methyltetrahydrofuran glass in the region of the calculated S_0 - T_1 transition, but no phosphorescence signal was observed. A long-lived luminescence observable by eye following intense broad spectrum irradiation was attributed to delayed fluorescence. In the matrix, intense overlapping photoinduced EPR signals of two species, one of them assignable to the triplet state, can now be observed easily. The EPR signal of the other species looks like that of a triplet also, and more work is underway to reach a definitive assignment.

In another development, the fluorescence polarization and fluorescence

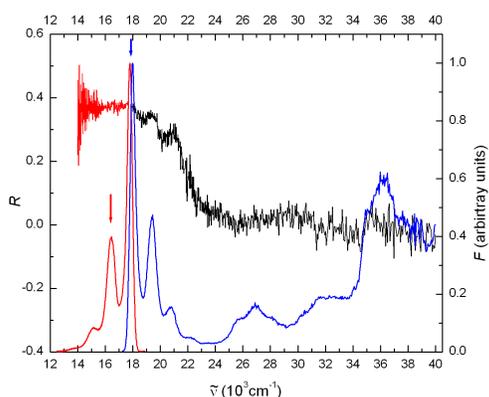


Figure 2. Spectra of Cibalackrot. Blue: absorption. Red: fluorescence and fluorescence anisotropy. Black: excitation anisotropy.

excitation polarization spectra of Cibalackrot in a 2-methyltetrahydrofuran glass were measured as a part of an effort to obtain full understanding of its excited electronic states (Figure 2). The triplet rise-time for Cibalackrot in benzene solution was examined by flash-photolysis using a 5 ns pump pulse. While the triplet reaches its maximum at 30 ns, additional analysis using a fs pump pulse is required to properly fit the data and determine the rise-time. The EELS operating program has been updated to work with the recently upgraded electronics, and we are currently working toward measurements to determine the first triplet energy of Cibalackrot.

A new pentacene derivative, 2,2,10,10-tetraethyl-6,14-bis-(tetrabutylethynyl)-1,3,9,11-tetraoxa-dicyclopenta[*b,m*]pentacene, has been synthesized. This readily soluble pentacene is expected to be more stable than native pentacene.

Progress was also made on the theory front by the group of our collaborator Mark Ratner. Previously, it was assumed that no system/bath interaction would provide decoherence processes that might either aid or hurt the efficiency of the exciton fission process. Ratner's group (doctoral student Danny Powell, Postdoctoral Nicolas Renaud, and Research Fellow Yuri Berlin) have now spent time examining decoherence processes, which could be important at two points. (i) Once the fission process is completed and (in the four-electron, four-level picture) the configuration shown as A in Figure 3 is obtained, decoherence is necessary to produce two independent triplets, one with $m_s = 1$ and one with $m_s = -1$. This process can be aided by spatial separation through diffusion, but in bridged dimeric structures, decoherence is necessary. (ii) The initial double tunneling process that goes from the photoexcited state (S_1S_0) via a virtual charge-transfer state to the state A involves two tunneling processes (if the one-

electron, as opposed to two-electron, part of the Hamiltonian governs the evolution). Here, decoherence might well destroy the process, because the tunneling intermediates might not be attainable.

We have designed a model based on our earlier results using a simple Redfield-type decoherence picture, and are now evaluating the effects of decoherence. Preliminary results seem quite promising – not much decoherence is really necessary for the state A to break up into the two separated triplets, and that is good news. The formation of state A by the tunneling model seems to some extent robust to dephasing, but we are not yet sure about relaxation terms.

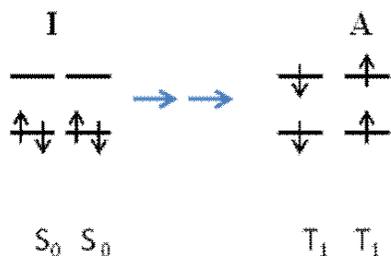


Figure 3. The configurations I and A in the singlet fission process (see text).

In the following quarter, we continued with the preparation of a workshop on singlet fission to be held in Golden, CO, on May 9-10. Over two dozen participants actively engaged in the study of singlet fission have registered. The article for SPIE Newsletter has been completed and submitted.

Work on a full paper describing the photophysics of weakly coupled dimers of **1** continued. The constrained DFT calculations that we have performed suggested that the transformation of the charge-separated species to another short-lived species with a similar spectrum at high temperatures could be due to intermolecular charge transfer to a ground-state dimer, resulting in a radical cation and a radical anion of the weakly coupled dimer. Our collaborators at NREL have started to test this possibility by examining the effect of ground state concentration of the dimer solution.

The photomodulation apparatus built in the Boulder laboratory was re-configured and is now working very well for the red dimer of **1** and for other samples. When we tried to use it on nanocrystals of **1**, however, we found that even with a nanocrystal sample from freeze-pump-thaw degassed THF injected into Ar-bubbled aqueous solution, the excitation source used in the photomodulation experiment proved to be too intense, and the particles were destroyed rapidly, probably due to reaction with residual oxygen. Freeze-pump-thaw cycles on water will be necessary although this may be tricky. Also, we will try to find another poor solvent to use that is easier to work with than water.

Considerable progress was made with Cibalackrot. We have obtained an X-ray structure on a tiny single crystal (on the LBL cyclotron) and used it to analyze the XRD powder pattern obtained on thin films. As a result, we now know the orientation of the crystallites on a quartz substrate: their (011) plane is parallel to the surface. Now, if the moment directions of the S_0 - S_n and T_1 - T_n transitions were known, we could evaluate the effect of film anisotropy on the observed transient triplet absorption and transient ground state bleaching, and evaluate the absolute triplet yield from the apparent yield of 45%. We tried hard to obtain the absolute transition moment directions experimentally, but failed to dissolve enough of the compound in stretched polymers. We have therefore

turned to theory and used the TDDFT method to obtain these data. It is encouraging that the relative polarization directions for S_0 - S_n transitions agree very well with our polarized fluorescence excitation data. The computation of the T_1 - T_n transition moments is now almost complete.

We have continued our efforts to observe phosphorescence from the second long-lived intermediate in the strongly coupled red dimer of **1** but even in a rigid solution saturated with xenon gas no emission was detected.

In the group of our collaborator at Northwestern, programming for calculations of decoherence in the singlet fission process using the stochastic surrogate Hamiltonian approach is now underway.

In the next quarter, the workshop on singlet fission took place on May 9-10 within the framework of our collaboration with NREL. It was financed from other sources. It went smoothly and was very useful. The participants agreed to set up a world-wide informal network for exchange of information on singlet fission.

Work on a paper on two weakly coupled 1,3-diphenylisobenzofuran dimers was brought to near completion. Our collaborators at NREL have continued the study of temperature and concentration dependent transient absorption spectra of the weakly coupled 1,3-diphenylisobenzofuran dimer **3** in DMSO. It was however not clear whether the unique decay channel observed at higher temperatures is concentration dependent and could be due to an intermolecular charge transfer from a dipolar state of one dimer molecule to the ground state of another. An extensive data set has been collected and was being analyzed.

Computational work on the issue of intermolecular charge transfer has been nearly completed. The geometries of the radical cation and radical anion of the dimers **2** and **3** were optimized at the level of B3LYP/SVP (TURBOMOLE). The optimized geometries were subjected to single point energy calculation in the presence of a COSMO dielectric ($\epsilon = 46.7$) at the level of B3LYP/SVP (NWChem). The results showed that the charge and spin localize on one half of the dimer and are consistent with the calculations performed previously for the monomer **1**. The results for the energies of these species are collected in the following table:

Species	Gas phase relative energies (kcal/mol) ^a	Solvated relative energies (kcal/mol) ^a
2 (ground state)	0.00	0.00
2 (^{•+} , ^{•-})	96.03	65.67
2 (^{•+})	133.88	110.84
2 (^{•-})	-25.20	-54.44
3 (ground state)	0.00	0.00
3 (^{•+} , ^{•-})	85.78	60.64
3 (^{•+})	133.68	110.53
3 (^{•-})	-24.58	-54.81

The question of whether singlet fission occurs in nanosized crystals of 1,3-diphenylisobenzofuran is of interest for their possible use as sensitizers on TiO₂ nanoparticles. We have made progress in the synthesis of these nanoparticles in solution, characterization of their size, and measurement of their triplet excited state spectra using photomodulation. The synthesis uses the standard reprecipitation method, in which the compound is dissolved in a good solvent and then injected into a

rapidly stirring poor solvent (water). The resulting suspension of particles is degassed by freeze-pump-thaw cycles. The UV-visible spectrum of the reprecipitated sample is broadened and red shifted from the spectrum of the monomer. Two differently shaped spectra have been observed which we believe represent the two conformers that we reported previously for films of this compound. Dynamic light scattering (DLS) is used to assess particle size. 1,3-Diphenylisobenzofuran is very sensitive to oxygen and sufficient removal of oxygen levels needed for sample stability under irradiation has been a challenge. So far, no excited state spectrum from this sample has been successfully taken due to the degradation of the sample when irradiated.

Also work on a publication on singlet fission in Cibalackrot has progressed. We now have computational (TD-DFT) results for both S_0-S_n and T_1-T_n transition moments and oscillator strengths from Zdenek Havlas, our collaborator in Prague, and have examined these with respect to observed spectra and experimentally determined molecular orientation in the thin film. It appears that a correction will need to be made for the roughly 45% triplet quantum yield that resulted from the simplest assumption of parallel singlet and the true value of triplet yield from singlet fission will be closer to 60 - 70%. The setup for angle-dependent transient absorption experiments has been optimized and will now be used for additional thin film measurements on Cibalackrot, which will aid in finalizing the triplet quantum yield.

Cibalackrot nanocrystals have also been prepared. This compound offers a larger number of choices of poor solvent for the reprecipitation method than does 1,3 diphenylisobenzofuran, and methanol was chosen. The UV-visible spectrum was broadened as expected for small particles. A triplet-triplet spectrum of the cibalackrot monomer in solution was recorded, with triplets being produced by intersystem crossing. A triplet-triplet spectrum which was similar in shape but blue shifted by about 15 nm was recorded for the sample made by the reprecipitation method. DLS measurements will be important to determine particle size.

Our collaborators at Northwestern University have continued their theoretical work on singlet fission, specifically on decoherence properties within the singlet/triplet/quintet manifold of the initial excited state, and its time evolution. Using the stochastic surrogate model, they have shown that the analysis within this extended manifold is quite sensitive to the overall exoergicity of the step from the S_1S_0 to the (TT) components. With too large an exoergicity, there is an effective "reflection" of density, and the final fission efficiency drops. This result is still preliminary, but if true, it could have major implications on the selection of chromophore candidates for singlet fission. In a sense, this result is in agreement with the so-called "inverted regime" in electron and exciton transfer that was introduced by Marcus a half century ago. In both situations, the energy released by the electronic or excitonic motion must be accepted by the vibrations and polarization degrees of freedom. If the energy released is too large, the process rate is reduced strongly.

Work Planned for this Quarter: In collaboration with our partners at NREL, we have completed our investigation of the nature of the previously mysterious additional dipolar intermediate observed for the weakly coupled dimer **3**, but not for the otherwise very similar dimer **2**, at elevated temperatures. This was achieved by comparison with the independently obtained spectra of the radical cation and radical anion of **3**, secured on our samples by Dr. John Miller, a collaborator at Brookhaven National Laboratory who performed pulse radiolysis. The results showed unambiguously that this putative intermediate actually is a 1:1 mixture of $3^{(+)}$ and $3^{(-)}$, formed by a fairly unusual intermolecular electron transfer between the intramolecular charge transfer state $3^{(+,-)}$ and the ground state of **3**. The results are in very good agreement with the results of calculations at geometries of the radical cation and radical anion of **2** and **3** that were optimized in the presence of solvent. They show that the intermolecular charge transfer is energetically favorable for **3** but unfavorable for **2**. What remains to be attempted is a determination whether the transformation of the intramolecular dipolar intermediate $3^{(+,-)}$ into the triplet of **3**, which is the only process observed at ordinary temperatures, and a similar transformation of $2^{(+,-)}$ into the triplet of **2**, occur by intersystem crossing or as a second step of singlet fission. This determination requires an accurate count of the triplets formed upon the disappearance of one molecule of $3^{(+,-)}$ or $2^{(+,-)}$, which would be one if intersystem crossing occurs and two if singlet fission occurs. This measurement is very difficult due to the low overall triplet yield, and it is now being attempted by our NREL collaborator, Dr. Justin Johnson. We are waiting with the publication of our results for **2** and **3** until this last piece of information can either be obtained or found to lie beyond the reach of present technology. Since stepwise singlet fission has never been observed before, this would be a significant result.

The publication of our extensive results on singlet fission in a thin layer of Cibalackrot has also been postponed, since a re-examination of its transient absorption spectra at higher sensitivity revealed the presence of a previously unsuspected additional intermediate whose nature remains to be established. This might perhaps be an ion pair and measurements of the absorption spectra of the radical cation and radical anion of Cibalackrot by pulse radiolysis are being planned at Brookhaven. This result does not affect the validity of our previous conclusion that triplet is formed by singlet fission in an about 70% yield, but it may help to complete our understanding of the fate of the molecules that do not form triplets. We know that some of them fluoresce. The yield of fluorescence increases dramatically as temperature is lowered, suggesting that the observed stabilization of the S_1 state by Davydov splitting moves its excitation energy below that of twice the triplet excitation energy in the solid, even though it is above in the isolated molecule. The situation is being clarified by a combination of triplet sensitization measurements in solution, intended to determine the triplet excitation energy by bracketing, and EELS measurements on a thin layer of the solid.

Work with the strongly coupled red dimer of **1** focused on the nature of the second long-lived intermediate. We have been attempting to measure and interpret its EPR spectrum, and need the EPR of triplet **1** first. This has proven to be elusive, since

the steady-state EPR spectrum, whose measurement we are set up for, must be obtained in the absence of molecular rotation. In high-viscosity media sensitizer diffusion is suppressed and triplet sensitization is inefficient. Intersystem crossing in **1** is too slow to produce any observable triplet, even in a glass saturated with xenon. We are now building an apparatus that should permit the observation of EPR of triplet **1** in a xenon matrix, in the hope that it might be formed under these conditions.

The study of nanocrystal formation from **1** and from Cibalackrot has proceeded apace. A reliable protocol for the synthesis of these particles has now been established. Those of **1** are produced by injection of a solution in an organic solvent such as THF into water and their size has been established by dynamic light scattering as ~50 nm across. Complete removal of oxygen sufficient for guaranteeing photostability turned out to be difficult and the measurement of triplet-triplet absorption spectra of these particles using the photomodulation apparatus constructed in Boulder is now being carried out in a flow cell constructed for the purpose. Particles of Cibalackrot are produced by injection into methanol and in this case the determination of particle size is not yet complete.

Finally, Prof. Mark Ratner, our subcontractor at Northwestern University, has made considerable advances in understanding the effects of decoherence and environmental parameters on the rate of singlet fission. In a paper that is about to be submitted, he and a postdoc, Dr. Nicolas Renaud, use the stochastic surrogate Hamiltonian approach to simulate relaxation and decoherence using a non-perturbative density matrix approach and a Slater determinant basis set in a simple quantum mechanical model for singlet fission. The coherent competition between the two-electron direct process and the one-electron indirect process is addressed specifically and a counter-intuitive decrease in triplet yield is predicted when the two-electron coupling term strength is increased. Interesting environmental effects on triplet yield are predicted.

Significant Accomplishments This Period: The nature of the high-temperature intermediate formed in polar solvents from **3**, but not from the otherwise very similar **2**, has been established by a combination of experimental and computational work. A new transient intermediate has been identified in a thin film of Cibalackrot, but its nature is presently not understood. Procedures for nanocrystal formation and characterization have been optimized. Theoretical understanding of the quantum mechanical nature of the singlet fission process has been enhanced.

Status:

Task 1. Predict a batch of new SF chromophore structures. This has been done.

Task 2. Synthesize a selected new SF chromophore. This has been done.

Task 3. Set up and test equipment for triplet-triplet absorption measurements at CU Boulder. This has been done.

- Task 4:** Predict new sensitizer chromophore structures. This has been done.
- Task 5:** Develop a density matrix formalism for singlet fission. This has been done.
- Task 6.** Synthesize new singlet fission sensitizers suggested by the theoretical work. This has been done.
- Task 7.** Synthesize a new chromophore. This has been done.
- Task 8.** Develop procedures for aggregate formation and photophysical characterization. This has been done.
- Task 9.** Predict new sensitizer structures. This has been done.
- Task 10.** Synthesize new sensitizers. This has been done.
- Task 11.** Synthesize new chromophore. This has been done.
- Task 12.** Preparation of suitable aggregates. This has been done.
- Task 13.** Write Marcus theory code for singlet fission. This has been done.
- Task 14.** Synthesize new sensitizers. This has been done.
- Task 15.** Finalize aggregate formation procedures. This has been done.

Patents: None.

Publications/Presentations/Travel:

Schwerin, A. F.; Johnson, J. C.; Smith, M. B.; Sreearunothai, P.; Popović, D.; Černý, J.; Havlas, Z.; Paci, I.; Akdag, A.; MacLeod, M. K.; Chen, X.; David, D. E.; Ratner, M. A.; Miller, J. R.; Nozik, A. J.; Michl, J. "Toward Designed Singlet Fission: Electronic States and Photophysics of 1,3-Diphenylisobenzofuran", *J. Phys. Chem. A* **2010**, *114*, 1457.

Greyson, E. C.; Vura-Weis, J.; Michl, J.; Ratner, M. A. "Singlet Fission in Organic Dimers: Maximizing the Triplet Yield in the Regime of Localized Excitation and Fast Coherent Electron Transfer", *J. Phys. Chem. B* **2010**, *114*, 14168..

Greyson, E. C.; Stepp, B. R.; Chen, X.; Schwerin, A. F.; Paci, I.; Smith, M. B.; Akdag, A.; Johnson, J. C.; Nozik, A. J.; Michl, J.; Ratner, M. A. "Singlet Exciton Fission for Solar Cell Applications: Inter-Chromophore Coupling", *J. Phys. Chem. B* **2010**, *114*, 14223.

Johnson, J. C.; Nozik, A. J.; Michl, J. "High Triplet Yield from Singlet Fission in a Thin Film of 1,3-Diphenylisobenzofuran", *J. Am. Chem. Soc.* **2010**, *132*, 16302.

Smith, M. B.; Michl, J. "Singlet Fission", *Chem. Rev.* **2010**, *110*, 6891.

Michl, J.; Johnson, J. C.; Nozik, A. J. "Toward Photocurrent Enhancement by Singlet Fission" SPIE Newsletter, published online Jul. 12, 2011, <http://dx.doi.org/10.1117/2.1201106.003755>.

Oral presentations of the results were made at the Fordon Research Conference on Photochemistry at Easton, MA, (July 10 - 15), at a WATOC satellite meeting in La

Coruna in Spain (July 23-24), at the ACS National Meeting in Denver, CO (Aug. 28-31), and at the ISTCP-VII meeting in Tokyo, Japan (Sept. 2-8).

Status Summary Tables:

Attached.