oxygen, the geminal effect is affected very little.

When the methyl group is replaced by a CN group, there is a very small destabilizing interaction between OH and CN. Harcourt et al. estimated a 4.8 kcal/mol destabilization for the geminal interaction of CN with OH based on the equilibrium for the addition of HCN to formaldehyde,[14] whereas Beckhaus et al. found that the $\Delta H_f°$ of $(CH_3)_3CCH(OCH_3)CN$ implies no stabilizing interaction.[15] This latter result is in accord with our calculational result.

There is a significantly larger destabilizing interaction between CN and OF in **8** than between CN and OH, resulting from the increased electronegativity of OF. We also find a modest destabilizing interaction (about 3 kcal/mol) between CN and OBH_2 in **7**. If we combine the effects of OF and OBH_2 to roughly model OTf, we reach the conclusion that the interaction of OTf with a strong electron-withdrawing group is significantly destablizing.[16] Returning to the relative stabilities of **1** and **2**, the major factor is the geminal destabilization between CN and OTf in compound **2**, which is about 7–9 kcal/mol. The remaining difference is attributed to the difference in alkyl/CN stabilization between **1** and **2**, which is about 1–2 kcal/mol.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research.

Supplementary Material Available: Table of calculated total energies of various small hydrocarbons and their F, CN, OH, OF, and OBH_2 derivatives (1 page). Ordering information is given on any current masthead page.

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(16) This model may not be adequate if the CN group is replaced by a bulky group such as CF_3, because of possible CF_3/Tf steric interactions.

Photoinduced Spin-Polarized Radical Ion Pair Formation in a Fixed-Distance Photosynthetic Model System at 5 K

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Photoinduced, multistep charge separation in bacterial 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.[1] The chromophores within the reaction center are positioned at precise distances and orientations to ensure that the electronic coupling between P^+ and Q^- is sufficiently weak to allow $P^+–Q^-$ to live for about 100 ms.[2] At long distances, the electron–electron exchange interaction, *J*, 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.[3] 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. Such spectra have been reported extensively for both bacterial and green-plant reaction centers,[4–6] but have not been observed previously in rigid model systems. Recently, we developed criteria for achieving high quantum yield charge separation in porphyrin-based donor–acceptor systems at cryogenic temperatures.[7] Using this information as a predictive model, we synthesized compound **1**, TAPD–ZP–NQ, which consists of a zinc porphyrin primary electron donor, ZP, positioned between a naphthoquinone electron acceptor, NQ, and an *N,N,N,N*-tetraalkyl-*p*-phenylenediamine secondary electron donor, TADP. Compound **1** undergoes two-step, sequential charge separation at 5 K to yield a radical ion pair that possesses an overall 23-Å center-to-center distance,[8] *a 4-ms lifetime*, and *spin polarization* as indicated by EPR.

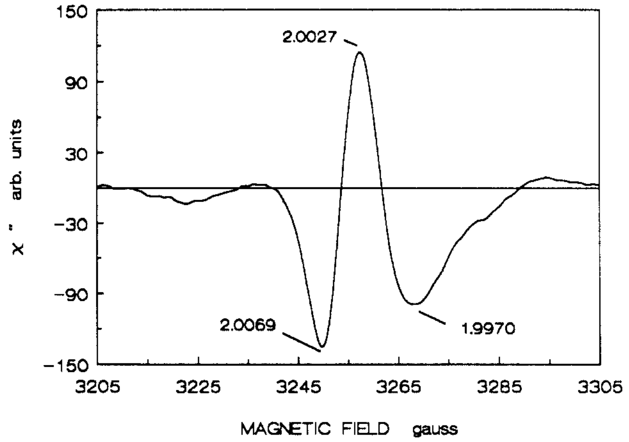

Figure 1. Integrated EPR signal of the spin-polarized radical ion pair resulting from irradiation of 5×10^{-5} M **1** in butyronitrile at 5 K using 540-nm light, modulated at 500 Hz, with lock-in detection: microwave power 5 mW, ν = 9.13 GHz, Varian E-9 EPR spectrometer.

Compounds **1** and **2** were prepared as follows: 2-formyltriptycenonaphthoquinone,[9] 3,3′-diethyl-4,4′-dimethyldipyrrylmethane,[10] and 5-formyl-*N*-(*p*-nitrophenyl)isoindoline[11] were condensed in CH_2Cl_2 with $BF_3·Et_2O$ catalyst[12] to yield the statistical mixture of porphyrinogens. The porphyrinogens were oxidized to porphyrins with chloranil at room temperature and separated on silica gel. The nitro group was reduced with $SnCl_2/HCl$ and dimethylated with $NaBH_3CN/CH_2O$,[13] to give **2** in 15% overall yield based on the starting aldehydes (mass spectrum: FAB calcd 1047, found M + 4 1051). The porphyrin was metalated quantitatively with $ZnOAc_2$ in $CHCl_3/MeOH$ to yield **1**. Compound **3** was prepared in 11% overall yield by a

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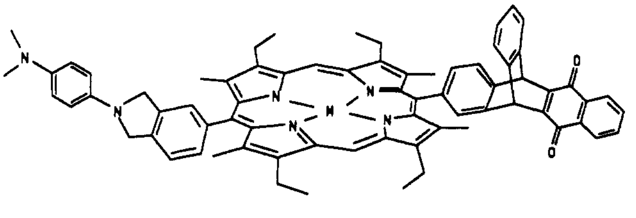
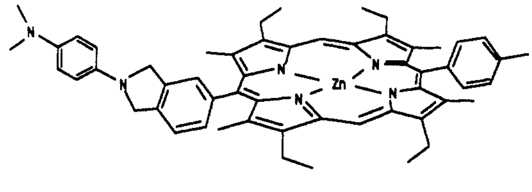
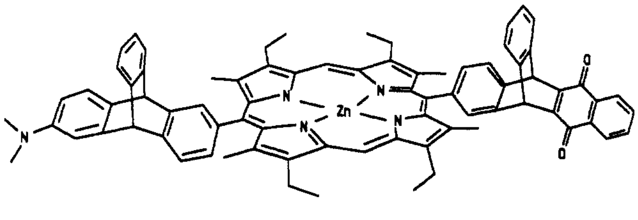
procedure analogous to that used for **1** by replacing the quinone aldehyde with *p*-tolualdehyde. Compound **4** was prepared by quantitative Zn insertion into the corresponding free base synthesized previously.[14]



1: M = Zn, 2: M = 2H



3



4

The energetics of electron transfer within **1** at room temperature in butyronitrile were determined from electrochemical measurements of its redox potentials and the fluorescence spectrum of ZP.[7,15] At room temperature, the energies of TAPD–^{1*}ZP–NQ, TAPD–ZP$^+$–NQ$^-$, and TAPD$^+$–ZP–NQ$^-$ in butyronitrile are about 2.15, 1.29, and 0.84 eV, respectively. We estimate that the corresponding energy levels in solid butyronitrile are about 2.15, 1.99, and 1.84 eV, respectively.[7] Picosecond transient absorption and emission measurements[16] show that the primary reaction, TAPD–^{1*}ZP–NQ → TAPD–ZP$^+$–NQ$^-$, occurs in $\tau < 10$ ps, while the secondary reaction, TAPD–ZP$^+$–NQ$^-$ → TAPD$^+$–ZP–NQ$^-$, occurs with $\tau = 0.5$ ns. Charge recombination within the long-lived ion pair, TAPD$^+$–ZP–NQ$^-$, occurs with a 4-ms time constant. Details of these measurements will be reported later.

The EPR spectrum of TAPD$^+$–ZP–NQ$^-$ is shown in Figure 1. This spectrum is displayed in the absorption mode so that lines with positive intensity are absorptive, while lines with negative intensity are emissive. Extensive control experiments were performed to assign the origin of this signal. At 5 K, the TAPD$^+$ and NQ$^-$ free radicals display Gaussian lines: TAPD$^+$, $g_{\rm iso}$ = 2.0030, fwhm = 35 G; NQ$^-$, $g_{\rm iso}$ = 2.0047, fwhm = 5 G. Removing the Zn atom from the porphyrin in **1** makes the initial electron transfer reaction endergonic in the solid state. Thus, excitation of the porphyrin in **2** results only in formation of its lowest excited triplet state which shows a strong EPR signal with zero field splitting parameters $|D| = 0.0451$ cm^{-1} and $|E| = 0.0041$ cm^{-1}. Replacement of the NQ in **1** by a *p*-tolyl group, **3**, results in no observed electron-transfer reactions at 5 K. Replacing the TAPD moiety by *N,N*-dimethylaniline in **4** also results in no photoinduced EPR signals. Since the *N,N*-dimethylaniline moiety oxidizes at 0.78 V vs SCE,[14] the secondary electron transfer in **4** is endergonic.

The spectrum in Figure 1 can be attributed to two radicals, TAPD$^+$ with a broad line width at lower *g* factor and NQ$^-$ with a narrow line width at higher *g* factor. Polarization is observed on a millisecond time scale because the spin–lattice relaxation times of the radicals are long at 5 K. Spin polarization of TAPD$^+$–ZP–NQ$^-$ can result from two mechanisms. The first mechanism is the usual radical-pair mechanism, RPM, of CIDEP.[17] S–T_0 mixing in TAPD–ZP$^+$–NQ$^-$ is followed by polarization transfer to a noninteracting radical pair TAPD$^+$–ZP–NQ$^-$, i.e., $J = 0$. The second mechanism assumes that TAPD$^+$–ZP–NQ$^-$ is itself an interacting spin-correlated radical pair, i.e., $|J| \sim 0.1–10$ G.[18-20] In this case, S–T_0 mixing in TAPD$^+$–ZP–NQ$^-$ can also produce polarized spectra.

If spin polarization in TAPD$^+$–ZP–NQ$^-$ results from the RPM of CIDEP, all polarization produced from differences in hyperfine interactions within the precursor radical TAPD–ZP$^+$–NQ$^-$ is lost, and only "net" polarization due to Δg differences between ZP$^+$ and NQ$^-$ remains. Thus, if $J < 0$, $\Delta g > 0$, and the initial state is a singlet, the RPM of CIDEP predicts that the NQ$^-$ signal should be absorptive, while the TAPD$^+$ signal should be emissive. However, the spectrum in Figure 1 cannot be described in such simple terms. The RPM of CIDEP also requires that the initial radical pair lives sufficiently long for polarization to develop. The 0.5-ns lifetime of TAPD–ZP$^+$–NQ$^-$ is probably too short for this to occur.[17] On the other hand, if the correlated radical pair mechanism is operative, a pair of partially overlapping anti-phase doublets is expected.[18-20] This mechanism should give rise to a polarization pattern similar to that observed for **1**, P700$^+$–A$_1^-$ in photosystem I of green plants,[4] and P865$^+$–Q$^-$ in bacterial reaction centers.[5] Since the spin-polarized EPR signal from TAPD$^+$–ZP–NQ$^-$ closely resembles those from photosynthetic organisms, and since we know the structure of **1**, the magnitudes of the spin–spin interactions and the relative orientations of the donors and acceptors in the proteins should be similar to those in **1**. We are preparing derivatives of **1** in which the orientation of TAPD$^+$ relative to NQ$^-$ is changed. This will allow us to investigate the dependence of the spin-polarized signal on the anisotropic spin–spin interactions between the radicals. Comparisons of the EPR signals from these molecules with those from photosynthetic proteins may yield structural information concerning the distances and orientations of the donors and acceptors within the proteins. Additional work is currently in progress on deuterated derivatives of **1** to narrow the TAPD$^+$ signal in order to aid in simulating the spectrum based on a new approach to describing the EPR spectra of correlated radical pairs.[21]

Our results show that it is now possible to study charge separation over fixed distances and orientations using magnetic resonance as well as optical studies. These studies should give us a direct measure of the electronic coupling between an electron donor–acceptor pair as a function of structure and environment and may lead to a better understanding of electron transfer in photosynthesis.

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