Michael T. Colvin

Northwestern University
Department of Chemistry
2145 Sheridan Road
Evanston, IL 60208
Ph: (847) 491-4855
Email: m-colvin@northwestern.edu

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Summary of work while a Link Energy Fellow

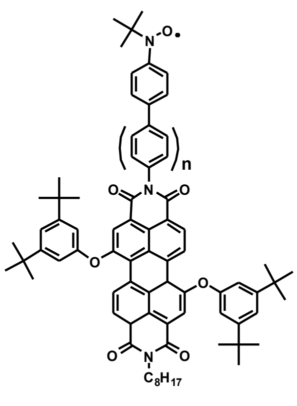
Introduction: Electrons have an intrinsic property called spin, which is found in one of two states, an "up" and a "down". The spin state of an electron can be observed and differentiated by applying an external magnetic field and inducing transitions with microwaves. The bulk of my graduate work has focused on *understanding, controlling, and transferring* spin information in molecular systems in the presence of light. If we can understand and transfer spin information it could be used for quantum computing which could revolutionize computing and information processing. This undertaking is difficult and at this point remains largely unexplored in organic molecular systems, requiring fundamental understanding how spin evolution occurs in molecular systems, how to impart information into these systems and direct its movement. We have chosen to examine stable organic free radicals covalently attached to chromophores, and donor-bridge-acceptor systems which undergo charge separation upon photoexcitation. In addition to my main project I have also been involved in several other projects: examining how bridge dynamics affects charge separation, recombination, and triplet-triplet energy transfer in donor-bridge-acceptor systems, understanding how the redox state of a molecule can induce motion along the backbone of a molecule. My research have or will result in 4 first author, and 8 co-author papers during the duration that I was a Link fellow, which are listed at the end of this summary. Several more first author and co-author publications should result within the next year from projects begun while a Link fellow.

I. Enhanced Intersystem Crossing in doublet-triplet systems

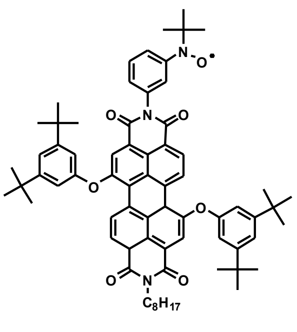
One of the requirements for spintronic applications to be useful is to have a large portion of the spins in either the “up” or “down” state, which is commonly called polarization. Polarization in a system can result from transitions induced by microwave pulses, or by quantum mechanical effects as a result of mixing between two or three electrons.[1-7] We explored how polarization evolves in three spin systems, where two unpaired spins reside on the same molecule, a triplet, while the third resides on a separate part of the molecule, a doublet. It has been known for several decades that mixing between triplets and doublets results in polarization that is unmatched by the polarization from microwave pulses. These interaction have largely been studied in solution based systems where the triplet and doublet diffuse towards each other.[7] However, the interaction between triplets and doublets had not been explored in rigid systems that would be required in real world systems, that would be in the solid state.

A. *Ultrafast Enhanced Intersystem Crossing in Radical Chromophore Systems*

We have studied how the presence of a stable radical results in ultrafast intersystem crossing from the singlet state of an organic chromophore to produce highly spin polarized quartet and doublet states. For these experiments we employed a chromophore based on perylene-3,4:9,10-bis(dicarboximide) (PDI). This chromophore has a fluorescence quantum yield approaching unity[8] and essentially a zero quantum yield of triplet formation by ordinary spin-orbit induced intersystem crossing (SO-ISC).[9] This makes the PDI molecule ideal for



1 (n=0), 2 (n=1)



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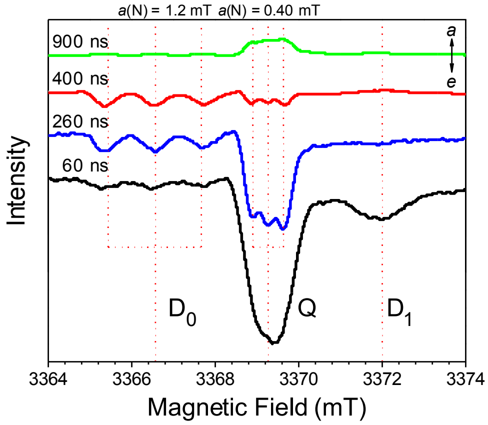
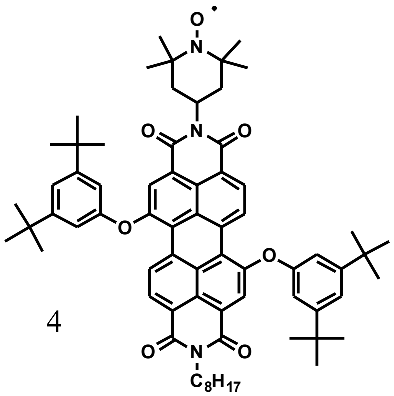


Figure. 1. W-band TREPR spectra of **1** in toluene at 295K following a 7 ns, 532 nm laser pulse.

studying other mechanisms of intersystem crossing leading to polarized high-multiplicity states. These states have well-defined initial polarizations, an initial condition that is critical for their potential application in the development of spintronic devices. Time-resolved transient optical absorption and EPR (TREPR) spectroscopies are used to probe the interaction of ^{1*}PDI with a stable *t*-butylphenylnitroxide radical (BPNO$^{\bullet}$) at specific distances and orientations. The BPNO$^{\bullet}$ radical is connected to the PDI with the nitroxide and imide nitrogen atoms either *para* (**1**) or *meta* (**3**) to one another, as well as through a second intervening *p*-phenylene spacer (**2**). Transient absorption experiments on **1-3** reveal that ^{1*}PDI undergoes ultrafast enhanced intersystem crossing (EISC) and internal conversion with $\tau \cong 2$ ps to give structurally dependent 8-31% yields of ^{3*}PDI. Energy and electron transfer quenching of ^{1*}PDI by BPNO$^{\bullet}$ are excluded on energetic and spectroscopic grounds.

TREPR experiments at high magnetic fields (3.4 T, 94 GHz) show that the photogenerated three-spin system consists of the strongly-coupled unpaired electrons confined to ^{3*}PDI, which are each more weakly coupled to the unpaired electron on BPNO$^{\bullet}$ to form excited doublet (D_1) and quartet (Q) states, which are both spectrally resolved from the BPNO$^{\bullet}$ (D_0) ground state (Figure 1). The initial spin polarizations of D_1 and Q are emissive for **1** and **2** and absorptive for **3**, which evolve over time to the opposite spin polarization. The subsequent decays of D_1 and Q to ground state spin polarize D_0. The rates of polarization transfer depend on the molecular connectivity between PDI and BPNO$^{\bullet}$, and can be rationalized in terms of the dependence on molecular structure of the through-bond electronic coupling between these species. The observed spin polarization of the three-spin system in **1-3** is attributed to the recently proposed “reversed quartet mechanism” or RQM.[2] The data show that we can control both the magnitude and the rates of spin evolution within these systems by application of specific structural changes. The ability to control the time evolution of coherent spin states is an important requirement for spintronics applications capable of operation at room temperature.

B. Competitive Electron Transfer and Enhanced Intersystem Crossing



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Next we examined how changing the communication between the chromophore and radical would affect the photophysical processes observed. A stable 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) radical was also covalently attached at its 4-position to the imide nitrogen atom of PDI to produce TEMPO-PDI, **4**, having a well-defined distance and orientation between TEMPO and PDI. Transient optical absorption experiments in toluene following selective photoexcitation of the PDI chromophore in TEMPO-PDI show that EISC occurs with τ = 45 ± 1 ps, resulting in formation of TEMPO-^{3*}PDI, while the same experiment in THF shows that the electron transfer reaction TEMPO-^{1*}PDI → TEMPO$^{+\bullet}$-PDI$^{-\bullet}$ occurs with τ = 1.2 ± 0.2 ps and thus competes

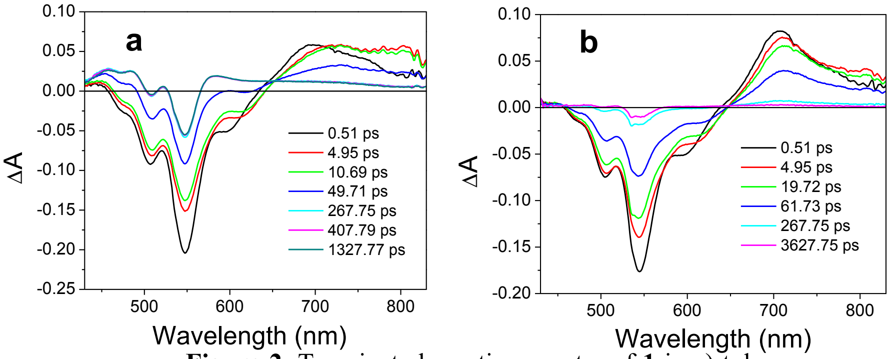


Figure 2. Transient absorption spectra of **1** in a) toluene and b) THF at the times indicated.

effectively with EISC. TREPR spectroscopy on the photogenerated three-spin system TEMPO-^{3*}PDI in toluene at 295 K initially shows a broad signal assigned to spin-polarized ^{3*}PDI, which thermalizes at longer times and is accompanied by formation of an emissively-polarized TEMPO radical. No signals are observed in THF at 295 K. The TREPR spectrum of TEMPO-^{3*}PDI at 85 K in toluene shows an emissive signal due to TEMPO and a broad triplet signal due to ^{3*}PDI having a spin polarization pattern characteristic of overpopulation of its T$_0$ sublevel. This unusual spin polarization pattern does not result from radical pair intersystem crossing because electron transfer does not occur at 85 K. The observed spin polarization of ^{3*}PDI cannot be readily explained by mechanisms discussed previously, leading us to propose a new spin polarization mechanism, which requires that the radical and attached triplet are in the weak exchange regime.

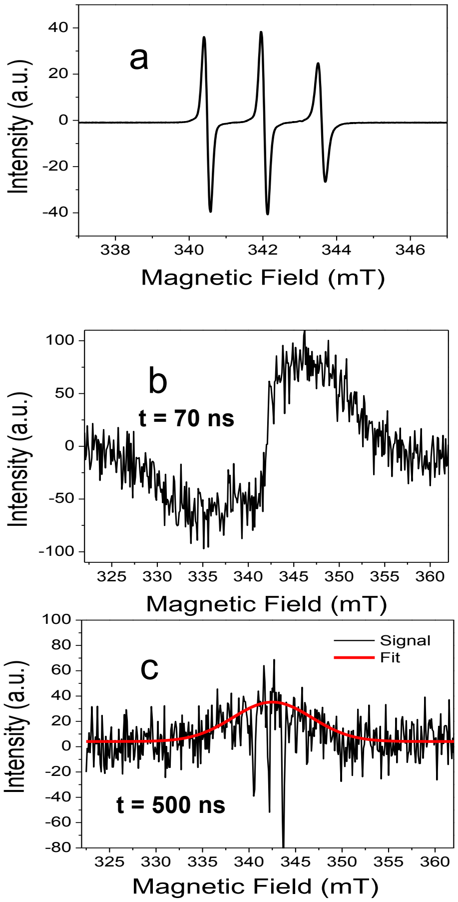
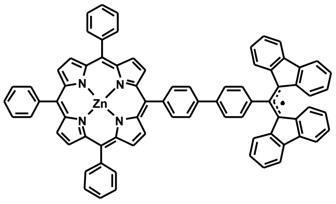


Figure 3. EPR spectra of **1** at 295 K. a) CW EPR spectrum; b,c) TREPR spectra following a 7ns, 532 nm laser flash at times indicated.

C. Enhanced Intersystem Crossing and Enhanced Internal Conversion in a system where ISC is an allowed process in the absence of the radical

Molecules **5-10** were synthesized to develop systems in which one photogenerated strongly spin-polarized radical will transfer its polarization through a poly(p-phenylene) linker to a more distant radical. ZnTPP is the central chromophore to which *α,γ*-bisdiphenylene-βphenylallyl (BDPA$^{\bullet}$) and *t*-butylphenylnitroxide (BPNO$^{\bullet}$) are attached. Femtosecond transient absorption spectroscopy was used to obtain the triplet state formation dynamics of ZnTPP within this series. The data show that BDPA$^{\bullet}$ in **5-7** enhances the intersystem crossing rate (EISC) of ^{1*}ZnTPP only slightly (τ = 1.5 ns vs. 2.4 ns for ^{1*}ZnTPP alone), while BPNO$^{\bullet}$ in **8-10** causes EISC with τ = 3.7, 27, and 200 ps, respectively. The different intersystem crossing rates are indicative of the degree to which varying the molecular structure changes the electronic coupling between ZnTPP and the BPNO$^{\bullet}$ or BDPA$^{\bullet}$ radicals. The weak coupling between BDPA$^{\bullet}$ and ^{3*}ZnTPP results from the properties of the BDPA$^{\bullet}$ SOMO. This differential interaction of BDPA$^{\bullet}$ and BPNO$^{\bullet}$ radicals with the ^{1*}ZnTPP to produce ^{3*}ZnTPP will prove useful in designing systems in which ^{3*}ZnTPP can selectively polarize BPNO$^{\bullet}$ followed by polarization transfer to BDPA$^{\bullet}$.



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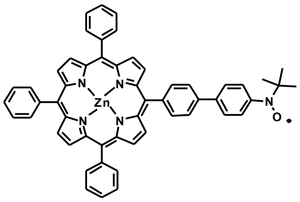

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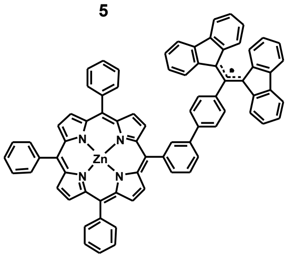

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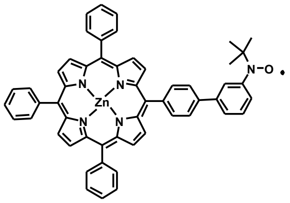

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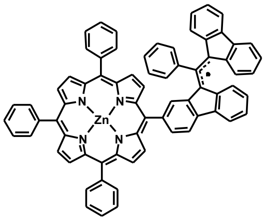

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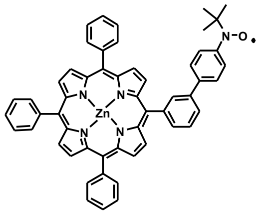

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TREPR was used to study the interaction of ^{3*}ZnTPP with the appended free radical, giving rise to excited quartet and doublet states. As the radical and its connectivity are varied, a wide variety of behavior is observed. The TREPR spectra for **5-7** all exhibit an emissive signal due to BDPA$^{\bullet}$ at long times (e.g. **5** in Figure 4). The spectra at early times are consistent with the observation of ^{3*}ZnTPP at room temperature,[10] and are indicative of a weak spin-spin exchange interaction, 3*J*, between ^{3*}ZnTPP and BDPA$^{\bullet}$. However, the behavior of **8-10** is quite different.

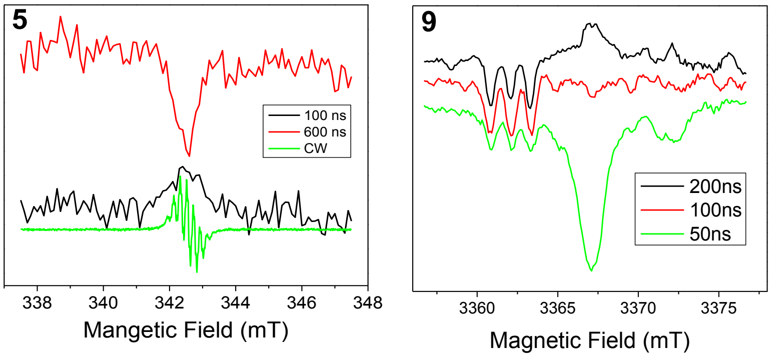


Figure 4. TREPR in toluene of **5** and **9** at 295K. The spectra of **5** were obtained at X-band, while those of **9** were obtained at W-band.

For example, at early times the TREPR spectrum of **8** shows a single absorptive feature, which is a result of a polarized BPNO$^{\bullet}$ signal overlaid with the quartet signal of the three-spin ^{3*}ZnTPP-BPNO$^{\bullet}$ system. As the quartet signal decays, the ^{14}N hyperfine splittings of BPNO$^{\bullet}$ become apparent and eventually decay in about 10 μs. In contrast, the spin dynamics of **9** is typical of the reversed quartet mechanism (Figure 4),[2,11-12] while the **10** exhibits a single broad resonance.

The TREPR results on the molecules featured here show that the magnitude of 3J, which couples ^{3*}ZnTPP to the radical is critical to the spin polarization mechanism. For a large 3J (e.g. **8** and **10**), the interaction between the doublet and quartet state can actually be turned off, and polarization inversion is not observed. For modest values of 3J (e.g. **9**), the RQM mechanism frequently is observed, while for small 3J values (e.g. **5**-**7**), the doublet and quartet state are energetically nearly degenerate and spin relaxation is too fast to allow for the appearance of the doublet and quartet polarization. Thus, structural control of 3J can be used to develop systems that tailor the spin polarization mechanism for particular spintronics applications.

II. Bridge Dynamics of Donor-Bridge-Acceptor Systems.

In addition to my work with multi-spin systems I have also been involved in research that explores how charges, and spin move in systems that have the same donor and acceptor, but a different bridge in between. This gives our group a unique ability to study how charge movement is affected by the energetic and dynamics of the bridge connecting the donor and acceptor.

A. Phenyl Series

Understanding the pathways into and out of charge separated states is vital to prolonging the lifetime of the state, increasing the likely hood that the energy stored can be used effectively.[13] Generally there are at least two pathways out of a charge separated state, namely singlet and triplet recombination.[14-15] By employing transient optical magnetic field effects and time resolved EPR we were able to determine all relevant parameters including how the coupling varies as a function of distance, the overall charge recombination rate and the relative contributions of singlet and triplet charge recombination.

B. Cross Conjugated series

Perhaps the most important criteria for artificial photosynthesis is to create a long lived charge separated state with near unity quantum yield, whose energy can be harvested and stored in chemical bonds.[13] Unfortunately, this is difficult synthetically and while it has been accomplished by us and others it generally requires iterative synthesis to extend the distance between the donor and acceptor, which usually requires additional synthetic steps and decreased synthetic yield. Cross-conjugation is defined as "…a compound possessing three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other. The word conjugated is defined here in the classical sense of denoting a system of alternating single and double bonds."[16] We use cross-conjugated bridge to show that we can extend the lifetime of the charge separated state without sacrificing the quantum yield of charge separation or involve iterative synthetic steps.

C. Fluorenone and Phenyl-ethnyl series

To date two mechanisms for charge separation and recombination are considered, superexchange and hopping.[17-21] In superexchange the electron moves from the donor to the acceptor in one concerted step, without spending any time on the bridge. In hopping the electron moves from the donor to the bridge and then from the bridge to the acceptor. To determine the mechanism of charge transfer a series of molecules where the bridge is extended is usually synthesized and the rate of electron transfer is measured as a function of distance.[22-23] Generally, superexchange will have a exponential distance dependence, while hopping will scale inversely with the distance.[24] By using a fluorenone bridge we are able to observe the electron on the bridge directly by transient absorption as the electron moves from the donor to acceptor. We have also explored how a phenyl-ethnyl bridge impacts the mechanism of charge transfer. The energy of putting an electron on the phenyl-ethnyl bridge is significantly higher than the fluorenone bridge which is high enough to inhibit hopping from being a viable pathway for charge transfer. More will be discussed about these systems in Section III.

D. Magnetic Field Induced Switch in the Radical Pair Intersystem Crossing Mechanism

We have explored how triplet formation occurs in systems where the two electrons of the radical pair are strongly coupled. While RP-ISC has been observed in multiple donor-bridge-acceptor systems it has largely been unexplored in systems with a large exchange interaction. The exchange interaction is proportional to the coupling for charge separation and recombination, and thus can provide information about the rate of charge transfer.[25] We used transient optical techniques to monitor charge separation, and recombination. Subsequent to charge recombination we observe formation of a triplet. By varying the static magnetic field that

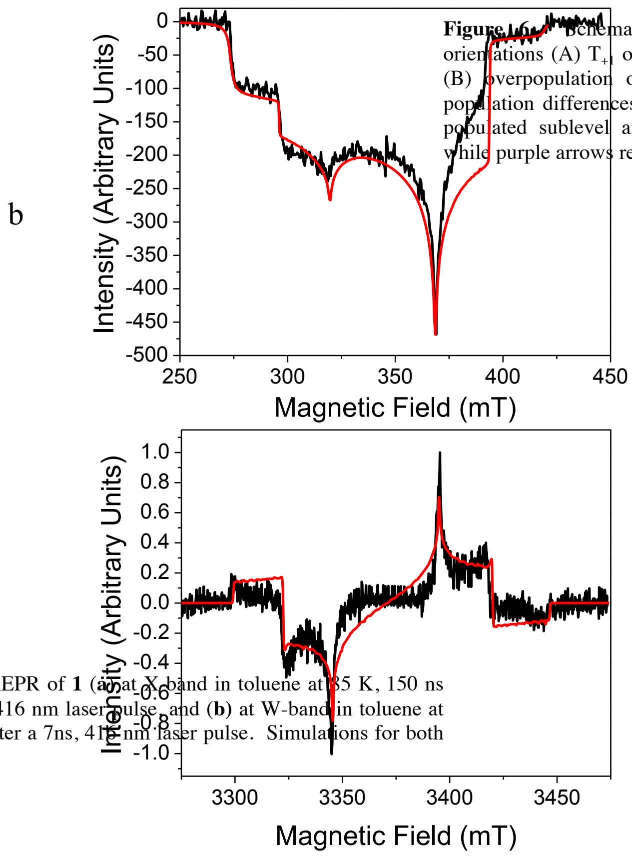


Figure 5. TREPR of **1** (**a**) at X-band in toluene at 85 K, 150 ns after a 7 ns, 416 nm laser pulse, and (**b**) at W-band in toluene at 85 K, 2 µs after a 7ns, 416 nm laser pulse. Simulations for both shown in red.

the triplet is produced in, the triplet yield is altered, and maximized when the magnetic field equals the exchange interaction, which we measured to be 210 mT at room temperature, and 130 mT at 77 K. To explore the mechanism by which the triplet was formed we obtained time resolved electron paramagnetic resonance at two magnetic fields, X-band (9.5 GHz, center field g~2 340 mT) and X-band (94 GHz, center field g~2 3400 mT). The spectrum consists of six transitions shown in Figure 6, with the polarization pattern giving information about the mechanism by which the triplet was formed. A switch in polarization pattern from e,e,e,e,e,e to a,e,e,a,a,e indicates that a change in the mechanism by which the triplet was formed occurred at the different magnetic fields.

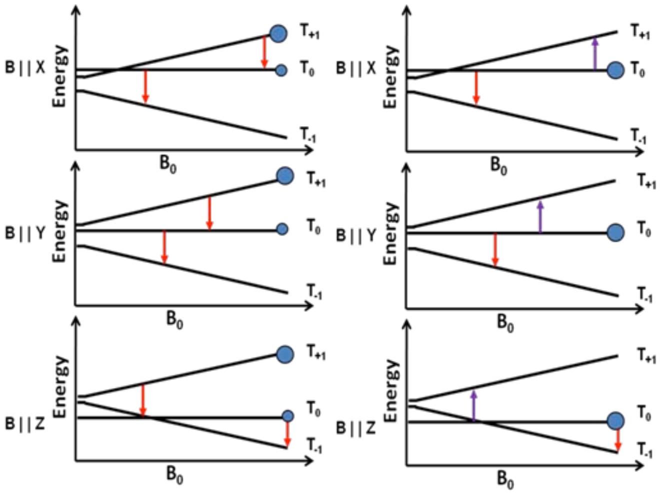
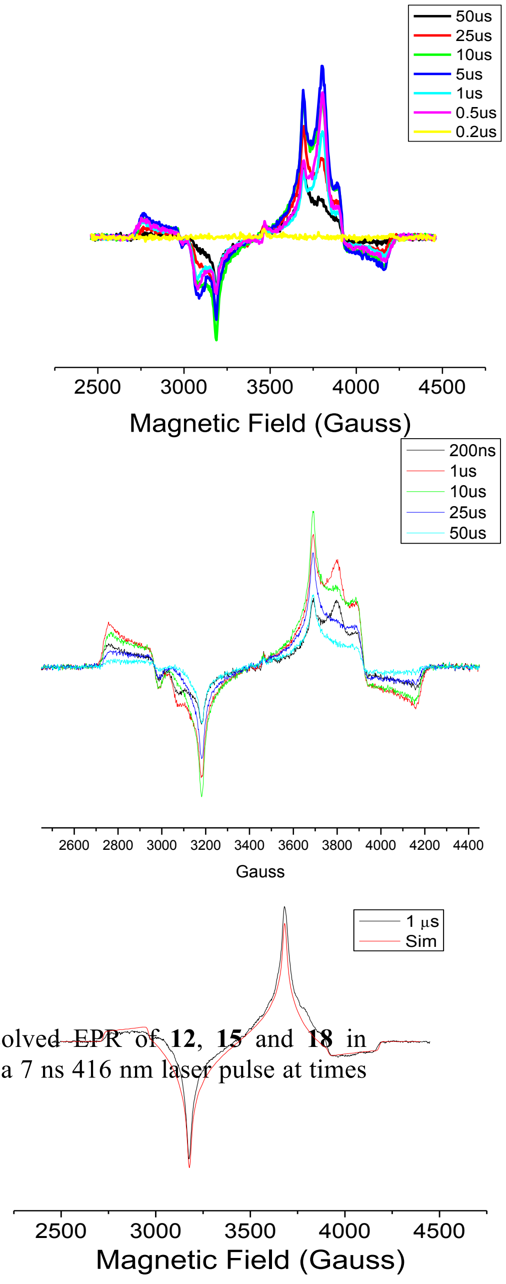


Figure 6. Schematic for EPR transitions in all three canonical orientations (A) T_{+1} overpopulated and some population on T_0 sublevels (B) overpopulation on T_0 sublevel. The blue circles represent the population differences of the three triplet sublevels relative to the least populated sublevel and the red arrows represent emissive transitions while purple arrows represent absorptive transitions.

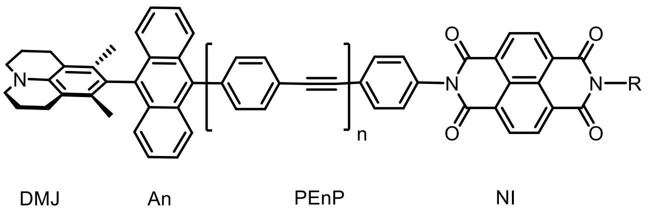
III. Energy Transfer in Donor-Bridge-Acceptor Systems

In photosynthesis several charge separation steps result in a radical pair with the radical cation located on the special pair, and the radical anion located on the second quinine termed Q_B. While most of this species is harvested to drive a proton gradient and subsequently carbon fixation, when this is not the case a triplet is formed on one of the chlorophylls of the special pair.[26] To prevent formation of singlet oxygen formation triplet-triplet energy transfer moves the triplet from the chlorophyll to a nearby caretonoid preventing degradation of the special pair.[26] Triplet-Triplet energy transfer requires two energetically accessible triplets, whose energy is sufficiently different to provide driving force for the transitions to occur.



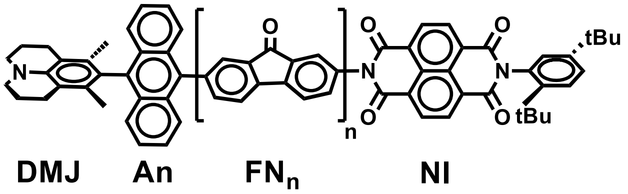
igure 6. Time-resolved EPR of **12**, **15** and **18** in oluene at 85 K after a 7 ns 416 nm laser pulse at times

We have chosen to employ TREPR to monitor TE_NT as a consequence of the timescale of TE_NT in our systems, and because it allows us to monitor the sublevels of the two triplets, and which ones are relevant to the TE_NT process.

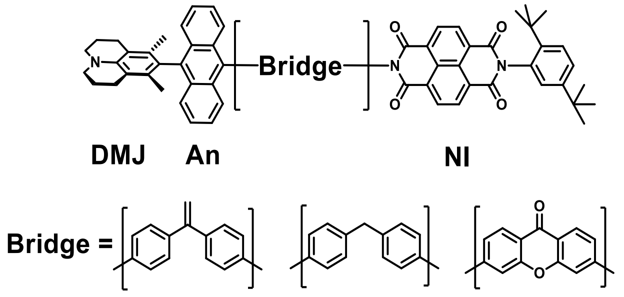


11-13 **(n=1-3, respectively)**

1,2: R = n-C_8H_{17} ;
3: R = 2,5-di-t-butylphenyl



14-16 (n = 1-3, respectively)

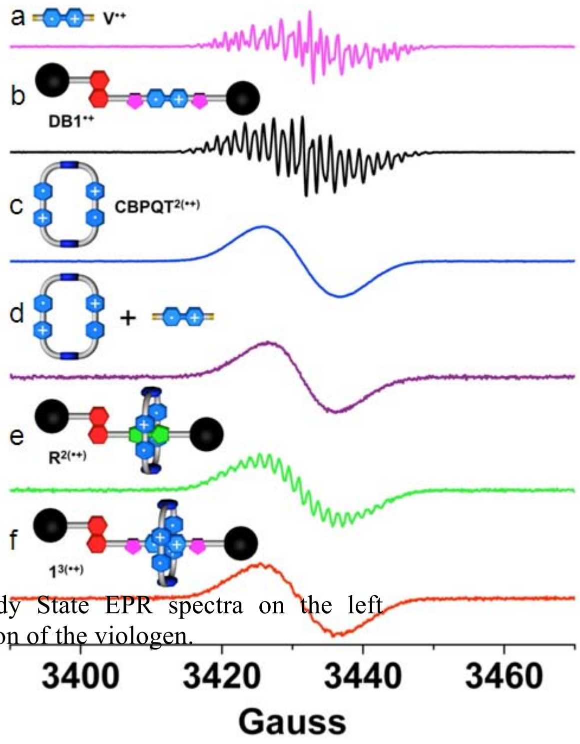


17 **18** **19**

Following charge separation and recombination two triplets are observed, ^{3*}An and ^{3*}NI, with the intensity of ^{3*}NI decreasing as the intensity of ^{3*}An increases, indicating that 1) ^{3*}NI is formed first, and 2) that triplet-triplet energy transfer from ^{3*}NI to ^{3*}An occurs on the microsecond timescale. The first observation indicates that hole transfer is preferred to electron transfer for charge recombination. This had been observed in similar systems with poly-phenyls acting as the bridge between the donor and acceptor.[27] This should be sensitive to the redox potentials of the bridge. As such we have chosen to examine fluorenone and phenyl-ethnyl as bridges, due to the large discrepancy in their reduction potentials. Our initial results indicate that hole transfer is preferred for both series, although significantly less than in the fluorenone series, and the triplet sublevels seem to play a role in the triplet-triplet energy transfer. A manuscript on this work will be forthcoming in the next few months.

IV. Using EPR to Elucidate Mechano-stereochemistry

The work presented in this section has been conducted in conjunction with the Stoddart research group at Northwestern. Their group is interested in how changes in the redox states of parts of molecules can induce motion of one component from one binding site to another site among several sites present in the molecule. Most of their work is based on NMR, steady state

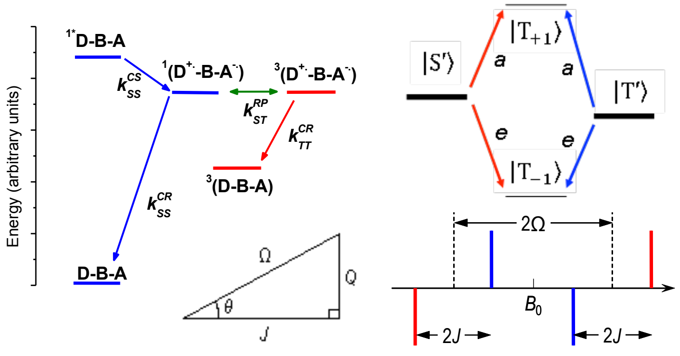


gure 8. Steady State EPR spectra on the left llowing reduction of the viologen.

visible spectroscopy, electro- and spectroelectro-chemistry. By utilizing EPR we can provide additional information about these processes. In total three projects have been carried out. The first project involved multiple viologens that they believed were interacting with each other. For these projects the Stoddart group was examining molecules where a cyclobis-paraquat-p-phenylene box was able to bind to several different sites on a molecule depending on the redox state of the sites and the cyclobis-paraquat-p-phenylene box. We were able to use EPR to determine that the cyclobis-paraquat-p-phenylene box was interacting with a reduced viologen on the molecules backbone forming a complex comprised of three viologens, the two from the box and one on the molecule. The second project involved two tetrathiafulvalene (TTF) units that were dimerized, in the ground state inside a cyclobis-paraquat-p-phenylene box. The TTF units are able to undergo two oxidations each, for a total of four redox states. Prior to our involvement the third oxidative state was a mystery, which we determined was disproportionating into the 2nd and 4th oxidative states. One of the primary interests in this molecule is it starts with both TTF units interacting with one another but must undergo a rotation away from one another due to electrostatic repulsion. The most recent work carried out is based on the TTF work. The Stoddart group has prepared a molecule where the TTF can be on one of two sites. The probability of TTF residing on each site was ascertained by monitoring the EPR signal intensity during a titration with iron perclorate. We have plans to examine the temperature dependence of this phenomenon in hopes of extracting information about the free energy for these processes.

V. Continuing work

I am interested in understanding the spin dynamics of multi-spin systems containing stable organic free radicals in the hopes of utilizing the electron spin to carry, store and transmit information. Spin is an intrinsic quantum mechanical property possessed by electrons and nuclei. The spin of the particle can be in one of two states, an “up” state and a “down” state, which can be treated like the 1 and 0 used in binary code. We are able to use microwave pulses to impart and detect spin information in multi-spin systems, which I use in my current projects on both stable and transient free radicals. Two of my projects involve spin correlated radical pairs (SCRPs) which are generated upon charge separation from a donor to an acceptor. SCRPs are generated because electrons move substantially faster than spin motion. Upon laser excitation an electron is moved from one part of the molecule to another, in an initial singlet configuration (because the two electrons were spin paired before transfer), but are mixed due to differences in the local magnetic environments of the two radicals. A schematic of SCRP mixing and EPR spectrum is shown in Figure 9.



A. “J-Jump” Experiment

The first project looks to use two photons at different wavelengths, the first laser pulse will generate the SCRP, while the second laser pulse will selectively move one of the electrons associated with the SCRP to a secondary acceptor. Through this methodology we hope to be able to answer two important questions, 1). can a second photon be used to generate a secondary radical pair, and thereby create a longer lived charge separated state? and 2). can we move the spin information inherently contained in SCRPs?

B. Spin Information Transfer mediated by SCRP.

The second project I am working on will use SCRPs to act as a conduit between two isolated stable organic free radicals across long distances. We have designed a donor-bridge-acceptor system that has a one radical connected to the donor, and a second distinguishable radical connected to the acceptor. These radicals and their location in the molecule are designed to have both radicals unable to participate in the redox chemistry of the molecule. In the steady state this molecule will have two radicals that do not communicate with one another. We can then impart spin information on one of the two radicals selectively with a microwave pulse. Next we use a photon to create a SCRP between the donor and acceptor, which interact with one another in an entangled quantum mechanical state. We expect that the donor and the first radical will interact with each other, as will the second radical and the acceptor; which will allow for spin information to flow from one radical to the other using the SCRP as a conduit for spin migration. We can thus move spin information without having to move the electron that possesses the relevant spin information.

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The discretionary funds were used to purchase replacement parts for our lasers and lab supplies, and to offset my attendance to the Electron Donor Acceptor Interactions Gordon Research Conference in August 2010.

Broader Impact of this Fellowship

This fellowship enabled me to focus on a research project that has not been studied in detail. My main thesis project is not a certainty to work, but has the possibility to revolutionalize information storage and transfer, so called quantum computing. I am not sure I would have been able to work on a high risk high reward project like this without this fellowship. Additionally, it enabled me to focus on multiple projects in addition to my main project as I was not funded solely one of my advisors grants. I found this to be extremely useful, as I was able to spend a non-negligible amount of time and effort on collaborative efforts that have yielded interesting results detailed previously in the summary of results section.