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Excited State Relaxation Dynamics of the Zinc(II) Tetraphenylporphine Cation Radical

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A new technique employed to study the photophysical properties of the zinc(II) tetraphenylporphine cation radical is reported. It employs a combination of controlled potential coulometry and femtosecond absorption spectrometry. The fast transient lifetime of 17 ps of the π-cation species originates in very efficient mixing of the a_{2u} HOMO cation orbital that places electronic density mainly on pyrrolic nitrogens and metal d-orbitals. That explains the lack of any emission of the cationic species. This nonradiative decay process might elucidate the processes taking place in photosynthetic systems when an electron is removed from the porphyrinic moiety and the hole is produced.

Introduction

Porphyrin π-cation radicals are known to play a crucial role in biological electron-transfer systems such as respiration and photosynthesis.[1−3] In the natural photosynthetic systems, as reported by Barkigia et al.,[4] chlorophylls, that are closely related to porphyrins, are the main chromophoric moieties that undergo one electron oxidation that starts the photosynthetic cycle.[5,6] A number of electron donor−acceptor linked systems have been designed, and their photodynamics have been examined to mimic photosynthetic charge separation.[7−14] Zinc(II) tetrapyrroles, which have a d^{10} electronic configuration of the central metal ion and contain no axial ligands, easily undergo one electron oxidation, forming stable π-system radical cation species.[15] On the basis of the electronic ground state configuration, the π-cation radicals have been categorized into those possessing a $^2A_{1u}$ or a $^2A_{2u}$ ground state.[2,16] The two highest occupied molecular orbitals of metalloporphyrins (a_{1u} and a_{2u}) are nearly degenerate, and their relative energies are dictated by many factors, including the nature and position of the porphyrin peripheral substitution, the central metal ion, the identity and disposition of the axial ligand, the environment, the temperature, and the symmetry of the molecule.[17,18] For zinc(II) meso-tetraphenylporphine, one electron oxidation proceeds with an electron removal from an a_{2u} orbital. This has direct influence on the interaction between the metal d-orbitals and the nitrogen orbitals of the tetrapyrrole macrocycle.[19] In this work, the zinc(II) meso-tetraphenylporphine radial cation species has been formed electrochemically in situ and studied by means of femtosecond absorption spectrometry to prove that this new technique could be used to elucidate the photophysical behavior of open shell species.

Experimental Section

Materials. Zinc(II) meso-tetraphenylporphine (Zn(II)TPP) (chlorine free) was obtained from Frontier Scientific, Inc., and used without further purification. The spectrophotometric grade acetonitrile and electrochemical grade *tert*-butylammonium hexafluorophosphate (TBAHP) have been purchased from Aldrich. Argon gas was obtained from AGA industries. A Pt wire electrode (99.99%, CH Instruments, Inc.), Pt wire (0.1 mm, Aldrich), and Pt gauze (woven from 0.07 mm wire, Aldrich) were used as auxiliary and working electrodes, respectively, in electrochemistry and spectroelectrochemistry.

Instrumentation. Spectroelectrochemical measurements were carried out by using a BAS Epsilon (bioanalytical system) electrochemical system. A standard three-electrode system was employed.[20−22] A platinum electrode functioned as the working electrode, and a CHI platinum wire electrode served as an auxiliary electrode. For the reference electrode, a Saturated Calomel Electrode (SCE) was used as the standard. The advantage of this approach is the minimization of the liquid junction potential.[20] Electrochemical oxidations and reductions (controlled potential coulometry) were also carried out by using the same system. A homemade spectroelectrochemical cell was used in the experiments. The cell consists of a 0.5 mm rectangular screw cap spectrophotometric cuvette that is fitted into the bottom of a Teflon beaker. A piece of platinum gauze, 100 mesh, woven from 0.07 mm diameter wire was used as a semitransparent working electrode. The electrode was placed in a 0.5 mm spectrophotometric cell and connected to the potentiostat output by a platinum wire. The potential applied to the electrode produced reduced or oxidized species that diffuse away from the semitransparent Pt electrode to saturate the 0.5 mm layer of the solution inside the spectrophotometric cell. The absorption spectra of the sample were taken as a function of time until the potential induced spectral evolution was complete. It usually took 1 or 2 min for the equilibrium to establish. This time may vary with the solvent. The spectroelectrochemical cell filled with pure solvent was used as a reference.

Electronic absorption spectra were recorded in acetonitrile using a Varian Cary 50 Bio single beam spectrophotometer. The pump−probe instrument for ultrafast transient absorption

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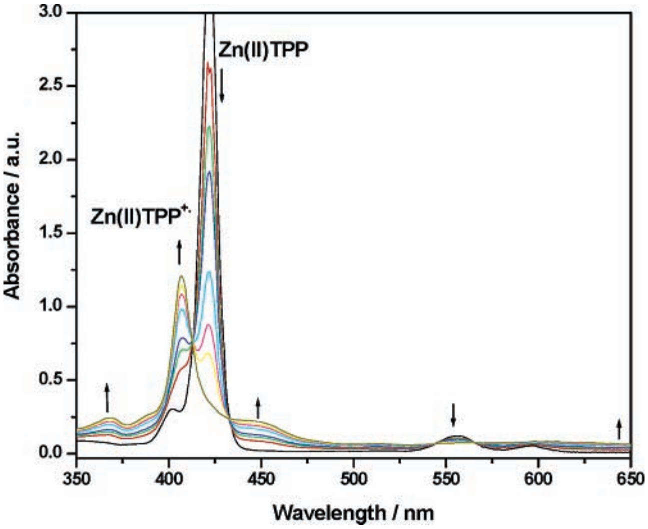

Figure 1. Oxidation of zinc(II) meso-tetraphenylporphine in acetonitrile. TBAHP was used as a supporting electrolyte.

measurements has been described previously.[23] The recent improvements to enhance signal-to-noise characteristics have been communicated elsewhere.[24] A Spectra-Physics Hurricane/Evolution Ti:sapphire combination generated 800 nm pulses of 130 fs duration at a rate of 1 kHz. In the current experiments, the excitation wavelength of 400 nm was derived from the second harmonic of the Ti:sapphire fundamental using a Super Tripler instrument (CSK Optronics). The excitation energy was 2 μJ/pulse.

Results

Spectroelectrochemical Studies of Zn(II)TPP Oxidation. The one electron oxidation of Zn(II)TPP in acetonitrile proceeded to completion at 0.8 V versus SCE with the appearance of several isosbestic points in the optical spectra taken during electrolysis (Figure 1).

The optical spectrum of oxidized porphyrin exhibited a sharp Soret band transition at 409 nm and a broad and featureless absorption in the 500−700 nm region showing the π-cation radical formation. The final (olive line in Figure 1) spectrum showed no indication of the 425 nm peak characteristic of the parent compound, indicating >99% conversion. The final spectrum was stable at room temperature at the applied potential. When the resulting greenish solution of the cation radical was electrochemically reduced, all of the starting material was recovered, indicating complete reversibility of the process.

Femtosecond Time-Resolved Potentiostatic Transient Absorption Spectrometry. Time-resolved absorption spectra in the Soret and Q band regions for the zinc(II) meso-tetraphenylporphine cation radical and its neutral counterpart in acetonitrile at 298 K, acquired using 130 fs excitation flashes at 400 nm, are shown in Figure 2.

At ~1 ps after excitation of the cation, bleaching of the ground state bands at 409 and 445 nm was accompanied by the appearance of a positive absorption over the 460−650 nm range of the spectrum (black line in Figure 2A). Over the following several tens of picoseconds, the derivative-shaped spectrum shifted slightly to the blue and decayed uniformly to the baseline, reflecting complete ground state recovery, with an isosbestic point near 470 nm (Figure 2A). The obscured features around 409 nm possibly result from pump beam interference. For comparison purposes, Figure 2B presents the transient spectral evolution of the neutral Zn(II)TPP species under the same experimental conditions prior to the application of positive potential. The spectral profiles of the two species and their temporal behaviors are clearly different in the presence and absence of applied voltage. The 30 ps spectrum of the neutral remained unchanged in intensity over the instrumental time window (1.5 ns).

Representative Soret and Q band region kinetic data are shown in Figure 3. At all wavelengths, the transient signals were fully developed within the instrument response function (~250 fs) and the resulting temporal change was fitted with a single exponential function added to a minor constant component (probably arising from an excited state of a small fraction of the parent porphyrin). The lifetimes of the transient signals shown in Figure 3 were 16.5 ps (445 nm) and 17.6 ps (495 nm). The lifetimes in the 470−650 nm band showed weak wavelength dependence ranging from 12 ps at the red edge to 18 ps at the blue.

Discussion

The spectrum of zinc meso-tetraphenylporphine cation radical (Figure 1) displayed features consonant with a π-cation species.[3,25] The Soret band was slightly blue shifted and weakened in intensity and the Q band region was featureless and broadened (Figure 1). These bands arise from those transitions that are responsible for the Soret and Q band transitions of the neutral

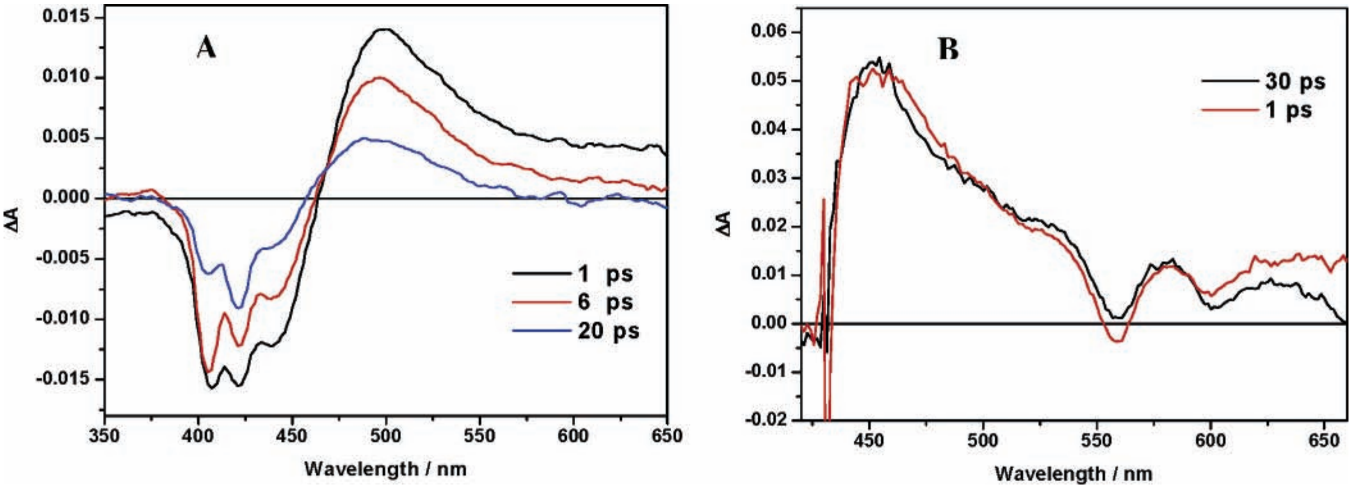

Figure 2. Absorption difference spectra in the visible region of (A) Zn(II)TPP$^{+\bullet}$ and (B) Zn(II)TPP in acetonitrile/TBAHP acquired following a 130 fs excitation pulse at 400 nm. The pulse energy was 2 μJ.

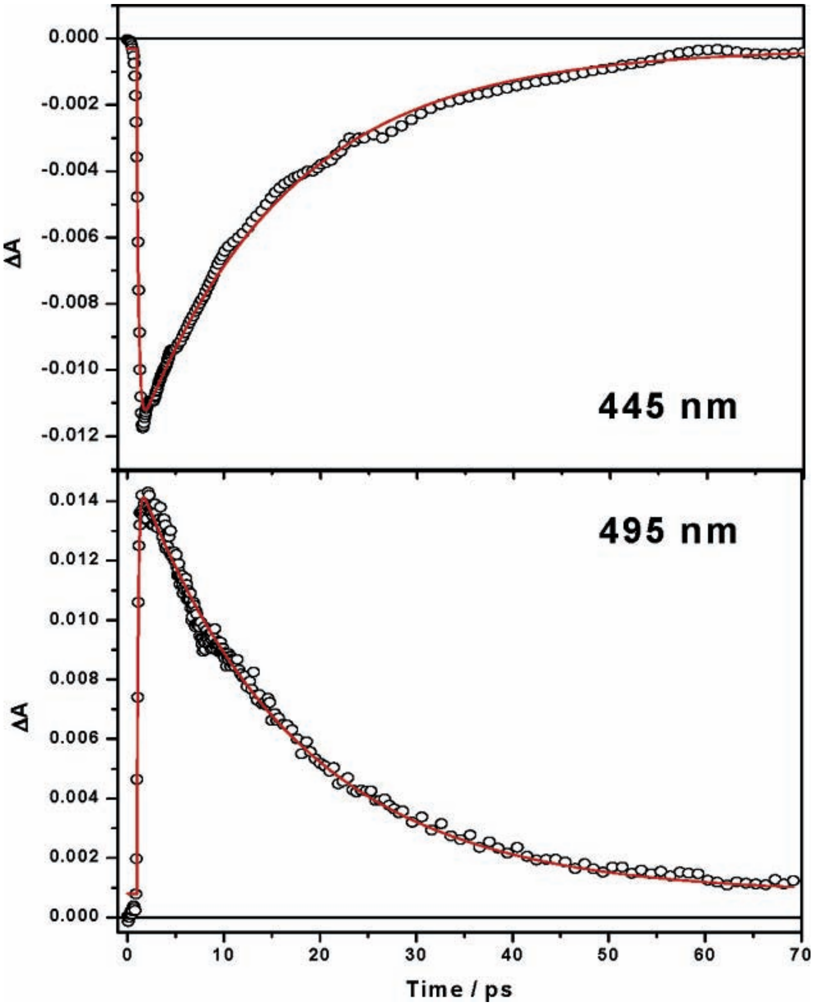

Figure 3. Representative kinetic data and the fits of the evolution of the absorption difference spectra of Zn(II)TPP$^{+\bullet}$ in acetonitrile/TBAHP from Figure 2A.

species, as reported by Fajer et al.[1] Extensive electron spin resonance (ESR) and electron paramagnetic resonance (EPR) studies of oxidized zinc porphyrin species[16,25−27] have shown that the ground electronic state has a $^2A_{2u}$ configuration after one electron has been removed from the $a_{2u}(\pi)$ highest occupied molecular orbital (HOMO), an orbital that places electron density mainly on the central nitrogens and the meso carbons.[28] However, the central metal remained indifferent to the oxidized ligand[29] and does not contribute to the ground electronic absorption spectrum. The lack of broad bands in the 800−950 nm region suggested the absence of any dimeric forms of the cationic species and excluded possible interference from the supporting electrolyte PF_6^- anion.[19]

The 400 nm excitation beam presumably populates a higher-lying $^2(\pi,\pi^*)$ excited state, which apparently undergoes rapid radiationless deactivation to the $^2(\pi,\pi^*)$ (D_1) state within the instrument response.[30] The D_1 excited state decayed with a lifetime of ∼17 ps during which the transient spectra narrowed and slightly shifted to the blue (Figure 2A), indicating a conformational/vibrational relaxation process.[31] Thus, the major excited state deactivation pathway for excited radical cation states examined here appears to be internal conversion from the lowest excited doublet state (D_1) to the doublet ground state (D_0). The lack of luminescence and the efficiency of the nonradiative deactivation mode presumably arise from the small energy gaps between the ground and excited states, evidenced by broad absorption bands in the Q band region.[32] As reported by Yu et al.,[33] the neutral form of zinc(II) tetraphenylporphine exhibits some early time picosecond kinetics which were assigned to vibrational/conformational relaxation processes. Our own observations (Figure 2B) of Zn(II)TPP showed small contributions of early time decays of 1.2 and 10 ps lifetime at wavelengths beyond 600 nm, essentially in agreement with Yu et al.[33] However, since the conversion to the radical cation was >99% (Figure 1) and comparing the spectral features of Zn(II)TPP and Zn(II)TPP$^{+\bullet}$ in Figure 2, it is clear that any contribution of the neutral species is small and appears only as a small residual offset signal. The analysis of the bleaching peaks at 409 and 425 nm revealed similar kinetics to those for the negative absorption signal presented in Figure 3 at 445 nm, except that the offset at 425 nm is greater, since that bleaching corresponds to the very intense Soret band transition of the neutral porphyrin. The vibrational relaxation process in the 470−650 nm band for the radical cation showed wavelength dependence of the time constants similar to that observed for the neutral species, though the analysis of the kinetics in the 600−650 nm region did not reveal any fast 1 ps component as in the case of parent porphyrin,[33] supporting the conclusion that the contribution of unoxidized porphyrin into the overall kinetics of the cationic species was negligible.

The central metal plays an important role in the deactivation of the excited state. Despite the fact that zinc has completely filled d-orbitals, it provides an efficient mixing of its orbitals with the π-system of the tetrapyrrole ring. Since the electron is removed from the a_{2u} orbital that has electronic density on the pyrrolic nitrogens directly attached to the central metal, the mixing is facilitated.[28]

Conclusion

The potentiostatic femtosecond transient absorption technique has been successfully used to investigate the excited state dynamics of the one electron oxidation product of zinc porphyrin. The deactivation pathway of the zinc(II) meso-tetraphenylporphine radical cation has been shown to be largely dependent on both the electronic and structural properties of the tetrapyrrole macrocycles. The primary mechanism for the excited state deactivation is believed to be an internal conversion of the higher doublet states into the ground state facilitated by the effective vibronic mixing of the d-orbitals of the central metal and π-orbitals of the ligand framework. The ultrafast relaxation process proves to be a very effective mechanism for the protection of the active chromophore in the photosynthetic center against the photodamage. Finally, the combination of controlled potential electrolysis and ultrafast absorption spectrometry has interesting applications for examining the excited state dynamics of reduced/oxidized states of compounds that are thermally unstable. In one further application, we have found the method to be useful in examining the deactivation dynamics of excited states of iron(II) porphyrins.

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