SOLVENT-DEPENDENT ABSORPTION AND ELECTRONIC RELAXATION DYNAMICS OF IRON (III) TETRA-4-N- METHYLPYRIDYLPORPHINE

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Abstract:

Solvent-dependent excited-state relaxation dynamics of iron (III) tetra-4-N-methylpyridylporphine (FeTMPyP) were investigated using steady-state and femtosecond spectroscopies. Soret absorption for water-dispersed FeTMPyP consisted of two spectrally broad components centered at 3.12 eV and 2.92 eV, corresponding to $\pi \rightarrow \pi^*$ and charge-transfer (CT) transitions. The CT transition exhibited inverse-dielectric-dependent energy shifts. Following 400-nm excitation, dynamics proceeded by femtosecond internal conversion from the initially prepared π^* state to the CT state, followed by solvent-dependent CT relaxation. The CT energy shifts and relaxation rates exhibited correlated dielectric dependences. CT absorption energy and relaxation dynamics of FeTMPyP are sensitive indicators of surrounding dielectric environments.

Introduction

Photo-driven processes involving synthetic and naturally occurring porphyrins have been of substantial interest due to their catalytic properties and biochemical importance.^{1,2,3,4} Metal centered porphyrins present unique photophysical properties due to their structure, which incorporates a metal atom bound to a stable π conjugated macrocycle. The photophysical functions of metalloporphyrins depend on the electronic properties of the bound metal, where the nature of the metal modifies the relaxation dynamics.^{5,6,7,8,9} Iron porphyrins are a special class of metalloporphyrins due to the variety of oxidation and spin states associated with the iron atom. The versatility of iron-centered porphyrins offers routes to prepare materials with optical, electrochemical, and magnetic functionality. The family of iron metalloporphyrins is also of great biological importance as a result of their role as the active site in hemoproteins present in living systems as agents to transport molecules, and because of the use of synthetic porphyrins in photodynamic cancer treatment.¹⁰ Iron porphyrin molecules can also function as an assembly agent to produce nanoparticle networks, using a molecular dimer bridging scheme.¹¹ Because iron porphyrins often function in unique and spatially confined environments, it is important to determine the influence of solvents on their optical and electronic properties.

The electronic absorption spectra of metalloporphyrins is dominated by two types of bands; the Soret band (~400 nm) and lower-energy Q bands that span visible wavelengths; both of these involve exciting (π,π^*) transitions of the porphyrin macrocycle.¹² The electronic absorption properties of porphyrins are based on the four-orbital model developed in the theoretical work of Gouterman.¹² Two nearly degenerate highest occupied molecular orbitals (HOMOs) and two degenerate pairs of lowest unoccupied molecular orbitals (LUMOs) produce four electronic transitions. The near ultraviolet (UV) to high-energy visible absorption peak

corresponds to the strongly allowed transition and is referred to as the Soret band. The weakly allowed optical transitions in the visible region of the spectrum are denoted Q bands. The electronic absorption properties of metalloporphyrins depend on the π -conjugated system of the porphyrin, whereas the relaxation properties are strongly influenced by the centrally ligated metal.^{5,6,13,14,15} Ultrafast spectroscopy has been an invaluable tool for understanding electronic dynamics in porphyrins.^{13,14,15,16,17,18} Metalloporphyrins containing metal atoms with unfilled d-orbitals [e.g. Ni(II), Cu(II), Fe(III)] have been shown experimentally to rapidly dissipate energy through a ligand-to-metal charge transfer (LMCT) channel, which is not efficient in the presence of filled d orbitals such as Zn(II)TPP.⁶

In this paper we describe the electronic excitation spectra and relaxation dynamics of iron (III) tetra-4-N-methylpyridylporphine (FeTMPyP) in a range of dielectric environments. The UV-Vis absorption spectra revealed two contributions to the Soret band where the lower-energy component was found to depend on the dielectric properties of the solvent, exhibiting an inverse dielectric-dependent red shift with decreasing dielectric constant. This lower energy component was assigned to a charge-transfer (CT) transition. Femtosecond transient absorption measurements on FeTMPyP also revealed dielectric-dependent relaxation rates. A model involving Soret band excitation, internal conversion, and a ligand-to-metal charge-transfer state (LMCT) relaxation process explains the excited state dynamics observed for FeTMPyP. Specifically, following Soret-band excitation using a 400-nm pump pulse, FeTMPyP electronic relaxation proceeded by femtosecond internal conversion from the π^* to CT states, followed by non-radiative relaxation within the C-T manifold of states; the time constant for the latter step spanned 520 fs (water) to 1.4 ps (1-propanol). Subsequent non-radiative electronic relaxation occurred over 2.8 ps (water) to 6.0 ps (1-propanol). The relaxation time constants exhibited

solvent dielectric dependences that correlated directly with the energy shift determined from linear absorption measurements. Based on these data, the charge-transfer steady-state absorption and time dependent transient signals of FeTMPyP provide sensitive indicators of the dielectric conditions of the iron porphyrin surrounding environment.

Experimental Methods

Preparation of FeTMPyP Monomer and Optical Characterization

FeTMPyP was purchased from Cayman Chemical Company. For FeTMPyP solutions, 0.1 mM FeTMPyP in solvent was prepared at room temperature. The solutions were vortexed and the pH was adjusted to pH 2 using 0.1 N HCl. At pH 2 FeTMPyP exists as the monoaquo ferric porphyrin species, $[\text{Fe(III)TMPyP(H}_2\text{O)}]^{19}$. The UV-Vis absorption spectra of FeTMPyP (pH 2) was measured in water, 3:1 water : methanol mixture, 1:1 water : methanol mixture, 1:3 water : methanol mixture, methanol (Macron Fine Chemicals), ethanol (Koptec), and 2-propanol (Sigma-Aldrich). All water used was 18.2 M Ω milli-Q filtered. Absorption spectra were collected using a Perkin Elmer (Lambda 950) spectrometer.

Femtosecond Time-Resolved Transient Absorption Experimental Setup

Transient absorption experiments were performed using an amplified 1-kHz, 800-nm Ti:Sapphire laser system that delivered 800-uJ pulse energies. The experimental setup has previously been described in detail.^{20,21} The amplified 90 fs pulse was characterized by frequency-resolved optical gating (FROG) pulse diagnostics.²² The compressed output of the amplified laser system was split into two beams (96:4) with the more intense arm serving as the pump pulse and the less intense one providing a broadband probe pulse. A 400 nm excitation pulse was generated by frequency doubling the pump portion of the fundamental output. For the

work reported here, the excitation pump pulse energy was held constant at 800 nJ/pulse. A visible continuum probe pulse that spanned 450 nm to 850 nm was generated by focusing the less intense portion of the amplified laser onto a sapphire plate. The pump-probe time delay was controlled using a retroflecting mirror mounted on a motorized linear translation stage. The probe and pump pulse were spatially overlapped at the sample and the probe pulse was spectrally dispersed on a silicon diode array. Time-dependent differential absorption spectra were determined by measuring the transmitted 1-kHz continuum pulse while modulating the pump pulse with a chopper at 500 Hz. Differential absorption spectra collected in this manner spanned from 450 nm to 800 nm. The instrument response time was determined from the non-resonant response of the pump and probe pulse in water, water:methanol (1:3; 1:1; 3:1) solutions, methanol, ethanol, and 2-propanol. An instrument response function of 150 fs was typical for the experiments described in this paper. Time-resolved transient absorption data were analyzed for select probe wavelengths using multi-component fitting methods developed in house.²¹

Results and Discussion

First, the electronic excitation spectrum of aqueous FeTMPyP was determined by measuring the linear UV-Visible absorption spectrum (Fig. 1a). Iron porphyrin is soluble over a broad pH range. At pH 2 FeTMPyP exists as the monomeric monoaquo ferric porphyrin species, [Fe(III)TMPyP(H₂O)],¹⁹ which exhibits two dominant overlapping peaks in the Soret region of the spectrum and two weaker bands appearing at 2.4 eV and 1.95 eV. The UV-Vis absorption spectrum for FeTMPyP in an aqueous solution (Fig. 1a) agreed well with literature reports, which attribute these features to a system containing the monomeric porphyrin species.^{23, 24} Previous reports for this iron porphyrin attribute the strong intensity of the two peaks to a

possible mixing of the $\pi \rightarrow \pi^*$ transitions and C-T transitions resulting in two components in the Soret band.²⁴

FeTMPyP was dispersed in a series of solvents to monitor the dielectric dependence of the absorption spectrum. The iron porphyrin was dispersed into 1:3, 1:1, and 3:1 water:methanol mixtures, methanol, ethanol, and 2-propanol solutions, which corresponded to dielectric constants that ranged from 80 (water) to 20 (2-propanol). The approximate dielectric constants of water and methanol solvent systems were calculated for 3:1, 1:1 and 1:3 water : methanol mixtures, where the ratios reflect the volume ratios. The dielectric constants were calculated using a previously reported method for determining these values for binary mixtures by using the weighted average of each component.^{25,26} Therefore the dielectric constant values for the water/methanol mixtures were calculated as follows $\epsilon_m = \Phi_1\epsilon_1 + \Phi_2\epsilon_2$ where ϵ_m , ϵ_1 , and ϵ_2 are the dielectric constants of the mixture and solvents 1 and 2, respectively.^{25,26} Using this method, the weight fractions, Φ_1 and Φ_2 , were determined for the water and methanol amounts used in the mixtures. The values of dielectric constants for 3:1, 1:1 and 1:3 water: methanol mixtures were calculated to be 70.1, 59.2 and 46.4, respectively.

All solutions were adjusted to pH 2 and characterized by measuring the absorption spectrum (Fig. 1b). The spectra obtained for FeTMPyP in the water:methanol mixtures, methanol, ethanol, and 2-propanol solutions exhibited changes in the relative peak amplitudes for the high- and low-energy Soret components as compared to the peak amplitudes observed in the aqueous FeTMPyP absorption spectrum. The ratio of the relative peak intensities, $I_{(\pi, \pi^*)} / I_{CT}$, changed from 1.20 to ~0.60 as the dielectric is changed from 80 to 20. As the solvent dielectric was changed, the low-energy Soret component shifted monotonically to longer wavelengths, whereas the high-energy component was unaffected by solvent.

Figure 1. (a) Steady-state absorption spectrum of FeTMPyP in aqueous solution. (b) Linear absorption spectra for FeTMPyP in several solvent dielectrics; the plot is truncated to emphasize the Soret absorption region. (c) First derivative of truncated absorption spectra for FeTMPyP in water (black), 3:1 water : methanol (cyan), 1:1 water : methanol (purple), 1:3 water : methanol (orange), methanol (red), ethanol (blue), 2-propanol (green) for the energy range 3.52 eV to 2.58 eV given in panel. (d) Inverse dependence of energy shift on dielectric constant of solvent. The energy shift, ΔE , is reported relative to the high energy ($\pi \rightarrow \pi^*$) component of the Soret band (3.1 eV).

In order to more accurately assign the peak energies that contributed to the Soret resonance feature, the first derivative of the absorption spectrum of FeTMPyP was calculated. (Fig. 1c). Specifically, peak positions were determined by identifying the downward-going

derivative features in the dAbs/dE spectra and calculating the peak energy from the midpoint between the maxima and minima inflection points. Using this method, two components centered at 3.12 eV and 2.92 eV were found to contribute to the Soret resonance feature in the absorption spectrum of FeTMPyP dispersed in water. In order to determine the dielectric-dependent energy shift of the Soret band components, the first derivative of the absorption spectrum of FeTMPyP was calculated for all solvents. The high-energy component remained at ~ 3.1 eV for all solvents. In contrast, the low-energy component exhibited a strong dielectric-dependent energy shift. First derivative results revealed peak energies for the lower energy contribution for water, 1:1 water : methanol mixture, methanol, ethanol, and 2-propanol to be 2.92, 2.91, 2.87, 2.86, 2.85 eV, respectively, corresponding a net energy shift of 70 meV as the dielectric was changed from water (80) to 2-propanol (20). The observed dielectric dependence of the amplitude and absorption wavelength of the low-energy component of the Soret band indicated that this peak reflected a charge-transfer absorption band, consistent with previous predictions.²⁴ The energy shift of this assigned charge-transfer state relative to the initially excited Soret state (3.1 eV) was found to have an inverse dependence on the dielectric constant of the solvent (Fig. 1d), as expected based on classical Coulomb estimates for charge transfer energies. In order to confirm this inverse dielectric dependence, the experimentally observed energy shift (ΔE) plotted versus the solvent dielectric constant (D) was fit using the following expression:

$$\Delta E = \left(\frac{q_1 q_2}{4\pi\epsilon^2 D} \right) = \left(\frac{A}{D} \right) \quad (1)$$

where A is a constant that accounts for coulomb charges and the dimensions of the charge-transfer complex. The resultant fit result is included as a solid black line in Fig. 1d.

In order to gain more insights into local solvent effects on iron porphyrin absorption and electronic properties, the excited state relaxation dynamics of FeTMPyP were also studied in the

same series of solvents using femtosecond time-resolved transient absorption measurements. The transient absorption spectra obtained for aqueous FeTMPyP following 400-nm excitation are portrayed in Figure 2a at several different pump-probe delay times, 0.35 ps, 0.85 ps and 3.30 ps, as denoted in the figure legend. These delay times were chosen to illustrate the time-dependent evolution of the transient spectra following excitation. For reference, the inverted ground-state excitation spectrum for FeTMPyP in water is given in Fig. 2a. In the transient difference spectra measured at 0.35 ps a positive-amplitude excited state absorption feature is observed at ~ 2.70 eV. The difference spectra obtained for aqueous FeTMPyP at pump-probe time delays of 0.35 ps and 0.85 ps contained a transient bleach at ~ 2.41 eV along with multiple excited-state absorption peaks in the range that extended from 2.25 eV to 1.65 eV. A low-amplitude transient bleach was also observed at the Q band transition energies (1.95 eV). However, it is noted that the differential absorption signal is offset to positive values because of spectral overlap with excited state absorption responses in this probe detection region.

Figure 2. (a) Transient absorption difference spectra collected following 400 nm excitation of FeTMPyP in water. Difference spectra measured at delay times 0.35 ps (black), 0.85 ps (red) and 3.30 ps (blue) following 400-nm excitation. (b) Single wavelength kinetic results for FeTMPyP dispersed in water. The black trace corresponds to the bleach recovery at approximately 2.4 eV. The kinetic trace in red corresponds to excited state relaxation.

Excited-state transient absorption spectra have been previously characterized for condensed-phase porphyrin systems.⁸ For Sn(IV), Zn(II) and Mg(II) porphyrin complexes an intense transient peak resulting from excited-state absorption by the $^1(\pi, \pi^*)$ state has been observed between 2.95 and 2.53 eV probe energies.⁸ Absorption by the excited $^1(\pi, \pi^*)$ state also generates a broad transient feature ranging from 2.48 eV into the near-infrared wavelength region.⁸ The detection of these two transient features in the difference spectra of aqueous

FeTMPyP indicated that $^1(\pi, \pi^*)$ excited states were accessed by the 3.1 eV pump pulse. The relaxation dynamics of a series of metalloporphyrins with partially filled 3-d shell transition metals such as Ni(II), Co(II), Cu(II) and Fe(III) porphyrins and closed shell Zn porphyrins, has been studied in the gas phase using 400 nm excitation and multi-photon-ionization pump-probe methods.^{5,6,9} For Fe(III), Ru(II), Co(II), Ni(II) and Cu(II) transition metal metalloporphyrins, a biexponential decay is observed with the initial S_2 excited state having a lifetime of ~100 fs, and second relaxation time constant in the picosecond range is observed.⁶ The ultrafast dynamics of iron (III) tetraphenylporphyrin chloride (Fe(III)TPPCL) in the liquid-phase – system, which is similar to the topic of this letter- reveal an electronic relaxation process on a time scale of 0.4-0.6 ps that involves the formation of a LMCT state.¹³

Taken together, previous results for Fe(III)TPPCL and our current data suggest the relaxation dynamics for the aqueous FeTMPyP proceeds through an intermediate charge transfer state. Figures 2b and 3a display the normalized single wavelength kinetic trace corresponding to the bleach recovery at approximately 2.4 eV compared to the excited state absorption signal detected using a probe energy of 1.8 eV. The calculated difference kinetics for the selected single wavelength traces reveal an additional first-order exponential component with an approximate 1 ps time constant (Fig. 3b). This was an indication of an intermediate electronic state that mediates the relaxation dynamics for the aqueous FeTMPyP. This intermediate process was also reflected in the apparent growth process detected in the 2.3-eV excited state absorption signal. The model we propose to describe these FeTMPyP transient data involve an initial ligand-based $\pi \rightarrow \pi^*$ excitation achieved by 400 nm pumping. (Fig. 4) The initial excited state relaxes by rapid internal conversion in the manifold of states that make up the Soret band. Further electronic relaxation into a charge transfer state that occurs in approximately 260 fs (for water). Subsequent

thermalization of the charge transfer manifold of states into a relaxed-charge-transfer configuration occurs on the sub-picosecond time scale (520 fs). Further thermalization proceeds with a time constant of 2.8 ps. These time constants are the reported averages resulting from five trials.

Figure 3. Normalized time-dependent transient signal amplitudes measured using 2.4 eV probe (black) and 1.8 eV probe (red). The time domain data are obtained from temporal analysis of the data shown in Figure 2. (b) Difference between single wavelength time-dependent transient signal amplitudes for the 2.4-eV bleach and 1.8-eV excited state absorption signals shown in panel (a). The difference reveals an additional relaxation component contributing to the ground-state bleach kinetics.

Figure 4. (Left) Proposed model for electronic relaxation of FeTMPyP in water following 400-nm excitation. Excited state S_n refer to (π, π^*) excited states of the porphyrin macrocycle. The charge transfer state, CT, involves an electronically excited porphyrin transferring an electron to the centrally ligated metal. (Right) The light gray box depicts solvent stabilization of the CT state. Stabilization of the CT states affects non-radiative relaxation rates following an energy-gap law, as described in the text and summarized in Figure 6.

In order to examine the kinetic model depicted in Figure 4 and determine the contributions from charge-transfer states to the FeTMPyP relaxation dynamics, the influence of the dispersing solvent on the ultrafast electronic decay rates were quantified by performing transient absorption measurements on FeTMPyP dispersed in a series of solvents that included water : methanol mixtures (3:1; 1:1; 1:3), methanol, ethanol, and 2-propanol. Indeed, these data were significantly dependent upon the solvent dielectric constant. The transient absorption difference spectra collected following 400 nm excitation of FeTMPyP in 2-propanol collected at pump-probe delay times, 0.26 ps, 1.30 ps and 5.70 ps contains a transient bleach feature along with multiple excited-state absorption peaks, similar in nature to water-dispersed FeTMPyP. (Fig. 5a) The time-resolved transient signals obtained from single wavelength probing of this

system are displayed in Figure 5b along with fitting results. Similar to the data obtained for water-dispersed FeTMPyP (Figure 2), the ground-state bleach for 2-propanol-dispersed porphyrin also included a low-amplitude picosecond component not observed for excited-state absorption detection.

Next, the time dependence of transient bleach signals for FeTMPyP dispersed in a series of solvents was examined. These data were fit using three exponential decay components and a non-decaying plateau function. The τ_1 time constant exhibited small dielectric dependence in going from water to water : methanol mixtures, but remained statistically invariant for all other solvents: 0.26 ± 0.10 (water), 0.20 ± 0.10 (3 :1 water : methanol), 0.20 ± 0.10 (1 :1 water : methanol), 0.15 ± 0.10 (1 : 3 water : methanol), 0.20 ± 0.10 (methanol), 0.20 ± 0.10 (ethanol), 0.20 ± 0.10 ps (1-propanol). The τ_2 time constant was strongly influenced by the dispersing dielectric. For FeTMPyP dispersed in 3:1 water : methanol mixture, 1:1 water : methanol mixture, 1 : 3 water : methanol mixture, methanol, ethanol, and 2-propanol, the second time constant was determined to be 0.55 ± 0.10 , 0.60 ± 0.10 , 0.70 ± 0.10 , 1.10 ± 0.1 , 1.20 ± 0.10 ps, and 1.40 ± 0.10 ps respectively; the 2-propanol data corresponded to an approximate 3-fold increase in the τ_2 time constant, with respect to water. The τ_3 time constant exhibited a smaller, but statistically significant dielectric dependence: 2.80 ± 0.10 , 3.30 ± 0.40 , 3.62 ± 0.90 , 5.30 ± 0.40 ps, 5.40 ± 0.20 ps, 6.00 ± 0.80 ps for 3:1, 1:1, 1:3 water:methanol mixtures, methanol, ethanol, and 2-propanol respectively, corresponding to a 2-fold τ_3 increase in going from water to 2-propanol. The time-dependent transient bleach recovery - monitored in the 2.4 – 2.3 eV region - obtained for FeTMPyP dispersed in several solvents are compared in Figure 6a, which clearly portrayed the effect of the local dielectric on the global relaxation dynamics over the picosecond time scale.

Figure 5. (a) Transient absorption difference spectra collected following 400 nm excitation of FeTMPyP in 2-propanol. Difference spectra measured at delay times 0.26 ps (black), 1.30 ps (red) and 5.70 ps (blue) following 400-nm excitation. (b) Single wavelength kinetic results for FeTMPyP dispersed in 2-propanol. The black trace corresponds to the bleach recovery at approximately 2.4 eV. The kinetic trace in red corresponds to excited state relaxation.

The solvent-dependent linear absorption data, along with the time-resolved transient absorption results suggested that the low-energy component of the Soret absorption band corresponded to a charge-transfer transition. The solvent-dependent trends observed for the kinetic data could be understood by considering the linear and transient absorption data together.

The energy shift of the charge transfer state was due to solvent stabilization of the CT state, which is reflected in the inverse dielectric-dependent shift of the CT absorption energy with respect to the higher energy π^* state. (Fig. 1d). The dielectric dependence of the time-resolved data is evident in the electronic relaxation time constants (Fig. 6b). The stabilization of the charge transfer state shifted the energy of the electronic charge-transfer state relative to the initial excited state prepared by the 400-nm pump pulse. The dielectric-dependent time constants, τ_2 , were found to directly correlate with the energy shift, ΔE (Fig. 6c.); the non-radiative (τ_2) relaxation time constant was directly related to the energy difference between the initial and final electronic states of the relaxation process. These findings supported a relaxation model that involved initial excitation followed by rapid internal conversion and subsequent relaxation to a charge transfer state with a dielectric dependent time constant τ_2 . Following relaxation into the charge transfer state, thermalization of the charge carriers accounted for the third time constant. Therefore, the solvent dependence of the electronic relaxation time constants resulted from dielectric stabilization of iron porphyrin charge transfer states.

Figure 6. (a) Time-dependent differential absorption signal monitored by probing the approximate 2.4 eV bleach transition for FeTMPyP dispersed in several solvents, described in panel legend. These data reflect the dielectric dependence of the bleach recovery. The fitting parameters involved three exponential components and a plateau function for all samples. Plot is truncated to first 10 ps following time zero. (b) Relaxation time constant τ_2 plotted against the dielectric constant of the solvent. (c) Relaxation time constant τ_2 plotted as a function of the ΔE , where ΔE is the energy change between the initially formed state upon excitation and the proposed charge transfer state.

Conclusions

We have investigated the influence of solvent dielectric on the linear absorption and the electronic relaxation dynamics of FeTMPyP dispersed in a series of solvents. A multi-component feature in the Soret region of the spectrum dominated the linear absorption spectrum for FeTMPyP in water. These intense absorption components resulted from a mixing of the $\pi \rightarrow \pi^*$ and charge-transfer (C-T) electronic transitions. The lower energy component shifted by 70 meV to lower energy with decreasing dielectric constant of the dispersing medium. This shift was due to stabilization of this charge transfer state when the solvent dielectric constant was changed. Transient absorption experiments were carried out to study the electronic relaxation of FeTMPyP dispersed in water and polar protic solvents. The proposed model for FeTMPyP involves internal conversion after excitation, followed by charge transfer and thermalization of the charge transfer band. The solvent influenced the charge transfer dynamics as a result of the dielectric-induced stabilization of the electronic CT state. The dielectric-dependent time constant, τ_2 , correlated linearly with the energy shift of the proposed charge-transfer state relative to the initially prepared state. Based on these results, the FeTMPyP charge-transfer transitions provide a sensitive indicator of the dielectric conditions of the surrounding environment. The results from this study suggest that the charge transfer state of this iron porphyrin can be used as a spectroscopic probe to observe changes in the local environment of complex systems. Furthermore, a complete understanding of the functional role of metalloporphyrins requires a full description of the influence of the local dielectric on their optical and electronic properties.

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