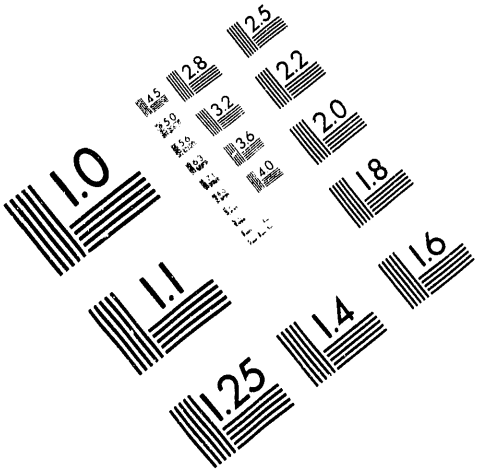
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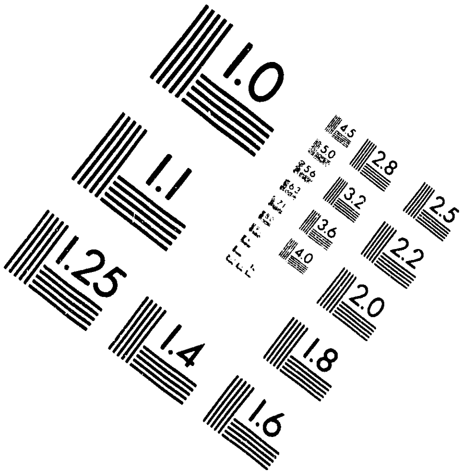
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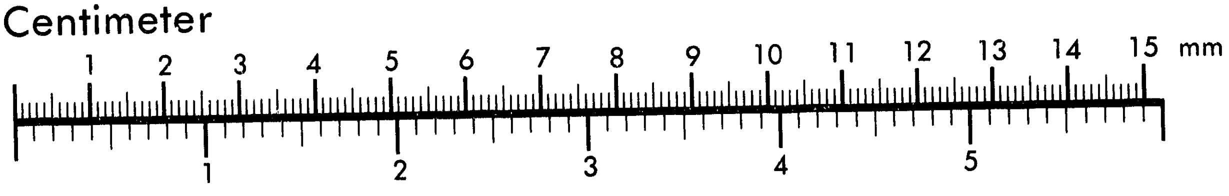
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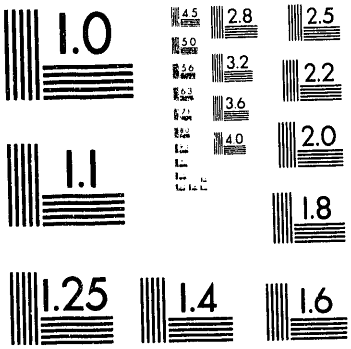
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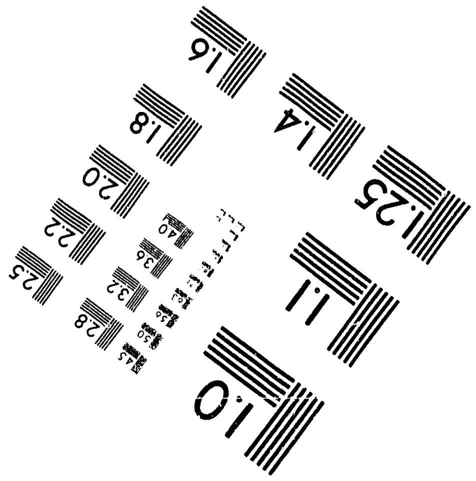
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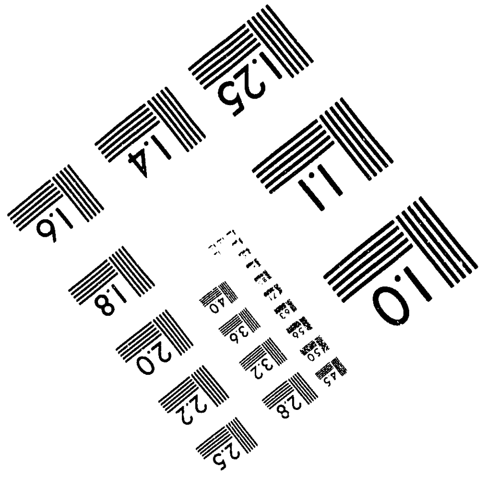
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Invited talk, 17th DOE Solar Photochemistry
Research Conf., Brainerd, MN, June 6-10, 1993

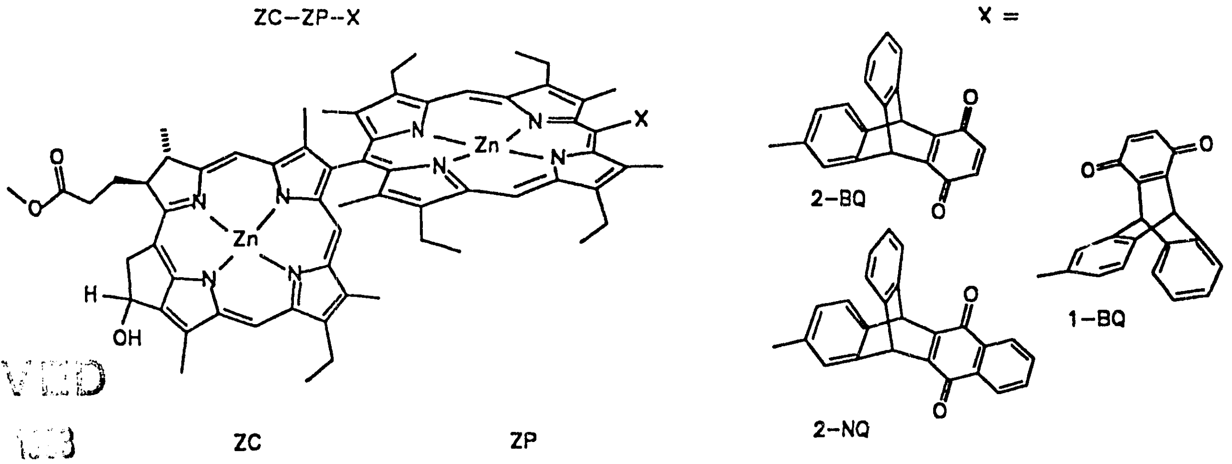
ULTRAFAST PHOTOINDUCED ELECTRON TRANSFER REACTIONS IN SUPRAMOLECULAR ARRAYS: STUDIES OF ELECTRONIC COUPLING AND SOLVATION

Michael R. Wasielewski, Gary P. Wiederrecht, and Walter A. Svec

Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

Photoinduced charge separation reactions form the basis for energy storage processes in both natural and artificial photosynthesis. Recent research in our laboratory focuses on developing supramolecular arrays that produce long-lived charge separation by limiting the electronic coupling between the separated charges, and on the role of solvation in determining the rates and energetics of photoinitiated electron transfer reactions.

Over the past two years we have developed a unique series of supramolecular arrays that for the first time closely mimic the electronic coupling that up until now was observed only for long-lived radical pairs that are produced in photosynthetic systems in glassy solids. 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, which results in the appearance of spin-polarized EPR spectra. Photoexcitation of the ZC-ZP-X molecules illustrated below initiates single-step charge separation reactions: ^{1*}ZC-ZP-XQ -> ZC^{+}-ZP-XQ^{-}, with $\tau < 10$ ps and 90+% quantum yields in glassy solids at cryogenic temperatures. There is no evidence for formation of intermediates involving the porphyrin on time scales > 200 fs. The radical ions of the pairs are about 18 Å apart, which results in long-lived radical pairs, $\tau = 1\text{-}4$ *ms*. Moreover, the radical pairs retain a memory of the singlet spin state in which they were born by exhibiting *spin-polarization* as indicated by EPR.



Spin polarization within ZC^{+}-ZP-XQ^{-} results from weak spin-spin coupling. S-T_0 mixing in ZC^{+}-ZP-XQ^{-} 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 each 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, these molecules 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

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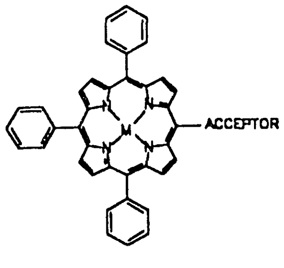
This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract W-31-109-Eng-38.

separation and storage process is highly optimized in these molecules. 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.

A series of 36 fixed-distance donor-acceptor molecules using porphyrin donors, triptycene spacers, and 9 different acceptors has been prepared. These molecules are used to probe the dependence of photoinduced charge separation rates on free energy of reaction as a function of solvent both in liquid and solid solution. Data has been obtained on the rates of charge separation in dioxane, 2-methyltetrahydrofuran, butyronitrile, toluene, chlorobenzene, and benzonitrile. The range of free energies explored spans three-quarters of the total energy available from excitation of the porphyrin to its lowest excited singlet state. The rate constant *vs* free energy relationships obtained show that 1) the energy of the ion-pair state is very sensitive to solvent polarity, 2) restricting solvent motion results in destabilization of the ion pair by 0.8 eV as predicted by the dielectric continuum model of solvation, 3) rate constants for nonadiabatic electron transfer at large free energies of reaction remain large when $-\Delta G > \lambda$, 4) the total reorganization energy for the donor-acceptor molecules containing zinc porphyrin donors is 0.3 eV larger than that for the donor-acceptor molecules containing the corresponding free base porphyrin donors, 5) the electronic coupling for photoinduced charge separation from the lowest excited singlet state of the ZnP-acceptor molecules is about 5 x larger than that for the corresponding H_2P-acceptor molecules, and 6) semi-classical electron transfer theories can be used to model the results obtained.

DONORS:



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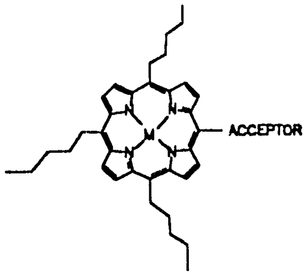
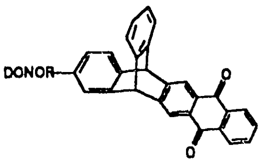


C: M = 2H, D: M = Zn

ACCEPTORS:



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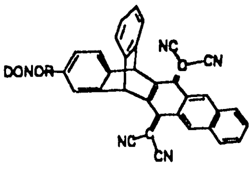

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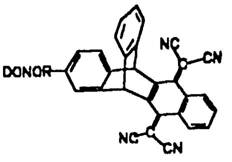

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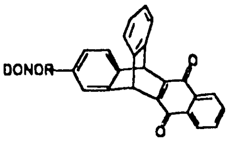
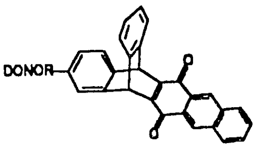


B



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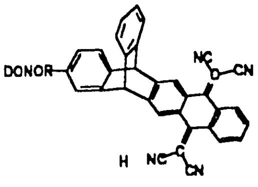

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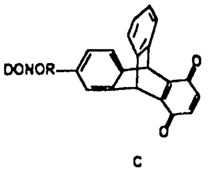
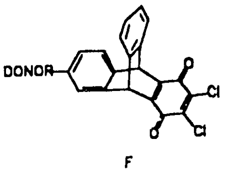


C



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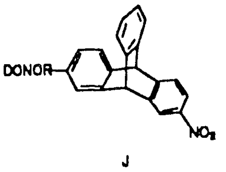

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Michael R. Wasielewski

1. SPIN-POLARIZED RADICAL ION PAIR FORMATION RESULTING FROM TWO-STEP ELECTRON TRANSFER FROM THE LOWEST EXCITED SINGLET STATE OF A FIXED-DISTANCE PHOTOSYNTHETIC MODEL SYSTEM AT 5 K.
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D. W. Minsek, N. C. Yang, M. P. Niemczyk, W. A. Svec,
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H. A. Frank, R. Farhoosh, R. Gebhard, J. Lugtenburg,
D. Gosztola, and M. R. Wasielewski
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G. P. Wiederrecht, S. Watanabe, and M. R. Wasielewski
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