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ULTRAFAST PHOTOINDUCED ELECTRON TRANSFER REACTIONS IN SUPRAMOLECULAR ARRAYS:
FROM CHARGE SEPARATION AND STORAGE TO MOLECULAR SWITCHES

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Photoinduced charge separation reactions form the basis for energy storage processes in both natural and artificial photosynthesis. Moreover, rapid, reversible photoinduced electron transfer reactions are a class of photophysical phenomena that can be exploited to develop schemes for optical switching. Examples from each of these fields will be discussed.

Photoinduced, multi-step charge separation in bacterial photosynthetic reaction centers proceeds from the lowest excited singlet state of the dimeric bacteriochlorophyll electron donor in two steps to yield a weakly interacting dimer cation - quinone anion radical pair, P^+-Q^- , separated by 28 Å. At long distances the electron-electron exchange interaction, $2J$, between radicals within a charge separated ion pair is sufficiently weak that differences in local magnetic fields surrounding each radical result in $S-T_0$ mixing of the radical pair spin sublevels. This mixing produces a non-Boltzmann population of the spin sublevels of the radical pair and may result in the appearance of spin-polarized EPR spectra. Photoexcitation of 1, ZC-ZP-NQ, at 5 K results in the single-step charge separation reaction: ${}^1\text{ZC-ZP-NQ} \rightarrow \text{ZC}^+-\text{ZP-NQ}^-$, with $\tau = 10$ ps with a 90+% quantum yield. There is no evidence for formation of intermediates involving the porphyrin on time scales > 1 ps. The radical ions of the pair are 22 Å apart, which results in a long-lived radical pair, $\tau = 2$ ms. Moreover, the radical pair retains a memory of the singlet spin state in which it was born by exhibiting *spin-polarization* as indicated by EPR.

ZC

ZP

NQ

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Spin polarization within $\text{ZC}^+-\text{ZP-NQ}^-$ results from weak spin-spin coupling. $S-T_0$ mixing in $\text{ZC}^+-\text{ZP-NQ}^-$ is driven principally by the anisotropic dipolar spin-spin interaction, D . The exchange interaction $2J$ is close to 0. Since both the distance and orientation of the two radicals within the pair are known, the spin-polarized EPR spectra can be modeled using reasonable values for the exchange and dipolar interactions, in addition to the anisotropic g -tensors of the radicals. Thus, molecules such as 1 can be used as structural probes for systems such as green plant PS I and PS II, which exhibit radical pair EPR spectra, but have unknown donor-acceptor orientations and distances. The critical balance of energetics and electronic interactions necessary to produce spin-polarization in the solid state demonstrates that the charge separation and storage process is highly optimized in this molecule. Molecules of this type are being used as prototype systems for developing the basic concepts necessary to produce efficient solar energy conversion and storage devices.

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Molecular electronic switches, wires, micro-sensors for chemical analysis, and opto-electronic components for use in optical computing are currently under active investigation. The principal advantages of using molecules in these applications are high component density, increased response speeds, and high energy efficiency. The design and production of energy-efficient, state-of-the-art electronic devices depends increasingly on the ability to produce ever-higher densities of circuit elements within integrated circuits. Since photoinduced electron transfer processes within molecules can take place on a picosecond time scale, it should be possible to produce efficient devices that respond very rapidly. An essential requirement for photodriven molecular electronic components is photostability. Molecules that employ reversible electron transfer reactions for optical switching should possess both speed and photostability advantages over molecular switches based on photochemical changes in molecular structure.

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We have designed an electron donor-acceptor-donor molecule, **2**, consisting of two porphyrins, HP, rigidly attached to N,N'-diphenyl-3,4,9,10-perylenebis(dicarboximide), PBDCI, that exhibits light intensity dependent optical switching using two ultrafast electron transfer reactions. Excitation of the porphyrins within this molecule with femtosecond laser pulses results in single or double reduction of the acceptor depending on the light intensity. The singly- and doubly-reduced electron acceptors absorb light strongly at 713 nm and 546 nm, respectively. Since these absorption changes are produced solely by electron transfers, this molecular switch effectively has no moving parts, and switches significantly faster than photochromic molecules that must undergo changes in molecular structure.

The photophysical behavior of **2** constitutes a light intensity dependent optical switch. As the light intensity is increased, **2** switches from being a strong transient absorber at 713 nm to one in which the transient absorption occurs at 546 nm. Such molecules could be used to modulate two light beams at different colors on a picosecond time scale. Moreover, **2** can switch using two different excitation wavelengths. Since the PBDCI molecule absorbs strongly at 526 nm ($\epsilon = 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and possesses a 2.3 eV lowest excited singlet state, excitation of PBDCI initiates the first electron transfer to produce $\text{HP}^+ - \text{PBDCI}^-$. The second electron transfer is initiated by a second 585 nm photon that is absorbed principally by the remaining ground state porphyrin. Thus, this molecule is capable of performing logic operations.

In previous work we found that porphyrin-acceptor molecules dissolved in glassy media require ΔG for charge separation to be at least -0.8 eV to insure quantum yields approaching unity. Metalation of the porphyrins in **2** with zinc increases the free energy available for the two electron transfer steps to -1.0 eV and -0.8 eV, respectively, so that picosecond molecular switching using **2** in glassy media such as polymers should occur. This opens up the possibility of developing molecular electronic devices based solely on electron motion within donor-acceptor complexes. We are currently exploring these possibilities.

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