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Porphyrin−Quinone Electron Transfer Revisited. The Role of Excited-State Degeneracy in Ultrafast Charge Transfer Reactions

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Abstract: Ultrafast time-resolved anisotropy experiments in which electronically excited [5-(1′,4′-benzoquinonyl)-10,15,20-triphenylporphinato]magnesium (MgPQ) was probed with polarization both parallel and perpendicular to the pump pulse have been carried out in a variety of solvents. These results show that the photoinduced electron transfer process involving the locally-excited MgP*Q state is solvent independent, while the thermal charge recombination reaction is solvent dependent. Moreover, these studies indicate that the photoinduced charge separation reaction may be rate-limited by electronic population equilibration between near degenerate porphyrin Q_x and Q_y levels.

Introduction

Electron transfer model systems featuring porphyrin and quinone redox entities have figured prominently in mechanistic studies of biologically relevant charge transfer processes.[1−13] Porphyrin−quinone (PQ) model systems in which the quinone is fused directly to the porphyrin periphery therefore have a special relevance in the development of a fundamental understanding of rapid biological electron transfer (ET) reactions.[9−13] Although the importance of these compounds as structurally simple models that feature large donor−acceptor (D−A) electronic coupling has long been recognized,[14] only recently has the state of the art in time-resolved spectroscopy evolved to allow examination of these systems on sufficiently fast time scales.[11,13]

We have recently reported ultrafast time-resolved anisotropy experiments in which electronically excited (5,10,15,20-tetraphenylporphinato)magnesium (MgTPP) was probed with polarization both parallel and perpendicular to the pump pulse.[15] Key results of these studies showed that the emission of the initially prepared MgTPP electronically coherent excited-state ensemble decayed with three time constants: 210 fs, 1.6 ps, and 100 ps. The fast (210 fs) time constant corresponds to the loss of coherence between the Q_x and Q_y components of the E_u excited state of porphyrin; the second fastest constant (1.6 ps) corresponds to the decay of an incoherent Q_x, Q_y ensemble having a nonstatistical mixture of Q_x and Q_y populations.[15,16] The slow (100 ps) decay is simply the reorientation time of the electronically dephased E_u excited state of MgTPP. Since the two electronic decay processes have time scales comparable with that of photoinduced charge separation ($^1k_{ET}$) and thermal charge recombination (k_{CR}) ET reactions of PQ complexes,[11,13] we

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decided to reexamine such a PQ system to ascertain the effect of degenerate electronic excited-state dynamics on such processes. To accomplish this, time-dependent anisotropy measurements were carried out with [5-(1′,4′-benzoquinonyl)-10,15,20-triphenylporphinato]magnesium (MgPQ).

Experimental Section

Materials. All manipulations involving MgPQ were carried out under nitrogen previously passed through an O_2 scrubbing tower (Schweizerhall R3-11 catalyst) and a drying tower (Linde 3 Å molecular sieves). Standard Schlenk techniques were employed to prepare dry, degassed solutions of MgTPP, MgPQ, [5-(1′,4′-dimethoxyphenyl)-10,15,20-triphenylporphinato]magnesium and [5-(1′,4′-dihydroxyphenyl)-10,15,20-triphenylporphinato]magnesium for optical and transient optical spectroscopy. These spectroscopic studies utilized Schlenk-style fluorescence cells that have been described previously.[17] All solvents were obtained from Fisher Scientific (HPLC Grade). Tetrahydrofuran (THF), toluene, and cyclohexane were predried over 4 Å molecular sieves and then distilled from Na/benzophenone under N_2. Pyridine and acetone were distilled under N_2 from barium oxide and anhydrous K_2CO_3, respectively. $CDCl_3$ was used as an NMR solvent and dried by distillation from CaH_2 under vacuum. All reagents were obtained from Aldrich. Pyrrole was distilled under vacuum and stored under N_2. BBr_3 was transferred to a 100 mL storage tube, deoxygenated by three freeze/pump/thaw cycles, and stored under N_2. Benzaldehyde, 2,5-dimethoxybenzaldehyde, magnesium perchlorate, and lead(IV) oxide were used as received. Chemical shifts for ^{1}H NMR spectra are relative to residual protium in the deuterated solvents ($CDCl_3$, $\delta = 7.24$ ppm, or benzene-d_6, $\delta = 7.27$ ppm). Chemical shifts for ^{13}C NMR spectra are relative to deuteriochloroform solvent ($CDCl_3$, $\delta = 77.00$ ppm). All J values are reported in hertz. Chromatographic purification of the porphyrin molecules utilized basic alumina, 60−325 mesh (Brockman Activity Grade I), obtained from EM Science.

Instrumentation. Electronic spectra were recorded on an OLIS UV/vis/NIR spectrophotometry system that is based on the optics of a Cary-14 spectrophotometer. Emission and excitation spectra were recorded on a Perkin-Elmer LS 50B fluorescence/phosphorescence spectrometer.

[5-(1′,4′-Dimethoxyphenyl)-10,15,20-triphenylporphinato]magnesium. 5-(1′,4′-Dimethoxyphenyl)-10,15,20-triphenylporphyrin and its magnesium derivative were synthesized from benzaldehyde, 2,5-dimethoxybenzaldehyde, pyrrole, and $MgClO_4$ according to literature methods.[18,19] This compound was purified by column chromatography on basic alumina (Brockman Activity Grade I) using hexane/chloroform as the eluent; eluent polarity was gradually increased during chromatography (0−50% $CHCl_3$). ^{1}H NMR (250 MHz, benzene-d_6): δ 9.26 (m, 8H), 8.39 (m, 6H), 8.00 (d, 1H, $J = 3.1$), 7.59 (m, 9H), 7.35 (dd, 1H, $J = 8.9, 3.1$), 7.07 (d, 1H, $J = 9.0$), 3.58 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (60 MHz, $CDCl_3$): δ 152.20, 150.08, 149.93, 149.87, 149.72, 144.12, 143.83, 135.77, 134.65, 133.86, 131.97, 131.61, 131.36, 126.96, 126.17, 122.10, 121.65, 121.30, 114.25, 112.30, 56.85, 55.94. Vis (toluene): 406 (4.31), 426 (5.23), 564 (3.84), 602 (3.54). FAB MS: *m/e* 696 (calcd 696).

[5-(1′,4′-Benzoquinonyl)-10,15,20-triphenylporphinato]magnesium (MgPQ). [5-(1′,4′-Dimethoxyphenyl)-10,15,20-triphenylporphinato]magnesium was first deprotected with BBr_3 to give [5-(1′,4′-hydroxyphenyl)-10,15,20-triphenylporphinato]magnesium and subsequently oxidized to the MgPQ complex by reaction with PbO_2 utilizing experimental methods identical to those described previously for the preparation of other porphyrin−quinone complexes.[1a,20] ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.84 (m, 8H), 8.19 (m, 6H), 7.72 (m, 9H), 7.29 (s, 1H), 7.08 (s, 2H). ^{13}C NMR (60 MHz, $CDCl_3$): δ 188.48, 150.41, 150.12, 149.91, 149.73, 143.47, 143.41, 137.74, 137.06, 136.87, 134.64, 134.55, 132.94, 132.27, 131.93, 129.55, 127.18, 126.27, 122.42. Vis (toluene): 404 (4.62), 426 (5.70), 560 (4.12), 598 (3.56). FAB MS: *m/e* 666 (calcd 666). Immediately prior to any transient optical measurements, MgPQ was subject to an additional chromatographic purification on basic alumina. MgPQ was judged to be sufficiently pure for use in the transient experiments if the sample was totally lacking an emission spectrum (i.e., not even *trace* amounts of porphyrinic impurities such as [5-(1′,4′-dimethoxyphenyl)-10,15,20-triphenylporphinato]magnesium or [5-(1′,4′-dihydroxyphenyl)-10,15,20-triphenylporphinato]magnesium could be present) and the recovery of the signal to 0 at short delay times ($t < 30$ ps) in an optical pump−probe experiment, verifying the lack of residual fluorescence. This method of assessing purity is more meaningful for the types of spectroscopic studies described herein than elemental analysis since it is possible for porphyrin−quinone complexes to analyze properly yet have trace amounts of impurities that affect the photophysics.

Transient Optical Studies. The MgPQ kinetic experiments were performed with a femtosecond spectrometer that has been described before.[15] Briefly, a colliding pulse mode-locked dye laser, pumped by 3−5 W of a continuous wave argon ion laser at 514 nm, produces two beams of ~60 fs pulses centered at 620 nm. One beam is amplified to pulse energies of 2−4 μJ in a multipass amplifier pumped by a copper vapor laser at 8 kHz. The beam is attenuated and then split into excitation and probing arms. One arm is reflected by a mirror fixed to a programmable stepper motor, providing the variable delay between the pump and probe pulses. Immediately prior to the sample lens, the pump beam passes through a horizontal polarizer, while the probe beam passes through a polarizer oriented 45° to the horizontal. A polarizing beam splitter separates the parallel and perpendicular probe components; the transmitted parallel and perpendicular beams are then directed to separate detectors. The experimental design outlined above allows simultaneous measurement of the two quantities required for the calculation of the anisotropy. The magic angle signal was reconstructed from these traces by taking the sum of the parallel signal and twice the perpendicular signal. In the experiments the samples were pumped with a pulse centered at 620 nm and the subsequent dynamics probed by white light continuum pulses, generated in a 2 mm quartz cell containing ethylene glycol. The zero of delay was determined through cross-correlation in a thin (300 μm) KDP doubling crystal.

Results

In contrast to the electronic absorption spectra of MgTPP and the MgPQ precursors [5-(1′,4′-dimethoxyphenyl)-10,15,20-triphenylporphinato]magnesium and [5-(1′,4′-dihydroxyphenyl)-10,15,20-triphenylporphinato]magnesium, the electronic absorption spectrum of MgPQ has a number of distinct features (Figure 1): (i) the Q(0,0) and Q(1,0) bands in the electron transfer model complex are significantly reduced in intensity and lie at higher energy than in MgTPP and (ii) the MgPQ absorption spectrum features a broad band, the position and width of which depend markedly on solvent polarity; this transition we assign to a charge transfer (CT) absorption. The spectra of MgPQ in cyclohexane, toluene, pyridine, acetone, and THF (Figure 2) were fitted with a nonlinear least squares fitting program based on the simplex method. The Soret band and the various Q bands were represented by Lorentzian line

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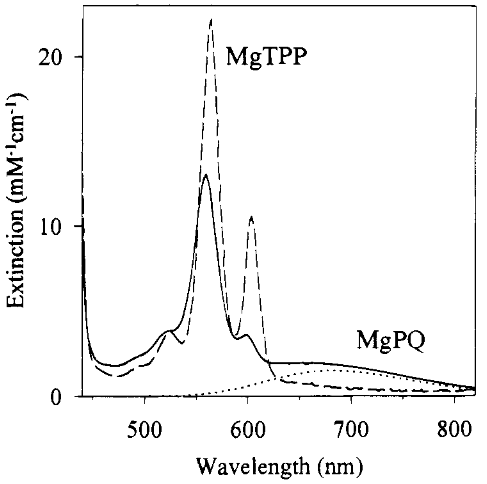

Figure 1. Absorption spectrum of MgTPP (dashed line) and MgPQ (solid line) in toluene. The dotted line is the charge transfer band as found from the data-fitting method described in the text.

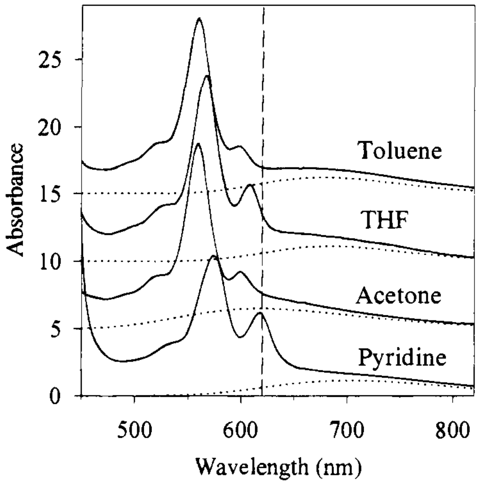

Figure 2. Solvent dependence of the absorption spectrum of MgPQ. The solid line is the experimental spectrum, the dotted line is the deconvoluted charge transfer absorption band, and the vertical dashed line indicates the position of 620 nm (the laser excitation wavelength).

shapes. Since the CT band did not show any obvious structure, it was represented by a Gaussian line shape, i.e.

$$I(\omega) \propto \exp\left\{\frac{-(\hbar\omega - \lambda_T + \Delta G^0)^2}{4\lambda_T k_B T}\right\} \quad (1)$$

where λ_T is the total (inner sphere plus outer sphere) reorganization energy, ω the angular frequency, and ΔG^0 the energy of the 0−0 transition of the CT band (i.e., the driving force for the thermal charge recombination reaction). From these fits, it is found that the reorganization energies are 4900 ± 500 cm^{-1} in THF, 4900 ± 230 cm^{-1} in cyclohexane, 4900 ± 500 cm^{-1} in toluene, 7200 ± 900 cm^{-1} in pyridine, and 11000 ± 3400 cm^{-1} in acetone. The experimental values of the reorganization energies are consistent with a calculation using Onsager's continuum cavity description.[21] The driving force for k_{CR} varies from (9.7 ± 0.5) × 10^3 cm^{-1} (1.20 ± 0.06 eV) in THF to (7.8 ± 0.8) × 10^3 cm^{-1} (1.0 ± 0.1 eV) in pyridine. Note that in the coordinating solvents (such as pyridine) the porphyrin Q absorption bands are red shifted. The transition dipole moment of the CT band, estimated from the area of the absorption in the electronic spectrum obtained in pyridine, is 1.78 ± 0.07 D.

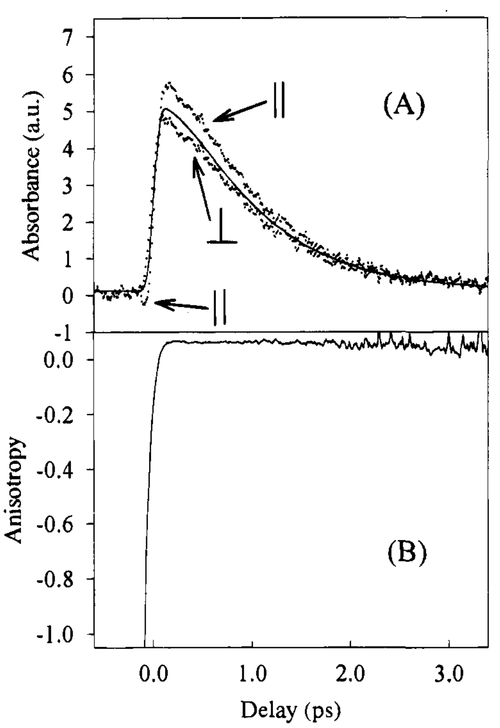

Figure 3. MgPQ kinetic data obtained in pyridine at respective pump and probe wavelengths of 620 and 650 nm: (a) pump−probe data taken with the probe pulse polarization parallel and perpendicular to the pump pulse; the solid curve is a fit to the magic angle data as described in the text; (b) anisotropy of the data shown in (a).

When the sample is pumped at 620 nm, a transient absorption can be observed at 650 nm (Figure 3A) that is assigned to absorption from the excited charge transfer state on the basis of previous studies.[11a,22] A fit of the magic angle data at this wavelength in THF and pyridine shows that the dynamics are quite complex: an initial, instantaneous (pulse width limited) rise is followed by a slower rise and subsequent decay. In THF, 60% of the signal rises instantaneously, 40% rises with a time constant of 350 ± 10 fs, and the signal decays with a time constant of 1.34 ± 0.02 ps. In pyridine, 65% of the signal rises instantaneously, 35% rises with a time constant of 360 ± 40 fs, and the signal decays with a time constant of 760 ± 40 fs. The data obtained in toluene, in contrast, show only an instantaneous rise and a decay with 6.0 ± 0.1 ps. The amplitudes of the instantaneous and slow rises can be understood from mathematical fitting of the static spectra: in toluene, the ground state absorption at 620 nm is dominated by the CT transition, whereas the ratio of CT to Q extinction coefficients at 620 nm in THF and pyridine is considerably smaller (approximately 1). The deconvoluted amplitudes of the instantaneous and slower rise in THF and pyridine follow the same pattern; therefore, the slow rise in the signal at 650 nm must be due to the conversion of the MgPQ locally-excited state (MgP*Q) to the CT state (MgP^+Q^-), while the decay is due to the charge recombination reaction that regenerates the ground state from MgP^+Q^-. The ET rate constants are listed in Table 1. In contrast to the data obtained in THF and pyridine, the decay in toluene is biexponential; a fast, 570 ± 80 fs, component is tentatively assigned to relaxation of the vibrationally hot CT state, a reasonable assumption since neither MgP*Q nor MgP^+Q^- should be expected to thermally equilibrate on the time scales of these ET events. This thermal relaxation is most

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Table 1. Rate Constants for Intramolecular ET Reactions of MgPQ as a Function of Solvent

solvent	${}^1k_{ET}$ (s^{-1}) (^{1}MgP*Q → MgP$^+$Q$^-$)	k_{CR} (s^{-1}) (MgP$^+$Q$^-$ → MgPQ)
pyridine	$(2.78 \pm 0.31) \times 10^{12}$	$(1.32 \pm 0.07) \times 10^{12}$
THF	$(2.86 \pm 0.08) \times 10^{12}$	$(7.46 \pm 0.11) \times 10^{11}$
toluene		$((1.66 \pm 0.02) \times 10^{11})^b$

[a] Experimental conditions: [MgPQ] = 1 mM; 20 °C. [b] MgP$^+$Q$^-$ undergoes vibrational cooling with a time constant of 570 ± 20 fs.

likely not observed in THF and pyridine because the charge recombination rate in these solvents is too close to the rate of thermalization of vibrational energy.

Figure 3B shows the anisotropy of the pump–probe signal at 650 nm in pyridine. The anisotropy has an asymptotic value close to 0.1 (about 0.05) as expected for transitions with near degenerate states.[16,22] At delay times short compared with the pulse width the anisotropy attains negative values as small as −1. Although our pulse width is on the order of 60 fs, we can estimate from the data that this negative anisotropy decays to the asymptotic value in approximately 30 fs. In a "pure" signal from MgPQ (that is, a signal that consists purely of a transient bleach or a transient absorption) an anisotropy between 0.7 and 0 is expected[16] since the MgPQ molecule has at most 4-fold symmetry. An anisotropy of −1 can only be obtained when the total signal is composed of both a transient absorption signal and a transient bleach (or stimulated emission) signal where both signals have a different (but not necessarily negative) anisotropy. This can be seen as follows: if the signal is composed of components labeled i, with parallel component p_i, perpendicular component o_i, anisotropy r, and total strength $c_i = p_i + 2o_i$ (the magic angle signal), then the net anisotropy of a signal consisting of two components is given by

$$r = \frac{p_1 + p_2 - o_1 - o_2}{c_1 + c_2} \tag{2}$$

Thus, if c_1 is positive (transient absorption) and c_2 is negative (transient bleach), c_1 and c_2 can cancel each other, giving rise to a total anisotropy that can range from plus to minus infinity. It also follows that if $r_1 = r_2$, then the anisotropy of the signal is equal to the anisotropy of its components. The anisotropy data therefore prove that there is a fluorescence signal at 650 nm that decays in approximately 30 fs since it reaches its asymptotic value with this time constant. The signal with laser pulses polarized parallel to each other (see Figure 3A) actually exhibits a small transient bleach at negative delay times ($\tau \approx -30$ fs). An attempt was made to fit the parallel and perpendicular data sets simultaneously, including a bleaching signal that decays with a time constant on the order of 30 fs. From this fit it can be concluded that the data are not consistent with an anisotropy of the bleach signal of 0.7 but are consistent with an initial anisotropy of 0.4. The time resolution of the experiment is insufficient to determine the anisotropy and decay time of the bleach signal accurately. Since the time resolution of the experiment is expected[15] to be high enough to resolve dephasing of a coherently excited E$_u$ level pair, the anisotropy of approximately 0.4 implies that the pump pulse only excites a single level.

At 620 nm, the characteristic[11a,22] porphyrin cation-radical absorbance can also be observed as well as a transient absorption that is due to the formation and decay of a vibrationally hot ground state (decaying with a characteristic time constant of 13 ps), similar to what has been observed by other researchers.[10,11a,14c] Probing at wavelengths shorter than 620 nm shows instantaneous bleaching of the ground state (replica hole formation), and recovery at the charge recombination rate constant and transient absorption due to hot ground states.

Discussion and Conclusion

The photoinduced, charge separation ET time constants in THF and pyridine are indistinguishable: 350 ± 10 and 360 ± 40 fs, respectively. This is quite remarkable considering that the driving force for the ET reaction changes by approximately 0.3 eV on changing the solvent. The charge recombination reaction, on the other hand, is solvent dependent (see Table 1) and slows by an order of magnitude on going from pyridine to toluene.

The solvent independence of the ${}^1k_{ET}$ rate constants can be explained using a simple model. Note that in Figure 1 the Q bands are greatly reduced in intensity and blue-shifted in MgPQ relative to MgTPP, suggesting a strong mixing of the locally-excited state with the CT state has taken place. In MgTPP as well as in [5-(1′,4′-dimethoxyphenyl)-10,15,20-triphenylporphinato]magnesium and [5-(1′,4′-dihydroxyphenyl)-10,15,20-triphenylporphinato]magnesium, the electronically excited state is doubly degenerate; it is likely, however, that, in MgPQ, Q$_x$ and Q$_y$ mix differently with the CT state since the 4-fold symmetry of the porphyrin moiety dictates that one of these states has a node in the π-electron density on the carbon that connects to the quinone moiety. One of these levels (Q$_x$) thus gives rise to the intense CT absorption, while the other (Q$_y$) is less perturbed. As discussed in the previous section, the early time ($\tau < 30$ fs) dynamics is consistent with a bleaching signal with an anisotropy of 0.4, not 0.7. This bleaching signal (and the negative anisotropy in the total signal) was not observed in toluene. Since substantial fluorescence is expected at 650 nm in THF and pyridine (MgTPP has strong fluorescence at 650 nm), this observation indicates that a coherent superposition of Q$_x$ and Q$_y$ states is not excited, in agreement with the proposed lack of molecular 4-fold symmetry of MgPQ. MgP$^+$Q$^-$ is formed from the decay of MgP*Q with a time constant of 350 fs, so another explanation is needed for the 30 fs component. We suggest that the faster process is due to a dynamic Stokes shift of the fluorescence of the Q$_y$ state. At times longer than 30 fs, the anisotropy is close but not equal to 0.1 for almost all delay times, further indicating that the 4-fold symmetry of the porphyrin is broken by the quinone moiety fused to the porphyrin edge in MgPQ.

The MgP*Q → MgP$^+$Q$^-$ ET time constant of 350 fs that we observe here is 5 times smaller than the 1.6 ps required for Q$_y$ → Q$_x$ population transfer in MgTPP.[15] The population transfer between the degenerate level pair in MgTPP is driven by solvent fluctuations that couple the Q$_x$ and Q$_y$ levels through the polarizability of the E$_u$ state.[16] In MgPQ, since the Q$_x$ and Q$_y$ levels are not degenerate and will be more polarizable due to the mixing with the CT state, it may be expected that this rate of population transfer will be enhanced relative to that in MgTPP. This suggests that the photoinduced ET process from the locally-excited state may be rate-limited by electronic population decay from the Q$_y$ level to the nearly degenerate Q$_x$ level that is mixed with the CT state. In other words, the ET reaction is a transition from $|Q_y\rangle$ to $|\alpha Q_x + \beta CT\rangle$ where α and β are mixing coefficients. Since coupling between the Q$_y$ and the CT state is expected to be small due to the symmetry of the porphyrin moiety and since the ET reaction rate is experimentally found to be insensitive to the energy of the CT state, the reaction rate may be determined by the coupling between Q$_x$ and Q$_y$.

In conclusion, we suggest that the near invariant time constant for photoinduced charge separation in THF and pyridine has its origin in the time required for population transfer from the porphyrin Q_y excited state to the Q_x state. We have determined the rate of such a population exchange between the degenerate level pair of MgTPP; the 1.6 ps time constant for this process in MgTPP is of comparable magnitude to the 350 fs, solvent independent, photoinduced charge separation reaction time constant determined in our studies of MgPQ. Thus, the photoinduced, ultrafast ET process that involves the porphyrin locally-excited state may be governed entirely by the rate of population transfer between near degenerate Q_x and Q_y levels in MgPQ. Processes similar to those discussed here may need to be considered in interpreting ultrafast electron transfer experiments of biologically important systems that involve degenerate or near degenerate excited states.[23] For example, the primary donor of the bacterial photosynthetic reaction center consists of a pair of bacteriochlorophylls (the special pair); the lowest excited states of the special pair consist of a pair of levels sufficiently close in energy[24] that they might play a role similar to that of the E_u states in MgPQ.

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