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Investigations of Biomimetic Light Energy Harvesting Pigments

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). Nature uses chlorophyll and other porphyrinic pigments to capture and transfer light energy as a preliminary step in photosynthesis. The design of synthetic assemblies of light harvesting and energy directing pigments has been explored through synthesis and characterization of porphyrin oligomers. In this project, pigment electronic and vibrational structures have been explored by electrochemistry and dynamic and static optical measurements. Transient absorption data reveal energy transfer between pigments with lifetimes on the order of 20 - 200 picoseconds, while Raman data reveal that the basic porphyrin core structure is unperturbed relative to the individual monomer units. These two findings, along with an extensive series of experiments on the oxidized oligomers, reveal that coupling between the pigments is fundamentally weak, but sufficient to allow facile energy transfer as the predominant excited state process. Modeling of the expected quantum yields for energy transfer within a variety of arrays was accomplished, thereby providing a tool to guide synthetic goals.

Background and Research Objectives

The development of molecular-scale information processing systems requires the creation of molecular devices that function as wires, gates, memory elements, sensors, and related components. One of our labs (Lindsey) recently developed a molecular photonic wire consisting of an array of pigments 90 Å in length, shown in Figure 1.¹ Absorption of a photon of visible light by an input chromophore at one end of the array leads to emission of a photon by an output chromophore at the opposite end of the array. The quantum yield of energy migration from input to output is estimated to be 76%. In this project, we defined multiple goals. First, we wished to understand the differences and similarities of the ground state porphyrin structures of isolated molecules as compared with those

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incorporated into arrays. Second, we wished to measure the excited state dynamics, especially the energy-transfer processes. Third, we wanted to design and test a porphyrin oligomer in which the energy transfer could be switched on and off. Finally, we found that the similarities between the inherent relaxation processes of the component monomers within the oligomers was such that we could develop a mathematical tool based on matrix eigenvalue eigenvector equations to predict the efficiency of energy transfer in such weakly coupled structures.

Importance to LANL's Science and Technology Base and National R&D Needs

Molecular-based design represents one of the new paradigms in materials science. Electronic materials with bulk properties derived from a molecular basis set is a goal of many research programs in this country and elsewhere. That such materials can be realized has been demonstrated by nature in a variety of ways, including photosynthetic, structural, and sensor functions with molecular-based designs. Thus, design of materials following such bio-inspired approaches is a goal of central importance to national and LANL goals in energy technology, security, and materials economy.

Scientific Approach and Accomplishments

Biomimetic light-harvesting materials must have several properties. First, they must exhibit efficient energy transfer. Natural systems exhibit energy transfer lifetimes on the order of one picosecond (ps), which predominate the excited state processes.² Second, assemblies of pigments into a molecular-based biomimetic system must yield predictable electronic and dynamic properties. If each new synthetic assembly is a unique system with properties unrelated to similar structures, then there can be little capability to design and synthesize an assembly with desired properties.

These two properties, efficient but predictable energy transfer, are somewhat at odds. Efficient energy transfer requires coupling between pigments while strong coupling will yield an assembly that in no way relates to its component monomers, thus hampering the ability to predict energy-transfer properties. The diarylethylene-linked phenyl porphyrin arrays designed by Lindsey at North Carolina State University (see Figure 1) satisfy both criteria. First, as demonstrated by transient absorption measurements from our laboratory (Publication 2), energy transfer, which occurs on ps timescales, is the prominent excited state process in such assemblies. Second, again based on photodynamics data, the excited state processes in competition with energy transfer, such as triplet yield, fluorescence, and

non-radiative decay, occur on nanosecond timescales in a fashion quite similar to that of the individual pigments.

These results have been supported by Raman analysis of the molecular structure, and by electron paramagnetic resonance studies of selectively oxidized arrays. Thus, we have satisfied our first and second goals of understanding the similarities and differences of the assemblies as compared with the individual components and understanding the excited-state dynamics.

Our third goal of designing an array in which energy transfer could be switched on and off was met by incorporating a redox center in the porphyrin arrays. Thus, we found that excitation of arrays comprised of Zn and free-base porphyrins leads to rapid energy transfer to the free base, where the excited state is trapped and leads to fluorescence. Upon incorporation of a Mg porphyrin into the arrays, switching of the free-base fluorescence was made possible via oxidation of the Mg chromophore. We demonstrated that this switching was reversible by correlating the absence or presence of free base fluorescence with repeated oxidation and reduction of the Mg center (Publication 1).

Our final goal of a design tool for assembling pigment arrays with predictable properties was met by using matrix mathematical expressions to solve the eigenvalue equations for energy transfer within an array of porphyrins. In this approach, we assumed that the pairwise interactions observed experimentally for energy transfer could be mapped into extended arrays. As a result of solving these coupled kinetics equations, we can now predict the results of random or selective excitation of a weakly coupled array of pigments of any geometry and including random or directed energy transfer (Publication 7).

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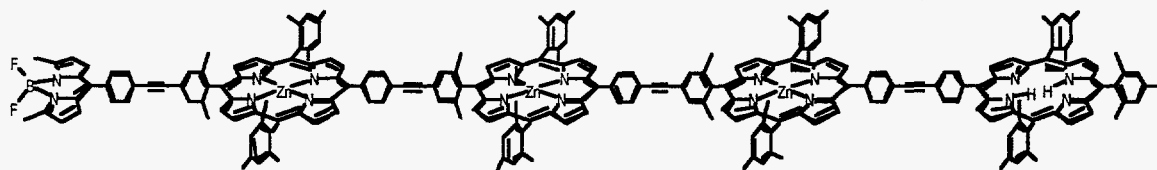


Figure 1. A molecular photonic wire: excitation at the dipyrrole fragment leads to emission from the terminal free base with approximately 76 % efficiency.