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Synthesis and Spectroscopy of a Series of Substituted N-Confused Tetraphenylporphyrins

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A series of N-confused tetraphenylporphyrins (H_2NCTPPs) with substituents on either the para- or the 3,5-positions of the *meso* phenyl rings were prepared using Lindsey conditions. Both electron-withdrawing and electron-donating groups were chosen in order to probe the effects of peripheral substitution on the properties of the macrocycles. The series includes 5,10,15,20-tetra-(4-R-phenyl) N-confused porphyrins (where R = bromo (**1**), iodo (**2**), cyano (**3**), methoxy (**4**), 2′,5′-dimethoxyphenyl (**5**), or ethynyl (**6**)) and 5,10,15,20-(3,5-di-*tert*-butylphenyl) N-confused porphyrin (**7**). Absorption and steady-state fluorescence measurements were carried out, and quantum yields were measured for all compounds in both dichloromethane (CH_2Cl_2) and dimethylacetamide (DMAc).

Introduction

Porphyrinic macrocycles are found in a variety of natural systems, including the light harvesting complexes[1–3] and photosynthetic reaction centers in green plants, where they assist in light harvesting and initiate the charge separation process, and heme-based metalloenzymes such as hemoglobin and myoglobin, where they bind and transport oxygen for metabolic needs.[4] Free-base and metalloporphyrin derivatives have been extensively studied in order to understand and reproduce these natural processes outside of the protein environment.[5]

The effects of substitution at the macrocycle periphery on the photophysical properties of porphyrins have also been thoroughly investigated. Deviations from planarity caused by bulky substituents,[6] changes in electronic interactions due to the donor/acceptor properties of the substrate, and the position of the substituent have all been shown to affect properties such as redox potentials,[7] absorption spectra[8] and fluorescence quantum yields.[9] Investigating the fundamental chemistry and photophysical processes of porphyrinic macrocycles, therefore, continues to be crucial to understanding their role in biological systems.

Unlike normal porphyrins, the chemistry of porphyrin isomers such as N-confused tetraphenylporphyrins (H_2NCTPPs) (also called 2-aza-21-carba-5,10,15,20-tetraarylporphyrin and inverted tetraphenylporphyrin) has yet to be fully explored. H_2NCTPP differs structurally from tetraphenylporphyrin (H_2TPP) by inversion of one pyrrole ring, resulting in three nitrogens and one carbon at the macrocycle core, and the inverted nitrogen at a β-position at the periphery of the macrocycle. N-Confused porphyrins can exist as two tautomers in solution depending on the polarity of the solvent. In polar solvents such as DMF or dimethylacetamide (DMAc), the externally protonated tautomer is more stable, presumably due to hydrogen bonding or dipole−dipole interactions between the external N−H bond and the solvent. However, in nonpolar solvents such as chloroform or CH_2Cl_2, the internally protonated tautomer is more stable. Figure 1 shows both N-confused porphyrin tautomers in comparison to porphyrin.

The structural changes in the macrocycle leads to a decrease in symmetry and a reduction in aromaticity as

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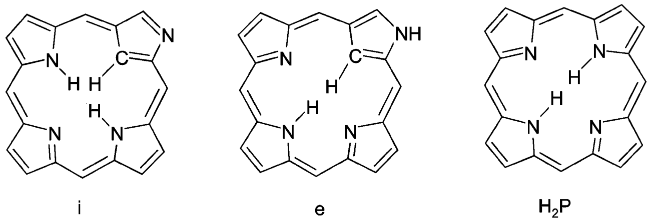

FIGURE 1. Structures **i** and **e** are the internally (nonpolar solvents) and externally (polar solvents) protonated tautomers of N-confused porphyrin; freebase porphyrin (H_2P, right) is shown for comparison.

compared to H_2TPP,[10] as well as photophysical properties that compare favorably to chlorins[11,12] and porphyrins.[13] Both tautomeric forms have absorption spectra that are different from that of tetraphenylporphyrin (H_2TPP) and are characterized by red-shifted Soret and Q-bands.[14,15] The red-shifted absorption maxima are attributed to a break in the degeneracy of the e_g orbitals that results from a decrease in symmetry within the macrocycle.[15] The excited state properties of each tautomer are different from one another, with the internally protonated tautomer exhibiting a lower excited state energy and fluorescence quantum yield than the externally protonated tautomer.[15,16] The fluorescence lifetimes of both tautomers are comparable.[15] These properties indicate that N-confused porphyrins are viable alternatives to porphyrins and the difficult to prepare chlorins[17,18] in artificial light-harvesting systems and photonic arrays.[19−21]

In this paper, we report the synthesis of a series of seven $H_2NCTPPs$, where both electron-donating and electron-withdrawing groups have been substituted at the para-position or 3,5-positions of the *meso* phenyl rings (Figure 2). The role of the substituent on purification and final synthetic yield will be discussed. We have also probed the effects of the substituent in both tautomers of the macrocycle on properties such as absorption and fluorescence and compared the results to unsubstituted H_2NCTPP.

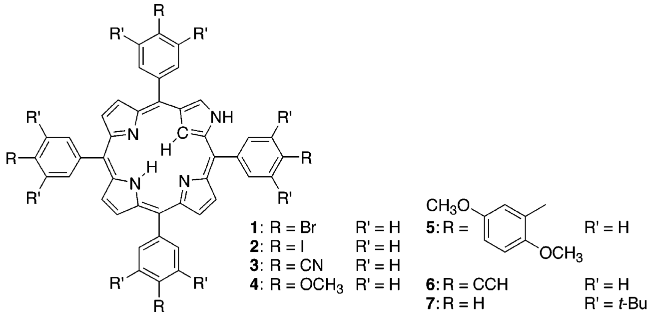

FIGURE 2. Structures of the N-confused porphyrins examined in this paper. Only the externally protonated form of each tautomer is shown.

Results and Discussion

Synthesis. While the synthesis of H_2NCTPP is known to be acid catalyzed,[22] the mechanism of the reaction has yet to be fully elucidated. Possible mechanisms in the literature include anion templating[23] and the presence of multiple orientations of tetrapyrromethane linkages that allow for ring closure by electrophilic attack at either the α- or β-pyrrole positions.[24] Typical yields (isolated) for the synthesis of unsubstituted H_2NCTPP using Lindsey conditions[25] are around 35%. For the seven compounds synthesized here, isolated yields ranged from 6.7% (**3**) to 26% (**5**), with the average yield being around

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TABLE 1. Summary of the Synthetic Data for N-Confused Porphyrins 1−7 and H_2NCTPP, Including % Yield of N-Confused Porphyrin and % Yield of Regular Porphyrin

N-confused porphyrin	% isolated yield	% yield of N-confused porphyrin	% yield of regular porphyrin
1	13	15	11
2	8	11	8.0
3	6.7	12	6.9
4	13	15	1.5
5	26	30	4.8
6	9.2	12	10
7	10	28	3.2
H_2NCTPP	35[a]	40[a]	<10[a]

[a] Taken from ref 25.

10% (Table 1). No obvious trends between yield (crude or isolated) and electronic structure are found, although it is tempting to cite the bulk of the para substituent as a factor in the N-confused porphyrin yield. For example, N-confused porphyrins **5** and **7**, which have 2,5-dimethoxybenzene and 3,5-di-*tert*-butyl substituents respectively, have larger crude yields by a factor of 2−3 than **1**−**4** and **6**. These yields are nonetheless lower than those observed for H_2NCTPP,[25] and it is difficult from the synthetic data presented here to provide a definitive comment on the structure−yield relationship.

Absorption Spectroscopy. The absorption spectra of H_2NCTPP are tautomer-dependent.[14,15] In DMAc, H_2NCTPP(e) is observed to have a Soret band red-shifted to 442 nm from that of H_2TPP (417 nm). The Q-bands are also observed to be red-shifted, with the $Q_x(0,0)$ band at 699 nm. Similarly, the Soret band for H_2NCTPP(i) in $CHCl_3$ absorbs at 438 nm and the low-energy $Q_x(0,0)$ band is at 724 nm. Because the MOs for H_2NCTPP are slightly distorted from the normal Goutermann four-electron four-orbital model by the decrease in symmetry in the macrocycle,[15] we anticipated observing absorption bands in **1**−**7** that were shifted further still from both H_2TPP and H_2NCTPP.

In general, the Soret band absorptions for the substituted H_2NCTPPs prepared here are red-shifted from those of H_2NCTPP by 3−7 nm in CH_2Cl_2 and 3−6 nm in DMAc (Table 2). Similarly, the Q-band absorptions (Figure 3) are red-shifted to varying degrees, with the amount depending upon both the substitution and Q-band transition. Interestingly, the magnitude and range of red-shifts in the Q-band region varies significantly more in CH_2Cl_2 than in DMAc, consistent with the out of plane distortion of the inverted pyrrole ring having an important impact on the interaction of the substituent with the ring. Minor deviations from H_2NCTPP are also observed for the extinction coefficient values, although most differences are on the order of a factor of 2.

Notable exceptions include compound **3** where the presence of the cyano group results in a bathochromic shift of 18 nm of the Soret band in DMAc (460 nm) from that of H_2NCTPP (442 nm), whereas in CH_2Cl_2 the band is only shifted to 444 nm (438 nm for H_2NCTPP). Similarly, the Soret band of **5** is significantly shifted in DMAc (459 nm) but only 445 nm in CH_2Cl_2. In addition, the extinction coefficients of the Soret and Q-bands for **5** and **6** are also unusually large compared to H_2NCTPP. In CH_2Cl_2, **5** has a Soret band extinction coefficient of 3.60×10^5 and a $Q_x(0,0)$ coefficient of 3.31×10^4, and **6** has a Soret band extinction coefficient of 2.81×10^5 and a $Q_x(0,0)$ coefficient of 2.40×10^4, all significantly higher than those observed for H_2NCTPP.

Fluorescence Spectroscopy. The fluorescence spectra[15] of N-confused porphyrins H_2NCTPP(i) and H_2NCTPP(e) are characterized by emission bands red-shifted from those of H_2TPP (Figure 4). The fluorescence quantum yield (Φ_{Fl}) and fluorescence lifetime (τ_{Fl}) also differ from each other and from H_2TPP, with the quantum yield for H_2NCTPP(e) greater than that of H_2NCTPP(i) by a factor of 2 ($\Phi_{Fl} = 0.0460$ vs $\Phi_{Fl} = 0.0227$, respectively),[16] and a slightly longer-lived fluorescence lifetime (i.e., 1.98 vs 1.60 ns,[15] respectively). These minor differences have been attributed[15] to a more rapid rate of internal conversion or intersystem crossing in H_2NCTPP(i) that results from the presence of the extra hydrogen atom in the interior of the A ring in the macrocycle that leads to a nonplanar geometry and favorable steric conditions for deformation.

TABLE 2. Summary of Absorption Data Obtained for Compounds 1−7, H_2NCTPP, and H_2TPP

compound	solvent	Soret (nm) ($\epsilon \times 10^5$ M^{-1} cm^{-1})	Q-bands (nm) ($\epsilon \times 10^4$ M^{-1} cm^{-1})			
1i	CH_2Cl_2	441 (1.21)	542 (0.971)	584 (1.35)	668 (0.0516)	728 (1.12)
1e	DMAc	447 (1.33)	552 (0.302)	597 (0.659)	646 (1.06)	699 (1.36)
2i	CH_2Cl_2	442 (1.16)	543 (1.08)	586 (1.23)	667 (0.265)	729 (0.804)
2e	DMAc	447 (1.06)	553 (0.295)	596 (0.536)	646 (0.978)	701 (1.24)
3i	CH_2Cl_2	444 (1.00)	543 (1.00)	587 (1.25)	658 (0.183)	726 (0.993)
3e	DMAc	460 (0.807)	550 (0.0800)	599 (0.267)	646 (0.387)	699 (0.600)
4i	CH_2Cl_2	441 (1.52)	548 (0.819)	592 (1.53)	682 (0.0504)	736 (1.29)
4e	DMAc	445 (1.08)	550 (0.214)	599 (0.548)	651 (0.774)	709 (1.01)
5i	CH_2Cl_2	445 (3.60)	546 (1.54)	591 (3.92)	677 (0.512)	732 (3.31)
5e	DMAc	459 (1.92)	556 (0.467)	601 (0.928)	651 (1.30)	706 (1.57)
6i	CH_2Cl_2	444 (2.81)	546 (1.41)	589 (2.89)	675 (0.455)	731 (2.40)
6e	DMAc	448 (1.33)	554 (0.338)	601 (0.660)	650 (1.09)	705 (1.41)
7i	CH_2Cl_2	441 (2.13)	543 (0.976)	585 (1.53)	672 (0.270)	728(1.34)
7e	DMAc	445 (0.832)	547 (0.302)	599 (0.632)	650 (1.04)	704 (1.36)
H_2NCTPP	$CHCl_3$[a]	438 (1.59)	539 (0.78)	580 (1.08)	665 (0.27)	724 (1.04)
H_2NCTPP	DMAc[a]	442 (1.19)	550 (0.2)	595 (0.61)	644 (0.95)	699 (1.24)
H_2TPP	$CHCl_3$[b]	419 (4.11)	515 (1.73)	550 (0.81)	590 (0.64)	645 (0.62)
H_2TPP	DMAc[c]	417 (4.85)	513 (2.08)	548 (0.967)	591 (0.669)	646 (0.605)

[a] Taken from ref 15. [b] Taken from: Dudic, M.; Lhoták, P.; Král, V.; Long, K.: Stibor, I. *Tetrahedron Lett.* **1999**, 40, 5949−5952. [c] Taken from: Datta-Gupta, N.; Malakar, D.; Rice, L.; Rivers, S. *J. Heterocycl. Chem.* **1987**, *24*, 629−632.

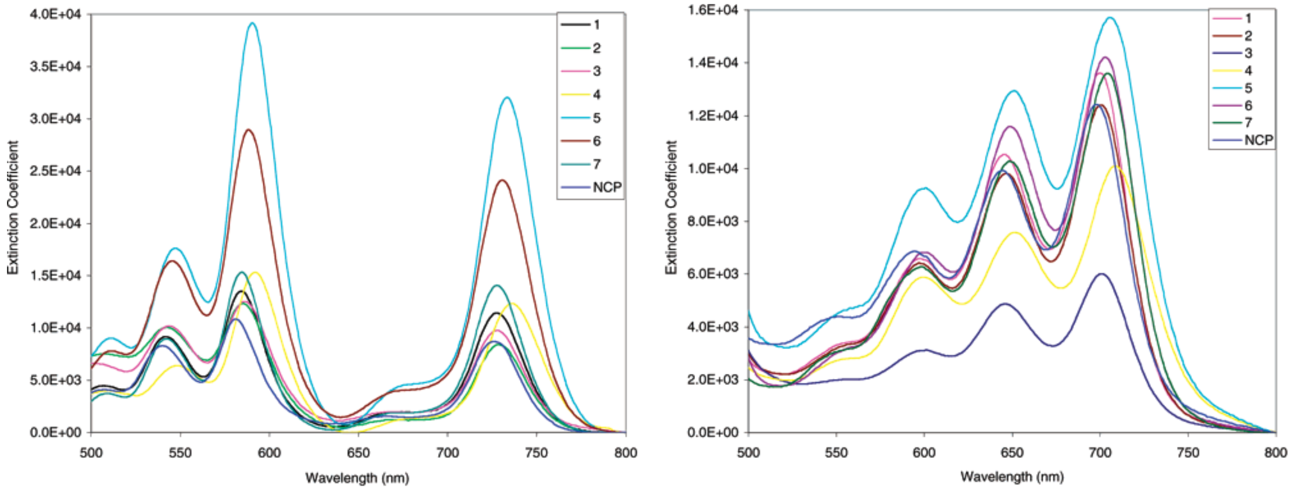

FIGURE 3. Expanded Q-band region in the absorption spectra of **1**−**7** and H_2NCTPP in CH_2Cl_2 (left) and DMAc (right).

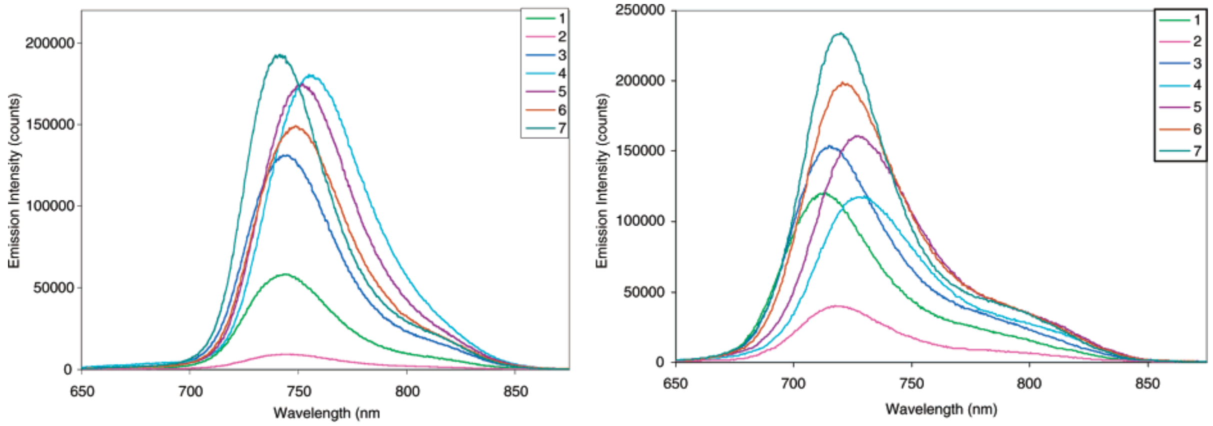

FIGURE 4. Fluorescence spectra of **1**−**7** in CH_2Cl_2 (left) and DMAc (right).

The steady-state fluorescence spectra of **1**−**7** have significantly red-shifted emission bands relative to those of both H_2TPP and H_2NCTPP, consistent with the red-shifted Soret and Q-bands observed in the absorption spectra (Figure 4, Table 3). The fluorescence spectra of **1**−**7** are dominated by large $Q_x(0,0)$ emission bands at ∼741−756 nm (in CH_2Cl_2) and ∼715−728 nm (in DMAc) and low-energy $Q_x(0,1)$ shoulders at ∼809−827 nm (CH_2Cl_2) and ∼777−789 nm (DMAc). The ratios of the areas of the $Q_x(0,0)$ and $Q_x(0,1)$ emission bands are significantly larger than those of H_2TPP and are similar to the ratios for the H_2NCTPP $Q_x(0,0)$ and $Q_x(1,0)$ absorption bands, a result that has been attributed to changes in the ground state ↔ Q-state excited-state transitions.[15]

Differences between the two tautomers are also observed in the fluorescence quantum yield data obtained for H_2NCTPPs **1**−**7**, with the Φ_{Fl} values smaller for tautomers **1i**−**7i**. The presence of the extra hydrogen atom at the macrocycle core of these tautomers leads to distortion of the inverted pyrrole ring out of the plane of the porphyrin macrocycle. Such a distortion provides a mechanism for enhanced nonradiative decay by either internal conversion or intersystem crossing.[15] This effect appears most pronounced for the halogen-containing compounds **1** and **2**, where intersystem crossing is further enhanced by the heavy atom effect resulting in a significant decrease in Φ_{Fl} for these H_2NCTPPs in CH_2Cl_2 relative to the Φ_{Fl} values in DMAc.

TABLE 3. Summary of Fluorescence Data for N-Confused Porphyrins 1−7, H_2NCTPP, and Tetraphenylporphyrins H_2TPP

compound	solvent	fluorescence maxima (nm)[a]	Φ_{FL}[b]	Stokes shift (cm^{-1})
H_2NCTPPi[c]	CH_2Cl_2	744, 815	0.023	371
H_2NCTPPe[c]	DMAc	713, 783	0.046	281
1i[c]	CH_2Cl_2	744, 818	0.0050	295
1e[c]	DMAc	713, 795	0.020	281
2i	CH_2Cl_2	747, 809	0.0010	331
2e	DMAc	718, 784	0.0073	337
3i	CH_2Cl_2	744, 823	0.020	333
3e	DMAc	717, 777	0.035	400
4i	CH_2Cl_2	754, 827	0.026	324
4e	DMAc	730, 789	0.031	406
5i	CH_2Cl_2	751, 825	0.026	346
5e	DMAc	726, 789	0.042	410
6i	CH_2Cl_2	749, 822	0.023	329
6e	DMAc	722, 788	0.049	334
7i	CH_2Cl_2	745, 823	0.033	313
7e	DMAc	720, 783	0.065	316
H_2TPP	CH_2Cl_2	649, 713	0.11	143
H_2TPP	DMAc	649, 714	0.15	95

[a] Excited at the Soret bands to avoid aggregation due to concentration effects. [b] Relative to the fluorescence of H_2TPP. Quantum yields were calculated using standard methods. [c] Taken from ref 16.

Substituent effects on the fluorescence quantum yield values of the para-substituted compounds **3**−**6** are not pronounced except for the aforementioned bromo- and iodo-containing H_2NCTPPs. In general, the Φ_{Fl} values for these compounds in CH_2Cl_2 range from approximately 0.020−0.025 and increase to 0.031−0.049 in DMAc. For the 3,5-di-*tert*-butyl-substituted H_2NCTPP **7**, the Φ_{Fl} values in both solvents are ~50% larger than the para-substituted compounds, indicative of the decrease in torsional motion about the *meso*-phenyl C−C bond brought about by the sterically demanding *tert*-butyl groups that decreases nonradiative decay.

Substituent effects on the photophysical properties of regular porphyrins are well-known.[13] The data presented here demonstrate that the photophysical properties of N-confused porphyrins are not only dependent upon substituent but also highly sensitive to the particular tautomer in solution. This unique solvent dependence makes them potentially very useful for incorporation into devices and arrays, where changing the tautomer can result in a significant change in the absorption energy and/or oscillator strength, and in the case of fluorescence, the fluorescence quantum yield.

Conclusion

A series of N-confused tetraphenylporphyrins (**1**−**7**) containing electron-withdrawing or electron-donating substituents on the *meso* phenyl rings were prepared in order to study substituent effects on synthetic yield and steady-state optical properties (absorption and fluorescence). Absorption spectra showed Soret and Q-bands for **1**−**7** that were red-shifted from those of H_2NCTPP in both CH_2Cl_2 and DMAc. The magnitude of these red-shifts in the Q-band region varied more in CH_2Cl_2, probably as a result of the distortion from planarity in the macrocycle that results from the inverted pyrrole ring. The fluorescence spectra also revealed red-shifted bands. The fluorescence quantum yields were found to be smaller for **1**−**7** in CH_2Cl_2 as a result of the ring distortion caused by the extra hydrogen atom in the macrocycle core that leads to enhanced rates of nonradiative decay.

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Supporting Information Available: Experimental procedures and spectroscopic details for the characterization (^{1}H, ^{13}C and TOF-MS data) of N-confused tetraphenylporphyrins **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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