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ARTICLES

Lowest Excited State of Oxovanadyl(IV) Tetraphenylporphyrin

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The excited-state relaxation dynamics and pathways of oxovanadyl(IV) tetraphenylporphyrin ($OV^{IV}TPP$) have been investigated by nanosecond time-resolved and steady-state emission, transient absorption, and transient resonance Raman spectroscopies. At room temperature, the emission spectrum shows a single broad featureless band centered near 790 nm in noncoordinating solvents such as toluene and benzene and at 814 nm in tetrahydrofuran (THF), whereas at 77 K the emission bands in the same solvents exhibit blue-shifts to 745 and 784 nm, respectively. Furthermore, the emission decay time in benzene increases from 40 to 60 ns with a decrease in temperature from 323 to 268 K. In contrast, the decay time in THF is ca. 10 ns, which is almost independent of temperature. The energy separation between the tripdoublet state ($^2T(\pi,\pi^*)$) and the tripquartet one ($^4T(\pi,\pi^*)$) under the proposed relaxation scheme of photoexcited $OV^{IV}TPP$ has been estimated to be ca. 500 cm^{-1} in benzene and toluene. The transient absorption spectra at room temperature denote a broad featureless absorption centered at around 480 nm with a ground-state bleaching at 555 nm. All the spectroscopic results including the transient Raman spectra led us to conclude that the electronic nature of the lowest excited state should be the tripquartet state ($^4T(\pi,\pi^*)$) at ambient temperature. The decay times for both photoinduced absorption and bleaching are similar and also in good accordance with the emission decay times as long as temperature and solvent are the same. The time-resolved emission spectra and wavelength dependent decay kinetics at 77 K reveal that the observed emission spectra apparently originate from three different emitting species. These observations are discussed in terms of postulating a quenching state (Q), which is thermally accessible from the tripdoublet state ($^2T(\pi,\pi^*)$) of $OV^{IV}TPP$ at room temperature.

Introduction

The photophysical properties of metalloporphyrins have been extensively investigated because these molecules have significance in biological functions such as oxidation−reduction processes. Especially, oxometalloporphyrins have attracted much attention as a model system for active sites of heme proteins such as peroxidase and cytochrome P_{450}'s,[1] which are known to be porphyrin cation radicals containing ferryl bonds, $Fe^{IV}-O$. Thus, oxovanadyl(IV) porphyrins, which also contain a stable $V^{IV}-O$ bond, may provide a convenient model system for further understanding of the electronic nature of reactive ferryl porphyrins.[2]

Oxovanadyl(IV) porphyrins are paramagnetic d^1 complexes[3] and consequently can be expected to exhibit peculiar photophysical behaviors similar to those of d^9 copper(II) porphyrins.[4] However, the photophysical properties of oxovanadyl porphyrins have not been studied in great detail even though the previous systematic resonance Raman studies have been done to elucidate the nature of the $O-V^{IV}$ bond.[2] The unpaired electron in the d_{xy} orbital for oxovanadyl porphyrins results in a splitting of the porphyrin ring triplet state arising from a strong interaction between the π electronic system of the porphyrin ring and the unpaired electron in the metal d_{xy} orbital. The resultant tripmultiplet ($^2T/^4T(\pi,\pi^*)$) states probably play significant roles in the relaxation dynamics of photoexcited oxovanadyl(IV) porphyrins, since the spin states of the lowest excited and ground porphyrin ring states are doublet ($^2S_1$ vs $^2S_0$). Furthermore, the unpaired electron can also invoke several charge-transfer transitions such as ring-to-metal (π(ring) → d(metal)), metal-to-ring (d(metal) → π(ring)), metal-to-metal (d(metal) → d(metal)), and their mixtures.[3] The previous studies on copper(II) porphyrins[4] proposed that the charge transfer and/or (d,d) states act as a quenching state in the deactivation process of photoexcited copper(II) porphyrins. However, the detailed electronic nature of the quenching state is still controversial.[4]

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It has been previously reported[3,5] that no fluorescence is detected for oxovanadyl(IV) porphyrins, but phosphorescence is observed from their $^2T/^4T(\pi,\pi^*)$ electronic manifolds at low temperatures. Particularly, the luminescence from oxovanadyl(IV) etioporphyrin ($OV^{IV}Etio$), β-substituted porphyrin, was reported to exhibit a main peak at 709 nm with weaker bands at 712, 725, and 755 nm. Their relative intensities vary with temperature. Gouterman et al.[3,5] assigned the main peak as the luminescence from the $^2T(\pi,\pi^*)$ state and the weaker ones as a superposition of the luminescence from the $^4T(\pi,\pi^*)$ state and its vibronic bands. The low-temperature luminescence of $OV^{IV}TPP$ consists of one broad peak centered at 758 nm, which is attributed to the tripquartet ($^4T(\pi,\pi^*)$) state, and its spectral feature as well as emission quantum yield is independent of temperature in the range 10−80 K.[5] However, the lifetime measurements exhibit a peculiar dependence on temperature and probe wavelength. Nevertheless, these complex behaviors of photoexcited oxovanadyl porphyrins have not been fully understood in the previous theoretical and experimental studies. To have a deeper understanding of the coupling of unpaired metal electrons with the porphyrin ring π electronic system, it is necessary to investigate the photophysics of oxovanadyl porphyrins not only in solid form at low temperatures but also in solution at relatively high temperatures. During the preparation of this paper, the room-temperature emission and absorption studies were reported.[6] However, the interpretation of this work is contradictory to the results of our current investigation. In the present work, the steady-state and time-resolved luminescence spectra have been recorded in both solid form at 77 K and solution at various temperatures in the range 268−333 K. Furthermore, the transient absorption and time-resolved resonance Raman spectra for $OV^{IV}TPP$ were measured in solution to correlate with the luminescence spectral data.

Experimental Section

Chemicals. $OV^{IV}TPP$ was purchased from Porphyrin Products, Inc. (Utha). The emission spectra of the raw samples consist of a strong emission band originating from free-base tetraphenylporphyrin (H_2TPP) at 650 and 720 nm and a much weaker luminescence around 790 nm at room temperature. To remove the fluorescing impurities, especially H_2TPP, the raw $OV^{IV}TPP$ was rigorously purified by extensive column chromatography on silica gel by using n-hexane/ethyl ether (7:3 v/v) mixture as an eluent. This type of procedure was found to be efficient for removing the emissive impurities. Purification two times by column chromatography was enough to reduce the emission from H_2TPP to negligible levels compared with the emission of $OV^{IV}TPP$. All the solutions studied in this work were prepared after freeze−pump−thaw cycles, keeping the porphyrin concentration lower than 10^{-4} M to prevent dimerization or aggregation.[7] The temperature was controlled within ±0.5 K in a brass block. The emission spectra and their kinetics at 77 K were obtained from a homemade liquid nitrogen Dewar.

Spectroscopic Measurements. The absorption and steady-state emission spectra were recorded on a UV−vis spectrophotometer (Cary 3E) and a SLM-AMICO 4800 spectrofluorometer, respectively. Time-resolved emission and transient absorption spectra were recorded by using a conventional flash photolysis setup based on a Q-switched Nd:YAG laser, a CW Xe arc lamp as a probe light source and a boxcar averager. The excitation source at 435 nm was obtained with a Raman shifter filled with H_2 by using the second harmonic (532 nm) of Nd:YAG laser. The temporal behaviors of the absorption and emission signals were detected with a Hamamatsu R958 photomultiplier tube of which the output was monitored by using a 500 MHz digital oscilloscope and then transferred to a microcomputer for further data processing. We have checked the validity of our experimental setup by measuring the emission temporal profile of H_2TPP of which the time constant is well established to be in the range 10−12 ns.[8] The obtained temporal profiles were manipulated with a global deconvolution method with an instrument response function (IRF) of the laser pulse.

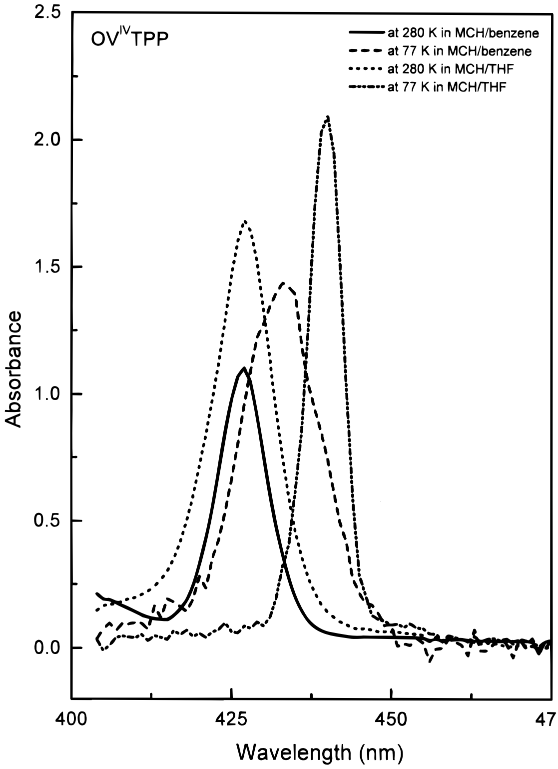

Figure 1. Ground-state near-UV absorption spectra of $OV^{IV}TPP$ in MCH/benzene and MCH/THF (10:1 v/v) at two different sample temperatures.

The transient Raman spectra were obtained by using the 532 and 457 nm pulses with a pulse width of ca. 8 ns. The probe pulse at 457 nm was generated by the D_2 Raman shifting of the second harmonic from a Q-switched Nd:YAG laser. The Raman spectra were collected with a HR 640 spectrograph (Jobin-Yvon), a gated intensified photodiode array detector (Princeton Instruments IRY700), and a pulse generator (Princeton Instruments FG100).[9]

Results

Absorption Spectra. Figure 1 shows the absorption spectra of $OV^{IV}TPP$ in the Soret band region at room temperature and 77 K. Since $OV^{IV}TPP$ is insoluble in pure methylcyclohexane (MCH), we used a mixture of MCH/other solvents (10:1 v/v) in order to obtain a transparent glassy medium at 77 K. At room temperature, the Soret band in MCH/benzene or MCH/toluene is almost identical with that in MCH/THF centered near 427 nm. At 77 K, however, the Soret band in MCH/THF is largely red-shifted to 441 nm while the Soret band in MCH/benzene or MCH/toluene is slightly shifted to 433 nm. It has been reported that the Soret band of copper(II) tetraphenylporphyrin ($Cu^{II}TPP$) in MCH exhibits a slight red-shift from 412 nm at 295 K to 417 nm at 77 K.[4d] Meanwhile, the strong basic solvents such as pyridine and piperidine are known to be ligated to the central metal ion at room temperature, and consequently, the Soret band of $OV^{IV}TPP$ has been reported to be largely red-

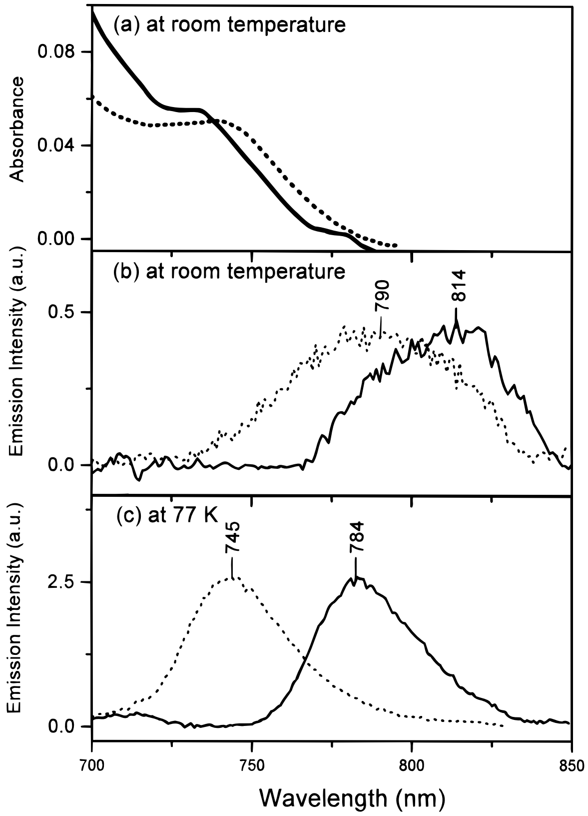

Figure 2. NIR absorption at room temperature (a) and luminescence (b and c) spectra of OV^{IV}TPP in MCH/benzene (dotted lines) and in MCH/THF (10:1 v/v) (solid lines) at room temperature (b) and 77 K (c).

shifted to 440 nm.[2a] These observations imply that OV^{IV}TPP strongly interacts with THF at 77 K compared with other noncoordinating solvents such as benzene or toluene.

We have tried to find evidence of an absorption band, if any, other than normal Q-bands especially in the region of 600−800 nm at 77 K attributable to the $^2S_0(\pi,\pi^*)-^2T_1(\pi,\pi^*)$ transition,[10] since the $^2S-^2T$ transition is a spin-allowed transition and thus the extinction coefficient is expected to be relatively high compared with other spin-forbidden transitions such as $^2S-^4T$ transition. However, we have failed to find any evidence of its presence at porphyrin concentrations less than 10^{-4} M. This is probably due to a very small extinction coefficient of the $^2S-^2T$ transition. Harima et al.[6] have recently reported the S−T absorption for 6.7×10^{-3} M solution in $CHCl_3$ at room temperature, of which the peak and molar extinction coefficient were estimated to be at 733 nm and 5 M^{-1} cm^{-1}, respectively. The similar near-infrared (NIR) absorption band was already reported in copper(II) porphyrins and was assigned to be the spin-allowed $^2S_0-^2T_1(\pi,\pi^*)$ transition. We also observed a similar absorption band in highly concentrated porphyrin solutions in noncoordinating solvents such as benzene and toluene as well as THF (see Figure 2).

Temperature Dependence of Steady-State Emission Spectra. The emission spectra of OV^{IV}TPP in benzene and THF at room temperature are displayed in Figure 2b. Since the emission intensity in THF at room temperature is too weak to be detected with a CW light source, we employed the second harmonic of pulsed Nd:YAG laser as an excitation source. The emission bands for OV^{IV}TPP at room temperature are centered at 790 and 814 nm in benzene and THF, respectively. We also observed that the emission band of OV^{IV}TPP in toluene is similar to that in benzene. There is no change in the overall spectral feature with a variation in the excitation energies either at the Soret or at the Q-band as long as the solvent is the same. The luminescence excitation spectra in the two different solvents are the same, indicating that the different luminescence spectra originate from the same molecular species under investigation (not shown).

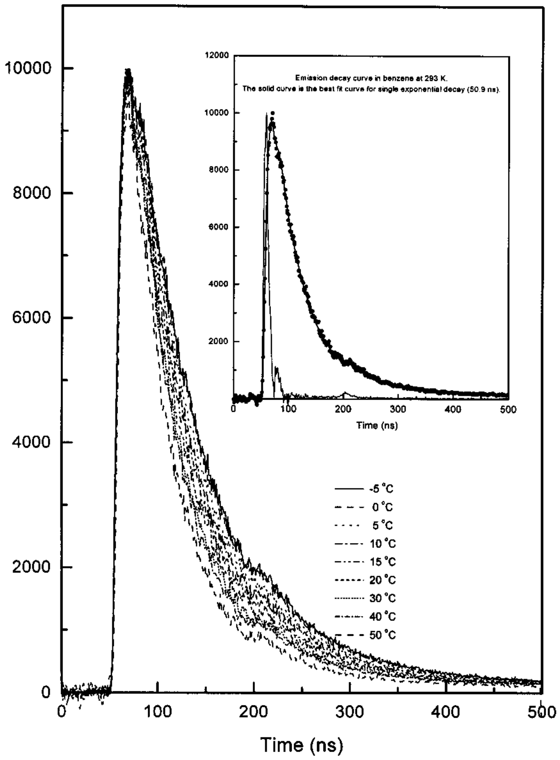

Figure 3. Temporal decay profiles of the emission intensity for OV^{IV}TPP in benzene at temperatures between 268 and 323 K. Inset displays the typical fitting result with the instrument response function.

Figure 2c shows the CW emission spectra of OV^{IV}TPP in the two different solvents at 77 K. Although the emission spectrum in MCH/benzene exhibits a maximum around 745 nm, which is slightly blue-shifted from the reported value of 758 nm in a PMMA matrix,[5] the emission maximum in MCH/THF is observed at 784 nm. The solvent-dependent shifts in the emission bands are in good accordance with the shifts in the absorption spectra (see Figure 1). These observations led us to suggest that the THF solvent ligates to OV^{IV}TPP at low temperatures and then alters the energy levels of the emitting states. Nevertheless, the observed large Stokes shifts in various solvents indicate that the emitting state cannot be simply assigned to the lowest excited singlet state ($^2S_1(\pi,\pi^*)$).

Kinetics of OV^{IV}TPP and Their Temperature Dependences. At temperatures between 268 and 323 K in benzene, toluene, and THF, no apparent change was observed in the emission spectral feature of OV^{IV}TPP except the emission intensity.[6] However, its decay kinetics in benzene and toluene strongly depends on temperature (Figure 3). All the temporal profiles were found to be well fitted to a single-exponential decay. On the other hand, in THF the decay time of ca. 10 ns is almost independent of temperature. The temperature dependent decay times in benzene and toluene are listed in Table 1 along with that in THF. Assuming that the inherent radiative lifetime of the emitting state is quite long compared with nonradiative relaxation processes, the Arrhenius plots of the data (Figure 4) give a good linearity for all the solvents employed in this work. The activation energies are estimated to be 480 ± 20 and 520 ± 20 cm^{-1} in benzene and toluene, respectively.

TABLE 1: Luminescence Decay Times of OV^{IV}TPP in Three Different Solvents at Various Temperatures

	lifetimes (ns)		
temp (K)	benzene	toluene	THF
268	63.5	75.2	10.6
273	63.2	69.8	10.5
278	58.4	68.2	10.5
283	55.7	62.0	10.3
287	53.1	59.4	10.4
293	50.1	57.1	10.1
303	46.8	53.7	10.2
313	44.9	50.3	9.8
323	40.5	45.0	10.3

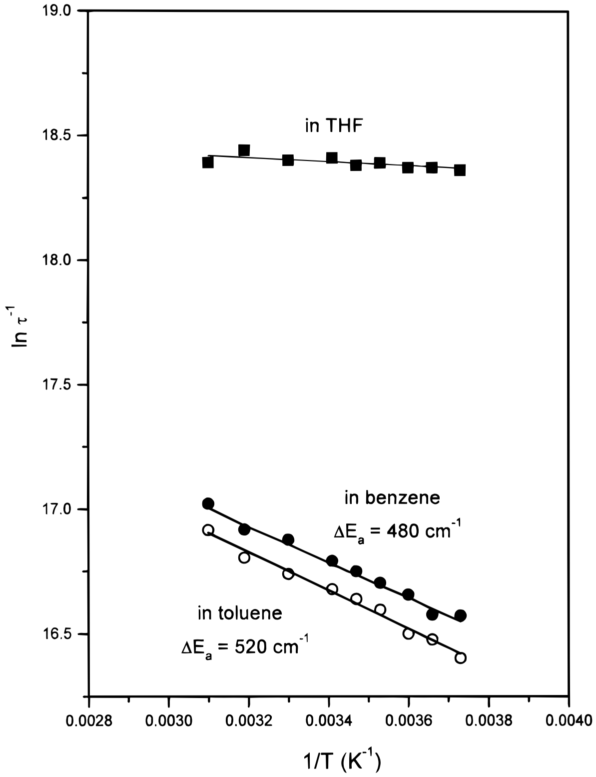

Figure 4. Arrehenius plot of the emission decay kinetics for OV^{IV}TPP in pure benzene (●), toluene (○), and THF (■) at temperatures betweeen 268 and 323 K.

It has to be pointed out that the emission decay time constants are almost independent of the probe wavelengths in the temperature range 268−323 K. In contrast, at 77 K the decay profiles are dependent on the probe wavelengths (Figure 5). With an increase of the probe wavelength from 720 to 760 nm, the overall emission decay time gradually decreases. With a further increase of the probe wavelength up to 800 nm, however, the decay profiles exhibit a slight increase in the decay times. These results are partly consistent with the wavelength dependence of the emission lifetimes reported by Gouterman et al.[5a]

All the decay profiles were well reproduced with fast (5−8 μs) and slow components (20−30 μs). The fitting parameters are listed in Table 2 for each probe wavelength. Even though it is difficult to gain an insight into the electronic nature of the emitting state from its decay time only, the variation of the relative amplitudes in the two decay components with a change in the probe wavelengths (inset in Figure 5) suggests that the emission spectra of OV^{IV}TPP at 77 K is the superposition of at least three different emission bands. Although it is difficult to precisely estimate the decay time constant for each emitting state because of the spectral congestion, the fast component has a lifetime of 5−6 μs, and the other two slow components observed at shorter and longer wavelengths have lifetimes of 24 and 30 μs, respectively. By using three Gaussian line shape functions and the fitting parameters listed in Table 3, we reconstructed the time-resolved emission spectra (Figure 6) in which the emission bands at 77 K exhibit a blue-shift with an increase of the time delay. From this simulation, the shifts in emission maxima with an increase of time delay can be explained by the contribution of the moderately fast decaying component centered at 13 300 cm^{-1}, compared with the other emission bands at 13 600 and 12 700 cm^{-1}.

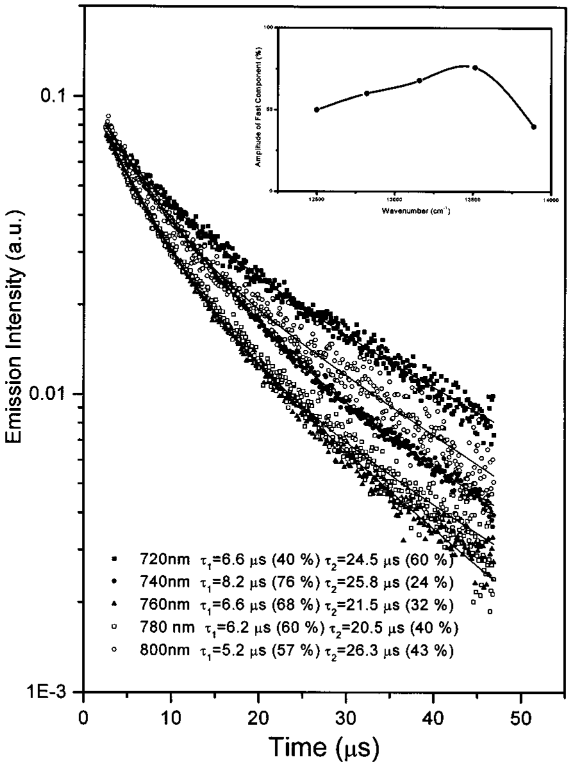

Figure 5. Temporal decay profiles of the emission intensity for OV^{IV}TPP at various probe wavelengths following 532 nm excitation at 77 K. The amplitudes of the fast component at various probe wavelengths are displayed in the inset

TABLE 2: Probe Wavelength Dependence of the Emission Decay Times of Photoexcited OV^{IV}TPP in MCH/Toluene (10:1 v/v) at 77 K

	fast component		slow component	
probe wavelengths (nm)	lifetime (μs)	amplitude (%)	lifetime (μs)	amplitude (%)
720	6.6	40	24.5	60
740	8.2	76	25.8	24
760	6.6	68	21.5	32
780	6.2	60	20.5	40
800	5.2	57	26.3	43

TABLE 3: Fitting Parameters of the Time-Resolved Emission Spectra of OV^{IV}TPP in MCH/Toluene (10:1 v/v) at 77 K upon 532 nm Excitation

		peak 1		peak 2		peak 3	
temp (K)	time delay Δt (μs)	position (cm^{-1})	fwhm (cm^{-1})	position (cm^{-1})	fwhm (cm^{-1})	position (cm^{-1})	fwhm (cm^{-1})
77	0.5−1.5	13 556	364	13 292	530	12 709	931
77	5−6	13 591	362	13 322	526	12 625	1006
77	20−21	13 654	330	13 366	471	12 720	957
293	0.1−0.12					12 715	947

It is also interesting to note that the peak position and width of the emission band located at 12 700 cm^{-1} are almost identical

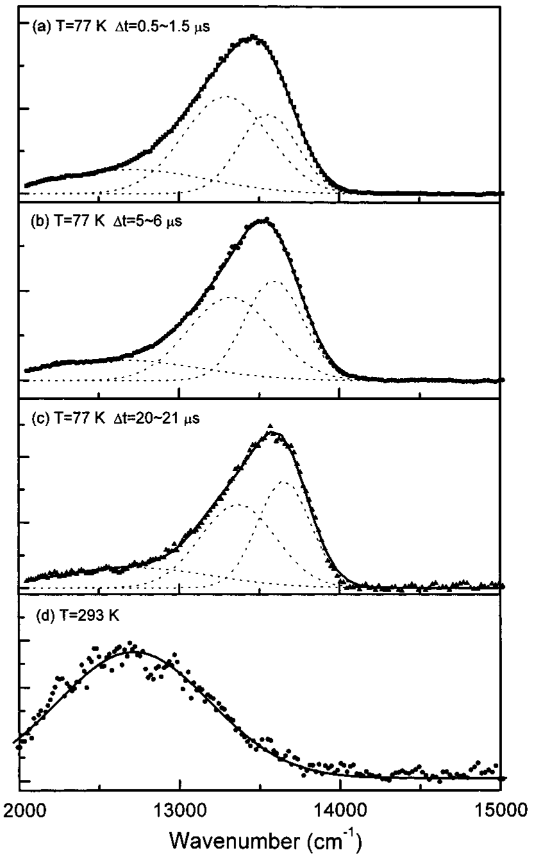

Figure 6. (a−c) Time-resolved emission spectra of $OV^{IV}TPP$ in MCH/toluene (10:1 v/v) at various time delays following excitation at 532 nm at 77 K. (d) The emission spectra at room temperature for the same sample is displayed for comparison.

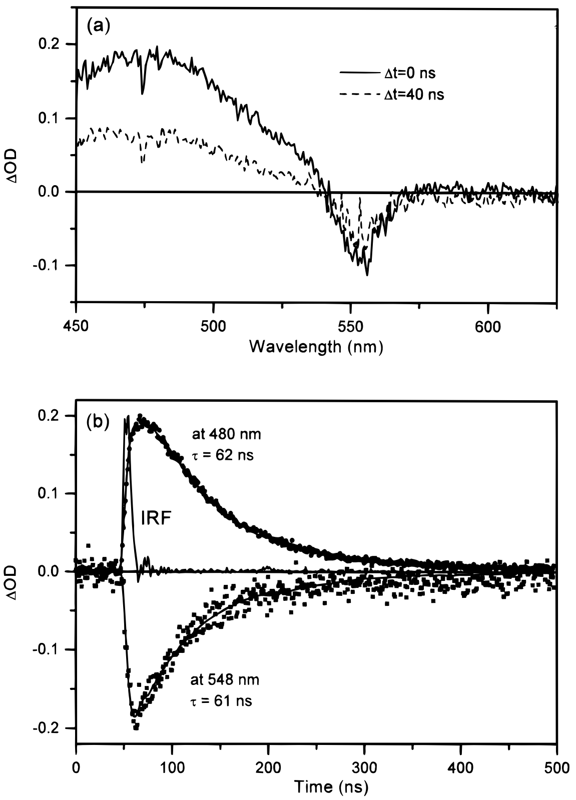

Figure 7. (a) Transient absorption spectrum of $OV^{IV}TPP$ in benzene following photoexcitation at 435 nm at 278 K. (b) Temporal decay profiles of the photoinduced absorption at 480 nm and the ground-state bleaching at 548 nm.

with those observed at room temperature as shown in Figure 6. These observations led us to conclude that the emitting state at the lowest energy at 77 K is assignable to that at room temperature under the assumption that the energy of the state is not altered significantly with a change in the environment from liquid to solid. Furthermore, the band at 12 700 cm^{-1} is also tentatively assignable to the lowest excited state formed during the deactivation process of photoexcited $OV^{IV}TPP$. This tentative assignment is also supported by the transient absorption measurement (see below). If this is the case, the difference in energy between the lowest excited state (12 700 cm^{-1}) and the higher one at 13 300 cm^{-1} is surprisingly close to the activation energy estimated in noncoordinating solvents such as benzene and toluene.

Nanosecond Transient Absorption and Time-Resolved Resonance Raman Studies. Transient absorption spectra measured immediately after photoexcitation of $OV^{IV}TPP$ with 8 ns, 435 nm flash are shown in Figure 7a. The broad spectral feature of the photoinduced absorption band extended to 500 nm accompanied by the bleaching of the Q-band did not change with either time delay or temperatures between 268 and 323 K. Furthermore, no prominent difference in the spectral feature was observed with changes in the excitation wavelength from 435 to 532 nm. Figure 7b shows the temporal profiles of both the photoinduced absorption signal at 480 nm and the ground-state bleaching signal at 548 nm in benzene at 278 K. It is interesting to see that the two decay profiles exhibit the same decay time within experimental error as long as temperature and solvent are the same. The estimated decay time from the transient absorption measurements is also in good agreement with the emission decay time measured in the same solvent at the same temperature.

Meanwhile, the transient absorption decay kinetics of $OV^{IV}TPP$ strongly depend on temperature and solvent. These dependencies in the excited-state kinetics induced by the variation in temperature and solvent are the same as those from the emission decay kinetics. These observations also led us to conclude that the emissive state of $OV^{IV}TPP$ at room temperature, which is the lowest excited state, is also responsible for photoinduced absorption.

To obtain Raman spectra of the emissive transient species, the probe pulses at 457 nm were employed to be in resonance with the photoinduced absorption shown in Figure 7a. Figure 8 shows the transient Raman spectra of $OV^{IV}TPP$ in THF measured by using 532 nm pump and 457 nm probe pulses with a time delay of 10 ns. The peak positions of the porphyrin skeletal modes such as ν_2, ν_4, ν_1 and the phenyl internal mode ϕ_4 for the ground-state Raman spectra are in good accordance with the reported values.[2] No change was observed in the Raman spectral feature under the probe-pulse-only configuration in the interval before and after exposure to the pump pulse at 532 nm (parts a and c of Figure 8). Upon photoexcitation at 532 nm, however, the relative intensity of the ϕ_4 mode is remarkably enhanced as shown in Figure 8d. It has been well established that this enhancement accompanied by an appearance of a weak broad band near 1500 cm^{-1} is characteristic of the triplet state resonance Raman spectra of normal metallo- and/or free-base porphyrins.[11] It was also apparent that the almost identical spectral feature of the transient Raman spectrum was observed in benzene and toluene solvents, although it is difficult

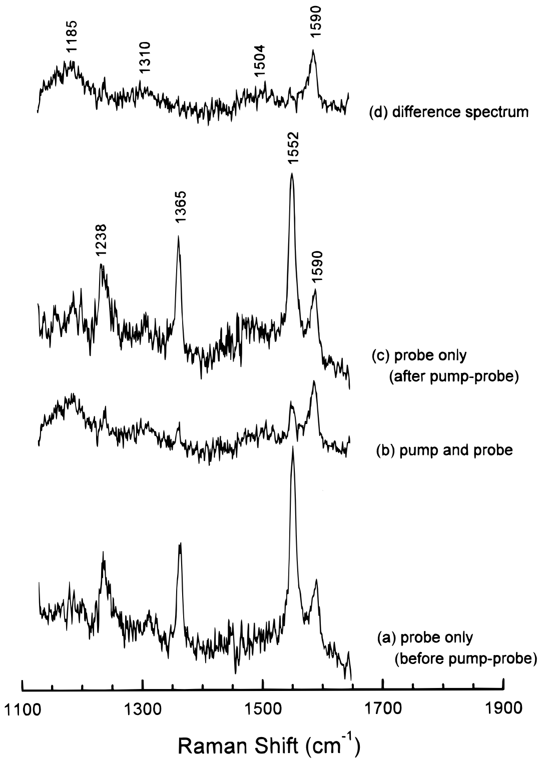

Figure 8. Time-resolved transient RR spectra of OV^{IV}TPP in THF by using 532 nm pump and 457 nm probe pulses measured at 10 ns time delay. The porphyrin concentration and the laser power were kept constant at less than 10^{-5} M and 1 mJ/pulse, respectively. The probe-only spectrum before (a) and after (c) the illumination by the pump pulse are displayed to check that no photodegradation has occurred.

to obtain the spectra with a good signal-to-noise ratio because of the spectral complexity from the strong Raman bands of the solvents.

Discussion

We have observed that the relaxation kinetics of photoexcited OV^{IV}TPP strongly depend on temperature and solvent from time-resolved emission and photoinduced absorption measurements. To explain our results observed at temperatures between 268 and 323 K, we propose a state energy diagram as shown in Figure 9 with the aid of an energy-level diagram that is generally accepted in the photophysics for copper(II) porphyrins.[4,12] It is to be noted that copper(II) porphyrin is also paramagnetic and its electronic configuration is d^9. So it would be reasonable to suppose that the photophysical properties of photoexcited OV^{IV}TPP show some resemblances to those of Cu^{II}TPP. Like Cu^{II}TPP, the odd electron in the central metal of OV^{IV}TPP results in the splitting of the lowest excited triplet state of the porphyrin ring. This interaction results in the tripdoublet (^{2}T(π,π*)) and tripquartet (^{4}T(π,π*)) states as depicted in Figure 9.

The transient Raman and absorption spectral features as well as the large Stokes shifts in the emission spectra at temperatures between 268 and 323 K reveal that instead of the singdoublet state (^{2}S(π,π*)), one of the tripmultiplet (^{2}T/^{4}T(π,π*)) states is responsible for the observed luminescence. Considering the spin states of the tripmultiplet states, most of photoexcited OV^{IV}TPP species mainly relaxes to the tripdoublet (^{2}T(π,π*)). The fact that no fluorescence was detected under any experimental condition in this work strongly suggests that the fast relaxation from ^{2}S$_1$(π,π*) to ^{2}T(π,π*) should be a major deactivation route for photoexcited OV^{IV}TPP. Among the tripmultiplet states, the tripquartet (^{4}T(π,π*)) lies in energy below the tripdoublet (^{2}T(π,π*)) by Hund's rule. Thus, it is relevant to suppose that the electronic nature of the state responsible for the observations in this work at temperatures between 268 and 323 K is the tripquartet state (^{4}T(π,π*)). This assumption was, in part, supported by an energy difference larger than 1500 cm^{-1} between the NIR absorption band, which was attributed to the ^{2}S$_0$(π,π*)–^{2}T(π,π*) transition, and the room-temperature emission maximum. Furthermore, the investigations of the luminescence spectral features and their relaxation dynamics at 77 K will again support the above criteria (see below).

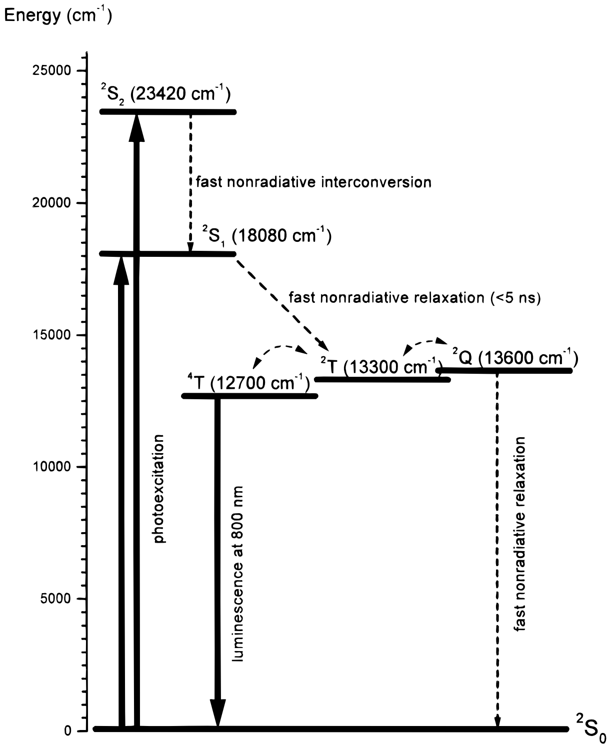

Figure 9. Proposed energy-level diagram for OV^{IV}TPP in noncoordinating solvents such as benzene and toluene at room temperature between 268 and 323 K. The locations of the electronic states in this figure are estimated from our measurements (see text).

The relatively weak luminescence of OV^{IV}TPP compared with other normal metalloporphyrins such as Zn^{II}TPP ($\phi_{\text{fluo}} = 0.04$ at 298 K, $\phi_{\text{phos}} = 0.012$ at 77 K)[13] implies that the tripquartet state cannot be populated directly from the lowest excited singlet state (^{2}S$_1$(π,π*)). It would be more probable that the tripquartet state is thermally equilibrated with the tripdoublet state as indicated by the blue-shifted emission at 77 K (Figure 2c). If the tripquartet (^{4}T(π,π*)) state is in thermal equilibrium with the tripdoublet (^{2}T(π,π*)) one, the strong temperature dependence of the decay time constant for the tripquartet state can also be understood by the relaxation scheme. Furthermore, the extremely weak room-temperature luminescence led us to suppose that a nonradiative relaxation process, which is also thermally accessible from the equilibrated tripmultiplet states, plays an important role in the overall deactivation process of photoexcited OV^{IV}TPP (see Figure 9). This proposed relaxation route can be explained by a quenching state (Q), which will be discussed below.

If the above considerations have some validity to describe the relaxation process of photoexcited OV^{IV}TPP, the following scenario at temperatures between 268 and 323 K can be proposed as shown in Figure 9. The initially populated

$^2S_1(\pi,\pi^*)$ state decays rapidly to the $^2T(\pi,\pi^*)$ and then relaxes mainly to the ground state nonradiatively via a proposed Q state with a minor contribution of the deactivation to the moderately long-lived $^4T(\pi,\pi^*)$ state. The resultant kinetic scheme is so complex that several assumptions are necessary to derive further information such as temperature dependence. First, the tripmultiplet states ($^2T/^4T(\pi,\pi^*)$) are assumed to be rapidly equilibrated thermally just after photoexcitation to the $^2S_1(\pi,\pi^*)$ state. Second, the relaxation processes from the $^2T(\pi,\pi^*)$ to the ground state through either a proposed Q state or a nonradiative transition are fast compared to the intersystem crossing to the $^4T(\pi,\pi^*)$ state. Finally, radiative or nonradiative deactivation to the ground state from the $^4T(\pi,\pi^*)$ state is independent of temperature and slow compared with the thermal activation to the $^2T(\pi,\pi^*)$, which will eventually relax to the ground state. These assumptions are partly supported by the failure to observe any luminescence from either the $^2S_1(\pi,\pi^*)$ or the $^2T(\pi,\pi^*)$ state at temperatures between 268 and 323 K. We obtained a linear Arrhenius plot as shown in Figure 4 at temperatures between 263 and 323 K. The good linearity again led us to accept our proposed relaxation scheme of photoexcited $OV^{IV}TPP$.

Prior to further discussion of the data at 77 K, it is appropriate to review briefly the previous investigations of this complicated system. Gouterman et al.[5] already reported that the spectral feature and relative emission quantum yield of the photoluminescence of $OV^{IV}TPP$ in poly(methyl methacrylate) (PMMA) matrix do not change at temperatures between 10 and 80 K. Meanwhile, the photoluminescence studies on paramagnetic metalloporphyrins such as $Cu^{II}TPP$[5] and $ClCr^{III}TPP$[14] revealed that the longer is the probe wavelength, the slower become the luminescence lifetimes. These probe wavelength dependences of the lifetimes have been well illustrated by theoretical consideration by Gouterman et al.[5] in which the transition from the $^2T(\pi,\pi^*)$ to the $^2S_0(\pi,\pi^*)$ lies higher in energy and is faster than that from the $^4T(\pi,\pi^*)$ to the $^2S_0(\pi,\pi^*)$. However, the lifetime of 16 μs for photoexcited $OV^{IV}TPP$ has been reported to be reduced to 13 μs with an increase in the probe wavelength from 726 to 745 nm.[5a] In addition to this peculiar phenomena, Gouterman et al.[5] mentioned the abnormally fast lifetimes of photoexcited $OV^{IV}TPP$ compared with other diamagnetic metalloporphyrins at low temperatures.

Without considering the contribution of the weak emission band at 12 700 cm^{-1} in Figure 6, our experimental observations are consistent with the previous ones.[5] Our observations, however, led us to assign the emission band at 790 nm as a radiative transition, $^4T(\pi,\pi^*)-^2S_0(\pi,\pi^*)$. As a result, the probe wavelength dependence of the lifetimes is now normal, since the decay times for the two emission bands centered at wavelengths shorter than 760 nm are faster than that of longer wavelength emission at 790 nm. Even though the above discussion can roughly explain the overall emission spectra at low temperatures, it is not possible to distinguish clearly which one of the other two emission bands at shorter wavelengths corresponds to the transition $^2T(\pi,\pi^*)-^2S_0(\pi,\pi^*)$. If photoexcited $OV^{IV}TPP$ follows the proposed relaxation scheme in Figure 9 even at 77 K, there are two possible radiative transitions other than the previously mentioned $^4T(\pi,\pi^*)-^2S_0(\pi,\pi^*)$ transition: one may be $^2T(\pi,\pi^*)-^2S_0(\pi,\pi^*)$ and the other $Q-^2S_0(\pi,\pi^*)$. Even though we do not have any conclusive information on the electronic nature of the proposed Q state, the activation energy estimated in this work in noncoordinating solvent is useful for helping with the assignment as follows. If the proposed Q state is not thermally populated directly from the lowest excited tripquartet state, then the activation energy corresponds to the energy gap (ΔE_{DQ}) between the $^2T(\pi,\pi^*)$ and $^4T(\pi,\pi^*)$ states. Considering both the activation energy and the peak positions of the three emission bands shown in Figure 6, it is possible to tentatively assign the two emission bands centered at 13 300 and 13 600 cm^{-1} as the transitions of $^2T(\pi,\pi^*)-^2S_0(\pi,\pi^*)$ and $Q-^2S_0(\pi,\pi^*)$, respectively, which are mostly quenched at the higher temperatures.

It is noteworthy that the estimated activation energy values as well as the energy of the emitting state of the $^4T(\pi,\pi^*)$ are dependent on the solvent nature. Accompanied by the change in solvents from a noncoordinating solvent such as benzene or toluene to a weakly coordinating one like THF, the energy of the emitting state at ambient temperature decreases from 12 700 to 12 000 cm^{-1} along with a decrease in the activation energy. Meanwhile, the absorption band due to $^2S_0(\pi,\pi^*)-^2T_1(\pi,\pi^*)$ at room temperature remains almost intact with a change in solvents from toluene to THF as shown in Figure 2, while the emission band maximum in THF is observed to be at longer wavelength than that in toluene or benzene. These solvent dependences could be explained, in part, by the supposition that photoexcited $OV^{IV}TPP$ has a strong interaction with the oxygen-containing solvent THF to result in the lowering of the energies of the tripmultiplet states and by a proposed quenching state (Q) as well as by their differences in energy. Furthermore, the low-temperature absorption (Figure 1) and emission spectra (Figure 2) clearly demonstrate that THF ligates to $OV^{IV}TPP$ to result in a six-coordinate vanadyl(IV) porphyrin.[2a] If this is the case, the energy difference between the tripmultiplet states ($^2T(\pi,\pi^*)$ vs $^4T(\pi,\pi^*)$) is strongly affected by the solvent nature, which in turn affects the decay time constant of the lowest excited state of photoexcited $OV^{IV}TPP$.

Finally, it is necessary to discuss the electronic nature of the proposed Q state of $OV^{IV}TPP$. The similarities can be found in the previous studies related to copper(II) porphyrins that have an odd electron in the central metal d orbital like $OV^{IV}TPP$. Many theoretical and experimental investigations have been carried out to elucidate the electronic nature of a proposed Q state for copper(II) porphyrins.[15] In concordance with the generally accepted proposition in the case of copper(II) porphyrins, the proposed Q state for $OV^{IV}TPP$ might be one of the possible charge transfer (CT) states such as ring-to-metal (π(ring)−d(metal)), metal-to-ring (d(metal)−π(ring)), and metal-to-metal (d(metal)−d(metal)), or their mixtures. All the above proposed CT states have doublet spin states. This consideration suggests that the quenching state cannot be directly populated from the tripquartet state. At this moment, however, we cannot definitely confirm the electronic nature of the proposed Q state of $OV^{IV}TPP$, since no previous study on this aspect has been reported yet to our knowledge. We are now in the process of doing experiments to obtain further information on the electronic nature of the proposed Q state.

Conclusion

The experimental observations described in this work show that the relaxation dynamics of photoexcited $OV^{IV}TPP$ are rather complicated because of the presence of unpaired electron in the d_{xy} orbital of the central metal. By measurement of the luminescence decay profiles, transient absorption, and ground-state bleaching signals at temperatures between 268 and 323 K, the lifetime of the lowest excited state of $OV^{IV}TPP$ was determined. The emission spectral feature and its decay time exhibit a strong temperature and solvent dependence. These observations can be reasonably explained by proposing an energy-level diagram with a quenching state, which is prerequisite for explaining the nonluminescent properties from the $^2S_1(\pi,\pi^*)$ and $^2T(\pi,\pi^*)$ states at room temperature. On the basis of the temperature-dependent lifetimes, we estimated the energy difference between the tripdoublet and tripquartet states to be ca. 500 cm^{-1} in noncoordinating solvents. We also found that the temperature dependent lifetimes of the emission bands originating from the tripmultiplets at 77 K are consistent with the activation energies. When the solvent is changed to a weakly coordinating one, THF, the decay time of the lowest-excited state of OV^{IV}TPP was reduced to 10 ns, which was also found to be almost independent of temperature.

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