**CHEMICAL
PHYSICS
LETTERS**

Excitation relaxation of zinc and free-base porphyrin probed by femtosecond fluorescence spectroscopy

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Abstract

Fluorescence rise and decay times of zinc porphyrin (ZnP) and free-base porphyrin (H_2P) were measured using a fluorescence up-conversion method. The observed fluorescence signals were analyzed to be a sum of three exponentials: 150 fs, 600 fs, and 1.5 ns for ZnP; and 90 fs, 1.5 ps, and 12 ns for H_2P. The two fastest components of 150 and 600 fs for ZnP are associated with the decay processes of $B \rightarrow Q$ internal conversion and the vibrational relaxation in the Q state, respectively. The short-lived components of 90 fs and 1.5 ps for H_2P are correlated with the decay processes of $Q_y \rightarrow Q_x$ internal conversion and the vibrational relaxation in the Q_x state, respectively. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

There have been numerous attempts to construct synthetic analogues to biological molecular systems to obtain a deeper understanding of the sequential and cooperative reactions observed in nature [1–16]. A variety of porphyrin oligomers have been prepared as models for photosynthetic reaction centers [5–16] and through steady-state and time-resolved spectroscopies advances have been made toward understanding the electronic properties and the porphyrin–porphyrin interaction occurring in these systems. In these highly organized donor/acceptor (D/A) molecules, electron or energy transfer can

occur in a time regime of < 10 ps. These intramolecular processes are expected to compete effectively with other relaxation processes available to the electron or energy donor such as an internal conversion and a vibrational relaxation. Although much progress has been made in understanding the photodynamics occurring in these molecules, a complete picture of the excited state dynamics in a porphyrin moiety has yet to be obtained. There have been two studies reporting the direct measurement of the B state lifetime of a porphyrin derivative, zinc tetraphenylporphyrin (ZnTPP), using a fluorescence up-conversion method [17,18]. Chosrowjan et al. report lifetimes of 3.5 and 0.75 ps in acetonitrile and dichloromethane, respectively, [17] while Gurzadyan and coworkers observed a biexponential decay of fluorescence with 60–90 fs and 2.35 ps components correlated with vibrational relaxation in the B state

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and internal conversion from the B state to the Q state (B → Q), respectively [18].

We have previously reported experiments aimed at elucidating the relaxation processes of three kinds of zinc porphyrin dimers and a circular trimer [19]. These studies revealed that following photoexcitation in resonance with B band absorption B → Q internal conversion occurs within 30 fs. This relaxation process is followed by excitation delocalization within the Q state in a time scale of tens to hundreds of fs. The present study is aimed at extending our understanding of porphyrin excited state dynamics by investigating the monomeric units of the zinc dimers and circular trimer. Specifically, we are concerned with obtaining information on the internal conversion and vibrational relaxation occurring in zinc porphyrin (ZnP) and free-base porphyrin (H$_2$P) immediately after B band excitation. Through a combination of ground state electronic absorption, steady-state emission, and femtosecond fluorescence spectroscopy, the excited state relaxation dynamics of ZnP and H$_2$P are discussed.

2. Experimental

ZnP and H$_2$P were synthesized by the method previously reported [7]. All the samples were prepared as benzene solution at $\sim 10^{-5}$ M. Each sample was degassed by repeated freeze–pump–thaw cycles just prior measurement.

The steady-state absorption and fluorescence spectra were recorded with a JASCO Ubest-50 spectrophotometer and a Hitachi F-4500 fluorescence spectrometer, respectively. Fluorescence decay curves were measured with a femto second fluorescence up-conversion system described in detail elsewhere [19]. Briefly, the fluorescence was excited with the second harmonic of a Ti:sapphire laser (Spectra-Physics, Tsunami, 840 nm, 80 MHz) pumped with a diode-pumped solid state laser (Spectra-Physics, Millennia X). To avoid polarization effects, the angle between the polarizations of the excitation and probe beams were set to the magic angle by a $\lambda/2$ plate. The sum-frequency signal of the Raman line in pure benzene excited with the second harmonic yielded an instrumental response function of 200 fs FWHM. In order to reconstruct

the transient spectra, the fluorescence intensities in the wavelength region of 520–620 nm were corrected using the correction factors that were obtained for matching the integrated fluorescence up-conversion signals of β-carotene with its steady-state fluorescence. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Absorption and fluorescence spectra

Absorption and fluorescence spectra are depicted in Fig. 1. For ZnP, there are two absorption bands, the B band (Soret band) in the near-UV ($\lambda_{max} = 412.0$ nm) and the Q band in the visible ($\lambda_{max} = 538.5$ and 572.9 nm). Two peaks in the Q band are assigned to $Q(1,0)$ and $Q(0,0)$, respectively. When the effects of substituent groups are assumed to be negligibly small, H$_2$P and ZnP belong to the symmetry group of D_{2h} and D_{4h}, respectively. The break of symmetry of the porphyrin ring by the central proton axis changes the
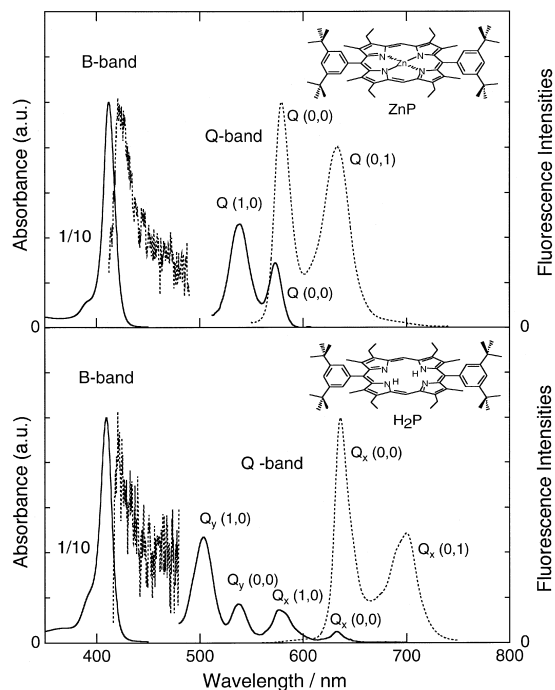

Fig. 1. Absorption (solid lines) and fluorescence (dashed lines) spectra of: (a) ZnP and (b) H$_2$P.

absorption spectra from a two-banded (D_{4h}-type) to a four-banded (D_{2h}-type) spectrum. Thus, Q(0, 0) splits into $Q_x(0, 0)$ and $Q_y(0, 0)$ separated by ~ 3000 cm^{-1} for H$_2$P. As depicted in Fig. 1, the absorption spectrum of H$_2$P consists of an intense B band ($\lambda_{max} =$ 409.6 nm), and two Q bands: Q_y band ($\lambda_{max} = 503.2$ and 537.2 nm) and Q_x band ($\lambda_{max} = 576.4$ and 632.0 nm). Each Q band has a vibronic structure corresponding to the vibronic origin and the first excited vibronic level of the excited state.

The fluorescence spectrum of ZnP displays intense fluorescence originating from the first excited singlet state, S$_1$ or Q state. This Q band fluorescence has two peaks at 578.8 nm (Q(0, 0)) and 633.0 nm (Q(0, 1)). In addition to the Q band fluorescence, weak B band fluorescence originating from the second excited singlet sate, S$_2$ or B state is also observed. The fluorescence quantum yield ratio, ϕ_F^Q / ϕ_F^B, is ~ 400. Weak B band fluorescence has also been reported for ZnTPP [18,20]. An estimate of the lifetime of the excited B state following B band excitation can be made based upon the results of the absorption, steady-state emission data and the previously reported lifetime of the Q band fluorescence of 1.5 ns [7]. Since the B band absorption is estimated to be 22 times larger than that of the Q band, and the fluorescence quantum yield ratio is ~ 400, the lifetime of the B state is estimated to be ~ 200 fs. The fluorescence spectrum of H$_2$P exhibits intense Q_x fluorescence with two local maxima at 636.2 nm ($Q_x(0, 0)$) and 700.2 nm ($Q_x(0, 1)$). Although the B fluorescence was observed in the steady-state spectrum, its intensity was too weak to estimate a lifetime. The fluorescence lifetime of the Q_x band was measured to be 12 ns [7].

3.2. Excited state relaxation of ZnP

Fig. 2a shows the fluorescence rise and decay curves observed for ZnP at 470, 560, and 580 nm. The fluorescence signal of the B band (470 nm) is represented by a monoexponential decay with a time constant of 150 ± 10 fs. In contrast to the B band fluorescence signal, the fluorescence monitored at 580 nm (Q(0, 0) band) is best represented by a sum of a rise of 150 ± 10 fs and a decay of > 50 ps. The fast rise component shows a good correlation between the B state population decay and the Q state
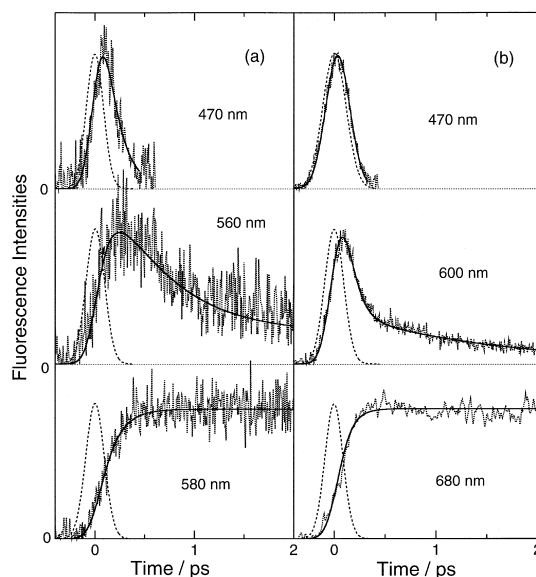

Fig. 2. Fluorescence rise and decay curves measured with a fs up-conversion method observed at: (a) 470, 560, and 580 nm for ZnP; and (b) 470, 600, and 680 nm for H$_2$P. The excitation wavelength is 420 nm, corresponding to excitation to the B band. The signal observed at 680 nm was detected by a lock-in amplifier.

population rise. This trend is in agreement with that observed for ZnTPP [18] and therefore the time constant of 150 fs can be associated with the B $\rightarrow$ Q internal conversion process. This time constant is in rough agreement with the estimated lifetime of the B state (see Section 3.1). The time constant obtained here is much shorter than that obtained for ZnTPP, 2.4–3.5 ps [17,18], although the energy gap between the B and the Q bands for ZnP is almost the same as that for ZnTPP. This is probably due to the substitution of methyl, ethyl, and/or phenyl groups onto the porphyrin ring. This point should be extensively investigated for zinc porphyrin derivatives before a comprehensive picture of the effects of substituent groups on relaxation processes is put forward.

Fig. 3a shows the reconstructed time-resolved fluorescence spectrum of ZnP together with its Q band absorption spectrum. It is clear from this figure that the fluorescence spectrum changes with time. At early time, there is significant intensity to the blue of the Q(1, 0) band. As time progresses, there is an intensity alternation until the Q band fluorescence observed in the steady-state spectrum is replicated.
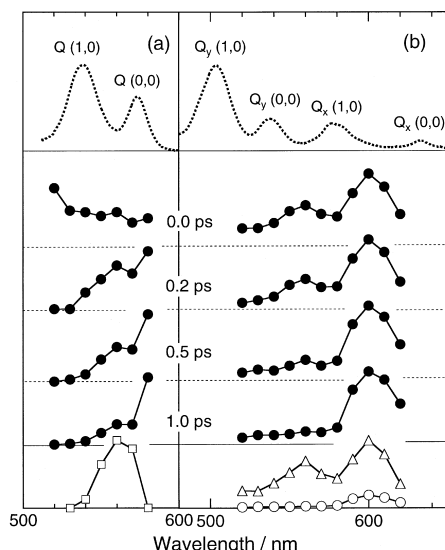
3.3. Excited state relaxation of H_2P

Fig. 3. Time-resolved fluorescence spectra and the absorption spectra in the Q region (dashed line): (a) ZnP and (b) H_2P. Spectral profiles of short-lived components are shown at the bottom: (a) 600 fs for ZnP; and (b) 90 fs (triangle) and 1.5 ps (circle) for H_2P.

In addition to the intensity change that reflects the $B \rightarrow Q$ internal conversion time of 150 fs, a band with a peak around 560 nm is recognized. In the wavelength region of 550–570 nm, the fluorescence signals are best represented as a combination of a rise of 150 ± 20 fs and two decays of 600 ± 30 fs and > 50 ps. Amplitudes of these three components are dependent upon wavelength. A spectral profile of the 600 fs decay component is shown in the bottom window of Fig. 3a. There is a direct correspondence of this component with the 600 fs lifetime in the transient fluorescence spectra. This band is located at an energetically higher level than $Q(0, 0)$, indicating that the 600 fs fluorescence should originate from a higher energy state(s). The fluorescence signals in the wavelength region where the 600 fs decay component is observed contains a rise component of 150 fs. This implies that a fluorescence with a 600 fs decay time is emitted from the Q state after the internal conversion from the B state. It is therefore reasonable to assign the 600 fs component to fluorescence originating from a vibrationally excited state(s) in the Q state and this time constant reflects the vibrational relaxation time in the Q state.

Fig. 2b shows fluorescence rise and decay curves observed at 470, 600, and 680 nm. The sum-frequency signal of the fluorescence at 680 nm was detected with a lock-in amplifier (NF circuit design block, 5610B) to avoid noise caused by the probe pulse. The B fluorescence (470 nm) decays within the time resolution of the instrument and no rise component is resolved in the wavelength region of 520–620 nm. This suggests that the $B \rightarrow Q_y$ internal conversion occurs within ~ 40 fs. The fluorescence signal observed at 600 nm is represented by a sum of three decay components; 90 ± 10 fs, 1.5 ± 0.1 ps, and > 50 ps, whereas that at 680 nm contains a rise of 90 ± 20 fs and a decay of > 50 ps.

Fig. 3b shows the time-resolved fluorescence spectrum of H_2P together with its Q_y and Q_x absorption spectrum. Immediately after excitation, the transient fluorescence spectrum exhibits two peaks at 560 and 600 nm. The relative intensity of the former band decreases with the passage of time, and only the peak at 600 nm is recognized at 1 ps. Fluorescence decay curves in the wavelength region of 520–620 nm are expressed as a sum of three decays, 90 fs, 1.5 ps, and > 50 ps, as shown for that at 600 nm. Individual contributions from these three components depend on the wavelength (the bottom window of Fig. 3b). The spectral profile of the 90 fs component shows two peaks at 560 and 600 nm. The energy difference between these peaks is ~ 1200 cm^{-1}, which is thought to be totally-symmetric vibrations of a porphyrin ring with 1130–1580 cm^{-1} due to the stretching vibrations of the C–C, C=C and/or C–N bonds, according to Raman spectroscopy [21,22]. On the other hand, the 1.5 ps component has a peak at 600 nm.

Two candidates for the origin of these two short-lived components are conceivable: (1) after the $Q_y \rightarrow Q_x$ internal conversion within the time resolution of system, a vibrational relaxation from highly excited levels occurs with a time constant of 90 fs, followed by a vibrational relaxation from the lowest excited level in 1.5 ps; and (2) after the $Q_y \rightarrow Q_x$ internal conversion with a time constant of 90 fs, the vibrational relaxation in the Q_x state occurs in 1.5 ps. In case (1), two bands at 560 and 600 nm are assigned to the $Q_x(2, 0)$ fluorescence (and higher

states, $Q_x(n, n-2)$) and the $Q_x(2,1)$ fluorescence ($Q_x(n, n-1)$), respectively. Since a $(2,0)$ transition is considerably weak against $(0,0)$ and $(1,0)$ transitions for absorption [20], the $(2,0)$ transition might be weak for fluorescence. The 90 fs component has an intense band at 560 nm, suggesting that this component should not be attributed to the $Q_x(2,0)$ ($Q_x(n, n-2)$) fluorescence. We therefore conclude that case (2) is more adequate for the relaxation of H_2P. In case (2), these two bands are explained as due to the $Q_y(0,0)$ ($Q_y(n,n)$) and $Q_y(0,1)$ ($Q_y(n, n+1)$) fluorescence bands, which show the mirror–image relationship to the Q_y absorption spectrum. The decay time of Q_y fluorescence is in good agreement with the rise time of the Q_x fluorescence observed at 680 nm.

4. Summary

We have examined the relaxation process of free-base porphyrin and zinc porphyrin by means of ground state electronic absorption, steady-state emission and femtosecond fluorescence spectroscopy. The relaxation processes of ZnP in benzene after B band excitation are summarized as follows (Fig. 4): (1) internal conversion from the B state to the Q state occurs with a time constant of 150 fs, followed by (2) vibrational relaxation in the Q state with a time constant of 600 fs, and finally this is followed by (3) Q state decays with a lifetime of 1.5 ns. The excited state dynamics following B band excitation of H_2P are consistent with the following four-step process: (1) an initial rapid internal conversion from the B state to the Q_y state taking place within 40 fs, followed by (2) internal conversion from the Q_y state to the Q_x state in 90 fs, followed by (3) vibrational relaxation in the Q_x state in 1.5 ps, and finally (4) Q_x state decay back to the ground state with a lifetime of 12 ns.

Recently, there has been intense interest in applying time-resolved spectroscopy to organic molecules in solution. An increasing amount of experimental data is becoming available for kinetic parameters of photophysical processes from higher (electronically and/or vibrationally) excited states. This present study provides additional information for ultrafast
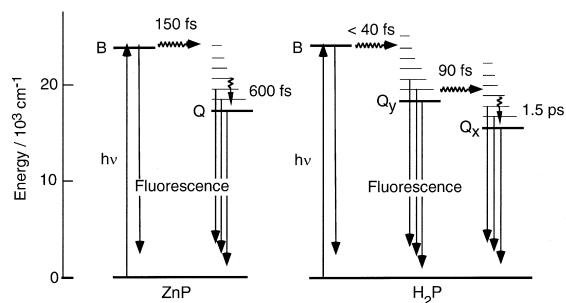

Fig. 4. Relaxation processes of ZnP and H_2P in benzene after excitation to the B band.

relaxation processes in solution and fundamental data for understanding of the relaxation kinetics in biological and artificial molecular systems.

Acknowledgements

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