

Final Report

DOE Award Number DE-FG02-01ER15270

Awardee: Department of Chemistry, University of Illinois

Project Title: “A Combined Synthetic, Spectroscopic and Theoretical Approach to the Rational Design of Photophysical and Photochemical Properties of Dendrimers”

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Executive Summary

The research performed during the period of Award DE-FG02-01ER15270 was dedicated to achieving an improved understanding of artificial solar light-harvesting molecules. These organic molecules may be components of low-cost solar energy systems. We were interested in a particular class of such molecules, multibranched dendrimers, which can mimic the light-harvesting function of the biological light-harvesting complex. The dendrimers investigated were composed of a phenylene ethynylene (PE) framework which had previously been shown to exhibit very high energy harvesting efficiencies. Using both theoretical and experimental methods, we found that the energy-containing excited states in these conjugated networks begin as localized states, but quickly undergo a limited delocalization to a new state which determines the energy transfer rate. By achieving an improved understanding of the fundamental photophysics of PE dendrimers, we are now in a position to evaluate their potential as light-harvesting components of low-cost solar cells. In addition, we also demonstrated the phenomenon of exciton fission in a single covalent molecule for the first time. Exciton fission represents a way to double (in principle) the yield of electron-hole pairs generated by solar photons, and thus represents a way to significantly increase the efficiency of organic solar cells. Both accomplishments

represent significant steps toward the realization of low-cost, “plastic” solar energy conversion technology that will eventually supplant fossil fuel sources.

Comparison of Accomplishments and Goals

In our original research proposal, we had three main goals:

- 1) Characterize the photophysics of phenylene ethynylene dendrimers in order to understand the molecular origin of their high light-harvesting efficiencies.
- 2) Design and characterize molecular assemblies which exhibit the phenomenon of exciton fission, whereby a single high energy excited state spontaneously splits into two lower energy excited states.
- 3) Design and characterize molecular assemblies which exhibit the phenomenon of exciton fusion, whereby a two low energy excited states spontaneously fuse into a single high energy state.

Since the total funding of our proposal was less than originally requested, we decided to concentrate on goals 1) and 2). Both of these goals were accomplished during the period of research support. After some initial work on goal 3), we decided not to pursue it.

Summary of Project Activities

1) Energy Transfer in Phenylene Ethynylene Dendrimers

The light-harvesting phenyl-ethynylene (PE) dendrimers originally synthesized by Moore and coworkers have very high energy transfer efficiencies. These molecules are unique in that they are multichromophoric systems where the chromophore serves as both a structural and optical

element. The strong overlap of the chromophore units raises the question of whether the energy transfer mechanism is purely incoherent, Forster transfer between segments or whether it involves more complicated through-bond interactions.

Early work on these systems showed that the absorption spectra were relatively insensitive to the number of chromophores in the dendrimer, despite the fact that their small separations should lead to strong electronic coupling. This lack of coupling suggested that the excited state wavefunctions were localized on individual segments, and that Forster transfer should be the dominant energy transfer mechanism. We have synthesized the series of molecules shown in Figure 1, with the goal of understanding their photophysics as a prelude to a detailed treatment of the energy transfer that occurs in the larger dendrimers. While the absorption spectra are consistent with localization of the absorbing state along individual dendrimer arms, dramatic changes in the emission spectrum and fluorescence dynamics indicate that the emitting state is quite different from the absorbing state [1].

To investigate the origin of this effect, we used *ab initio* quantum chemistry to investigate the nature of the excited states of these molecules. In order to accurately model

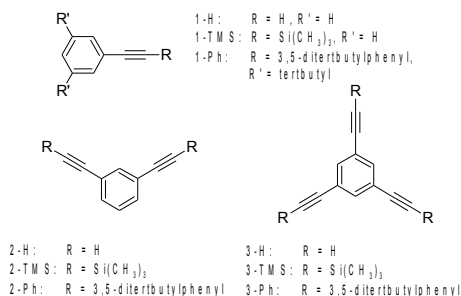
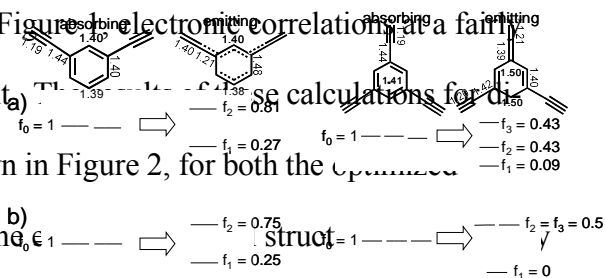
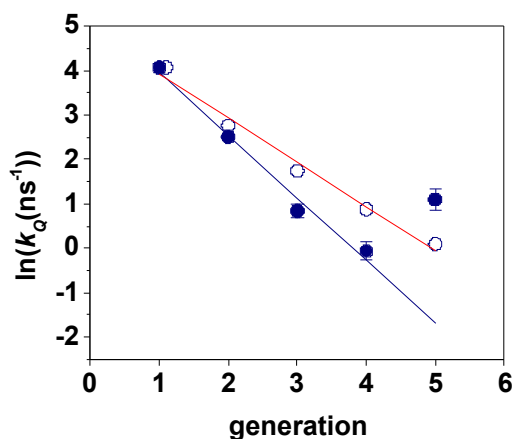


Figure 1. Model PE dendrimers studied to determine excited state photophysics.

these states, even for the simplest molecules in Figure 2, electronic correlations at a high level (CASPT2) must be taken into account. The results of these calculations for dendrimers **2-H** and **3-H**, are shown in Figure 2, for both the ground and excited state nuclear geometries. The electronic level structure is different in the two geometries: in the absorbing geometry, **2-H** has three excited states that are nearly degenerate, corresponding to excitation of the three arms of the molecule. In the emitting geometry, the lowest energy state, from which emission occurs,



absorbing states. This rearrangement of the level structure is due to a geometry-dependent electronic coupling. As the molecule relaxes on the excited state, its changing nuclear structure causes changes in the electron density and thus the electronic coupling between the three ethynyl segments. The change in coupling then leads to new, low-lying states with weaker oscillator strengths and more delocalized wavefunctions. This observation is significant because it shows that these entirely conjugated systems can demonstrate novel photophysical phenomena, e.g. new states not visible in the absorption spectrum but which can be harnessed to improve light harvesting in engineered molecules [2].



efficiency decreases exponentially with dendrimer size, as shown in Figure 3. This

Figure 3. Experimental(●) and calculated(○) fluorescence quenching rates ($\ln(k_q)$) versus dendrimer size (in units of generation). The linear least squares fit(—) to first 4 experimental points yields a slope of 1.4, while the linear least squares fit(---) to the 5 calculated points yields a slope of 1.0.

exponential decrease with generation can be predicted by a simple model that takes into account the increasing number of pathways for the excitation to navigate. Furthermore, the absolute energy transfer rates can only be understood in terms of the delocalized states identified above. These states actually slow down energy transfer due to their energy shift and lower oscillator strength, but some of this is counterbalanced by a decrease in separation due to the extended nature of the states. A simple model based on Forster transfer with the delocalized excited state as the donor and the localized ground state as the acceptor gave good agreement with the experimental data. The overall rate of energy transfer from the periphery to the core of these dendrimers decreases exponentially with dendrimer size, as expected due to the exponentially increasing number of pathways available to the excitation. The net effect of the excited state delocalization in PE dendrimers is to decrease the efficiency of the transfer. While this class of molecules is interesting from the standpoint of its unique photophysics, it probably does not present a viable long-term solution to the problem of light-harvesting for organic solar cells [12].

In collaboration with the Thayumanavan group at U. Massachusetts, we tried to take advantage of the excited state delocalization in the meta-linked compounds to create electron transfer diodes. A pair of donor-bridge-acceptor electron transfer complexes, with a carbazole donor and a naphthalimide acceptor connected by either a para- or meta-conjugated phenylene ethynylene bridge, were synthesized and studied using time-resolved and steady state spectroscopy. These experiments showed that the charge separation times, which depend on the coupling of the donor and acceptor through the excited bridge moiety, are similar for both the meta- and para-bridged molecules. The charge recombination time,

however, is a factor of ten slower for meta-bridged molecule than for the para-bridged molecule. Thus an electron-donor pair linked by a meta-conjugated bridge could have very rapid excited state electron transfer, thanks to the ability of the bridge to support electronic conjugation in the excited state. Once the forward transfer is complete, however, the bridge reverts to its ground state, and back electron transfer is suppressed. These results are related to changes in the electronic coupling of the bridge depending on its electronic state, and show that meta-conjugated bridges provide a possible motif for the design of asymmetric molecular wires which preferentially transfer electrons in the forward direction [8].

To complement our studies on rigid, conjugated PE dendrimers, we also examined energy and charge transfer dynamics in flexible non-conjugated dendrimers. These bifunctional molecules are capable of funneling energy from the periphery to the core followed by a charge transfer process from the core to the periphery, and were synthesized in the Thayumanavan group at U. Massachusetts. The energy and electron donors involved a diarylaminopyrene unit incorporated at the periphery of these dendrimers. The energy and electron acceptor was a benzthiadiazole moiety located at the core of the dendrimer. The backbone of the dendrimers was benzyl ether based. A direct electron transfer quenching of the excited state of the periphery or a sequential energy transfer – electron transfer pathway are the two limiting mechanisms of the observed photophysical properties. We found that the latter mechanism was dominant in these dendrimers. The energy transfer occurs on a picosecond timescale, while the charge transfer process occurs on a nanosecond time scale. The lifetime of the charge separated species was found to be in the range of microseconds. Energy transfer efficiencies ranging from 80% to 90% were determined using both steady-state and time-resolved

measurements, while charge transfer efficiencies ranging from 70% to 80% were deduced from fluorescence quenching of the core. The dependence of the energy and charge transfer processes on dendrimer generation was analyzed in terms of the backfolding of the flexible benzyl ether backbone, which leads to a weaker dependence of the energy and charge transfer efficiencies on dendrimer size than would be expected for a rigid system [6].

To further examine the role of dendrimer topology in determining energy and charge transfer rates, we examined the photophysics of a series of molecules consisting of a benzthiadiazole core surrounded by a network of benzyl ether arms terminated by aminopyrene chromophores, which function as both energy and electron donors. Three classes of molecules were studied:

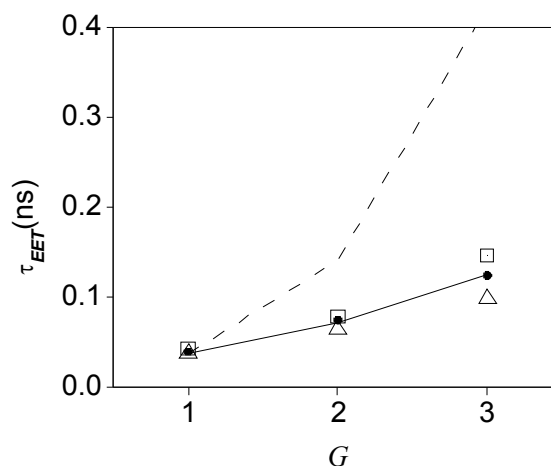


Figure 4. Energy transfer time, τ_{EET} , versus generation for **L** (linear, filled circles), **D** (difunctionalized, open squares), and **F** (fully decorated, open triangles) dendrimers. The flexible $(G+3)^3$ (solid line) and rigid $(G+3)^6$ (dashed line) models are shown normalized to the **1L** value, where G is the generation number.

dendrimers whose peripheries are fully-decorated with aminopyrene donors (**F**), disubstituted dendrimers whose peripheries contain only two donors (**D**), and linear analogs in which a pair of benzyl ether arms link two donors to the central core (**L**). The electronic energy transfer and charge transfer rates were determined by fluorescence lifetime measurements on the energy donors and electron acceptors, respectively. In all three types of molecules, the energy transfer times scaled as the square root of the generation number G , consistent with the flexible nature of the benzyl ether framework. This result was

consistent with our previous results as well. Transient anisotropy measurements confirmed that donor-donor energy hopping does not play a major role in determining the energy transfer times. The charge transfer dynamics occurred on the nanosecond timescale and lead to stretched exponential decays, probably due to conformational disorder. Measurements at 100°C confirmed that conformational fluctuations play a role in the CT dynamics. The average CT time increases with G in the **L** and **D** molecules but decreases for the **F** dendrimers. This divergent behavior with increasing G was attributed to the competing effects of larger donor-acceptor distances (which lengthen the CT time) versus a larger number of donors (which shorten the average CT time). This work illustrated two important points about light-harvesting and charge separation dendrimers. First, the use of a flexible dendrimer framework can lead to a more favorable scaling of the EET time (and thus the light-harvesting efficiency) with dendrimer size, relative to what would be expected for a fully extended dendrimer. Second, fully-decorated dendrimers can compensate for the distance-dependent slowdown in CT rate as G increases by providing additional pathways for the CT reaction to occur [13].

In addition to our spectroscopic studies of dendrimers, we also developed a femtosecond three-pulse $\chi^{(5)}$ polarization anisotropy experiment [3]. This experiment was used to examine the time-dependence of the rotational diffusion of Coumarin 153 in polar liquids. By probing the polarization anisotropy decay at various points during the molecule's excited state lifetime, a time-dependent diffusion coefficient was found in several solvents. This anomalous behavior is consistent with the relaxation of the solvent friction to accommodate the solute's excited state charge distribution. Rotational diffusion times measured immediately after photoexcitation by two-pulse $\chi^{(3)}$ experiments appear to reflect a nonstationary bath dynamics, rather than the equilibrium friction of the solvent.

The development of this experiment was driven by the desire to use it to monitor the nonstationary dynamics of energy transport in molecular assemblies. We recently applied it to exciton diffusion in a conjugated polymer, and plan to apply it to energy migration in dendrimer systems as well.

We also examined model light-harvesting systems using numerical calculations [4]. The problem of electronic energy transfer in a network of two-level systems coupled to a single trapping site was investigated using a simple Haken-Strobl model with diagonal disorder. The goal was to illustrate how the trapping time T_{trap} , coherence time T_d , and molecular topology all affect the overall efficiency of a light-harvesting network. Several issues were identified that need to be considered in the design of an optimal energy transfer network, including the dephasing-induced decoupling the trap from the rest of the network, the nonlinear dependence of trapping rate on the coherence time, and the role of network size and connectivity in determining the effect of the coherence time on efficiency. There are two main conclusions from this work. First, there exists an optimum combination of trapping time and coherence time which will give the most rapid population transfer to the trap. These values are not in general the shortest trapping time and the longest coherence time, as would be expected based on rate equation models and/or simple considerations from previous analytical results derived for the Haken-Strobl model in an infinite system. Second, in the coherent regime, where T_d is longer than the other relevant timescales, population trapping in a finite system can be suppressed by quantum interference effects, whose magnitude is sensitive to the molecular geometry. Suggestions for possible methods of observing such effects were discussed. These results provide a qualitative framework for quantum coherence and molecular topology into account for the design of covalent light-harvesting networks with high energy transfer efficiencies.

Finally, we have developed and tested new methods for excited electronic state dynamics which are applicable to large dendrimeric and donor-bridge-acceptor molecules [5, 16-18]. These methods are based on a hybrid quantum mechanical/molecular mechanical description, where the light-absorbing molecule is intended to be described quantum mechanically and the molecular mechanics description is used to model the surrounding environment, for example solvent. The quantum mechanical portion of the problem is described using new multireference semiempirical methods, which are explicitly reparameterized using high-level *ab initio* data. We showed that such methods can be transferable [18], so that one can determine parameters for weakly-interacting subsystems independently. This provides a possible route to modeling donor-bridge-acceptor type molecules, as parameters for the donor, bridge, and acceptor can be determined independently. In any case, the method was shown to be accurate (by comparison to direct *ab initio* dynamics) for excited state dynamics of the paradigmatic aromatic chromophore benzene [5]. The computational cost is more than an order of magnitude less than *ab initio* molecular dynamics methods. Future applications will include excited state electron and/or energy transfer in molecules, including the influence of solvent environments.

2) Exciton Fission

Tetracene has the property that its triplet state is at almost half the energy of its first singlet. Absorption to the singlet thus results in a state which has sufficient energy to produce two triplets in a process known as “exciton fission.” In this case, one photon can theoretically produce two photochemical products, with an effective quantum yield greater than 100%. A photophysical study of the covalently linked tetracene dimer 1,4-bis

(tetracen-5-yl)benzene, shown in Figure 5, confirmed this hypothesis. While the dimer's steady state spectroscopy is similar to that of monomeric tetracene, it also exhibits a long-lived fluorescence signal in solution and solid polyethylene films, which is absent in the monomer. The origin of this long-lived fluorescence signal was the intramolecular recombination of the two triplets to reform

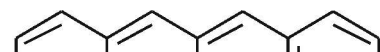
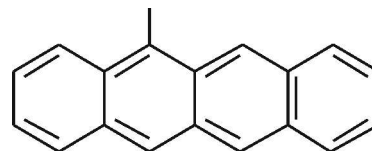


Figure 5. Tetracene dimer used to demonstrate intramolecular exciton fission. The two tetracenes provide sites for the two triplet states to reside on after fission of a single singlet state.



the emissive singlet state. The behaviour of this long-lived component as a function of temperature and oxygenation provides evidence that a small (<1%) fraction of the singlet excited states undergoes fission into two triplet states, which recombine on the order of 100 ns. A kinetic model based on this mechanism fits the fluorescence decay data quantitatively [9].

Products: Journal Publications (in chronological order)

1. "Meta-Conjugation and Excited State Coupling in Phenylacetylene Dendrimers," K. M. Gaab, A. L. Thompson, J. Xu, T. J. Martinez, and C. J. Bardeen, *J. Am. Chem. Soc.* **125**, 9288-9289 (2003).
2. "Variable Electronic Coupling in Phenylacetylene Dendrimers: The Role of Förster, Dexter, and Charge-Transfer Interactions," A. L. Thompson, K. M. Gaab, J. Xu, C. J. Bardeen and T. J. Martinez, *J. Phys. Chem. A* **108**, 671-682 (2004).
3. "Nonstationary Rotational Diffusion in Room Temperature Liquids Measured by Femtosecond Three-Pulse Transient Anisotropy," K. M. Gaab and C. J. Bardeen, *Phys. Rev. Lett.* **93**, 056001/1-056001/4 (2004).
4. "The effects of connectivity, coherence, and trapping on energy transfer in simple light-harvesting systems studied using the Haken-Strobl model with diagonal disorder," K. M. Gaab and C. J. Bardeen, *J. Chem. Phys.* **121**, 7813-7820 (2004).
5. "Excited State Direct Dynamics of Benzene with Reparameterized Multireference Semiempirical Configuration Interaction Methods," A. Toniolo, A. L. Thompson, and T. J. Martínez, *Chem. Phys.* **304**, 133-145 (2004).

6. "Energy and Electron Transfer in Bifunctional Non-Conjugated Dendrimers," K. R. J. Thomas, A. L. Thompson, S. V. Aathimanikandan, C. J. Bardeen and S. Thayumanavan, *J. Am. Chem. Soc.* **127**, 373-383 (2005).
7. Dependence of the two-photon absorption cross section on the conjugation of the phenylacetylene linker in dipolar donor-bridge-acceptor chromophores," S. Lee, J. K. Thomas, S. Thayumanavan and C. J. Bardeen, *J. Phys. Chem. A* **109**, 9767-9774 (2005).
8. "Using meta-conjugation to enhance charge separation versus charge recombination in phenylacetylene donor-bridge-acceptor complexes," A. L. Thompson, T. S. Ahn, K. R. J. Thomas, S. Thayumanavan, T. J. Martinez and C. J. Bardeen, *J. Am. Chem. Soc.* **127**, 16348-16349 (2005).
9. "Evidence for exciton fission and fusion in a covalently linked tetracene dimer," A. M. Mueller, Y. S. Avlasevich, K. Muellen and C. J. Bardeen, *Chem. Phys. Lett.* **421**, 518-522 (2006)
10. "Light-harvesting dendrimers," A. Nantalaksakul, D. R. Reddy, C. J. Bardeen and S. Thayumanavan, *Photosynthesis Res.* **87**, 133-150 (2006).
11. "Dendrimer analogues of linear molecules to evaluate energy and charge-transfer properties," A. Nantalaksakul, R. R. Dasari, T.-S. Ahn, R. Al-Kaysi, C. J. Bardeen, and S. Thayumanavan, *Org. Lett.* **8**, 2981 -2984, (2006)
12. "Light-harvesting in carbonyl-terminated phenylacetylene dendrimers: the role of delocalized excited states and the scaling of light-harvesting efficiency with dendrimer size," T. S. Ahn, A. L. Thompson, P. Bharathi, A. M. Muller and C. J. Bardeen, *J. Phys. Chem. B*, accepted for publication.
13. "Energy and charge transfer dynamics in fully decorated benzyl ether dendrimers and their di-substituted analogs," T. S. Ahn, A. Natalaksakul, R. R. Dasari, R. O. Al-Kaysi, A. M. Müller, S. Thayumanavan, and C. J. Bardeen, *J. Phys. Chem. B*, submitted for publication.

In addition to the above publications which were entirely supported by the DOE grant and explicitly acknowledge the DOE, the following publications were the result of partial support from the DOE:

14. "Probing Every Layer in Dendrons," K. Sivanandan, S. V. Aathimanikandan, C. G. Arges, C. J. Bardeen and S. Thayumanavan, *J. Am. Chem. Soc.* **127**, 2020-2021 (2005).
15. "Effect of Guest Molecule Flexibility in Access to Dendritic Interiors," S. V. Aathimanikandan, B. S. Sandanaraj, C. G. Arges, C. J. Bardeen and S. Thayumanavan, *Org. Lett.* **7**, 2809-2812 (2005).

16. "Computation of Reaction Mechanisms and Dynamics in Photobiology," S. Olsen, A. Toniolo, C. Ko, L. Manohar, K. Lamothe, and T. J. Martínez, in Computational Photochemistry, Ed. M. Olivucci (Elsevier, Amsterdam, 2005).
17. "Competitive Decay at Two and Three-State Conical Intersections in Excited State Intramolecular Proton Transfer," J. D. Coe and T. J. Martínez, *J. Amer. Chem. Soc.* **127**, 4560-4561 (2005).
18. "Photochemistry from First Principles and Direct Dynamics," A. Toniolo, B. Levine, A. Thompson, J. Quenneville, M. Ben-Nun, J. Owens, S. Olsen, L. Manohar, and T. J. Martínez in Computational Methods in Organic Photochemistry, Ed. A. Kutateladze (Marcel-Dekker, New York, 2005).