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CONTROLLING PHOTOINDUCED ELECTRON TRANSFER RATES IN DONOR-SPACER-ACCEPTOR MOLECULES BY CHANGING THE ELECTRONIC PROPERTIES OF THE SPACER

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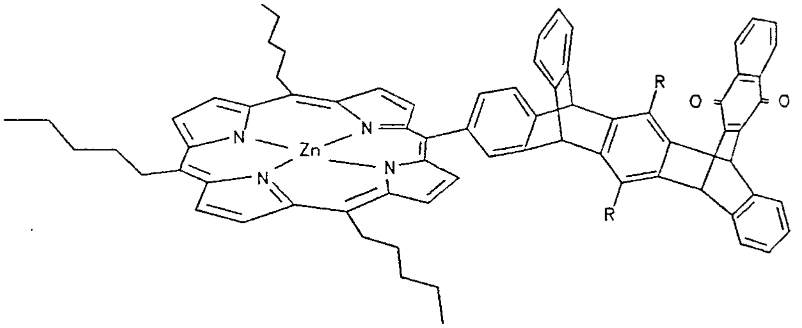
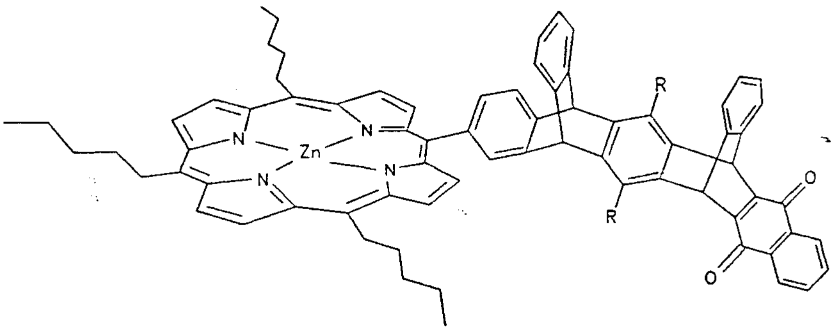
The electron donors and acceptors in photosynthetic reaction centers are positioned at precise distances and orientations relative one another to promote efficient charge separation and to impede charge recombination. However, the nature of the medium that lies between each individual donor-acceptor pair is thought to have a large influence on the observed rates of electron transfer. For example, in the bacterial photosynthetic reaction center a bacteriochlorophyll molecule lies between the dimeric bacteriochlorophyll donor and the bacteriopheophytin acceptor. The π systems of these chromophores lie at large angles relative to one another (about 70°) in an approximate edge-to-edge configuration. It is thought that mixing low-lying, ionic, virtual states involving the intermediate bacteriochlorophyll and the donor and/or acceptor with the locally excited state of the donor leads to a greatly increased rate of charge separation. This mechanism is known as superexchange. In general, molecules possessing low-lying π molecular orbitals can contribute strongly to a superexchange mechanism for electron transfer. However, there are few experimental tests of superexchange in donor-acceptor molecules, especially those involving excited state electron transfers. Moreover, the impact of low-lying virtual states possessing charge transfer character on the photophysics of porphyrin and chlorophyll donor-acceptor molecules remains unclear. Our approach to these problems is to synthesize and study a series of rigid donor-acceptor molecules in which the effects of changing the orbital energies of the donor, acceptor, and intervening spacer molecules are not convolved with changes in conformation.

Four fixed-distance porphyrin-quinone molecules, **1-syn**, **1-anti**, **2-syn**, and **2-anti**, were synthesized. These molecules possess a zinc 5-phenyl-10,15,20-tripentylporphyrin electron donor attached to a naphthoquinone via a rigid pentiptycene spacer. The central benzene ring of the spacer



1-anti: R = H and **2-anti**: R = OCH_3



1-syn: R = H and **2-syn**: R = OCH_3

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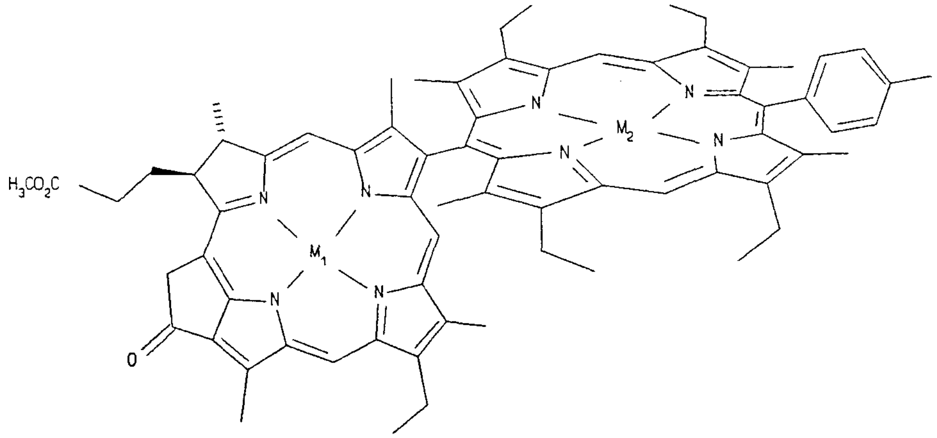
is unsubstituted in **1** and possesses p-dimethoxy substituents in **2**. The naphthoquinone is oriented either **syn** or **anti** to the porphyrin across the spacer. These molecules provide information concerning the orientation dependence of electron transfer between the porphyrin and the quinone, and the dependence of this transfer on low-lying ionic states of the spacer. The rate constants for the oxidation of the porphyrin lowest excited singlet state by the naphthoquinone are **1-syn**: 8.2 x 10^9 s^{-1}; **1-anti**: 1.7 x 10^{10} s^{-1}; **2-syn**: 8.5 x 10^9 s^{-1}; **2-anti**: 1.9 x 10^{10} s^{-1}. The corresponding rate constants for the porphyrin cation - naphthoquinone anion recombination reaction are **1-syn**: 1.4 x 10^{10} s^{-1}; **1-anti**: 2.5 x 10^{10} s^{-1}; **2-syn**: 5.0 x 10^{10} s^{-1}; **2-anti**: 8.2 x 10^{10} s^{-1}. The rate constants for the **syn** isomers are uniformly a factor of about 2 slower than those of the **anti** isomers. The charge separation reaction rates for **1** and **2** are similar, while the ion pair recombination reactions are about 3-4 x faster in **2** than in **1**. The conformational effect is attributed to better overlap of the spacer wave functions in the **anti** vs the **syn** conformation, while the increase in recombination rate for 2 over 1 is attributed to a superexchange interaction involving an electronic configuration of the spacer in which the dimethoxybenzene cation contributes.

Molecules **3-6** possess a chlorophyll molecule rigidly bound to a porphyrin such that the π systems of both macrocycles are constrained by steric interactions to be perpendicular to one another. The structures of these molecules are solvent independent. The electronic coupling between the two macrocycles is sufficiently weak that the ground state optical absorption spectra of both the porphyrin and the chlorophyll are not strongly perturbed. In molecules **3-6** excitation of the porphyrin results in sub-picosecond singlet energy transfer to the chlorophyll. The lowest excited singlet states of molecules **3** and **4** exhibit lifetimes and fluorescence quantum yields that are solvent polarity independent and do not differ significantly from those of chlorophyll itself. Molecule **5**, however, displays a lowest excited singlet state lifetime and fluorescence quantum yield that is strongly solvent polarity dependent. The fluorescence lifetime is about 4 ns in toluene (ϵ = 2.4) and decreases to about 100 ps in butyronitrile (ϵ = 20). Since the fluorescence quantum yield of **5** decreases proportionally with the decrease in fluorescence lifetime, non-radiative decay is strongly enhanced for **5** in polar media. However, picosecond transient absorption measurements show no evidence for a distinct charge separated intermediate. This is consistent with the fact that the energy levels of hypothetical charge separated states within **5** lie above that of S_1 and are therefore virtual states. Molecule **6** also displays distinctive solvent dependent photophysics. Not only is non-radiative decay strongly enhanced in **6** as solvent polarity increases, picosecond transient absorption measurements show that ion pair formation occurs within **6** in about 5 ps in polar solvents, such as butyronitrile. The ion pair recombines in about 100 ps. Molecule **6** is the only compound in the series 3-6 for which redox potentials predict that $ZnChl^-$ - $ZnPor^+$ lies about 0.1 eV below S_1 and is therefore a real state as opposed to a virtual state.



3: M_1=M_2=2H; **4**: M_1=Zn, M_2=2H; **5**: M_1=Zn, M_2=Zn; **6**: M_1=2H, M_2=Zn

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