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Photophysical Properties of Conformationally Distorted Metal-Free Porphyrins. Investigation into the Deactivation Mechanisms of the Lowest Excited Singlet State

Steve Gentemann,[1a] Craig J. Medforth,[1b] Timothy P. Forsyth,[1b] Daniel J. Nurco,[1b] Kevin M. Smith,[1b] Jack Fajer,[1c] and Dewey Holten*,[1a]

Contribution from the Department of Chemistry, Washington University, St. Louis, Missouri 63130, Department of Chemistry, University of California, Davis, California 95616, and Department of Applied Science, Brookhaven National Laboratory, Upton, New York 11973

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Abstract: Time-resolved and steady-state optical data are presented for a series of substituted free-base porphyrins. The porphyrins are grouped into "normal" and "perturbed" categories based on observed photophysical behavior, and the distinctions between the two classes correlate well with the conformations of the molecules. Normal porphyrins qualitatively and quantitatively follow the deactivation pathways traditionally reported for planar metal-free porphyrins. In contrast, the out-of-plane distortion in a series of sterically-crowded porphyrins results in unusual optical properties and enhanced radiationless decay of the $^1(\pi,\pi^*)$ excited state. In particular, macrocycle distortions increase the rates of **both** the internal conversion and intersystem crossing decay pathways. Enhanced internal conversion of $^1(\pi,\pi^*)$ to the ground state in the perturbed porphyrins is interpreted as arising from an enhanced Franck–Condon factor associated with a structural reorganization in the excited state. Enhanced intersystem crossing from $^1(\pi,\pi^*)$ most likely arises from increased spin–orbit coupling caused by the nonplanarity of the macrocycle. These results demonstrate that structural perturbations of porphyrin macrocycles, imposed by peripheral substitution *in vitro* or the protein environment *in vivo*, can result in significant changes in electronic properties, including the rates and yields of the fundamental excited state deactivation processes.

Introduction

Interest in the role that conformational distortion of porphyrins may play in the function of these molecules in biological systems has prompted the synthesis of many substituted porphyrins in which deformations from planarity are induced by crowding of substituents at the periphery of the macrocycle.[2–4] While environmental effects are believed responsible for altering porphyrin skeletal conformations in heme and photosynthetic proteins,[5,6] distortions arising from steric repulsion between ring substituents in dodecasubstituted model compounds nonetheless provide useful insights into the electronic and vibrational properties of nonplanar prosthetic groups and chromophores *in vivo*. Crystal structures for many highly substituted tetrapyrroles reveal that multiple substituents can indeed force the porphyrin ring from planar to ruffled or saddle-shaped conformations.[2,4] Molecular mechanics calculations furthermore accurately predict these nonplanar conformations.[7] Electronic and vibrational spectroscopic investigations of substituted porphyrins have been initiated to address the consequences of such macrocyclic deformations. Resonance Raman spectroscopy has been used previously to probe the effects of crowding by peripheral substituents on the vibrational structure of a series of nickel(II) porphyrins.[8] Electronic absorption and emission spectroscopies have also revealed the significant influence of ring nonplanarity on the optical properties of substituted free-base and metalated porphyrins.[7,9,10]

The available information regarding the electronic structure of sterically crowded porphyrins has been generally restricted to data obtained by steady-state methods such as ground-state absorption or fluorimetry. For example, previous work has shown that the fluorescence from the lowest excited $^1(\pi,\pi^*)$ state (S_1) to the ground state (S_0) of a dodecasubstituted free-base porphyrin is broadened and red shifted in comparison to tetraphenyl- or octaethylporphyrin and occurs with a reduced quantum yield.[10a] The origins of the spectral shifts and reduction in quantum efficiency have not been delineated, however. Increased rates of intersystem crossing (k_{ISC}) from S_1 to the lowest triplet excited state (T_1), $S_1 \rightarrow S_0$ internal conversion (k_{IC}), and intramolecular charge transfer have been proposed as possible mechanisms.[10,11] The relative contributions of these radiationless processes are not readily distinguishable solely from steady-state optical data. In the present work, we employ both steady-state and time-resolved optical techniques to investigate a series of planar and nonplanar metal-free porphyrins (Scheme 1). The results support previous assessments of the electronic properties of sterically crowded porphyrins and provide details of the mechanisms of excited-state deactivation. Specifically, nonplanar porphyrins display large absorption/fluorescence shifts (Stokes shifts), significantly reduced fluorescence quantum yields, and shortened excited singlet state lifetimes.

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* Author to whom correspondence should be addressed.

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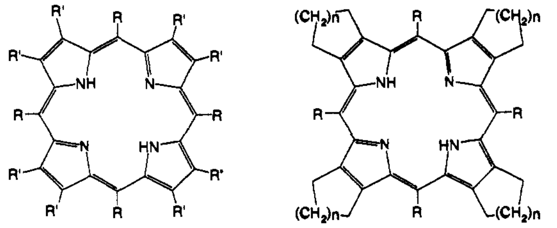
Scheme 1. Structure and Nomenclature of Substituted Free-Base Porphyrins



H_2DPP	$R = R' = C_6H_5$
H_2OMTPP	$R = C_6H_5$ $R' = CH_3$
H_2OETPP	$R = C_6H_5$ $R' = CH_2CH_3$
$H_2O(p\text{-}i\text{PrP})P$	R = H R' = *para*-*iso*propyl-C_6H_4
$H_2T(3,4,5\text{-OMeP})P$	$R = (3,4,5\text{-}OCH_3)\text{-}C_6H_2$ $R' = H$
H_2TPP	$R = C_6H_5$ $R' = H$
H_2OEP	$R = H$ $R' = CH_2CH_3$
$H_2TC_5T(3,4,5\text{-OMeP})P$	$R = (3,4,5\text{-}OCH_3)\text{-}C_6H_2$ n = 1
H_2TC_7P	R = H n = 3
H_2TC_7TPP	$R = C_6H_5$ n = 3
$H_2TC_7T(3,4,5\text{-OMeP})P$	$R = (3,4,5\text{-}OCH_3)\text{-}C_6H_2$ n = 3

Experimental Section

H_2TPP and H_2OEP were purchased from Porphyrin Products (Logan Utah). All other porphyrins were prepared using the general procedures described elsewhere.[2-4,12a,b] When necessary, triethylamine was added to samples to deprotonate any porphyrin dications to the neutral species. HPLC grade toluene and CH_2Cl_2 were used in all experiments and were dried by passage through basic alumina prior to use. Ground-state absorption spectra were obtained on a Perkin-Elmer Lambda 3B spectrophotometer. Fluorescence spectra of ~10 μM deaerated solutions of porphyrin at room temperature were acquired on a Spex Fluorolog II operated in a right angle detection geometry employing a cooled Hamamatsu R928P photomultiplier tube. Emission spectra were corrected for detector spectral sensitivity. Transient absorption spectra were obtained using a pump-probe apparatus previously described.[12c] Excitation flashes (1 mJ, 30 ps at 532 nm) pumped the Q bands of all porphyrins, and a weak white light pulse probed transients up to 12 ns after excitation. Emission lifetimes >1 ns were determined using an experimental arrangement described elsewhere having an instrument response of 2.5 ns fwhm.[13] Argon-bubbled samples for time-resolved emission were usually ~50 μM and excited with 30 ps pulses at 532 nm having an energy less than 50 μJ/pulse.

Results

Steady-State Absorption Spectra. Ground-state absorption spectra for most porphyrins investigated have been previously reported.[2,4,12a,b,14] Porphyrins that we will classify as "normal" on the basis of their overall photophysical behavior display absorption spectra with Q (visible) and B (near-UV) bands comparable in relative intensity and wavelength with H_2TPP and H_2OEP. For example, the longest wavelength electronic absorption band for these complexes, assigned as the $Q_x(0,0)$ band,[14] lies between 620 and 650 nm (Table 1). Those porphyrins classified as "perturbed" on the basis of their overall behavior generally show broadened, red-shifted Q and B bands relative to normal free-base porphyrins [e.g., the $Q_x(0,0)$ $S_0 \rightarrow S_1$ band lies past ~690 nm]. All of the porphyrins (normal and perturbed) listed in Table 1 generally have extinction coefficients for the $Q_x(0,0)$ band in the range 4000–6000 M^{-1} cm^{-1}. Likewise, the Soret (or B) bands of the normal-type porphyrins have intensities similar to H_2TPP or H_2OEP, while those of the perturbed compounds appear to be roughly one-half as intense.

Steady-State Fluorescence Spectra. The emission spectra also group the porphyrins into normal and perturbed categories. Normal fluorescence behavior includes (*i*) a quantum yield comparable to H_2TPP ($\phi_f = 0.11$)[15] or H_2OEP ($\phi_f = 0.16$),[16] (*ii*) small (~100 cm^{-1}) absorption/emission "Stokes" shifts between the $Q_x(0,0)$ absorption and $Q_x(0,0)$ fluorescence peaks (as in H_2TPP and H_2OEP), and (*iii*) vibronic structure and bandwidths similar to H_2TPP and H_2OEP. In contrast, perturbed emission spectra are characterized by (*i*) lower quantum yields (<0.01), (*ii*) larger absorption/emission shifts (~900 cm^{-1}), and (*iii*) generally only a single, broad (~1500 cm^{-1} fwhm) fluorescence band with no clear vibronic structure.

The fluorescence spectra of $H_2T(3,4,5\text{-OMeP})P$, H_2TC_7P, and $H_2TC_7T(3,4,5\text{-OMeP})P$ shown in Figure 1 illustrate the difference between the two types of emission. The emissions of $H_2T(3,4,5\text{-OMeP})P$ and H_2TC_7P represent examples of normal behavior. The spectrum of $H_2T(3,4,5\text{-OMeP})P$ is virtually superimposable on that of H_2TPP while the spectrum of H_2TC_7P is likewise nearly identical to that of H_2OEP. The quantum yields of $H_2T(3,4,5\text{-OMeP})P$ ($\phi_f = 0.10$) and H_2TC_7P ($\phi_f = 0.20$) compare quite well with those of H_2TPP and H_2OEP, respectively (Table 1). Both porphyrins exhibit only modest $Q_x(0,0)$ absorption/fluorescence shifts (70 cm^{-1} for $H_2T(3,4,5\text{–OMeP})P$ and 110 cm^{-1} for H_2TC_7P) which are comparable to the small shifts observed for many substituted normal free-base porphyrins.

Table 1. Free-Base Porphyrin Steady-State Photophysics

porphyrin[a]	$Q_x(0,0)$ absorption, nm	$Q_x(0,0)$ fluorescence, nm	absorption/emission shift, cm^{-1}	quantum[b] yield, ϕ_f
normal				
H_2TPP	645	651	142	0.11
H_2OEP	623	624	26	0.16
H_2TC_7P	620	623	70	0.20
$H_2T(3,4,5\text{-OMeP})P$	650	655	110	0.10
$H_2O(p\text{-}i\text{PrP})P$	635	640	120	0.10
$H_2TC_5T(3,4,5\text{-OMeP})P$	640	647	170	0.06
perturbed				
H_2TC_7TPP	720	770	900	0.007
H_2OETPP	705	750	850	0.005
H_2OMTPP	690	738	940	0.003
H_2DPP	718	772	975	0.006
$H_2TC_7T(3,4,5\text{-OMeP})P$	718	770	940	0.009

[a] Solvent is deaerated toluene at 295 K except for $H_2TC_7T(3,4,5\text{-OMeP})P$ and H_2TC_7TPP where CH_2Cl_2 was used. [b] Calculated assuming yields for H_2TPP ($\phi_f = 0.11$[15]) and H_2OEP ($\phi_f = 0.16$[16]); error in all yields is ±10% except for $H_2TC_7T(3,4,5\text{-OMeP})P$ and H_2TC_7TPP which may be overestimated by ~50% due to poor solubility.

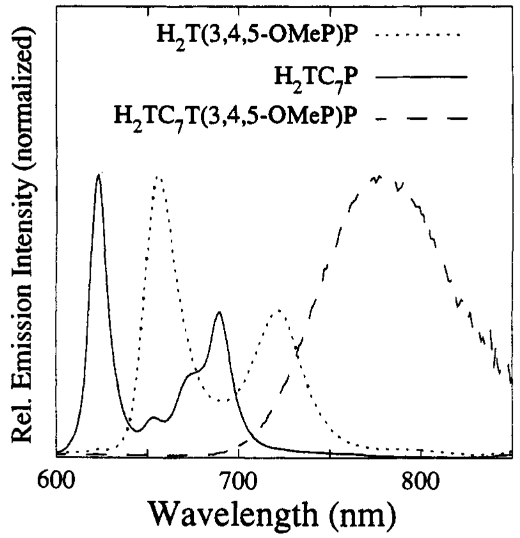


Figure 1. Room temperature corrected fluorescence spectra obtained by excitation into the Q bands: H_2TC_7P (—), $H_2T(3,4,5\text{-OMeP})P$ (···), and $H_2TC_7T(3,4,5\text{-OMeP})P$ (- - -).

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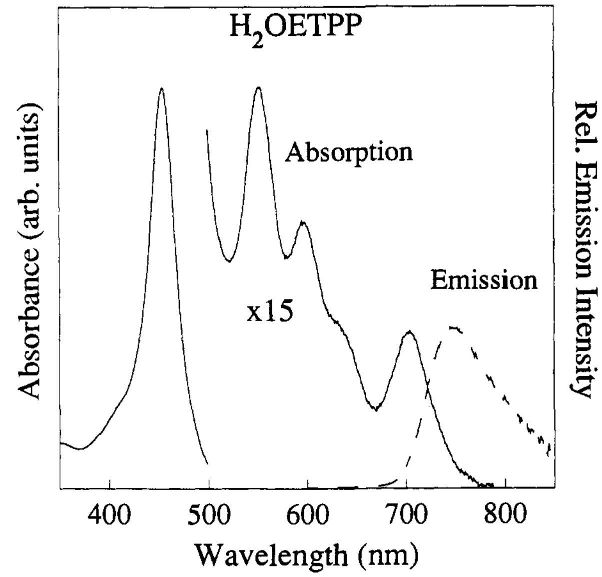

Figure 2. Ground-state absorption (—) and fluorescence (- - -) spectra of H_2OETPP. Absorbance between 500 and 800 nm is multiplied by the indicated factor for clarity. Emission intensity is normalized to the $Q_x(0,0)$ absorption for comparison.

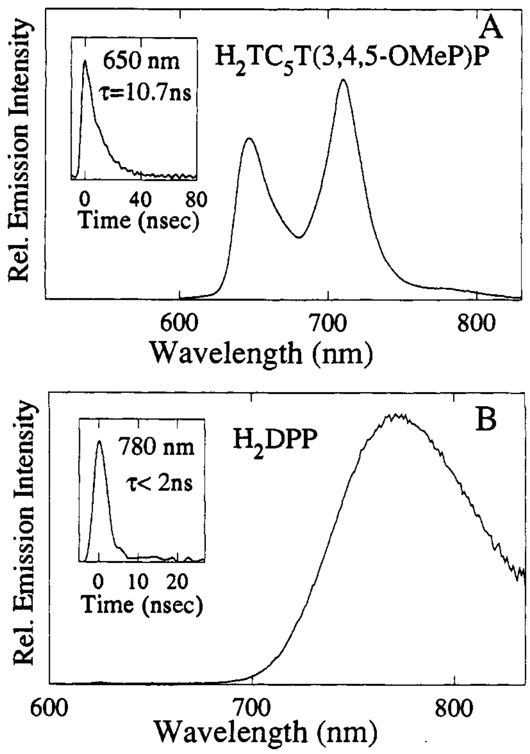

Figure 3. Steady-state fluorescence spectra of $H_2TC_5T(3,4,5\text{-OMeP})P$ (A) and H_2DPP (B) obtained by excitation into the Q bands. The insets show the time evolution of the emission detected at the indicated wavelengths; τ is the observed fluorescence lifetime obtained from an exponential fit to the data deconvolved from the instrument response.

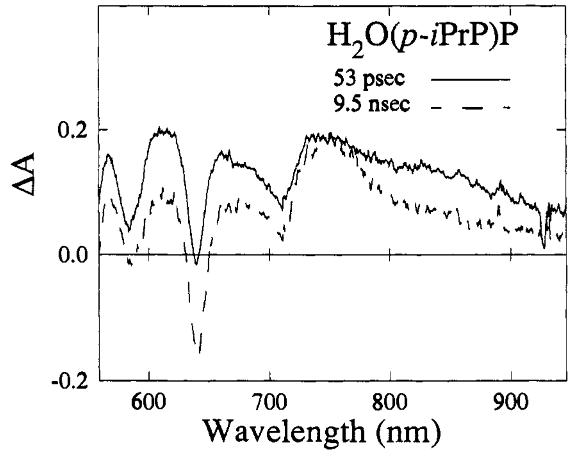

Figure 4. Time-resolved difference absorption spectra of $H_2O(p\text{-}i\text{PrP})P$ obtained at the indicated times after excitation with a 30-ps, 532-nm flash.

On the other hand, the fluorescence spectrum of $H_2TC_7T(3,4,5\text{-OMeP})P$ is quite perturbed. The immediately distinctive characteristics of the emission profile of $H_2TC_7T(3,4,5\text{-OMeP})P$ are a significant red shift and broadening compared to normal free-base fluorescence. In analogy with the normal porphyrins, we believe that the most reasonable assignment of the fluorescence from the perturbed porphyrins is that it represents Q_x emission, with the breadth reflecting unresolved vibrational structure (*vide infra*). The quantum yield of fluorescence of $H_2TC_7T(3,4,5\text{-OMeP})P$ is reduced to 0.009, an ~10-fold lower yield than observed for all the normal free-base porphyrins reported in Table 1. Similarly broad, red-shifted, and weaker fluorescence is observed for H_2OETPP (Figure 2), H_2DPP (Figure 3B), and the other porphyrins in the perturbed category of Table 1.

Finally, a complex that is basically normal but slightly perturbed in its fluorescence behavior is $H_2TC_5T(3,4,5\text{-OMeP})P$. Although the $Q_x(0,0)$ fluorescence band is in the spectral range of the other normal porphyrins (<650 nm), the bands are broader and the $Q_x(0,0)/Q_x(0,1)$ intensity ratio is reversed (Figure 3A). The fluorescence yield of this complex ($\phi_f = 0.06$) is roughly half the typical value for the other normal complexes, although still an order of magnitude larger than the perturbed porphyrins (Table 1).

Transient Absorption. Time-resolved absorption spectra were obtained for all free-base porphyrins in the red to near-IR region. Figure 4 displays transient absorption difference spectra obtained for the normal complex $H_2O(p\text{-}i\text{PrP})P$ at 53 ps and 9.5 ns following excitation with a 30-ps flash. The spectra show a series of troughs embedded on a relatively flat excited-state absorption, typical of (π,π^*) states of metal-free porphyrins.[17] The troughs are identified as ground-state bleachings at 580 and 640 nm [$Q_x(1,0)$ and $Q_x(0,0)$, respectively, indicating depletion of the ground state] and stimulated emission at 640 and 710 nm [$Q_x(0,0)$ and $Q_x(0,1)$, respectively] coincident with the positions of the steady-state fluorescent emission from $H_2O(p\text{-}i\text{PrP})P$.[10a] The stimulated (by the weak white-light probe pulse) emission features in time-resolved difference spectra identify the transient state as the lowest $^1(\pi,\pi^*)$ excited state of the porphyrin ring[17c] (the 640-nm feature at early delay time contains equal contributions from the ground-state bleaching and $^1(\pi,\pi^*)$ stimulated emission). The initial spectrum has decayed roughly 50% by 9.5 ns as estimated by the decrease in absorption at ~850 nm and in the vicinity of the ground-state bleachings. However, the $Q_x(0,1)$ stimulated emission near 710 nm is still observed, indicating that the $^1(\pi,\pi^*)$ state is still present and decaying. Although these transient absorption results do not lend to a precise determination of the $^1(\pi,\pi^*)$ state lifetime, the extent of the decay observed over ~10 ns in Figure 4 is consistent with the time constant of ~13 ns determined from decay of fluorescence (see below).

The observation that the amplitude of the ground-state $Q_x(1,0)$ bleaching at 580 nm for $H_2O(p\text{-}i\text{PrP})P$ remains about the same amplitude (when referenced to the broad positive transient absorption) between 53 ps and 9.5 ns tends to suggest that the $^1(\pi,\pi^*)$ state does not decay significantly by internal conversion to the ground state but instead substantially to the $^3(\pi,\pi^*)$, or T_1, state. The persistence of transient absorption beyond 750 nm

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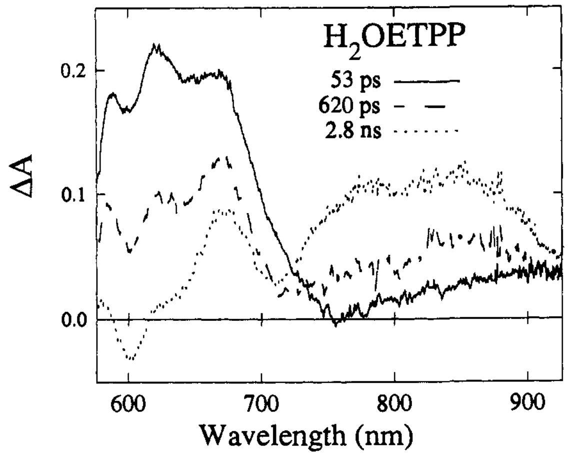

Figure 5. Transient absorption spectra of H_2OETPP obtained at the delay times shown after excitation with a 30-ps, 532-nm flash.

at long pump-probe delay times is consistent with this point of view based on optical data for porphyrin (π,π^*) triplets.[17] However, the fact that the data encompass less than one lifetime of the singlet decay does not allow a precise determination of the triplet yield, ϕ_T, for this compound. Similar transient absorption behavior is observed for the other normal porphyrins studied.

Figure 5 shows room temperature transient absorption data obtained for a perturbed complex, H_2OETPP, illustrating the decay of the $^1(\pi,\pi^*)$ state to a longer lived species. The 53-ps difference spectrum is described by a broad excited-state absorption upon which is superimposed bleaching of the ground-state absorption bands near 710, 645, and 600 nm and a broad stimulated emission extending from ~700 nm to past 850 nm (corresponding to the wavelength span of the broad spontaneous fluorescence in Figure 2). The time evolution of the spectra in Figure 5 shows the complete disappearance of the stimulated emission by 2.8 ns, while the ground-state bleachings persist (with intensity ratios comparable to those in the ground-state absorption spectrum of Figure 2 when referenced to the broad positive transient absorption). There is also a decrease in transient absorption between 600 and 700 nm in the time interval shown. Decay kinetics measured at 5-nm intervals across the spectral region shown are single exponential, with a time constant of 660 ps determined from global analysis of the data. The 2.8-ns spectrum of Figure 5 does not decay further within the longest pump-probe delay time of the transient absorption apparatus (~12 ns). While the long-lived (2.8 ns) spectrum does not exhibit absorption features completely diagnostic of a particular state, the broad background absorption to the red of the lowest-energy ground-state absorption band is, however, consistent with a porphyrin $^3(\pi,\pi)$ state.[17] This state appears to form with a reasonable yield, since the time evolution of the spectrum in Figure 5 suggests that the magnitude of the ground-state bleachings (when referenced to the broad transient absorption) does not decrease substantially as the $^1(\pi,\pi^*)$ state decays. However, since the excited state absorption of H_2OETPP in the vicinity of the bleaching at 600 nm may have a modest slope, we can only estimate a lower limit of ~50% for ϕ_T for this compound. This estimate is consistent with the value of ~0.55 obtained by other workers for this compound.[18]

Figure 6 displays transient absorption data obtained for two additional perturbed porphyrins, $H_2TC_7T(3,4,5\text{-}OMeP)P$ and H_2DPP, in the vicinity of the bleaching of the ground-state $Q_y(0,0)$ band near near 615 nm. For both compounds, the magnitude of the bleach (when referenced to the broad background absorption) remains nearly constant during decay of the $^1(\pi,\pi^*)$ state. This observation indicates a quantum efficiency for $S_1 \rightarrow T_1$ intersystem crossing of greater than 50% and perhaps as high as 90% for these two complexes.

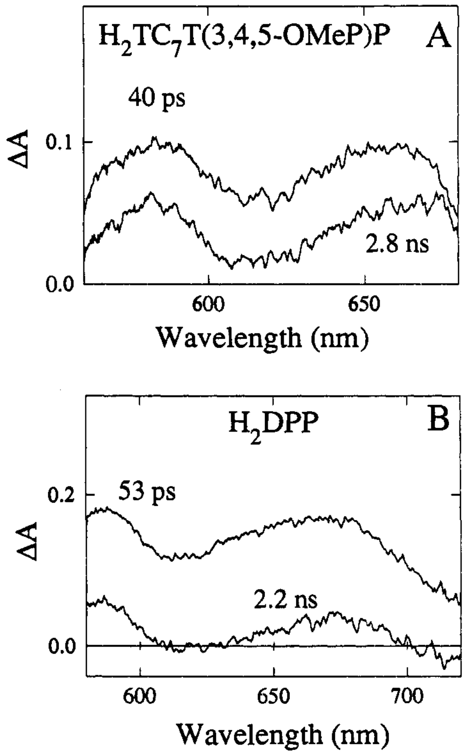

Figure 6. Transient absorption spectra of $H_2TC_7T(3,4,5\text{-}OMeP)P$ (A) and H_2DPP (B) in the region of the $Q_y(0,0)$ ground-state absorption bleaching obtained at the delay times indicated after excitation with a 30-ps, 532-nm flash.

The other perturbed type porphyrins investigated in this work display transient spectral characteristics and kinetic behavior similar to H_2OETPP, H_2DPP, and $H_2TC_7T(3,4,5\text{–}OMeP)P$ (Table 2). Stimulated emission in the early time transient absorption spectra of all compounds identifies the transient species $^1(\pi,\pi^*)$ for these complexes. All perturbed compounds have $^1(\pi,\pi^*)$ decay times less than 1 ns.

Time-Resolved Emission. The insets to Figure 3 display the fluorescence decay profiles of $H_2TC_5T(3,4,5\text{-}OMeP)P$ and H_2DPP. The normal type emission from $H_2TC_5T(3,4,5\text{-}OMeP)P$ shown in Figure 3A decays exponentially with a 10.7-ns lifetime throughout the entire emission spectrum shown. This lifetime compares well with the values of 10–20 ns obtained for the other normal porphyrins in this work (Table 2) and for many alkyl- or phenyl-substituted free-base porphyrins from previous studies.[16,19] The similarity of excited-state lifetimes of all these complexes clearly classifies them as a set distinct from the perturbed porphyrins. All the perturbed porphyrin emission decays (e.g. H_2DPP, Figure 3B inset) fall within the 2.5 ns instrument limit of the emission apparatus, consistent with the time constants of 400–850 ps accurately determined via picosecond transient absorption.

Discussion

Extensive theoretical studies have described the absorption and emission characteristics of free-base porphyrins.[20,21] Generally accepted theories ascribe the ground-state absorptions of porphyrins as transitions to $^1(\pi,\pi^*)$ states derived from $[a_{1u}(\pi), e_g(\pi^*)]$ and $[a_{2u}(\pi), e_g(\pi^*)]$ configurations, where $a_{1u}(\pi)$ and $a_{2u}(\pi)$ are the nearly degenerate porphyrin ring HOMOs and $e_g(\pi^*)$ are the degenerate ring LUMOs. Mixing of these configurations gives rise to the strongly allowed, near-UV Soret band and the less-intense, lower-energy, quasi-allowed Q bands. The effects of peripheral substitution on the optical properties of

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Table 2. Free-Base Porphyrin Time-Resolved Photophysics

porphyrin	$^1(\pi,\pi^*)$ lifetime[a]	triplet yield, ϕ_T	radiative[b] lifetime, ns	intersystem[c] crossing lifetime, ns	internal[d] conversion lifetime, ns
normal					
H_2TPP	14.7 ns	0.7[e]	134	22	77
H_2OEP	21.7 ns	0.7[e]	136	31	155
H_2TC_7P	20.0 ns	*f*	100	29	110
$H_2T(3,4,5\text{-}OMeP)P$	11.0 ns	*f*	110	16	55
$H_2O(p\text{-}i PrP)P$	13.3 ns	*f*	133	19	67
$H_2TC_5T(3,4,5\text{-}OMeP)P$	10.7 ns	*f*	173	15	45
perturbed					
H_2TC_7TPP	400 ps	>0.5[g]	57	0.8(0.4)	0.8(4.3)
H_2OETPP	660 ps	>0.5[g]	132	1.3(0.7)	1.3(7.0)
H_2OMTPP	640 ps	>0.5[g]	213	1.3(0.7)	1.3(6.6)
H_2DPP	830 ps	>0.5[g]	138	1.7(0.9)	1.7(8.8)
$H_2TC_7T(3,4,5\text{-}OMeP)P$	580 ps	>0.5[g]	64	1.2(0.6)	1.2(6.4)

[a] For normal porphyrins, measured from decay of spontaneous emission; lifetimes are ±0.1 ns. For perturbed porphyrins, measured from decay of transient absorption; lifetimes are ±30 ps. [b] Calculated from $\tau_{1(\pi,\pi^*)}/\phi_f$ (ϕ_f from Table 1). [c] Calculated from $\tau_{1(\pi,\pi^*)}/\phi_T$. For normal porphyrins, $\phi_T = 0.7$ is used. For perturbed porphyrins, the first value of τ_{ISC} shown is calculated using $\phi_T = 0.5$ while the value in parentheses is calculated using $\phi_T = 0.9$. [d] Calculated from $\tau_{1(\pi,\pi^*)}/\phi_{IC}$, where $\phi_{IC} = 1 - \phi_f - \phi_T$, *i.e.*, yield of direct conversion to the ground state from S_1 (values of ϕ_f from Table 1). For perturbed porphyrins, the first value shown is calculated using $\phi_T = 0.5$ while the second value in parentheses is calculated using $\phi_T = 0.9$. [e] Taken from ref 37. Note: reported values of ϕ_T ranges from as low as 0.67 (ref 38) to as high as 0.84 (ref 39) for H_2TPP. [f] Unable to estimate from transient absorption since $^1(\pi,\pi^*)$ decays by less than one lifetime over the maximum pump-probe delay of 12 ns. Therefore, the value of 0.7 for H_2TPP and H_2OEP was assumed. [g] Estimated from the lack of appreciable ground state bleaching recovery in the transient absorption spectra (see text).

many free-base and metalated porphyrins have also been described in detail.[21] Extensive series of β-octaalkyl- or $\alpha,\beta,\gamma,\delta$-tetraaryl-substituted porphyrins demonstrate the ability of peripheral substituents (especially via their electron donating/withdrawing nature) to modulate the energies of the porphyrin frontier MOs and the photophysical behavior of these complexes.

The normal porphyrins investigated in this study generally follow the documented photophysical behavior of β-octaalkylporphyrins (e.g. H_2OEP) or $\alpha,\beta,\gamma,\delta$-tetraarylporphyrins (e.g. H_2TPP). These extensively studied, generally planar macrocycles have fluorescence quantum yields of ~0.1 while phosphorescence is absent or present in yields below 10^{-5} at room temperature in the absence of any external heavy atom enhancement.[22] The typical positions of the $Q_x(0,0)$ absorption and fluorescence bands of H_2TPP and H_2OEP place the lowest excited $^1(\pi,\pi^*)$ state of these complexes at 1.9 and 2.0 eV, respectively. Previous studies of other octaalkyl- and tetraarylporphyrins have afforded similar $^1(\pi,\pi^*)$ state energies.[14,19b,23] Emission data in Table 1 likewise place the lowest excited singlet state of all the normal free-base porphyrins between 1.9 and 2.0 eV above the ground state. In contrast, the perturbed porphyrins studied have lowest $^1(\pi,\pi^*)$ states which lie ~1.7 eV above the ground state (as calculated from the average of the positions of the $Q_x(0,0)$ absorption and fluorescence bands).

Crystallographic data available for several of the perturbed free-base porphyrins investigated here indicate severely nonplanar conformations in the ground state induced by steric crowding of the peripheral substituents. H_2OETPP[24] and its Zn(II),[2a] Cu(II),[25] Co(II),[25] and Ni(II)[2c] analogs are all saddle-shaped[26] with the β-pyrrole carbons alternately displaced up and down from the average porphyrin plane by 1 Å or more. Crystalline H_2DPP[2d] is also saddle-shaped as are $Zn^{II}OMTPP$[2a] and $Ni^{II}TC_7TPP$.[27] In contrast, although an X-ray structure[2b] of $Ni^{II}TC_5T(3,4,5\text{-}OMeP)P$ shows the molecule to be "ruffled", EXAFS data indicate that it is planar in solution.[2c] Crystalline $Cu^{II}TC_5T(3,4,5\text{-}OMeP)P$ is also planar.[2b] Some degree of nonplanarity in the free-base derivative may thus account for its somewhat modified, but essentially normal, optical properties. The molecules substituted solely at the β-pyrrole positions are either planar or expected to be planar.[26]

The molecular orbital calculations on several distorted zinc(II) and nickel(II) porphyrins indicate that the saddle deformations destabilize the porphyrin HOMOs,[2c,6] accounting for the lower oxidation potentials and the red shifts of the ground-state absorptions (via a smaller HOMO/LUMO energy gap). The red-shifted absorption observed here (Table 1) and in previous studies on distorted free-base prophyrins is consistent with this point of view. Furthermore, data from Table 1 indicate a substantial "dynamic stabilization" of this emissive S_1 state in the nonplanar porphyrins compared to the initially prepared Franck–Condon configuration, i.e. the "Stokes shift" in absorption/emission. The data of Table 1 indicate that the perturbed porphyrins have not only red-shifted Q_x aborption bands but also substantial Stokes shifts between the absorption and fluorescence bands. The shifts are almost an order of magnitude larger than for the normal porphyrins. The classical explanation for large absorption/fluorescence Stokes shifts for polar molecules in polar solvents derives from solvent reorientation to give enhanced energetic stabilization of the $^1(\pi,\pi^*)$ state compared to the ground state.[28] The persistence of the substantial (~900 cm^{-1}) absorption/emission shift for the perturbed (and relatively nonpolar) porphyrins in nonpolar solvents such as toluene suggests that an additional reorganization in the excited state dominates the behavior of these complexes.[29] Large shifts also have been observed and interpreted similarly for several of the complexes by others.[18]

A reasonable mechanism for this excited-state restructuring is motion along a collective internal coordinate involving the planarity of the porphyrin macrocycle.[30] However, whether this coordinate shift reflects a less or more planar conformation in the excited state vs the ground state cannot be readily determined from the present experimental data. A shift toward a more planar conformation is thought to occur following formation of a (d,d) excited state of some nickel porphyrins as the macrocycle core expands to relieve electron repulsion originating from population of the metal $d_{x^2-y^2}$ orbital.[31] Although there is no such change in metal configuration for the free-base compounds studied here, it is possible that nonplanar metal-free porphyrins also undergo a shift toward a more planar geometry when electronic promotions to porphyrin LUMOs occur in (π,π^*) excited states. The barrier to such a conformational shift in the excited state may be large,

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(26) The nomenclature is that suggested by Scheidt and Lee (Scheidt, W. R.; Lee, Y. J. *Struct. Bonding (Berlin)* **1987**, *64*, 1). In a saddle conformation, alternate pyrrole rings are tilted up and down with respect to a least-squares plane through the 24 atoms of the porphyrin core, and the *meso* atoms lie in the least-squares plane. In a ruffled conformation, alternate pyrrole rings are twisted clockwise or anticlockwise about the metal–nitrogen bond and the *meso* carbon atoms are alternately above or below the least-squares plane through the 24 atoms of the porphyrin core.

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(28) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.

(29) Note that porphyrin–solvent π–π interactions that might induce Stokes shifts would be expected to be more likely with planar porphyrins, contrary to the effects observed here (see ref 5).

(30) Given the variety of peripheral substituents on the porphyrins in this study, it is unlikely that the perturbed photophysical behavior arises from substituent electronic effects. The most obvious feature of the perturbed porphyrins is their marked nonplanarity in the ground state which has been shown to affect their optical spectra, *i.e.* the energies of the π–π^* transitions (*vide supra*).

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however. Variable-temperature NMR experiments indicate that the activation barrier for inverting the saddle-shaped conformer of H_2OETPP in the ground electronic state is 18 kcal mol^{-1}.[2a] Also, while the energy minimized structure of NiDPP is calculated to a saddle conformation, a relaxed planar structure is predicted to lie ~25 kcal mol^{-1} above the nonplanar conformer.[2d] Alternatively, the perturbed free-base complexes may distort further from planarity in the $^1(\pi,\pi^*)$ state. Or, the perturbed porphyrins may shift to a different nonplanar conformation following photoexcitation. Indeed, X-ray structures of tetraarylporphyrins with halogens at the β positions show additional "ruffled" distortions superimposed on the saddle deformations.[32] A similar effect is found in the π-cation radical of Cu^{II}OETPP relative to that of the neutral complex.[33] Also, recent time-resolved ESR results for the triplet states of H_2OETPP and ZnOETPP suggest conformational excursions of the excited states from the canonical crystallographic structures of the molecules in their ground states.[24]

As noted in the Introduction, a central focus of this study is to elucidate the origin of the reduced fluorescence quantum yields for the sterically-crowded porphyrins. Previous studies on dodecaphenylporphyrins have raised several intriguing questions. An electron transfer process involving the strongly electronegative fluorines in H_2F_{20}DPP (R = C_6F_5, R′ = C_6H_5 in Scheme 1) was proposed as a quenching mechanism of the $^1(\pi,\pi^*)$ state, resulting in an lower observed fluorescence yield.[11] However, such weak fluorescence was subsequently reported for H_2DPP, a porphyrin lacking potential facile electron acceptors, indicating that the low quantum yields for both dodecaphenylporphyrins arise from increased rates of radiationless decay processes other than electron transfer.[10a,11] Reduced fluorescence yields have also been found for structurally-perturbed basket-handle porphyrins.[10b]

Our results on a series of perturbed porphyrins support the interpretation that radiationless processes other than electron transfer act to quench the lowest excited singlet state. We propose that the reduced quantum yields of emission in the perturbed, nonplanar porphyrins are a direct result of the decreased S_1 lifetimes whose reduction is due **both** to increased $S_1 \rightarrow T_1$ intersystem crossing **and** increased $S_1 \rightarrow S_0$ internal conversion rates. Natural radiative lifetimes of the nonplanar complexes in Table 2 appear to compare well to the ~120-ns lifetimes observed for the normal-type free-base porphyrins investigated here and previously.[15,23] This assessment is supported by radiative rates obtained directly from $^1(\pi,\pi^*)$ lifetime and fluorescence yield measurements (Table 2) or calculated from the integrated $S_0 \rightarrow S_1$ ground-state absorption bands.[34] We estimate that the triplet yields (ϕ_T) for the perturbed porphyrins are at least 0.5, and could be as high as 0.9 for several of the complexes based on the apparent lack of substantial ground-state recovery as $^1(\pi,\pi^*)$ decays (see e.g. Figure 6). Triplet yields of 0.5–0.9 place estimates on intersystem crossing times (τ_{ISC}) of ~1 ns for all perturbed porphyrins compared to ~20 ns calculated for the normal porphyrins (Table 2). (Note that even if the triplet yields for the perturbed compounds were as low as 0.1, a value clearly inconsistent with the transient optical data, the calculated value of τ_{ISC} would still remain shorter than that for the normal porphyrins.) The $^1(\pi,\pi^*)$ lifetimes and fluorescence yields give a calculated average internal conversion time (τ_{IC}) of ~1 ns for the nonplanar complexes if our estimated lower limit of $\phi_T = 0.5$ is employed and ~7 ns if $\phi_T = 0.9$. Hence, independent of reasonable estimates of the triplet yield, it is seen that the values of τ_{IC} for the perturbed porphyrins are at least an order of magnitude shorter than the average value of ~80 ns for the normal porphyrins. Thus, an important conclusion to be drawn from the calculated non-radiative lifetimes of Table 2 is that **both** non-radiative rates (k_{IC} and k_{ISC}) are increased in the perturbed porphyrins relative to the normal porphyrins.

The enhancement in both $S_1 \rightarrow S_0$ internal conversion and $S_1 \rightarrow T_1$ intersystem crossing in the nonplanar, perturbed porphyrins can be understood by noting that these radiationless decay processes are dependent on (*i*) vibrational wave function overlap (the Franck–Condon factor) between the electronic states involved and (*ii*) an electronic coupling term. An enhanced Franck–Condon factor for $S_1 \rightarrow S_0$ internal conversion in nonplanar complexes almost certainly results from the substantial S_1 reorganization (evidenced by the large absorption/fluorescence Stokes shift), and is supplemented by a reduced S_1–S_0 energy gap (via the energy-gap law for radiationless decay[28]). As noted above, the reorganization is most likely associated with additional structural excursions in the S_1 excited electronic state compared to S_0 for the perturbed porphyrins.

While intersystem crossing from S_1 to T_1 also could be enhanced via an improved Franck–Condon factor if there are larger structural differences between the two states compared to normal porphyrins, we believe that the increased intersystem crossing rate results primarily from enhanced spin–orbit coupling in the nonplanar complexes. Intersystem crossing in porphyrins is thought to depend on wave function overlap involving the central nitrogens of the macrocycle, and this may be facilitated by out-of-plane distortions in S_1, T_1, or both. Theoretical[35] and experimental[36] work on chlorophylls argues that intersystem crossing can be modulated by such nitrogen-centered perturbations. Thus, macrocycle distortions ultimately may be responsible for the increased rates of both internal conversion and intersystem crossing in the perturbed porphyrins, the former via an enhanced Franck–Condon factor and the latter via enhanced spin–orbit coupling.

Previous work has suggested that out-of-plane distortions in porphyrins and the associated changes in electronic and vibrational properties may have important consequences for their function in biological systems such as heme proteins and bacterial reaction centers.[5,6] The work presented here has further demonstrated the pronounced effects that structural perturbations can have on the electronic properties of the porphyrin system, and has revealed mechanisms by which the excited-state dynamics and fundamental decay pathways are modulated by structural parameters.

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