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ARTICLES

Ultrafast Spectroscopy of Free-Base N-Confused Tetraphenylporphyrins

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The photophysical characterization of the two tautomers (**1e** and **1i**) of 5,10,15,20-tetraphenyl N-confused free-base porphyrin, as well as the tautomer-locked 2-methyl 5,10,15,20-tetraphenyl N-confused free-base porphyrin, was carried out using a combination of steady state and time-resolved optical techniques. N-Confused porphyrins, alternatively called 2-aza-21-carba-porphyrins or inverted porphyrins, are of great interest for their potential as building blocks in assemblies designed for artificial photosynthesis, and understanding their excited-state properties is paramount to future studies in multicomponent arrays. Femtosecond resolved transient absorption experiments reveal spectra that are similar to those of tetraphenylporphyrin (H_2TPP) with either Soret or Q-band excitation, with an extinction coefficient for the major absorbing band of **1e** that was about a factor of 5 larger than that of H_2TPP. The lifetime of the S_1 state was determined at a variety of absorption wavelengths for each compound and was found to be consistent with time-resolved fluorescence experiments. These experiments reveal that the externally protonated tautomer (**1e**) is longer lived ($\tau = 1.84$ ns) than the internally protonated form (**1i**, $\tau = 1.47$ ns) by ∼369 ps and that the *N*-methyl N-confused porphyrin was shorter lived than the tautomeric forms by ∼317 ps (DMAc) and ∼396 ps (benzene). Steady-state fluorescence experiments on tautomers **1e** and **1i** and the *N*-methyl analogues corroborate these results, with fluorescence quantum yields (Φ_{Fl}) of 0.046 (**1e**, DMAc) and 0.023 (**1i**, benzene), and 0.025 (DMAc) and 0.018 (benzene) for the *N*-methyl N-confused porphyrin. The lifetime and quantum yield data was interpreted in terms of structural changes that influence the rate of internal conversion. The absorption and transient absorption spectra of these porphyrins were also examined in the context of DFT calculations at the B3LYP/6-31G(d)//B3LYP/3-21G(d) level of theory and compared to the spectra/electronic structure of H_2TPP and tetraphenyl chlorin.

Introduction

The optical properties and photophysical behavior of porphyrins, as well as their derivatives and analogues, continue to attract the interest of chemists because of their similarities to pigments found in biological organisms. This work is particularly useful for providing insight into the light-initiated dynamics of related biomolecules present in the light-harvesting complexes (LHCs) and photosynthetic reaction centers in purple bacteria and green plants. The light-harvesting centers (LHCII[1] in several green plant systems and LH2[2] and LH1[3] in purple bacteria) are comprised of various bacteriochlorophyll *a* (BChl*a*, i.e., B800, B850, and B880) pigments arranged in circular arrays. Structural data indicate[4,5] that a combination of hopping and exciton coupling among the BChl*a* pigments is responsible for the efficient electronic energy transfer (EET) within LH1 and LH2 upon absorption of light. Similarly, the photosynthetic reaction center (PRC) has evolved over time to facilitate photoinduced electron transfer (ET) from an electronically excited "special pair" of bacteriochlorophylls to a quinone acceptor through a series of fast intermediate steps.[4] Efforts to mimic both the LHC and PRC continue to fascinate chemists from the perspectives of solar energy conversion schemes using covalently bound[6,7] and supramolecular multiporphyrin arrays.[8,9,10]

The absorption characteristics of the $^1(\pi,\pi)$ and $^3(\pi,\pi)$ excited states of H_2TPP have been measured using ultrafast transient absorption spectroscopy[11] and provided a basis for the interpretation of energy and electron-transfer processes in a variety of complex arrays.[6−8] The excited-state spectrum of H_2TPP shows strong but nondistinct absorption features between the Soret- and Q-band bleachings that make identification of the nature of the excited-state difficult. The absorption bands in the 600 and 900 nm region, though less intense than those observed in the Soret region, have distinctive features that have been found to be useful in characterizing excited-state processes. The time-resolved dynamics of the S_1 state in this work was comparable to that obtained using time-resolved fluorescence measurements. Zewail and co-workers[12] recently reexamined the excited-state dynamics of H_2TPP using femtosecond-resolved transient absorption and fluorescence up-conversion experiments. In this work, excitation into vibrationally excited S_2 and S_1 states led to rapid intramolecular vibrational energy redistribution (100−200 fs), collisionally induced vibrational relaxation (1.4 ps), and thermal equilibration (energy exchange

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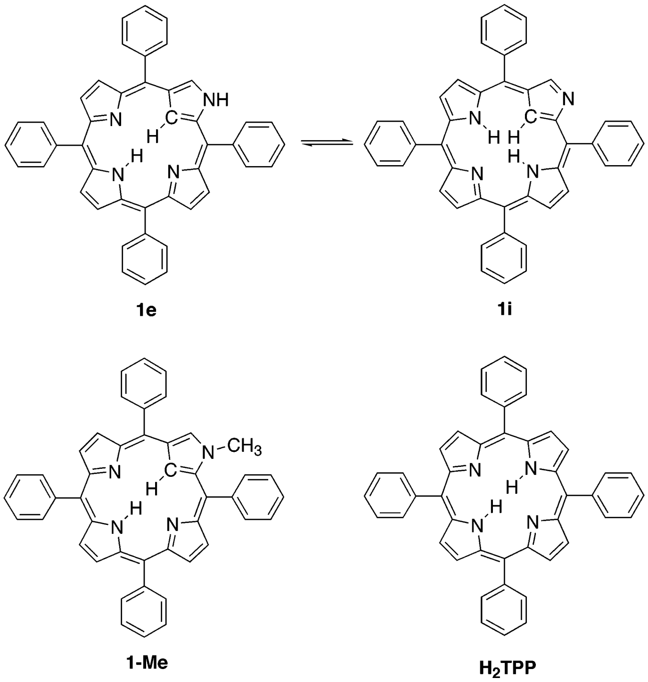

1e **1i** **1-Me** **H$_2$TPP**

Figure 1. Tautomeric forms of N-confused tetraphenyl porphyrin **1e** and **1i**, *N*-methyl N-confused tetraphenylporphyrin **1-Me**, and tetraphenylporphyrin (H$_2$TPP).

with solvent, 10−20 ps). The S$_2$ state decayed within ca. 50 fs to the S$_1$ state, whereas the equilibrated Q$_x$ state decayed by intersystem crossing on the ns time scale.

The spectroscopic features and properties of important porphyrin analogues such as BChl*a* and chlorins have not been examined in quite such detail. Nonetheless, the lifetimes of the S$_1$ state and quantum yields of various chlorins are known and are comparable to many porphyrins.[13] Time-resolved experiments have not yet been performed on many synthetic chlorins, although the fluorescence spectrum of tetraphenylchlorin has been reported[14] and the fluorescence lifetime (9.6 ns) and quantum yield (0.30) of a diarylchlorin has been reported.[15] Spectroscopic parameters of related free-base and zinc oxochlorins have also been reported by Lindsey, Holten, and Bocian.[16]

The high (D_{2h}, D_{4h}) symmetry of porphyrins and metalloporphyrins leads to a near degeneracy of the unfilled e$_g$ orbitals and results in weak, quasi-forbidden transitions in the Q-band region ($S_0 \rightarrow S_1$).[17] Unfortunately, this spectral region is primarily where solar irradiation reaches a maximum, and as a result, porphyrins are not found in organisms that utilize light-induced processes for cellular energy generation. Conversely, chlorins and BCHl*a* have a reduction in symmetry to C_s symmetry that results in a break in the degeneracy of the unfilled e$_g$ orbitals. The Q-band transitions in these analogues, as a result, are quasi-allowed and have significantly greater oscillator strengths, at lower energies, than the analogous porphyrins.[18] These strong, low-energy absorption properties make chlorins[19,20] very desirable for photonics applications and related devices.

N−Confused porphyrins (NCPs) represent attractive alternatives to both chlorins and porphyrins in photonics applications. NCPs are porphyrin isomers with one of the pyrrolic nitrogens facing outside the macrocycle and one C−H group oriented inward toward the core. These porphyrins, though differing from the parent tetrapyrrole by the inversion of only two atoms, exhibit different physical and chemical properties than normal porphyrins. Two NCP tautomers (**1e**, **1i** in Figure 1) are observed in solution.[21,22] Tautomer **1e** has an external N−H group and is favored in highly polar solvents such as DMF, where it presumably undergoes hydrogen bonding with the solvent. Tautomer **1i** has two internal N−H groups and is preferred in aromatic and halogenated solvents. The absorption spectra of both tautomers are characterized by Soret and Q-bands that are red-shifted to significantly lower energies and with larger extinction coefficients than those of tetraphenylporphyrin (H$_2$TPP).[21,22] Similarly to chlorin, the red-shifted absorption bands and increased oscillator strengths result[22] from a break in the degeneracy of the e$_g$ orbitals and a further splitting of the a$_{1u}$ and a$_{2u}$ orbitals in regular porphyrins that occur with the decrease in symmetry in this macrocycle.

We recently investigated the excited-state properties of NCPs **1e** and **1i** in solution using steady-state and time-resolved fluorescence spectroscopy.[22] The quantum yields of fluorescence (Φ_F) were found to be 0.023 in CH$_2$Cl$_2$ and 0.046 in dimethyl acetamide (DMAc),[23] and the corresponding fluorescence lifetimes (τ_F) were found to be 1.60 ns (CH$_2$Cl$_2$) and 1.98 ns (DMAc).[22] To characterize the absorption features of the S$_1$ state, we have extended this work to characterize the spectral and dynamic properties of the excited singlet and triplet states of NCPs **1e** and **1i** using ultrafast transient and time-resolved absorption spectroscopy. In this work, we also have included a parallel spectroscopic investigation of *N*-methyl N-confused tetraphenylporphyrin (**1-Me**) to investigate the spectroscopic ramifications of “locking in” one tautomeric form. We anticipate these experiments will provide a foundation for the subsequent use of NCPs in solar energy arrays and nanoscale molecular devices.

Experimental Section

Apparatus and Procedures. Femtosecond transient absorption measurements were performed in the Center for Laser and Optical Spectroscopy at the University of Akron. In these experiments, the output of a regeneratively amplified titanium-sapphire laser system, producing 130 fs pulses at a 1 kHz repetition rate with pulse energies of 3.5 mJ near 800 nm, was split into equal parts to generate the pump and probe pulse trains. For the pump, one-half of the fundamental light was either doubled for excitation in the Soret band or used to pump an optical parametric amplifier (OPA), the IR output of which was mixed with the residual fundamental to provide wavelengths between 437 and 635 nm. The pump pulse passed through a computer-controlled optical delay line (either 4 or 8 ns) and was focused with a 30-cm focal-length lens onto the sample cell, which was typically displaced several inches from the focal point to give an excitation spot size of ~450 μm. The pump power was varied from 0.07 to 3.5 μJ/pulse to study the power dependence of the measured dynamics. For transient dynamic measurements, the probe half of the fundamental was used to pump a second OPA. Probe wavelengths from 470 to 702 nm were produced by mixing or doubling the parametrically amplified IR light. Typical probe pulse energies used were from 0.01 to 0.5 μJ at the sample. A beam-splitter separated a small fraction of the probe beam for measurement by a photodiode before the probe crossed the pump beam at a small angle (~3°) in the sample cell, with the angle between pump and probe polarizations set at 54.7°. Comparison scans of cells containing pure solvent were recorded in conjunction with experiments under those conditions for which interference from solvent-induced transients were observed to be potentially significant.

Time-resolved fluorescence experiments were performed using the time-correlated single-photon counting (TCSPC) technique. The instrument used in this work utilized the pulses

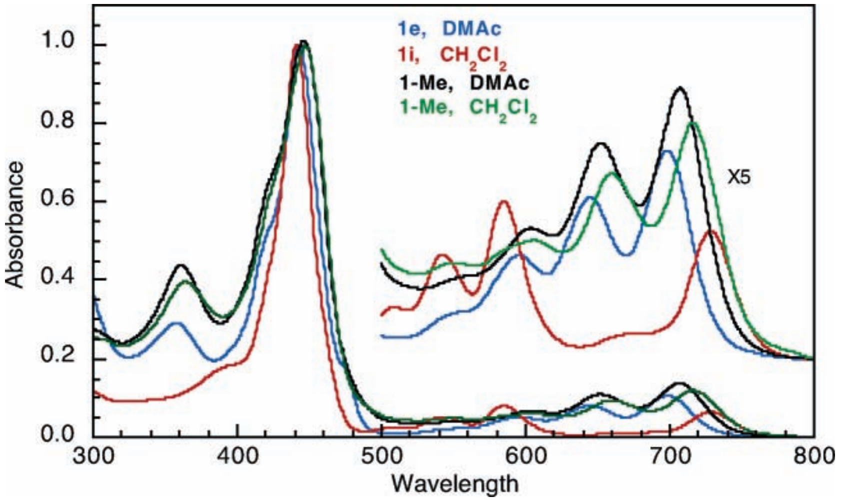

Figure 2. Absorption spectra of **1e** (DMAc, blue), **1i** (CH_2Cl_2, red), **1-Me** (DMAc, black), and **1-Me** (CH_2Cl_2, green). The spectra were normalized to the Soret band maximum; the Q-band region is shown expanded above by a factor of 5.

TABLE 1: Absorption Data for N-Confused Porphyrin Tautomers 1e and 1i and *N*-Methyl N-Confused Porphyrin 1-Me in CH_2Cl_2 and DMAc

compound	solvent	Soret (nm) ($\epsilon \times 10^4$ $M^{-1}cm^{-1}$)	Q-band (nm) ($\epsilon \times 10^3$ $M^{-1}cm^{-1}$)			
1i	CH_2Cl_2	437 (15.9)	539 (11.9)	580 (14.1)	665 (2.36)	724 (13.3)
1e	DMAc	442 (11.9)	550 (2.0)	595 (6.1)	644 (9.5)	699 (12.4)
1-Me	CH_2Cl_2	446 (10.3)	563 (2.4)	609 (4.4)	656 (8.9)	715 (12.2)
1-Me	DMAc	446 (10.5)	562 (3.2)	605 (5.6)	652 (10.0)	707 (12.9)

from a Coherent cavity dumped 702 dye laser pumped by the 527 nm output of a CW mode-locked Nd:YLF laser. The fluorescence signal was detected at 54.7° with an emission polarizer and depolarizer, using a Hamamatsu R3809U-51 red-sensitive multichannel plate detector (MCP). Data collection was accomplished with an Edinburgh Instruments data collection system, and analysis was done with a PicoQuant FluoFit decay analysis program. Time resolution on this instrument is estimated at ~7−9 ps. Time-resolved decays were fit such that values of $\chi^2 < 1.20$ were obtained. Error limits in these measurements are estimated at ±10%. All TCSPC experiments were run with argon-saturated benzene and DMAc solutions with optical densities of 0.15 at the excitation wavelength (582 nm excite/744 nm decay for **1i**, 594 nm excite/713 nm decay for **1e**, 600 nm excite/746 nm decay for **1-Me** in benzene, and 600 nm excite/733 nm decay for **1-Me** in DMAc).

Nanosecond transient and time-resolved absorption experiments were performed by exciting the NCP at 570 nm using the output of a Nd:YAG pumped dye laser (Rhodamine 6G) and monitoring the changes in absorption with the pulsed output from a 75W Xe arc lamp. Transient absorption experiments were acquired using an intensified CCD (ICCD) for detection and a 500 ns delay after the laser pulse. Time-resolved experiments were collected using a Hamamatsu R5108 PMT detector and a digitizing oscilliscope. The time-resolution on this system is estimated as ~10 ns. Pulse energies were kept to ~15 mJ to minimize multiphoton absorptions and triplet−triplet quenching reactions. Ground-state absorption and static fluorescence spectra were obtained as described earlier.[24]

Absorption spectra were recorded initially to confirm the quality of each sample prepared for use in femtosecond and nanosecond measurements and periodically to check for degradation over time. All solvents used for spectroscopic measurements were either Spectral or HPLC grade. The *N*-methyl NCP (**1-Me**) was prepared according to a literature procedure.[25]

Results and Discussion

Steady-State Absorption. Steady state absorption measurements have been previously reported for **1i** and **1e**[21,22] and are characterized by red-shifted Soret and Q-bands. The energy and oscillator strengths of these bands are highly dependent upon the particular tautomer. Tautomer **1e** (in DMAc) has a Soret band absorption at 442 nm and a Q-band region that gains intensity with decreasing energy (Figure 2). Tautomer **1i** (i.e., in CH_2Cl_2), on the other hand, has a Soret band at 437 nm and a Q-band structure similar to tetraphenylchlorin (H_2TPChl), with a very intense $Q_y(0,0)$ band at 724 nm as the dominant low-energy feature.[18] Replacement of the methyl group at the external nitrogen locks **1-Me** into tautomer **1e**, and its absorption spectra in both polar and nonpolar solvents was therefore expected to be similar to **1e**. The spectra of **1-Me** in CH_2Cl_2 and DMAc are shown in Figure 2 (Table 1). Both **1e** and **1-Me** (in both solvents) display a high energy band at 355−360 nm analogous to the N-band in normal porphyrins; this band is observed as a shoulder in **1i** at 388 nm.

As expected, the absorption spectra of **1-Me** in both solvents are similar to **1** in DMAc (i.e., **1e**) rather than in CH_2Cl_2 (i.e., **1i**), albeit with Soret and Q-band absorptions that are red-shifted from **1e**. In DMAc, the Soret band of **1-Me** is red-shifted to 446 nm, whereas the three lowest-energy (and most easily resolved) Q-bands are each red-shifted from **1e** by ~8−12 nm. In CH_2Cl_2, these shifts are slightly more pronounced, with the Soret absorption also at 446 nm, and the three low energy Q-bands now red-shifted between ~12−16 nm from those of **1e**. The solvatochromatic shifts are rather large compared to H_2TPP, which shows only minor absorption changes in different polarity solvents. Because the electronic structure of **1-Me** is unlikely to change substantially with changing solvent polarity, the observed solvatochromic shift is consistent with preferential stabilization of the excited state in more polar solvents in the so-called “externally protonated” tautomer of N-confused por-

TABLE 2: Steady-State and Time-Resolved Fluorescence Data for N-Confused Porphyrin Tautomers 1i and 1e and *N*-Methyl N-Confused Porphyrin 1-Me in Benzene and DMAc

compound	solvent	λ_{FL}	Φ_{FL}	τ_1 (ns)	Stokes shift (cm^{-1})
1i	benzene	744 815	0.023	1.47	371
1e	DMAc	713 783	0.046	1.84	281
1-Me	benzene	746 835	0.018	1.15	660
1-Me	DMAc	733 799	0.025	1.44	542

phyrins. The extinction coefficients of **1-Me** in both CH_2Cl_2[25] and DMAc are quite similar to that of **1e**.

Fluorescence Spectroscopy. The steady-state fluorescence spectra for tautomers **1i** and **1e** are characterized by maxima at 744 nm (**1i**) and 713 nm (**1e**), and both have weak shoulders extending into the red. The quantum yields of fluorescence (Φ_F) are also dependent upon the particular tautomer and have values of 0.023 (**1i**) and 0.046 (**1e**).[23] The corresponding fluorescence lifetimes (τ_F) are significantly shorter than that of H_2TPP and were previously determined by us to be 1.60 ns (**1i**, CH_2Cl_2) and 1.98 ns (**1e**, DMAc).[22] A slightly different detection setup, solvent (in the case of **1i**) and fitting program yielded slightly smaller, but still similar, values of 1.47 ns for **1i** in benzene and 1.84 ns for **1e** in DMAc. The replacement of the external hydrogen in **1e** with the methyl group in **1-Me** was expected to result in only minor changes in the fluorescence properties from those of **1e**. However, the fluorescence maxima (λ_{max}) for **1-Me** in both solvents are significantly red-shifted from those of **1e** (Table 2), with maxima in DMAc and benzene of 733 and 746 nm, respectively, compared to 713 nm for **1e** (DMAc). The Stokes shifts for **1-Me** in nonpolar (660 cm^{-1}) and polar (542 cm^{-1}) solvents are significantly larger than that of **1e** (281 cm^{-1}). The fluorescence quantum yields (Φ_{FL}) determined for **1-Me** in both solvents are significantly lower than **1e** as well and are consistent with the methyl group providing a mechanism for S_1 deactivation through an increase in the internal conversion rate constant (k_{IC}). Alternatively, although the structure of the **1-Me** has not yet been determined, the crystal structure of an N-substituted acetyl NCP[26] indicates a significant deviation from planarity; such a structural deformation could also account[22] for the decreased quantum yield in **1-Me**. The fluorescence lifetime (τ) of **1-Me** in both solvents was found to be best fit to a monoexponential decay (1.44 ns in DMAc and 1.15 ns in benzene). Both of these decay constants are smaller than that of **1e** (1.84 ns, Table 2) and are consistent with substitution at the external nitrogen providing a mechanism for excited-state deactivation.

Femtosecond Time-Resolved Absorption Spectroscopy. To probe the spectroscopic features and the dynamic properties of both tautomers of **1**, as well as that of **1-Me** in polar and nonpolar solvents, transient absorption spectra were obtained at a variety of time delays in both DMAc and toluene. Both Soret and Q-band excitation were used to examine the effects of excitation into the S_2 and S_1 states, respectively. The transient absorption spectrum in DMAc (**1e**) acquired at a 1 ps delay after 442 or 596 nm pump pulses is shown in Figure 3 (top), whereas the analogous spectra acquired in toluene (**1i**) with 437 or 585 nm excitation are shown in Figure 3 (bottom). The spectrum in DMAc at 1 ps with Q-band excitation (596 nm) is dominated by a strong absorption at ∼510 nm, with a shoulder to the blue at 485 nm. Depletion of the $Q_x(1,0)$ band is observed as weak negative absorption (bleach) at ∼645 nm. A second negative feature is observed at ∼710 nm and is attributed to a combination of the depletion of the $Q_x(0,0)$ absorption band and stimulated emission from the $Q_x(0,0)$ emission band. Excitation into the Soret band (442 nm) leads to slight changes in the transient absorption spectrum. First, the absorption centered at ∼510 nm in the Q-band spectrum is substantially broadened with an intense high-energy shoulder at 493 nm and a second prominent shoulder at 473 nm. Since the depletion from the pump beam is no longer present with this excitation wavelength, a weak absorption feature is observed at ∼620 nm. Depletion of the Soret band at 442 nm, the $Q_x(1,0)$ absorption band at 650 nm, and the combined $Q_x(0,0)$ bleach and $Q_x(0,0)$ stimulated emission (∼713 nm) are all observed as negative absorptions.

The transient absorption spectrum acquired in toluene with 585 nm excitation and a 1 ps delay shows an intense peak centered at ∼488 nm and a slight shoulder to the red at ∼535 nm. A second, less intense band is observed at ∼643 nm that is ca. one-third as intense as the main absorption peak. A negative absorbing feature is observed ∼730 nm that results from a combination of the bleach from the $Q_y(0,0)$ band at 724 nm and the $Q_y(0,0)$ stimulated emission band at 744 nm. The spectrum acquired with Soret band excitation at 437 nm, when scaled to the bleach/emission at ∼730 nm, shows a much more intense peak centered at ∼ 500 nm.[27] The shoulder that is observed at 535 nm with Q-band excitation is now more prominent and is blue-shifted to 525 nm. Instead of the relatively intense band at 543 nm, smaller bands at ∼570 nm and ∼626 nm are observed, as well as a less intense and broad band centered at ∼670 nm.

Transient absorption and time-resolved absorption experiments on the *N*-methyl NCTPP (**1-Me**) were also performed to investigate the potential for excited-state proton transfer, as well as any effects methylation might have on the excited-state spectrum and dynamics of NCTPP. Transient absorption spectra of **1-Me** in both DMAc and toluene acquired with excitation at the Soret band are shown at 1 ps after the laser pulse in Figure 4. In DMAc, the $S_1 \rightarrow S_n$ spectrum is characterized by a large absorption at 518 nm, ∼7 nm to the red of the $S_1 \rightarrow S_n$ absorption of **1e**. A poorly resolved negative absorption centered at ∼695 nm and extending toward ∼735 nm, attributed to a combination of the $Q_x(0,0)$ band bleach and the $Q_x(0,0)$ stimulated emission, is also observed. In toluene, the absorption maximum is found at ∼529 nm, which is substantially red-shifted from that of **1i** in toluene (488 nm) and is red-shifted 11 nm from **1-Me** in DMAc. The bleach of the $Q_x(0,0)$ absorption band and the stimulated emission is observed from ∼710−745 nm. Noticeably absent from the spectrum in toluene is the ca. 640 nm transition observed for tautomer **1i**.

To understand the differences in the transient spectra (i.e., absorption maxima, extinction coefficients) of the $^1(\pi,\pi^*)$ **1i** and **1e** excited states,[28] it is worth examining the ground-state electronic structures of these two molecules in comparison to H_2TPP and H_2TPChl. The electronic structures of **1i** and **1e** have been calculated previously at the B3LYP/6-31G(d)//B3LYP/3-21G(d) level of theory.[22] The relative energies of the interacting Gouterman orbitals for **1i** and **1e** are summarized together with those of H_2TPP and tetraphenylchlorin (H_2TPChl) in Figure 5. The absorption spectra of free-base porphyrins such as H_2TPP are characterized by low-energy $S_0 \rightarrow S_1$ transitions (Q-bands) that are nearly forbidden by parity rules and a more intense, higher-energy $S_0 \rightarrow S_2$ transition that is allowed (Soret band). The Q-band region in simple porphyrins generally decreases in intensity with decreasing energy. In H_2TPChl, the unoccupied orbitals are nondegenerate and substantially split in energy, resulting in the *y*-polarized Q-band transition (i.e., the $Q_y(0,0)$ band and its $Q_y(1,0)$ overtone) becoming weakly

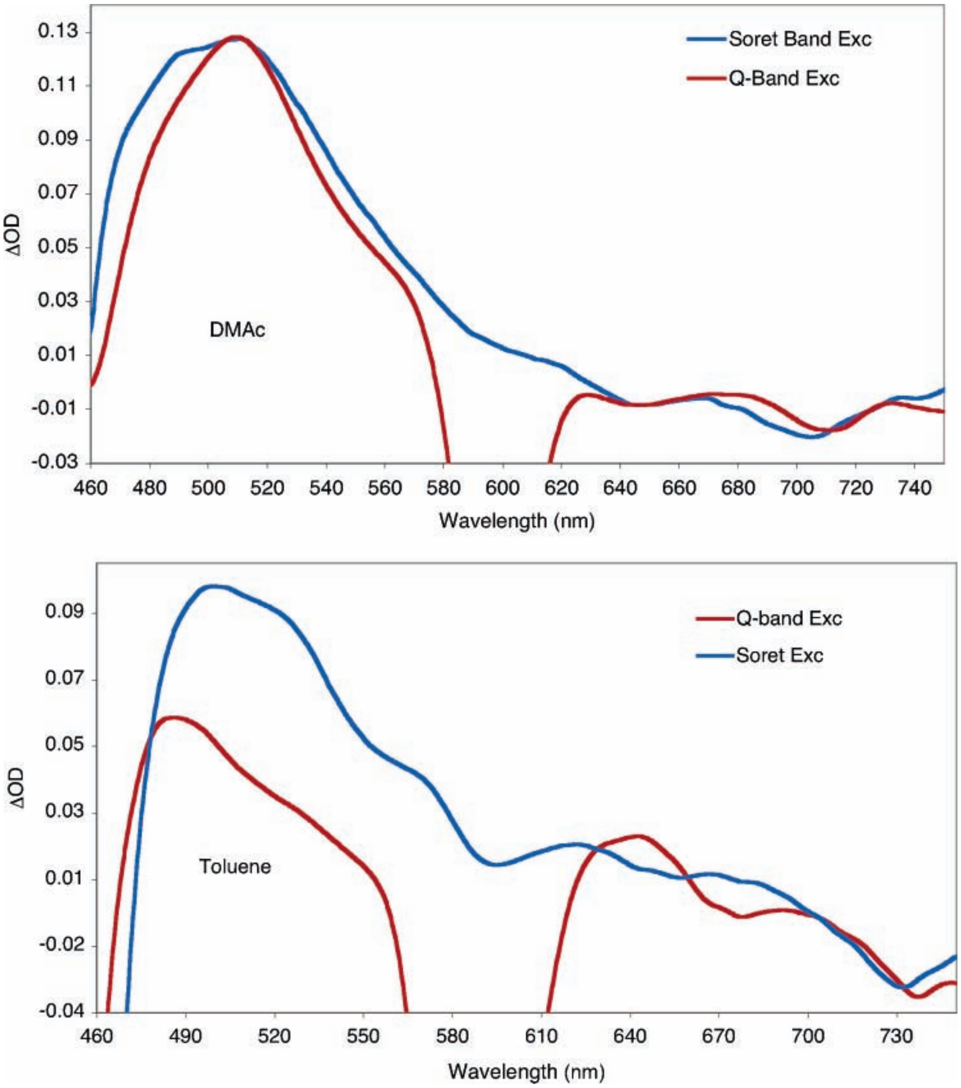

Figure 3. Transient absorption spectra of **1** in DMAc (top) and toluene (bottom) taken 1 ps after the laser pulse. Excitation was into either the Soret (blue spectra, 442 nm in DMAc and 437 nm in toluene) or Q-band (blue spectra, 596 nm in DMAc and 585 nm in toluene).

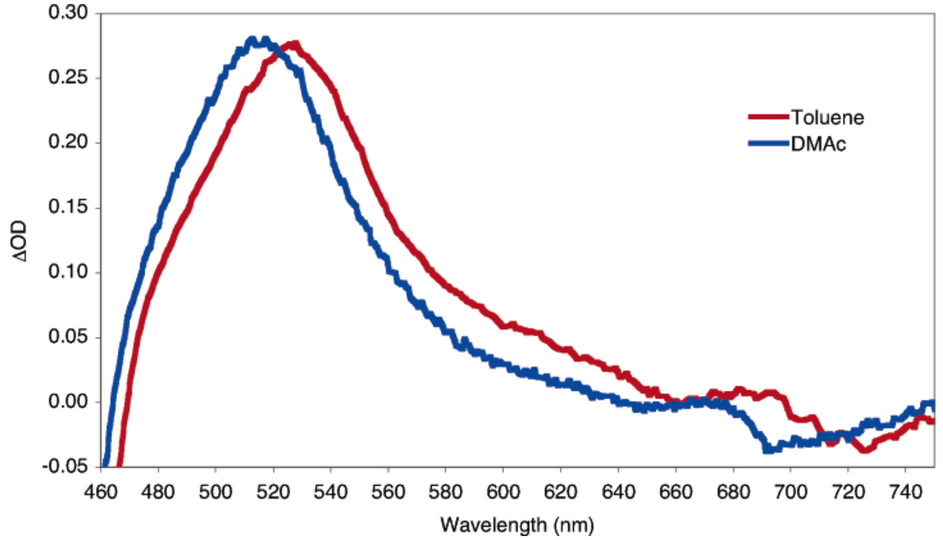

Figure 4. An overlay of the transient absorption spectra of **1-Me** in DMAc (blue) and toluene (red) taken 1 ps after the laser pulse using Soret band excitation (446 nm in DMAc and toluene).

allowed.[18,22] The result of this change is an increase in both the oscillator strength and a red-shift in the $Q_y(0,0)$ band.

For tautomer **1e**, both the unoccupied b_2 and a_2 and the occupied b_2 and b_2 orbitals[29] are nondegenerate. As a result, the absorption spectrum of **1e** becomes atypical of free-base porphyrins and exhibits Q-band absorptions that increase in intensity with decreasing energy. These transitions are weakly allowed because of the substantial break in degeneracy of the

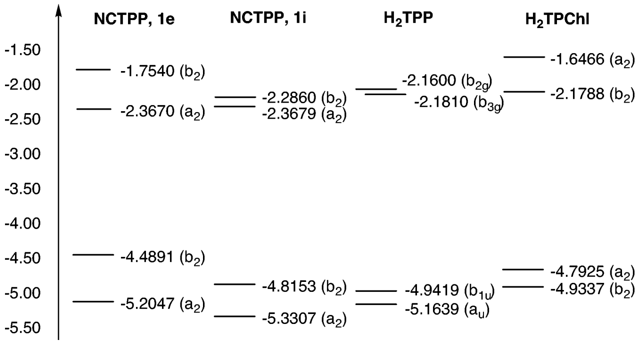

Figure 5. Orbital energies of NCTPPs **1e** and **1i**, as well as H$_2$TPP and H$_2$TPChl calculated at the B3LYP/6−31 g*//B3LYP/3-21 g level.[22]

TABLE 3: Transient Absorption Data for N-Confused Tetraphenylporphyrin Tautomers 1e and 1i and H$_2$TPP

		$^1(\pi,\pi^*)$	
compound	solvent	λ_{max} (nm)	ϵ (M^{-1}cm^{-1})
1i	toluene	488	—[a]
		643	—[a]
1e	DMAc	510	1.5×10^5
		620	6.9×10^3
H$_2$TPP	toluene	440	3.1×10^4

[a] Could not be determined because of the overlap between the Q$_y$(1,0) band of **1i** at 580 nm and a weak absorption feature in the same region in the transient absorption spectrum.

LUMO and LUMO+1 orbitals, which are split to higher and lower energy than those of H$_2$TPP, and the rather large increase in energy of the occupied b$_2$ orbital. These changes in orbital energy partly account for the red-shifted Soret and the Q-band absorptions observed in **1e**, as well as the increased oscillator strengths in the Q-band transitions. In tautomer **1i**, the b$_2$ and a$_2$ unoccupied orbitals are also nondegenerate and are lower in energy than the equivalent orbitals in either H$_2$TPP or H$_2$TPChl. The energy difference between the occupied b$_2$ and a$_2$ orbitals in **1i** is also much larger than is found for H$_2$TPP (a$_{2u}$ and a$_{1u}$) or H$_2$TPChl (a$_2$ and b$_2$). The changes in orbital energies in **1i** are the opposite of what is observed in H$_2$TPChl, for which the unoccupied a$_2$ and b$_2$ orbitals are substantially different energetically but the occupied a$_2$ and b$_2$ orbitals are more closely spaced together. The net result of the orbital changes is likely to be the same for both **1i** and H$_2$TPChl, however, and the Q$_y$(0,0) transition in **1i** is thus weakly allowed and has a relatively large extinction coefficient (at 724 nm) and a moderately intense Q$_y$(1,0) band (580 nm). With this information in hand, the $^1(\pi,\pi^*)$ excited-state spectra of **1i** and **1e**, as well as those of **1-Me**, can be discussed.

The transient absorption spectra of **1e** and **1i** acquired in toluene and DMAc (Figure 3), respectively, can first be compared as a function of excitation wavelength. The main absorption band at 488 nm in toluene is red-shifted 22 nm to 510 nm in DMAc, whereas the moderately intense band in toluene at 643 nm is blue-shifted in **1e** to ~620 nm and is much less intense.[30] The excited-state extinction coefficients for the spectrum in DMAc were calculated[11] in DMAc (Table 3) using the bleach of the Q$_x$(1,0) absorption band as a reference.[31] The 510 nm absorption in DMAc has $\epsilon \approx 1.5 \times 10^5$ M^{-1}cm^{-1} and the 620 nm band has $\epsilon \approx 6.9 \times 10^3$ M^{-1}cm^{-1}. The analogous values in toluene could not be calculated because the Q$_x$(0,0) band is obscured by one of the S$_1$ → S$_n$ transitions and the Q$_y$(1,0) band at 665 nm is too weak to observe as a negative feature. Holten et al.[11] have reported $\epsilon \approx 3.1 \times 10^4$ M^{-1}cm^{-1} for the main feature in the transient absorption spectrum of H$_2$TPP that is ca. a factor of 5 less intense than we report for **1e**. Holten has suggested[11] the absorption spectrum of the $^1(\pi,\pi^*)$ state of a regular porphyrin such as H$_2$TPP is probably best represented as a doubly excited $[a_u(\pi),b_{1u}(\pi)] \rightarrow [b_{2g}(\pi^*),b_{3g}(\pi^*)]$ configuration and not the configuration resulting from promotion of the already-excited electron that would result in the $[a_u(\pi),b_{1u}(\pi)] \rightarrow [a_u(\pi^*)]$ configuration. As noted previously,the ground-state electronic structures of **1e** and **1i** are different from that of H$_2$TPP, and given the nondegeneracy of the unoccupied a$_2$ and b$_2$ orbitals, it is therefore possible that the $[a_2(\pi),b_2(\pi)] \rightarrow [a_2(\pi^*),b_2(\pi^*)]$ configuration is not the only transition observed in the S$_1$ → S$_n$ transient spectra of **1e** and **1i**. Indeed, the appropriate transition for **1e** in particular, for which the a$_2$ and b$_2$ unoccupied orbitals are substantially different in energy, may well be $[a_2(\pi),b_2(\pi)] \rightarrow [a_2(\pi^*)]$ in nature. In all likelihood, the rich transient absorption spectra observed for **1e** and **1i** are a composite of two different transitions, each having different polarity. Such a scenario would explain the blue-shift of the low-energy absorption and the red-shift in the higher-energy absorption in DMAc, where the a$_2$ and b$_2$ unoccupied orbitals are more closely spaced together than in **1i**. This interpretation would explain the larger value of ϵ (i.e., more highly allowed S$_1$ → S$_n$ transitions) in **1e** compared to H$_2$TPP. Time-dependent density functional theory (TD-DFT) calculations are clearly necessary to evaluate these factors more fully, but these qualitative arguments provide a basis for interpretation of the observed spectra.

To fully probe the dynamics of the S$_1$ excited state, time-resolved absorption measurements were acquired with both Soret and Q-band excitation at several different probe wavelengths, in both DMAc and toluene (Table 4). Rise times for these spectra were universally laser pulse limited (<200 fs) and could not be resolved. In DMAc, excitation into the Q$_x$(1,0) band at 596 nm yielded decays in the spectral range 470−705 nm that were uniformly monoexponential. The average lifetime of the decays in the range of 470−560 nm was 1.71 ± 0.09 ns and varied little (<5%) over the observed spectral range. The recovery of the Q$_y$(0,0) bleach/stimulated emission with Q-band excitation was found to have a time constant of 1.92 (± 0.10) ns, longer lived than the absorption decays but nonetheless consistent with the TCSPC data (1.84 ns). Time-resolved decays for Soret band excitation produced similar results, where the decays were also fit to a single-exponential function. In the spectral range from 480 to 560 nm, the average excited-state lifetime was found to vary <5%, with a lifetime of ~1.62 ± 0.04 ns. Holten et al.[11] have previously indicated that time-resolved fluorescence is a more accurate indication of excited-state lifetimes and that the recovery of the Q$_y$(0,0) bleach/stimulated emission is a more accurate indicator of the porphyrin S$_1$ lifetime than the main transient absorption bands.

In toluene, excitation into both Soret and Q-bands resulted in monoexponential decays at all probe wavelengths examined. Excitation into the Q$_x$(1,0) band at 540 nm yielded decays in the spectral range of 480−525 nm region with an average lifetime of 1.40 ± 0.05 ns, whereas Soret band excitation produced slightly longer-lived decays of 1.45 ± 0.04 ns. The recovery of the Q$_y$(0,0) bleach/stimulated emission at 734 nm was obtained with both Q-band and Soret band excitation and was found to be 1.49 ± 0.11 ns (Q-band excitation) and 1.58 ± 0.12 ns (Soret band excitation). The data are consistent, within experimental error, with the lifetime determined by TCSPC measurements (1.47 ns).

N-Methyl N-confused tetraphenylporphyrin **1-Me** was also investigated in both DMAc and toluene, albeit with detection

TABLE 4: Time-Resolved Absorption Data for N-Confused Tetraphenylporphyrin Tautomers 1e and 1i

compound	solvent	$\tau_{\text{abs,Soret}}$ (ns)[a]	$\tau_{\text{abs,Q-band}}$ (ns)[b]	$\tau_{\text{bleach,Soret}}$ (ns)[c]	$\tau_{\text{bleach,Q-band}}$ (ns)[d]
1e	DMAc	1.62 ± 0.04	1.71 ± 0.09	1.95 ± 0.34	1.92 ± 0.10
1i	toluene	1.45 ± 0.04	1.40 ± 0.05	1.58 ± 0.12	1.49 ± 0.11

[a] Indicates the main transient absorption band was monitored upon Soret band excitation. [b] Indicates the main transient absorption band was monitored upon Q-band excitation. [c] Indicates the $Q_y(0,0)$ bleach was monitored upon Soret band excitation. [d] Indicates the $Q_y(0,0)$ bleach was monitored upon Q-band excitation.

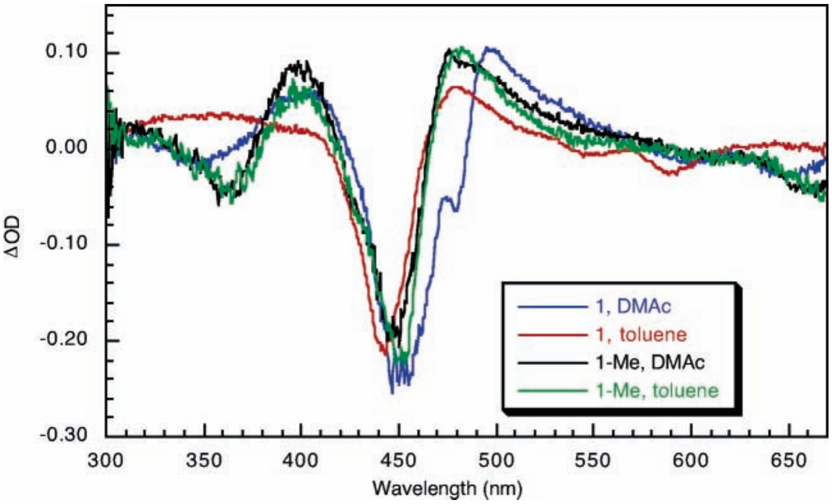

Figure 6. Transient absorption spectra of **1e** (DMAc, blue), **1i** (toluene, red), and **1-Me** in DMAc (black) and toluene (green) taken 500 ns after the laser pulse using $Q_y(0,0)$ band excitation (570 nm).

TABLE 5: Nanosecond Time-Resolved Transient Absorption Data for N-Confused Tetraphenylporphyrin Tautomers 1e, 1i, and *N*-Methyl N-Confused Porphyrin 1-Me in DMAc and Toluene

compound	solvent	λ_{pump} (nm)	λ_{probe} (nm)	τ_1 (μs)	τ_2 (μs)
1i	toluene	570	480	14 (75%)	45 (25%)
1e	DMAc	570	495	6.1 (89%)	27 (11%)
1-Me	toluene	570	480	2.0 (100%)	
1-Me	DMAc	570	480	3.1 (100%)	

solely at 510 nm, near the absorption maximum. In DMAc, excitation into either the Soret or Q-band gave similar results, with lifetimes of 1.52 ± 0.04 and 1.42 ± 0.02 ns, respectively. Similarly, in toluene a lifetime of 1.06 ± 0.01 ns was observed with either Soret or Q-band excitation. This value is, within experimental error, the same as that obtained using TCSPC (1.15 ns).

Nanosecond Time-Resolved Experiments. The triplet states of **1** and **1-Me** were studied in both polar (DMAc) and nonpolar (toluene) solvents using nanosecond transient absorption spectroscopy. Transient absorption spectra (Figure 6) were acquired by pumping the $Q_y(1,0)$ band of **1e** and the $Q_x(1,0)$ band of **1i** at 570 nm. The spectra of both compounds under both sets of solvent conditions are qualitatively the same, with each dominated by the Soret band bleach at ~445−450 nm and a pair of absorption bands at ~400 and 480 nm that are probably one single broad band, superimposed upon the Soret band bleach. The spectra of tautomer **1e**, as well as those of **1-Me** in both solvents, are largely featureless outside of this broad absorption band, and in fact, the spectra of **1-Me** are nearly superimposable on one another in both solvents. The triplet absorption spectrum of **1i** has an additional small absorption band centered at ~570 nm. The lifetimes obtained for both tautomers of **1** are biexponential, whereas the lifetimes of **1-Me** in both solvents are monoexponential and are significantly shorter lived (Table 5). The presence of a biexponential lifetime for **1e** and **1i** may be indicative of excited-state tautomerization; we intend to further explore this possible process in future work.

Conclusions

The spectroscopy of the S_1 and T_1 excited states of N-confused porphyrins **1** and **1-Me** in polar DMAc and nonpolar benzene and toluene were examined using a combination of steady-state and time-resolved optical spectroscopy. The excited-state S_1 lifetime of **1** in nonpolar solvents was found to be lower than that of **1** in polar solvents by ~369 ps. The excited-state S_1 lifetime of **1-Me** was found to vary substantially with solvent as well, with the lifetime in the nonpolar solvent ~290 ps longer lived. A comparison between **1** and **1-Me** indicates the methyl group increases the rate of nonradiative decay by ~317 ps in nonpolar and ~396 ps in polar solvents.

Several similarities and differences are evident when comparing the excited-state properties of **1e** and **1i** with regular porphyrins such as ZnTPP and H_2TPP. The S_1 lifetimes and fluorescence quantum yields **1e** and **1i** are comparable to those of ZnTPP, whereas their S_1 energies are significantly lower. The absorption features of the **1e**/**1i** S_1 states are slightly different from those of regular porphyrins and indicate they can be distinguished spectroscopically upon incorporation into multichromophore arrays. The most exciting aspect of these compounds, however, may be their steady-state absorption properties, which are different for each tautomer and from regular porphyrins. The fact that the tautomer, and therefore the absorption spectrum, can be switched as a function of solvent polarity is quite interesting and suggests these compounds might have other tautomer-dependent properties that might be exploited, both by themselves and as part of arrays.

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