Some singlet metastables do exist in these discharges.⁶⁴ Without the ability to experimentally "filter" discharge metastables, full elucidation of the mechanisms of production and conversion of singlet or triplet trimethylsilylnitrene in these experiments will probably await a thorough theoretical treatment.

Conclusions

The trimethylsilylnitrene radical, (CH₃)₃SiN, has been produced by the interaction of (CH₃)₃SiN₃ or (CH₃)₃SiNCO with metastable molecular nitrogen or argon and has been trapped and observed directly in nitrogen and argon matrices. Electron spin resonance data indicate that trimethylsilylnitrene has a triplet ground state, and the zero-field splitting and ¹⁴N hyperfine are consistent with a high concentration of spin density on the nitrogen

atom, as in other nonaromatic nitrenes. A number of infrared absorptions have been observed and preliminary assignments made. There is no strong evidence in either the ESR or IR data for $p_{\pi}-d_{\pi}$ bonding between the nitrogen and silicon atoms. The metastable energy transfer fragmentation method gives a different product distribution than direct photolysis or pyrolysis of the same precursors, favoring production of triplet molecules. However, singlet nitrenes are probably produced as well. The latter molecules may be involved in reactions that produce a silvlated imine, as seen in direct photolysis of the azide, or in reactions with CO to yield the trimethylsilyl isocyanate observed in other experiments.

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Picosecond Relaxation of Strongly Coupled Porphyrin Dimers

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Subpicosecond time-resolved absorption studies have been carried out on several lanthanide porphyrin complexes consisting of a Ce(IV) ion sandwiched between two strongly coupled cofacial porphyrin macrocycles. Following excitation, two relaxation processes having time constants of ~ 1.5 and ~ 10 ps are observed. The 1.5-ps process is attributed to excited-state deactivation to the electronic ground state via a low-lying ring-to-metal charge-transfer state. Relaxation of the resultant vibrationally excited ground electronic state can account for the complex spectral dynamics observed at longer times.

Introduction

Understanding the photophysical behavior of porphyrins and other chromophores within van der Waals distance is not only of much general interest but also may provide insights into how the electronic properties of the dimeric primary electron donor in bacterial photosynthetic reaction centers influence the initial stages of the charge separation process.^{1,2} The lanthanide porphyrin dimers provide an ideal series of molecules for studying the electronic structure and dynamics of strongly interacting porphyrins. These complexes, consisting of a lanthanide ion sandwiched between two porphyrin macrocycles, are distinguished from most previously studied dimers by their rigid structure, \sim 3-Å inter-ring separation, unusual electronic absorption spectrum, and, for the oxidized species, a prominent near-infrared absorption band.3-5

Recently, time-resolved absorption experiments on the sandwich dimers $Ce^{IV}(OEP)_2$ and $Ce^{IV}(TTP)_2$ using 30-ps flashes showed that the photoexcited complexes largely decay in ≤ 10 ps.^{6,7} It was proposed that this extremely fast nonradiative decay involved low-energy exciton and/or charge-transfer states, although the

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limited time resolution of the experiments did not permit identification of the key transient states or their kinetics. In this report, we present the results of steady-state and subpicosecond timeresolved absorption experiments on Ce^{IV}(OEP)₂, Ce^{IV}(TTP)₂, and a newly synthesized asymmetric dimer, Ce^{IV}(OEP)(TTP). These studies provide fundamental new information on the electronic properties and photophysical behavior of strongly coupled porphyrin dimers.

Experimental Section

 $Ce^{IV}(OEP)_2$ and $Ce^{IV}(TTP)_2$ were prepared according to the procedure of Buchler and co-workers.^{3b} A modification was developed to yield the mixed dimer, Ce^{IV}(OEP)(TTP), as follows. A 186.4-mg sample of H₂TTP (Porphyrin Products), 148.6 mg of H₂OEP (Aldrich), and 1 g of Ce^{III}(acac)₃·3H₂O (Strem) were refluxed in 50 mL of trichlorobenzene for 20 h. The trichlorobenzene was removed by rotary evaporation, and the crude product mixture was chromatographed on predried (160 °C overnight) activity I basic alumina (2.5 cm \times 25 cm column) with CH₂Cl₂ as the eluent. A small yellow/brown band of Ce(TTP)₂ was closely followed by a larger dark red band of Ce(OEP)(TTP). The third and largest of the dimer bands was the brown/red $Ce(OEP)_2$. The Ce(OEP)(TTP) fraction was rechromatographed in the same fashion. Smaller amounts of highly pure material also were obtained from the crude reaction product mixture by chromatography on predried (160 °C for 30 min) alumina G TLC plates $(20 \times 20 \text{ cm}^2)$; Analtech, spotted in CH₂Cl₂ and eluted with toluene).

The room-temperature ¹H NMR data for Ce(OEP)₂, Ce(TT-P)₂, and Ce(OEP)(TTP), recorded on a Varian XL-300 or VXR-500 spectrometer, are summarized in Table I. The NMR spectra of the two symmetric dimers agree with the literature data for these compounds.^{3a,b} The peak assignments for the new compound, Ce(OEP)(TTP), are based on integrated intensity ratios, proton decoupling experiments, and chemical shift comparisons with the symmetric complexes. During the course of our studies, we learned that Buchler et al. have synthesized the related molecule Ce(OEP)(TPP).⁴ Since our NMR data on Ce-(OEP)(TTP) are in accord with the NMR results of Buchler et

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TABLE I: Comparison of ¹H NMR Spectra of Ce Porphyrin Sandwich Complexes^a

molecule	solvent	ethyl CH ₃ (t)	tolyl CH ₃ (s)	endo CH ₂ (q)	exo CH ₂ (q)	m' (s)	m (s)	o' (s)	H _{pyr} (s)	H _{meth} (s)	o (s)
Ce(OEP) ₂	ь	1.68		3.85	4.20					9.10	
$Ce(TTP)_2$	С		2.67			6.27	7.02	7.90	8.13		9.45
Ce(OEP)(TTP)	ь	1.53	2.61	3.90	4.24	6.47	d	8.09	8.44	9.20	9.76

^a Resonances are listed in ppm relative to TMS (s = singlet; t = triplet; q = quartet). The spectra were recorded at 295 K. ^bToluene- d_8 . ^cCDCl₃. ^d Resonance obscured by solvent peak.

al. on Ce(OEP)(TPP), who have also determined the crystal structure of the latter complex, we defer to their article⁴ for a detailed structural analysis. Ground-state electronic absorption spectra (see Figure 1A) were recorded on a Perkin-Elmer Lambda 3B or Model 330 spectrometer. Our room-temperature spectra agree with those obtained by Buchler and co-workers.^{3a,b,4}

Time-resolved absorption measurements were carried out on a subpicosecond spectrometer described elsewhere.⁸ Samples having a concentration of about 500 μ M in a 2-mm path length cuvette were excited with a 350-fs 582-nm pulse ($\sim 200 \ \mu J$ focused to ~ 1.5 mm) and probed at various delay settings with a broad-band (370-950 nm) pulse. (Under these conditions, typically about 25% of the molecules in the excitation region were pumped.) Absorption difference spectra were measured in overlapping 150-nm wavelength intervals by using a two-dimensional data acquisition system employing a vidicon detector. These spectra were used to construct the broad-band spectra shown in Figures 2, 4, and 6. To account for dispersion in the probe pulse, which gives a difference of about 3 ps in the pump/probe delay between 400 and 500 nm, spectra in the blue region at delay times of <10 ps were generated by concatenating small (10-20 nm) regions of spectra acquired at the same effective delay time. The standard deviation in the measured difference absorption is typically ± 0.005 .

Fluorescence measurements were made on a Spex Fluorolog 2 spectrofluorometer. Low-temperature experiments utilized an Oxford Instruments DN704 cryostat equipped with a 3120 temperature controller. Spectral grade solvents were used for all measurements.

Results

Electronic Ground-State Absorption Spectra. The room-temperature ground-state optical absorption spectra for Ce(OEP)₂, Ce(OEP)(TTP), and $Ce(TTP)_2$ are shown in Figure 1A. All three dimers exhibit a blue-shifted Soret band compared to the case of monomeric^{9a,b} lanthanide porphyrins. The Q bands for the symmetric dimers, except for being broader, are basically at the same positions as found for monomeric complexes having the same macrocycle: $Ce(OEP)_2$ has a moderately strong Q(0,0) band at 573 nm and a weaker Q(1,0) band at 530 nm (solid spectrum), while for $Ce(TTP)_2$, a very weak Q(0,0) band is barely discernible near 590 nm, with the more intense Q(1,0) band located at 542 nm (dashed spectrum). On the other hand, the Q-band region of Ce(OEP)(TTP) is the average of neither the Q-band spectra of monomeric OEP and TTP lanthanide porphyrins nor the two symmetric dimers. The asymmetric dimer shows a broad band containing underlying features at 538, 558, and 578 nm (dotted spectrum in Figure 1A), as revealed in a second-derivative spectrum (not shown). These peaks can be seen more clearly in the 78 K spectrum shown in Figure 1B.

All three dimers show additional features not seen in the spectra of the monomeric lanthanide porphyrins (Figure 1). These features consist of a moderately intense band between 470 and 490 nm, a weak broad band between 625 and 665 nm, and a weaker absorption tailing past 1000 nm (see also refs 3b and 6). Ce(T-



Figure 1. Ground-state absorption spectra: (A) 295 K, Ce(OEP)₂ in toluene (solid), Ce(OEP)(TTP) in toluene (dotted), and Ce(TTP)₂ in CH₂Cl₂ (dashed); (B) 78 K, Ce(OEP)₂ (solid) and Ce(OEP)(TTP) (dotted) in 3-methylpentane. The 78 K spectra are normalized to unity at the Soret maxima. Absorbances in the 450-800-nm regions have been multiplied by the indicated factors.



Figure 2. Absorption difference spectra of $Ce(OEP)_2$ in toluene (~400 μ M) at 295 K taken 1 ps (solid) and 10 ps (dashed) after excitation. The 420-520-nm region of the 1-ps spectrum was obtained by concatenating spectra in adjacent small wavelength intervals at the same delay time as described in the Experimental Section. The 600-900-nm region of the spectra was acquired with a more concentrated sample (~2 mM) and then multiplied by 2 to give the indicated magnification. The inset shows the absorption difference spectrum of an ~3 mM sample at 295 K recorded at 0.6-ps (solid), 1.0-ps (dotted), and 3.3-ps (lower solid) delay times.

TP)₂, in addition, has a broad absorption centered near 950 nm, riding atop the weak tailing absorption (not shown).

Excited-State Spectra and Kinetics. Figure 2 shows the absorption difference spectra between 420 and 900 nm for $Ce(OEP)_2$ in toluene, observed at 1 and 10 ps after excitation with a 350-fs 582-nm flash. The spectra at these two times are representative of those observed during the fast and slow phases, respectively, of the biphasic excited-state absorption decay found for all three complexes. Typical kinetic traces and nonlinear least-squares fits to a dual-exponential function are shown in Figure 3. The results are summarized in Table II.

Most of the decay at both 295 and 180 K occurs during the fast phase, which for Ce(OEP)₂ was found to have a time constant of ~ 1.5 ps throughout the spectrum. Similar kinetic behavior

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Figure 3. Time evolution of the absorption difference of $Ce(OEP)_2$ in toluene at 430 nm recorded at 295 and 180 K (inset). The solid line represents a least-squares fit to a dual-exponential function.



Figure 4. Absorption difference spectrum at 295 K of Ce(OEP)(TTP) in toluene recorded at 1 ps (solid), 5 ps (dashed), 15 ps (dotted), and 90 ps (solid) after excitation. The blue portion of the 1-ps spectrum is a concatenated spectrum as described in the legend to Figure 2 and in the Experimental Section. Spectra acquired with a more dilute sample at 0.6 ps (solid), 1.3 ps (dotted), and 2.3 ps (dashed) are shown in the inset.

 TABLE II: Summary of Soret Region Transient Absorption Decay Kinetics^a

molecule	solvent	temp, K	τ_1 , ps	τ_2 , ps
Ce(OEP) ₂	toluene	295	$1.5 \pm 0.2 \ (65\%)$	6 ± 2
-	toluene	180	$1.2 \pm 0.5 (75\%)$	7 ± 2
	acetone	295	$2.5 \pm 0.6 (60\%)$	14 ± 3
	CH_2Cl_2	295	$1.5 \pm 0.5 (50\%)$	7 ± 2
$Ce(TTP)_2$	CH ₂ Cl ₂	295	1.5 ± 0.2 (80%)	9±3
Ce(OEP)(TTP)	toluene	295	1.8 ± 0.2 (85%)	10 ± 3
	toluene	180	$2.0 \pm 0.3 (80\%)$	10 ± 3

^aKinetics were measured between 420 and 440 nm for Ce(OEP)₂, between 440 and 470 nm for Ce(TTP)₂, and between 435 and 450 nm for Ce(OEP)(TTP). The fast component (τ_1) accounts for the percentage of the overall decay (and of the initial amplitude of ΔA) listed in parentheses ($\pm 5\%$). For Ce(OEP)₂ in toluene the time constant of the slower component (τ_2) varies from 5 ± 1 ps at 440 nm to 8 ± 1 ps at 420 nm. Such variations were observed for the other entries in the table, although systematic trends across the blue region of the transient absorption were not always as well pronounced. Therefore, we have simply listed the average value and standard deviation of τ_2 measured at 5-nm intervals across the blue region of the spectrum for each complex.

was observed for Ce(OEP)(TTP) in toluene at 295 and 180 K, with the fast, dominant phase of the decay having a time constant of ~ 2 ps (Figures 4 and 5). Ce(TTP)₂, studied only in CH₂Cl₂ because of low solubility, showed biphasic decay kinetics similar to the other two dimers (Table II).

For each dimer there are several wavelengths where ΔA appears to remain constant during the fast (1.5-2.5 ps) phase of the kinetics. These early-time isosbestic points (not at $\Delta A = 0$) are most clearly seen to the red of the Soret bleaching, at 392 nm for Ce(OEP)₂ in Figure 6A and at 403 nm for Ce(OEP)(TTP) in the inset to Figure 4. Additional isosbestic points in the series of difference spectra at very early times flank the bleaching of the 480-490-nm ground-state absorption band (Figures 4 and 6B).



Figure 5. Time evolution of the absorption difference of Ce(OEP)(TTP) in toluene at 440 nm recorded at 295 and 180 K (inset). The solid line represents a least-squares fit to a dual-exponential function.



Figure 6. Absorption difference spectra of $Ce(OEP)_2$ in toluene at 295 K: (A) dilute sample, recorded at 1 ps (solid), 1.6 ps (dotted), and 4 ps (dashed); (B) more concentrated sample, recorded at 1.3 ps (solid), 2.6 ps (dotted), and 4 ps (dashed); (C) same sample as in (B) recorded at 6.5 ps (solid), 10 ps (dotted), and 20 ps (dashed).

The 1.5-2.5-ps phase is accompanied by a substantial decay of bleachings in the ground-state absorption bands (Figures 4 and 6).

Quite distinct from the fast component, the time constant of the slower, smaller amplitude phase appears to be wavelength dependent. For example, for $Ce(OEP)_2$ in toluene the time constant of the slow phase appears to vary systematically from 5 ps near 440 nm to 8 ps at 420 nm. Similar trends are seen for $Ce(TTP)_2$ and Ce(OEP)(TTP), though such variations are largely within the standard deviation of the fitted lifetime values (Table 11). Additionally, a time constant of about 15 ps is observed for the slow component of the transient absorption decay centered at 510 nm for $Ce(OEP)_2$ and for recovery of the 490- and 540-nm band bleachings for Ce(OEP)(TTP) (see Figures 2 and 4). Perhaps the most clear and striking indication that the slow phase is more complex than the simple conversion of one state to another is the observation that, after a few picoseconds, the $\Delta A = 0$ point on the shorter wavelength side of the 480-490-nm band bleaching continuously shifts to shorter wavelengths as the transient absorption decays (see e.g. Figure 6C).

The Ce(IV) porphyrin dimers, in contrast to lanthanide porphyrin monomers, are nonluminescent.^{9,10} The only fluorescence observed from Ce(OEP)₂, Ce(TTP)₂, and Ce(OEP)(TTP) in toluene was from trace free-base impurities. From these measurements we place an upper limit of 2×10^{-6} on the fluorescence quantum yield for all three Ce(IV) dimers. The lack of fluorescence is in agreement with earlier work^{3a,6} on Ce(OEP), and Ce(TTP)₂, but we have now placed a more stringent upper limit on the quantum yield of this process. Similarly, no phosphorescence was observed in wavelength scans extending to 900 nm.

Discussion

Electronic Spectra and States. Traditionally, ground-state spectra of porphyrin dimers have been discussed in terms of exciton coupling between the monomer states.¹¹ The blue-shifted Soret band in the Ce(IV) porphyrin dimers compared to the spectra of monomeric complexes can be understood by using this approach.3b,6 However, exciton coupling between the macrocycles cannot account for the appearance of the two new bands in the 470-490and 620-670-nm regions which are observed in all of these dimers. In addition, the absence of a strong "OEP Q(0,0)" band in the mixed dimer, which is present in the symmetric OEP dimer, clearly shows that the two macrocycles are strongly coupled but in a manner inconsistent with a simple dipole-dipole interaction. Standard exciton theory predicts only small effects in the Q-band region because of the low oscillator strength of the monomer Q transitions.

The band near 470 nm in the Ce(IV) sandwich dimers is probably not a ring + metal CT transition. If it were, then its position should be dependent on the nature of the central lanthanide ion (via differences in the metal redox potentials). Such a dependence is not observed.^{3d} Similarly, we do not believe that the band in the vicinity of 650 nm is due to a ring ↔ metal CT transition. Rather, we believe that the additional "dimer" bands most likely represent new (π,π^*) absorptions that arise from transitions involving delocalized molecular orbitals. These dimer MOs are formed by strong coupling between the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ HOMOs and $e_g(\pi^*)$ LUMOs of one of the monomeric subunits with those of the other. This strong orbital interaction and splitting has been proposed⁵ to explain the near-IR absorption band in the spectrum of oxidized $Ce(OEP)_2$ and $Ce(TPP)_2$.^{3,5} The large splitting between the dimer bands located in the 470-490- and 620-660-nm regions with their respective Soret and Q counterparts (Figure 1) indicates that the couplings $\langle monomer_1 | H | monomer_2 \rangle$ are quite large, on the order of 10^3 cm⁻¹. At present, we cannot identify the orbital parentage of the new dimer transitions since orbitals in addition to the four-orbital set used to explain the monomer spectra probably need to be considered in view of the substantial π overlap in the sandwich complexes.^{12,13} Additionally, configuration interaction is probably substantial as it is for the monomers.¹⁰ The metal may also participate in the coupling of the monomeric π orbitals, although to a lesser extent as evidenced by the insensitivity of the optical properties of the lanthanide dimers to the nature of the metal.^{3e,5,16}

The ability to observe transitions between states derived from strongly interacting orbitals is of particular relevance to the bacterial photosynthetic reaction center. (Ring-to-ring chargetransfer transitions have often been discussed in this regard for the reaction center^{12,14,15} and some porphyrin dimers.^{13,17}) Recent

theoretical work has pointed out the importance of strong orbital interactions in determining the electronic properties of the dimeric electron donor in the reaction center.¹² However, it has not been possible to observe directly the weak transitions between states derived from delocalized molecular orbitals due to the masking effect of the strong Q_{γ} transitions of the chromophores and the resulting strong exciton coupling between them. On the other hand, the low oscillator strength and minimal exciton coupling of the Q bands of the lanthanide porphyrin dimers have given us a better opportunity to observe these weak transitions involving states of the dimer π system. We will report elsewhere on a detailed analysis of the optical spectra of the lanthanide porphyrin dimers as well as recent results^{18a} on the related Th(IV) sandwich complex,¹⁹ where the inclusion of strong interactions between the macrocycles is also required to explain the optical properties of the molecule.

Rapid Radiationless Decay of the Photoexcited Dimers. The transient spectrum observed for $Ce(OEP)_2$ at 0.6 ps has a broad band centered near 800 nm (Figure 2 and inset), although the exact shape and amplitude of the feature are difficult to ascertain since the bleaching of the ground-state absorption (Figure 1) will tail to beyond 750 nm. This near-IR feature suggests that the initially observed excited state may be a ring ${}^{3}(\pi,\pi^{*})$ state, since the ${}^3(\pi,\pi^*)$ state in monomeric metallooctaethylporphyrins routinely show an absorption peak in this region.²⁰ Although this assignment requires ultrafast intersystem crossing from the initially prepared singlet manifold of the ring to the triplet manifold, this is not unreasonable in view of the heavy central metal ion and the fact that instrument limited (<350 fs) formation of the ring triplet has been found in Cu(II) and Ru(II) porphyrins.²⁰ That the initially observed excited state is not the (π,π^*) state excited directly with the 582-nm flash follows from two observations. First, a near-IR feature like that observed in Figure 2 is not observed in the spectra of the lowest (π,π^*) state of porphyrin monomers, which instead show only a featureless absorption to the red of the Q-band bleachings, broken by characteristic stimulated emission features.²⁰ In addition, the upper limit of $2 \times$ 10⁻⁶ that our luminescence measurements place on the fluorescence quantum yield of the dimers corresponds to a (π,π^*) lifetime of \leq 200 fs,²¹ which is much shorter than the 1.5–2.5-ps lifetime we observed for the initial transient state in all three Ce(IV) porphyrin dimers that we investigated. However, we must keep in mind, as pointed out above in conjunction with our discussion of the ground-state absorption spectra, that the (π,π^*) excited states should be viewed as delocalized states of the strongly couuled dimer system, making it difficult to assign spectral features with certainty

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based on the properties of the monomer (π,π^*) states. One thing is clear, though; there is no a priori reason to expect that any of the (π,π^*) states of the dimer will radiationlessly decay *directly* to the ground state as rapidly as the 1.5-2.5-ps time constant that we observe for the excited-state decay and ground-state repopulation in these dimers (see also below). One or more lower energy excited states must be involved.

Yan and Holten proposed that, of all the excited states of the dimer, ring-to-metal charge-transfer (RMCT) excited states are the most likely to lie at low energy and to facilitate rapid deactivation.6 The electrochemically determined ring oxidation and metal reduction potentials^{3c,e,5} suggest that the lowest energy RMCT state for the Ce(IV) porphyrin dimers probably lies at $\leq 1 \text{ eV}$ above the ground state.²² This is far lower in energy than any of the (π,π^*) ring states, even when conservative limits for the exchange and Coulomb interactions are taken into account. The interpretation that RMCT states are crucial in the deactivation of the photoexcited Ce(IV) porphyrin dimers is also supported by recent work on the related Th(IV) sandwich complexes.¹⁸

Although we believe that the RMCT states play a crucial role in the ultrafast dynamics of the Ce(IV) sandwich complexes, a RMCT state probably is not the initially observed excited state. The RMCT states of these compounds are not expected to show the absorption feature observed near 800 nm for Ce(OEP)₂ (Figure 2 inset). This prediction is based on the fact that the ring cation of Ce(OEP)₂ has no absorption band between 700 and 1000 nm^{23} and the idea that the spectrum of the RMCT state should be roughly similar to that of the cation since the ring is oxidized in both species. However, we do not wish to press this analogy too strongly, since the simultaneous metal reduction in the RMCT state and the concomitant Coulomb effects might result in differences in the spectrum of the CT state compared to the case of the cation.

On the basis of this discussion, we believe that the following general scheme is the simplest model consistent with all of our observations on the ultrafast decay of the Ce(IV) porphyrin dimers:

$$(\pi,\pi^*)$$
 state $\xrightarrow{\tau_A}$ RMCT state $\xrightarrow{\tau_B}$

vibrationally excited ground state $\xrightarrow{10 \text{ ps}}$ ground state

Since the fast kinetic phase is accompanied by isosbestic behavior (e.g., Figure 4 inset and Figure 6a), the ratio of τ_A and τ_B must be quite large, i.e., either $\tau_{\rm A}$ < 350 fs and $\tau_{\rm B}$ ~ 2 ps or $\tau_{\rm A}$ ~ 2 ps and $\tau_{\rm B}$ < 350 fs. In other words, if the initially observed state is a ring (π,π^*) state, then the RMCT state that we believe facilitates the rapid deactivation must be too short-lived to be observed.

The dominant, 1.5-2.5-ps kinetic phase (Table II) is accompanied by a substantial decay of the bleachings in all the ground-state absorption bands (see Figures 4 and 6). In fact, we believe that the simplest interpretation of our data is that all the molecules return to the ground electronic state on this time scale. We believe that the slow component represents vibrational relaxation in the porphyrin dimer. This is reasonable considering that about 2 eV of electronic energy present in the initially prepared (π,π^*) state must be converted into vibrational degrees of freedom following the ultrafast relaxation to the ground electronic state

We favor this interpretation of the ~ 10 -ps spectral dynamics over the alternatives such as solvent dynamics or parallel deactivation pathways for several reasons. (1) Solvation dynamics is unlikely considering that the slow kinetic phase is present in

relatively nonpolar solvents such as toluene (see Figures 2-6). Also, although solvent relaxation times have yet to be measured for a number of aprotic solvents (e.g., acetone and CH_2Cl_2), current theory²⁴ and experiments on other aprotic solvents^{25a,b} suggest that the solvation time constants lie somewhere between the longitudinal ($\tau_{\rm L}$ = 0.35 ps for acetone and ~0.4 ps for CH_2Cl_2) and Debye ($\tau_D = 3.3$ ps for acetone and 1.5 ps for CH_2Cl_2) relaxation times,^{25c} both of which are significantly shorter than those of the slow phase (see Table II). (2) The slow phase is accompanied by a continuous shifting in the $\Delta A = 0$ points (see e.g. Figures 4 and 6C) and a variation of time constant with wavelength in the blue region which is seen most clearly for $Ce(OEP)_2$. (3) Similar complex spectral and kinetic behavior has been found recently in our laboratory during the first 20 ps after excitation of four-coordinate²⁶ and six-coordinate²⁷ Ni(II) porphyrins. These dynamics were shown to originate from a nonelectronic process such as vibrational relaxation or conformational changes. However, it is unlikely that such similar conformationally driven spectral dynamics should occur in all these porphyrins. Time-resolved measurements on a number of other large molecules indicate that up to 20 ps may be required for the flow of excess energy into the solvent,^{28,29} a time scale consistent with molecular dynamics simulations of intermolecular vibrational relaxation in heme proteins.³⁰ Additionally, it is likely that for porphyrins intramolecular vibrational relaxation may require several picoseconds or more.²⁶

It thus appears likely that vibrational relaxation is largely responsible for the complex dynamics in the Ni(II) porphyrins and for the similar 10-ps kinetic phase in the Ce(IV) dimers, representing here equilibration of a vibrationally excited ground electronic state.

Conclusions

We believe that three conclusions of general significance have emerged from our steady-state and subpicosecond resolution measurements on the Ce(IV) porphyrin sandwich complexes. (1) The very strong electronic coupling between the two rings of the dimer in these molecules must be taken into account in evaluating the ground-state absorption spectra and thus the electronic excited states. Simple exciton theory is not sufficient. (2) Electronic relaxation from the initially prepared (π,π^*) state to the ground electronic state involving an \sim 2-eV energy drop occurs extremely rapidly (\sim 2-ps) via a ring-to-metal CT state. The ultrafast rate implies excellent electronic and Franck-Condon factors for the deactivation process. (3) Ever increasing evidence is emerging that vibrational relaxation of photoexcited metalloporphyrins in solution occurs on a time scale of several picoseconds and is accompanied by a very complex time evolution of the transient absorption spectrum.

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⁽²²⁾ The first reduction of Ce(OEP)₂ occurs at -0.51 V (vs Ag/AgCl) and the first oxidation at +0.26 V. The reduction involves an orbital primarily metal in character whereas the oxidation is from an a_{1u} -like ring π orbital. The first reduction of Ce(TPP)₂ is at -0.16 V and oxidation at +0.79 V. Again, the reduction involves an orbital primarily metal in character, whereas the oxidation largely involves a ring orbital but is influenced by metal orbital participation.

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