Sequential Protonation of *meso*-(*p*-(Dimethylamino)phenyl)porphyrins: Charge-Transfer Excited States Producing Hyperporphyrins†

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Successive protonation by trifluoroacetic acid of *meso*-tetraphenylporphyrin derivatives bearing one, two, or four *p*-dimethylamino groups gives rise to new types of spectra. With one free amino group, the spectrum of the centrally protonated porphyrin shows a strong far-red band, a broad, flat absorption in the visible, and a less intense Soret band. With two or more free amino groups, the Soret band of the centrally protonated porphyrin is further split into two components. Complete protonation, including the peripheral amino groups, in all cases restores the spectral structure of the unsubstituted tetraphenylporphyrin dication. The spectra of the dianions of tetraanilino- and tetraphenylporphyrins are also similar. These results, and the related behavior of *p*-oxyphenylporphyrins and protonated Schiff base porphyrins, lead to a general interpretation of hyperporphyrin spectra in terms of charge-transfer excited states, involving charge movement either into or out of the porphyrin ring.

The ground-state and excited-state properties of porphyrins are influenced by peripheral or central substitutions which result in charge movement into or out of the macrocycle. Even in noncoplanar systems, such as tetraphenylporphyrins or their cations, substitution on the phenyl rings leads to well-defined effects on spectra and basicity which have been interpreted in terms of resonative interactions with the porphyrin ring.[1,2] Of particular interest is the marked broadening of the Soret band and the decrease of its peak extinction coefficient observed in ortho or para-amino-substituted *meso*-phenylporphyrins.[3,4] This has been attributed "to a charge-transfer interaction of the amine lone pair of electrons with the second excited state of the porphyrin, the transition to which is strongly allowed."[3] In agreement with this, stabilizing these lone pairs by acetylation or protonation of the amines restores the "normal" Soret structure.[3]

Much more striking effects are found in porphyrins for which quinonoid resonance structures involving such charge transfer can be written, such as *meso*-tetrakis(*p*-hydroxyphenyl)porphyrin in basic solution[5-7] or the dication of *meso*-tetrakis((*N*,*N*-dialkylamino)phenyl)porphyrin,[8] in which one postulates negative charge movement from the peripheral substituents toward the macrocycle (see below). In these cases, one finds again broadened or even "split" Soret bands and strongly enhanced and red-shifted absorption in the visible.[5-8] Such spectra are characteristic of the extensive class of "hyperporphyrins,"[9] as has been noted also in the case of metal-complexed *meso*-(*p*-hydroxyphenyl)porphyrins.[10,11]

To extend these observations and to clarify the nature of these changes, we have carried out systematic, sequential spectrophotometric titrations of mono-, di-, and tetra-*p*-dimethylamino-substituted *meso*-tetraphenylporphyrins. For the latter case, we cover the full range of eight proton additions, from the dianion to the completely protonated system. Closely related ^{1}H NMR data, taken at spectrophotometrically identified stages of protonation and which bear on the interpretations, are reported in the following paper.[12] These results and related studies help define in more general terms the molecular origins of hyperporphyrin spectra. We conclude that charge-transfer excited states, involving charge movement either into or out of the macrocycle, are responsible for the features of these spectra.

Experimental Section

Materials. Trifluoroacetic acid (TFA) and methylene chloride (reagent grade, Aldrich) were used as received. Porphyrins were prepared following established methods[13,14] as follows. Abbreviations: We use the notation $(DMA)_mPH_n^{(n-2)+}$, where m is the number of para-amino-substituted phenyls and n is the total number of protons added, centrally and peripherally, counting from the deprotonated porphyrin dianion, P^{2-}. The remaining $(4 - m)$ unsubstituted phenyls are understood to be present. Thus, PH_2 or $(DMA)_0PH_2$ is tetraphenylporphyrin itself.

meso-Tetraphenylporphyrin (I = $TPPH_2$ = $(DMA)_0PH_2$) was prepared by the method of Adler et al.[13]

5,10,15-Triphenyl-20-(4-(dimethylamino)phenyl)porphyrin (II = $(DMA)_1PH_2$). Samples of benzaldehyde (190 μL, 1.9 mmol, 7.5×10^{-3} M), 4-(dimethylamino)benzaldehyde (93 mg, 0.625 mmol, 2.5×10^{-3} M), and pyrrole (173 μL, 2.5 mmol, 10^{-2} M) were dissolved in 250 mL of CH_2Cl_2, then trifluoroacetic acid (963 μL, 12.5 mmol, 5×10^{-2} M) was added, and the solution was stirred for 20 min at room temperature. Then *p*-chloranil (490 mg, 2.0 mmol) was added to the dark-colored solution, and the mixture was warmed at 45 °C for 1 h. Then triethylamine (1.74 mL, 12.5 mmol) was added, the solution was concentrated, and a small amount of silica gel (~5 g, Si 60, 70–230 mesh) was added before evaporating the mixture to dryness. The dark powder was placed on top of a 8×4 cm silica gel column (Si 60, 70–230 mesh) poured with CH_2Cl_2. The porphyrins were eluted using CH_2Cl_2 followed by methylene chloride/ethyl acetate (4:1). Further separation via centrifugal thin layer chromatography (using a Chromatotron from Harrison Research, Inc.) on a 2-mm silica gel rotor afforded tetraphenylporphyrin (40 mg, 10.4%), **II** (80 mg, 19.5%), and a mixture of the cis- and trans-substituted porphyrins (70 mg, 16%): ^{1}H NMR ($CDCl_3$) δ −2.68 (s, 2 H,

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NH), 3.14 (s, 6 H, CH_3), 7.04 (m, 2 H, ArH), 7.78 (m, 10 H, PhH), 8.10 (m, 2 H, ArH), 8.25 (m, 5 H, PhH), 8.86 (m, 6 H, β-pyrrole), 8.99 (d, J = 4.5 Hz, 2 H, β-pyrrole); absorbance (CH_2Cl_2/EtOH 3:1) 418 (26 nm fwhm), 518, 556, 594, 650 nm.

Alternatively, a sample of 5,10,15-triphenyl-20-(4-aminophenyl)porphyrin[15] was reductively methylated[16] at room temperature in tetrahydrofuran with 37% aqueous formadehyde, $NaBH_3CN$, and acetic acid.

5,10,-o-C_5-strapped-15,20-Bis[4-(dimethylamino)phenyl]-porphyrin (III = $(DMA)_2PH_2$). Samples of bis(2-formylphenoxy)-pentane[17] (195 mg, 0.625 mmol, 2.5 × 10^{-3} M), 4-(dimethylamino)benzaldehyde (186 mg, 1.25 mmol, 5 × 10^{-3} M), and pyrrole (173 μL, 2.5 mmol, 10^{-2} M) were dissolved in 250 mL of CH_2Cl_2, then trifluoroacetic acid (965 μL, 12.5 mmol, 5 × 10^{-2} M) was added, and the solution was stirred at room temperature for 30 min. Then *p*-chloranil (460 mg, 1.88 mmol) was added, and the mixture was warmed at 45 °C for 1 h. The mixture was then neutralized with triethylamine and evaporated to give a dark, tacky powder. Flash chromatography (Si 60, 70–230 mesh, 5 × 5 cm) with CH_2Cl_2 (300 mL) eluted the bis-strapped porphyrins, and **III** eluted as a brown band with methylene chloride/ethyl acetate 1:1 (200 mL). TLC (silica, methylene chloride/ethyl acetate 19:1) showed the bis-strapped porphyrins (R_f's 0.75, 0.71), unreacted 4-(dimethylamino)-benzaldehyde, and **III** (R_f 0.45). No other porphyrins were observed by TLC analysis. Purification with semipreparative silica HPLC using methylene chloride/ethyl acetate 98:2 (3 runs) yielded the two atropisomeric bis-strapped porphyrins (2.0 mg, 0.39%) and **III** (11.5 mg, 2.3%): ^{1}H NMR ($CDCl_3$) δ −2.56 (bs, 2 H, NH), 0.55, 0.59 (m, 2 H, CH_2), 0.68, 0.75 (m, 2 H, CH_2), 0.99, 1.06 (m, 2 H, CH_2), 3.24 (s, 12 H, CH_3), 3.76, 3.83 (m, 2 H, CH_2), 3.88, 3.91 (m, 2 H, CH_2), 7.10, 7.18 (m, 4 H, ArH), 7.40, 7.44 (m, 2 H, ArH), 7.69, 7.76 (m, 4 H, ArH), 8.06, 8.14 (m, 4 H, ArH), 8.34, 8.42 (m, 2 H, ArH), 8.68 (s, 2 H, β-pyrrole), 8.79 (d, J = 4.5 Hz, 2 H, β-pyrrole), 8.88 (d, J = 4.8 Hz, 2 H, β-pyrrole), 8.89 (s, 2 H, β-pyrrole); ^{252}Cf plasma desorption mass spectrometry[18] $C_{53}H_{48}N_6O_2$, calcd 800.4, obsd 800.6; absorbance (CH_2Cl_2/EtOH 3:1) 428 (30 nm fwhm), 524, 566, 658 nm.

meso-Tetrakis(p-(dimethylamino)phenyl)porphyrin (IV = $(DMA)_4PH_2$) was prepared by a modified Adler–Longo procedure, using a 1:1 mixture of propionic and octanoic acids (POA) as solvent, instead of propionic acid alone.[19] This substantially improved the yield. To 700 mL of POA solvent was added 50 g (0.34 mol) of *p*-(dimethylamino)benzaldehyde, with stirring, under reflux. Gradually, 23 mL (0.34 mol) of pyrrole was added and the mixture refluxed for 45 min. The cooled solution was filtered, and the purple precipitate was washed with methanol and dried in air. Yield: 9.46 g (15%). Anal. Calcd for $C_{52}H_{48}N_8$: C, 78.39; H, 7.54; N, 14.07. Found: C, 78.14; H, 6.94; N, 12.88. Absorbance (CH_2Cl_2), λ (log ε) 662 (3.92), 575 (4.18), 526 (4.05), 436 (5.13). No peak attributable to chlorin was seen in the absorption spectrum (chlorin < 1%).

The notation and substitution patterns of these porphyrins are shown in Chart I.

Titration Procedure. Solutions (4.2 mL) in methylene chloride of porphyrins of known concentration (1.0–100 μM) were titrated directly in 1-cm absorption cells by successive additions of increasingly concentrated TFA (0.01–10 M), from a microliter syringe. The total volume change over a complete protonation sequence was negligible. After each addition, the solution was mixed, the cell restoppered, and the spectrum taken over the range 350–850 nm. The spectrophotometer was a Perkin-Elmer Model 522, interfaced with an X–Y recorder (Allen Datagraph, 900) and calibrated against NBS filters. Titrations with base were performed similarly, using solutions of sodium ethoxide in ethanol.

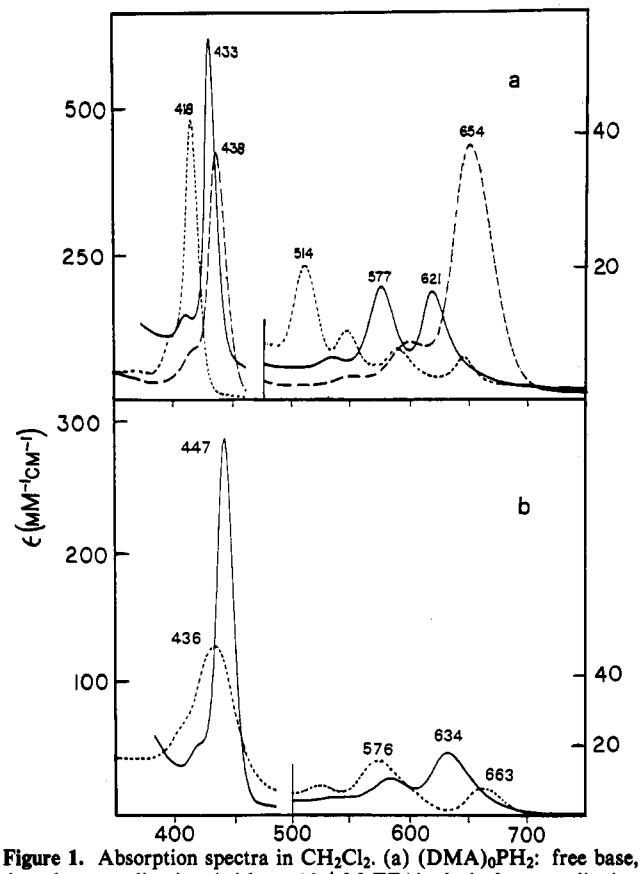
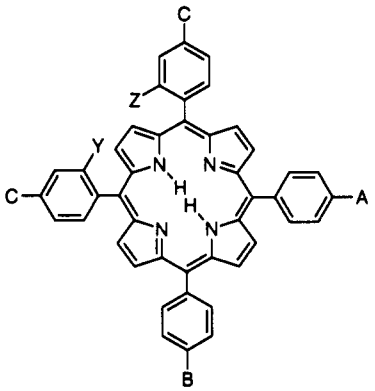


Figure 1. Absorption spectra in CH_2Cl_2. (a) $(DMA)_0PH_2$: free base, dotted curve; dication (with ~ 10^{-4} M TFA), dashed curve; dianion (with ~ 10^{-3} M NaOEt), solid curve. (b) $(DMA)_4PH_2$: free base, dotted curve; dianion, solid curve (with ~ 10^{-3} M NaOEt).

CHART I



Porphyrin Substitution Pattern

compound	A	B	C	Y	Z
I = $(DMA)_0PH_2$	H	H	H	H	H
II = $(DMA)_1PH_2$	$N(Me)_2$	H	H	H	H
III = $(DMA)_2PH_2$	$N(Me)_2$	$N(Me)_2$	H	$-O(CH_2)_5O-$[a]	
IV = $(DMA)_4PH_2$	$N(Me)_2$	$N(Me)_2$	$N(Me)_2$	H	H

[a] Y = Z linked by $-O(CH_2)_5O-$ chain.

Results

1. Normal and Anomalous Spectra: $(DMA)_4PH_2 \rightarrow (DMA)_4P^{2-}$. Figure 1a shows, for convenient reference, the spectra in methylene chloride of tetraphenylporphyrin ($(DMA)_0PH_2$) and its dication (TFA) and dianion (sodium salt). The spectra agree reasonably well with previous measurements of the free base and salts in benzene,[20] pyridine,[20] dimethylformamide,[1] or tetrahydrofuran.[21] Comparable spectra of $(DMA)_4PH_2$ free base and its dianion are given in Figure 1b. For both porphyrins, titration with base gave only single sets of good isosbestics, up to complete deprotonation, with no indication of monoanion formation, and

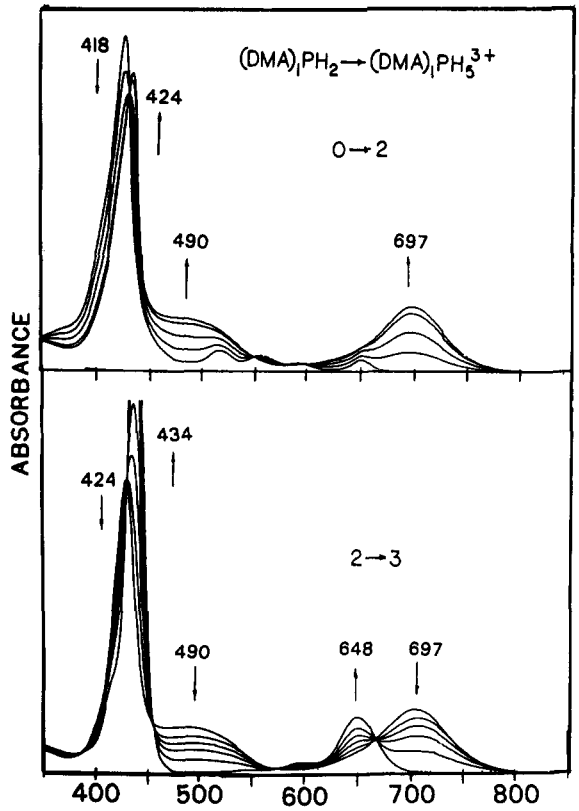


Figure 2. Spectrophotometric titration of $(DMA)_1PH_2$ with TFA. (a) Addition of two protons (0 → 2, A′ → B). (b) Addition of third proton (2 → 3, B → A). See Table I for [TFA] values at midconversions.

TABLE I: Titration of *meso*-Tetrakis(*p*-(dimethylamino)phenyl)porphyrins:[a] Spectral Types[b] and Acid Concentrations (× 10^{-3} M)[c]

	charge on porphyrin											
porphyrin $(DMA)_m$[d]	−2	0		+2		+3		+4		+5		+6
$(DMA)_0$	A[e]	A′	→ 0.05	A								
$(DMA)_1$		A′	→ 0.02	B	→ 20	A						
$(DMA)_2$		A′	→ 0.015	C	→ 6	B	→ 30	A				
$(DMA)_4$	A[e]	A″	→ 0.002	C	→ 0.5	C	→ 6	C	→ 40	B	→ 80	A

[a] Porphyrin concentration, 0.5–1.0 × 10^{-5} M, in CH_2Cl_2. [b] See text. [c] TFA concentration (× 10^{-3} M), corresponding to ~half-conversion for each successive stage. [d] m = number of *meso*-(dimethylamino)phenyl rings; $(4 - m)$ = number of unsubstituted meso phenyls. [e] With 10^{-3} M NaOEt.

was completely reversible on addition of acid. The spectrum of $(DMA)_4PH_2$, with three broad bands in the visible and a very broad Soret band, is "anomalous,"[4,8] but conversion to the dianion shifts the Soret band peak toward the red, sharpens it dramatically, and restores a more "normal" two-banded structure in the visible, as in the unsubstituted tetraphenylporphyrin dianion.[20,21]

2. $(DMA)_1PH_2 \rightarrow (DMA)_1PH_5^{3+}$. Spectra of successive acid-titration products of $(DMA)_1PH_2$ are given in Figure 2 parts a and b. Protonation occurs in two well-separated stages (Table I) both marked by good sets of isosbestics. The initial product, assigned to two proton additions (0 → 2) at the central nitrogens (see below), shows a somewhat reduced and slightly red-shifted (418 → 424 nm) Soret peak, the disappearance of the original broadened four-banded spectrum, and two new bands, a very broad, flat absorption around 490 nm and a strong far-red band at 697 nm, extending almost to 800 nm. The second step (2 → 3) at much higher [TFA] protonates the single peripheral amine,

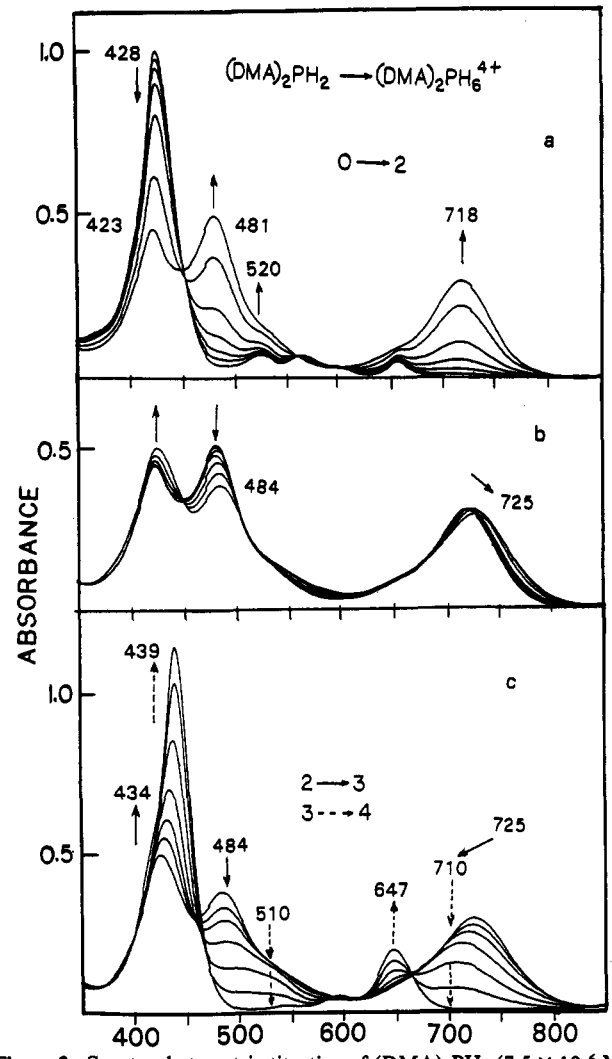


Figure 3. Spectrophotometric titration of $(DMA)_2PH_2$ (7.5 × 10^{-6} M; 1-cm cell) with TFA in CH_2Cl_2. (a) Addition of two protons (0 → 2, A′ → C). (b) Intermediate phase. (c) Addition of third proton (2 → 3, solid lines, C → B) and fourth proton (3 → 4, dotted lines, B → A). See Table I for [TFA] values at midconversions.

giving a "normal" porphyrin-acid spectrum, with a sharp Soret peak (434 nm) and single red band (648 mm) with a shoulder.

3. $(DMA)_2PH_2 \rightarrow (DMA)_2PH_6^{4+}$. Spectrophotometric titration of $(DMA)_2PH_2$ is shown in Figure 3. Initial protonation (0 → 2) occurs at very low acidity and again with good isosbestics. The first product now shows a "split Soret" structure, with components (423 and 481 nm) of about equal height, a broad extension around 525 nm, and a strong red band at 718 nm. Further titration at much higher acidity leads to somewhat overlapping proton additions which can be roughly resolved. In the second step (2 → 3), the long-wave component of the "split Soret" disappears leaving the broad, flat absorption around 510 nm, the high-energy component begins to recover (434 nm), and the far-red band moves to 710 nm and decreases in height (solid line in Figure 3c). Prior to this, there is some movement of this band further to the red (to 728 nm), which may belong to the second stage or result from ion association. The final addition (3 → 4; dotted lines in Figure 3c) forms again a "normal" porphyrin acid, with a sharp Soret peak (at 439 nm) and a single red peak at 647 nm. These changes and the final spectrum correspond closely to the final stage of $(DMA)_1$ (2 → 3) protonation.

4. $(DMA)_4PH_2 \rightarrow (DMA)_4PH_8^{6+}$. The spectral changes found for the diamino-substituted porphyrin appear now in more extreme form for the tetrasubstituted case (Figure 4), and the several stages of proton addition can be readily followed. Protonation results initially (0 → 2) in a sharply split Soret structure, in which the ratio of low-energy (470 nm) to high-energy (393 nm)

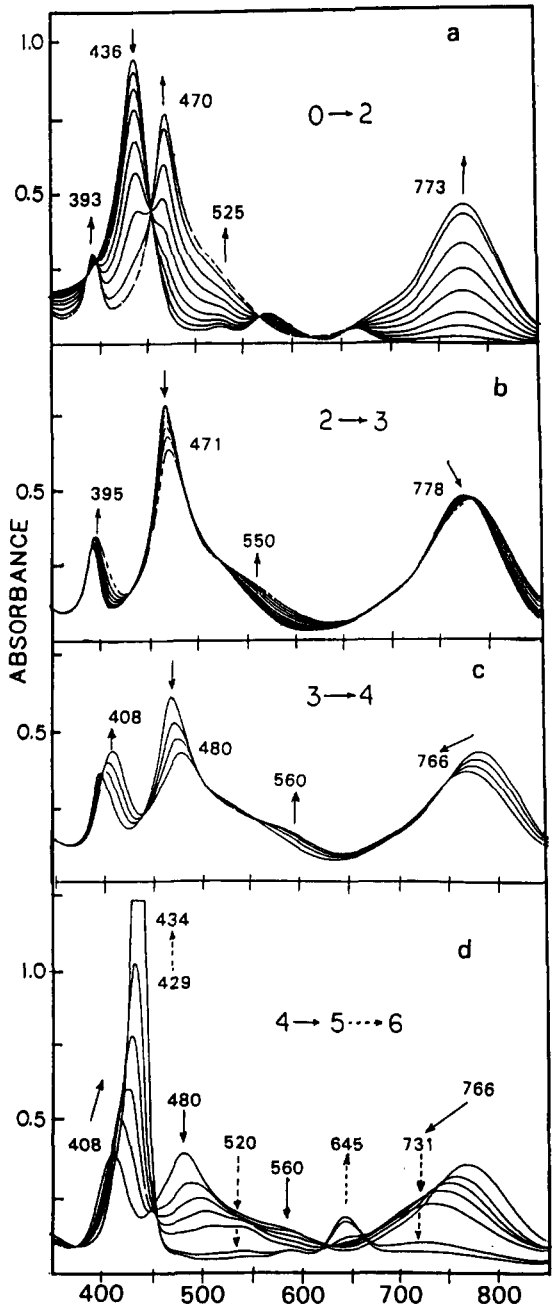


Figure 4. Spectrophotometric titration of $(DMA)_4PH_2$ (7.0×10^{-6} M; 1-cm cell) with TFA in CH_2Cl_2. (a) Addition of two protons (0 → 2, A″ → C). (b) Addition of third proton (2 → 3, C → C). (c) Addition of fourth proton (3 → 4, C → C). (d) Addition of fifth proton (4 → 5, C → B, solid lines) and sixth proton (5 → 6, B → A, dotted lines). See Table I for [TFA] values at midconversions. Final [TFA] = 0.15 M; final extinction coefficients for $(DMA)_4PH_8^{6+}$ ($\times 10^3$ M^{-1} cm^{-1}): 645 nm (26); 434 nm (234).

peaks is 2.6. An extended absorbance around 525 nm is again seen, together with an extremely strong far-red band at 773 nm. At much higher acidity (2 → 3), the split Soret ratio falls next to ~1.8, the peaks move slightly to the red, (395, 471, and 778 nm), and the extended absorption in the visible increases slightly. This is followed (3 → 4) by a further drop in the split-Soret ratio to 1.0, with slight movement to the red, and a shift in the far-red band to 766 nm. At this stage, with two amino groups still unprotonated, the spectral structure corresponds to that of $(DMA)_2PH_4^{2+}$ (Figure 3), but with a strongly shifted far-red band. The final two stages of protonation resemble those seen earlier. At $(DMA)_4PH_7^{5+}$, the long-wave component of the split Soret disappears, leaving a broad flat band around 520 nm, the Soret peak increases strongly, and the far-red band drops (4 → 5, solid lines in Figure 4d) and moves to 731 nm. Addition of the last proton (5 → 6, dotted lines in Figure 4d) results again in a "normal" porphyrin-acid spectrum with a very high Soret peak extinction at 434 nm and a red band at 645 nm.[22] The initial and final spectra in this protonation sequence agree well with the observations of Gunter and Robinson on $(DMA)_4PH_2$.[8]

TABLE II: Characterization of Spectral Types in $(DMA)_mPH_n^{(n-2)+}$

type	m	n	charge	red	Band Location, nm vis (flat)[a]	Soret[b]	ratio[c]
cation, A	0	4	+2	654		438	
(l = 0)[d]	1	5	+3	648		434	
	2	6	+4	647		439	
	4	8	+6	645		434	
cation, B	1	4	+2	697	490	424	
(l = 1)	2	5	+3	710	510	434	
	4	7	+5	731	520	429	
cation, C	2	4	+2	718	520	481/423	1.0
($l \geq 2$)	4	4	+2	773	525	470/393	2.6
	4	5	+3	778	550	471/395	1.8
	4	6	+4	766	560	480/408	1.0
anion, A	0	0	−2	621[e]		433	
(l = 0;4)	4	0	−2	634		447	

[a] Approximate values; band overlaps with Soret components. [b] Two values for split Soret components. [c] Ratio of heights of Soret components. [d] l = number of unprotonated amine groups. [e] Two-banded spectra in visible.

Discussion

1. Sites of Protonation and Effects on Basicity. Initial protonation of all the porphyrins studied, whether amino substituted or not, occurs at low [TFA] (Table I). Subsequent stages at much higher acidities are readily assigned to successive reactions of the several peripheral amino groups. Thus it is clear that in all cases addition occurs first at the central nitrogens of the porphyrin. Direct evidence for this is given by ^1H NMR studies, as described in the following paper.[12] Table I shows further that increasing the number of para amino groups increases the basicity of the pyrrole nitrogens. This presumably is the result of increasing charge delocalization in the ground state.[1] With progressive protonation, the basicity of the peripheral amino nitrogen decreases, reflecting charge and statistical effects.

2. Types of Spectra: Empirical Characterization. The acid–base titrations summarized in Figures 1–4 provide a rich variety of spectra. However, as already indicated, species with the same number of free peripheral amino groups have similar spectra, as indicated in Table II. These include, for example, all the fully protonated porphyrins, such as $(DMA)_0PH_4^{2+}$ and $(DMA)_4PH_8^{6+}$, or those with only two unprotonated amino groups, etc. It is evident that protonation of the lone pairs of the peripheral amino groups largely eliminates their effects on the spectra.

We now identify and discuss five types of spectra A, A′, A″, B, and C, which appear sequentially in the titrations (Tables I and II).

A, A′, A″ Type Spectra. These are typical so-called *regular porphyrin spectra*, whose theory is long established.[9] The excited states are based on the four-orbital model. There are two nearly degenerate HOMO orbitals b_1, and b_2 (symmetry in D_{4h}, respectively, $a_{2u}(\pi)$ and $a_{1u}(\pi)$) and two degenerate or nearly degenerate LUMO orbitals c_1 and c_2 (symmetry in D_{4h}, respectively, $e_{gy}(\pi^*)$ and $e_{gx}(\pi^*)$). In the case of metalloporphyrins the transitions from the HOMOs to the LUMOs give rise to the intense Soret or B bands around 400 nm and the weak visible or Q bands. In D_{4h} symmetry each absorption band arises from two degenerate excited states of x and y polarization. We refer to this as A type. As noted in Table II, for the *meso*-((dimethylamino)phenyl)porphyrins, A type spectra are observed when the

rings are fully protonated and in the deprotonated rings $(DMA)_0P^{2-}$ and $(DMA)_4P^{2-}$, which are square symmetric.

In the free base porphyrins, the degeneracy of x and y polarization is strongly lifted by the central proton axis.[9] As a result the two-banded visible spectrum Q(0,0) and Q(1,0) (this latter a vibronic band) splits into four bands $Q_x(0,0)$, $Q_x(1,0)$, $Q_y(0,0)$, and $Q_y(1,0)$. The Soret band is commonly broadened, but the x and y polarizations are rarely resolved and overlap.[9] We refer to this as the A′ type or D_{2h} spectrum.

A′ spectra are observed (Tables I and II) in the parent, uncharged free bases, $(DMA)_0PH_2$, $(DMA)_1PH_2$, and $(DMA)_2PH_2$. In the latter two, the Soret band is broadened and less distinct than in $(DMA)_0PH_2$. However, they are still considered to be A′ type since four bands are discernible in the visible. The spectrum of $(DMA)_4PH_2$ is somewhat anomalous, showing only a three-banded visible spectrum in CH_2Cl_2[8] (rather similar to that of the monoprotonated free base of TPP, $(DMA)_0PH^{1-}$ (ref 21)) and a diminished Soret. A possible reason for this may be the greater broadening effect of meso aminophenyl ring torsional oscillations compared to phenyl, associated with delocalization of the lone-pair electrons. We denote this three-banded visible spectrum as an A″ type spectrum. But in our view, A″ is still a "regular"[9] porphyrin spectrum, since no extra absorption bands appear, nor does an intense far-red band.

B Type Spectra are observed with the two central nitrogens protonated and with one unprotonated meso (dimethylamino)-phenyl substituent, as in $(DMA)_1PH_4^{2+}$, $(DMA)_2PH_5^{3+}$, and $(DMA)_4PH_7^{5+}$ (Table II). In all three cases, the spectrum reverts to A type with further acidification. These spectra are characterized by an intense far-red band in the 700–730-nm region, a broad and unusually flat absorption around 500–525-nm and a single weakened Soret band. The original visible band structure of the parent free base is absent.

C Type Spectra appear when the two central nitrogens are protonated and there are two or more unprotonated meso (dimethylamino)phenyl substituents, as in $(DMA)_2PH_4^{2+}$; $(DMA)_4PH_4^{2+}$, PH_5^{3+}, and PH_6^{4+}. These spectra exhibit an intense far-red band in the region 720–780 nm, a broad, flat absorption around 520–560 nm, and a characteristic doubled or split Soret structure, with low- and high-energy components around 470–480 and 390–425 nm, respectively. The ratio of the heights (low energy:high energy) of the split components increases as the number of unprotonated amino groups increase (Figure 4 parts b and c). Continued protonation forms successively B type and A type spectra, as above.

Theoretical Interpretation

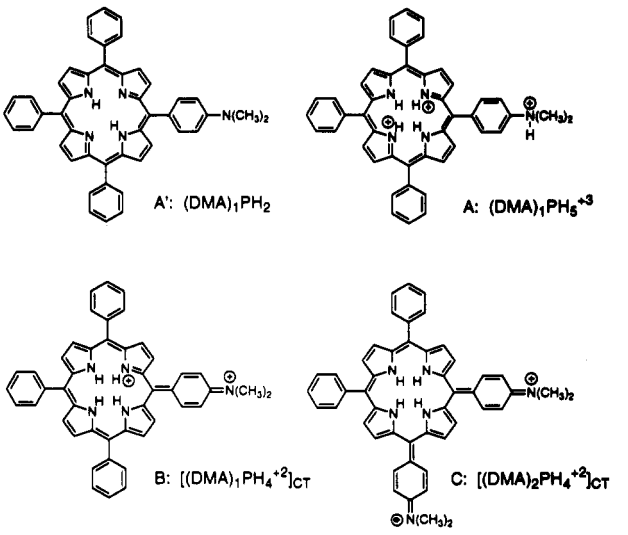
We propose that the B and C type spectra are *hyperporphyrins* in full analogy to the category developed by one of the authors:[9] "Hyperporphyrins show prominent extra absorption bands ($\epsilon > 1000\ M^{-1}\ cm^{-1}$) in the region $\lambda > 320$ nm, where normal porphyrins show only Q, B, and N(π,π^*) bands. There are two fairly well understood subclasses:

(1) p-Type are found with main-group metals in lower oxidation states, that is, Sn(II), Pb(II), ... The extra bands ... are due to charge transfer (CT) transitions $a_{2u}(np_z)(\text{metal}) \rightarrow e_g(\pi^*)(\text{ring})$.

(2) d-Type hyperporphyrins are found with transition metals in configurations d^m, $1 \le m \le 6$, that have holes in the $e_g(d_\pi)$ orbitals and relatively stable lower oxidation states. The extra bands ... are attributed to CT transitions $a_{1u}(\pi), a_{2u}(\pi)(\text{ring}) \rightarrow e_g(d_\pi)(\text{metal})$.

(3) The third group of unusual hyperporphyrins have been found ... where the extra bands appear to have other CT origins."[23]

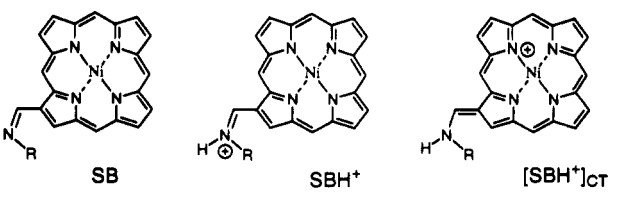
As pointed out in the previous section, regular porphyrin spectra arise from the four-orbital model: HOMOs $a_{2u}(\pi)$, $a_{1u}(\pi) \rightarrow$ LUMOs $e_g(\pi^*)$. In the p-type hyperporphyrin an extra orbital appears in the region of the HOMOs; in d-type hyperporphyrins extra orbitals appear among the LUMOs. In these sequentially



protonated ((dimethylamino)phenyl)porphyrins we propose that the extra orbitals responsible for the hyper spectra are filled π orbitals on the amino nitrogen atoms which permit transitions to the porphyrin LUMOs. The possibility that such charge-transfer transitions play a role in these species is indicated by the above resonance structures. Structure A′ is the usual ground-state free base porphyrin for $(DMA)_1PH_2$. Structure A is the expected protonated dication structure for $(DMA)_1PH_5^{3+}$. Structure B is a resonance form in which one of the central positive charges of the dication migrates out to the (dimethylamino)phenyl group. This corresponds to a charge transfer from the peripheral amino nitrogen to the ring. In resonance structures C, both of the central positive charges of the dication migrate out to two (dimethylamino)phenyl groups. No further migration is possible, nor can such migration occur to protonated amino groups. We believe that resonance structures B and C represent the charge-transfer *excited* states responsible for the B type and C type spectra respectively.

The most direct evidence for assigning these structures to excited states is given by ^1H NMR data in the accompanying paper.[12] Briefly, it is observed that addition of TFA leads to the same pattern of changes in the positions of pyrrolenine NH and β-pyrrole protons, whether the meso phenyl groups bear amines or not, despite the associated sharply different effects on the optical absorption spectra. Moreover, for the substituted systems, $(DMA)_1PH_2$ and $(DMA)_4PH_2$, the effects of TFA addition on the aminophenyl ring protons closely match those on the model compound, *N,N*-dimethyl-*p*-toluidine.[12] There is no indication of ground-state quinonoid structures, as such, in the ^1H NMR spectra of the acidified (aminophenyl)porphyrins.

Phenomena closely related to those described here occur in the case of metal complexes of Schiff base porphyrins (SB), as follows.



Ward, Chang, Young, and co-workers observed splitting of the Soret and development of an intense far-red band, resembling the C-type spectra above, when the nitrogen of the Schiff base was protonated (SBH^+).[24,25] Resonance Raman measurements showed very little effect of protonation on the ring vibration frequencies, and ^1H NMR indicated localization of the positive charge at the Schiff base nitrogen. Thus, in this case also, protonation does not markedly affect the ground state of the macrocycle. Molecular INDO-CI calculations by Hanson et al.

attribute the extra bands to an SB(π^*) orbital, where SB(π^*) denotes π^* contribution to the excited state from the substituent C=N.[26] In the protonated Schiff base, the charge-transfer resonance structure $(SBH^+)_{CT}$ involved in the hyperporphyrin spectrum describes charge movement from the porphyrin ring to the SB nitrogen. This structure clearly belongs to the excited state, not the ground state.

The normal D_{4h} spectrum, with a sharp Soret band, of the tetrakis((dimethylamino)phenyl)porphyrin dianion $(DMA)_4P^{2-}$ (Figure 1) indicates that the central negative charges oppose the effect of the peripheral lone pairs in establishing low-lying charge-transfer states, in accord with the above views.

Finally, we note the analogous spectra (with intense far-red bands and split Sorets), observed by Smith, for Sn^{IV} complexed in tetrakis (*p*-hydroxyphenyl)porphyrin,[10] and Milgrom, Jones, and Harriman, for several metal complexes of *meso*-tetrakis-(3,5-di-*tert*-butyl-4-(hydroxyphenyl))porphyrin, in basic media.[11] In particular, we note the striking similarity between the latter's spectrum for the basified nickel complex and that for $(DMA)_4PH_4^{2+}$ reported here. These authors have also noted the analogy to hyperporphyrin spectra. They propose a resonance structure for a "new chromophore," in which two negative charges from the phenoxide oxygens are transferred to the porphyrin nitrogen atoms, and suggest that the postulated nitride is stabilized by back-bonding to empty metal orbitals. Such a structure, even with back-bonding, will evidently be of quite high energy. We believe that, in analogy to the acidified Schiff base and ((dimethylamino)phenyl)porphyrins, the "new chromophore" suggested by Milgrom et al. actually represents the charge-transfer excited state.

The concept of hyperporphyrins was developed originally to explain the appearance of new bands in the spectra of certain metalloporphyrins. In that treatment,[9] the extra orbital providing the charge-transfer level was physically very close to the porphyrin π-system, either on the central metal or on an atom ligated to that metal. However, in the Schiff base porphyrins, the nitrogen atoms that were involved in the charge-transfer transition could be at the terminus of acroleinyl side chains, separated by two vinylic carbon atoms from the porphyrin ring.[24] In the ((dimethylamino)phenyl)porphyrins reported here, the peripheral nitrogen atoms that are the source of the postulated charge transfer transitions are separated by a phenyl ring from the porphyrin macrocycle. This is also the case for the oxyphenyl-substituted porphyrins studied by Smith[10] and by Milgrom et al.[11] Thus, if this viewpoint is correct, hyperporphyrins can occur generally if orbitals are present which make possible charge transfer either into or out of the porphyrin ring. Such orbitals, if suitably conjugated, may be substantially separated from the macrocycle. The resonance structures for the excited states, as given above, help explain such cases. The essential feature is the availability of charge-transfer levels, and there is evidently no special requirement for complexed metal.

To fully understand both the acidified ((dimethylamino)-phenyl)porphyrins and the basified oxyphenylporphyrins, calculations like those of Hanson et al.[26] would be needed. In particular such calculations might distinguish the new B type spectra from the C type, which are more typically like hyperporphyrins in showing two well-defined Soret bands. Pending such full calculations, the general interpretations offered here are qualitative. However, the spectral analogies are so clear that these speculations are well-grounded.

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