# Steric and Inductive Effects on the Basicity of Porphyrins and on the Site of Protonation of Porphyrin Dianions:

**Radiolytic Reduction of Porphyrins and Metalloporphyrins to Chlorins or Phlorins** 

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A series of sulfonated, water-soluble, phenyl-substituted porphyrins has been prepared, containing halogen or alkyl groups in the ortho, di-ortho or para positions. While the para-substituted compounds exhibited monomerdimer behaviour, all the ortho and di-ortho substituted porphyrins were monomeric in aqueous solution at 0.1 mol dm<sup>-3</sup> ionic strength. The proton basicities varied over a 10<sup>5</sup> range along the series, from the strongly basic tetra(4-methoxyphenyl) species to the weakly basic and less deformable sulfonated tetrakis(2,6-dichlorophenyl) porphyrin. Certain of these porphyrins and related metalloporphyrins were reduced by radiolytic methods in aqueous solutions. Pulse radiolysis studies provided the spectra of the short-lived  $\pi$ -radical anions and  $\gamma$ radiolysis led to formation of stable chlorins or phlorins, the products of two-electron reduction and protonation at the  $\beta$ -pyrrole or at the meso position, respectively. Whereas H<sub>2</sub>TPPS<sub>4</sub> [tetrakis(4-sulfonatophenyl)porphyrin] yields phlorin at all pH values, Zn<sup>11</sup>-, Al<sup>111</sup>-, In<sup>111</sup>- and Sn<sup>1V</sup>-TPPS<sub>4</sub> form phlorins at high pH but mostly chlorins at lower pH. The ratio of phlorin to chlorin production is enhanced by increased pH and by increased metal electronegativity. 2,6-Disubstitution at the phenyl rings diminishes the likelihood of phlorin formation while Nmethyl substitution at one of the central nitrogens of ZnTPPS<sub>4</sub> enhances phlorin formation. These and other results indicate that electron withdrawal from the porphyrin  $\pi$ -system enhances the ratio of phlorin/chlorin production. On the other hand, steric crowding around the meso position retards protonation at this site by preventing the geometric reorientation necessary for phlorin formation.

Many aspects of the dynamic coordination chemistry of porphyrins and metalloporphyrins in aqueous solution have been explored with the readily prepared and fully watersoluble negatively charged tetrakis(4-sulfonatophenyl)porphyrin (H<sub>2</sub>TPPS<sub>4</sub>) and to a lesser extent with tris(4sulfonatophenyl)monophenylporphyrin  $(H_2TPPS_3)$ .<sup>1-4</sup> Both compounds show monomer-dimer equilibria<sup>5,6</sup> near neutral pH, form higher aggregates in acid<sup>6,7</sup> and have  $pK_3$  and  $pK_4$  values of *ca.* 4.8.<sup>8,9</sup> Such behaviour severely limits the range of pH and porphyrin concentration in which many mechanistic studies can be done. We have sulfonated a variety of para, ortho and di-ortho substituted phenylporphyrins, rendering them water soluble, and examined the nature of the sulfonation products. While the para complexes show monomer-dimer behaviour, the ortho and di-ortho substituted derivatives are monomeric throughout the entire pH range. The  $K_a$  values for these sulfonated porphyrins vary by a factor of  $10^5$  across the series and are found to be relatively insensitive to the number of sulfonic acid groups present on a given porphyrin type, at the ionic strength examined.

Porphyrins (H<sub>2</sub>P) undergo several one-electron reduction steps to form  $\pi$ -radical anions, dianions and more highly reduced species. Metalloporphyrins (MP) undergo similar processes in addition to any redox reactions that may occur at the metal centre. The  $\pi$ -radical anions and the dianions are generally stable in aprotic solvents but undergo disproportionation and/or protonation in aqueous solutions. The products of these processes are either chlorins or phlorins. Chlorins and metallochlorins (H<sub>2</sub>PH<sub>2</sub> or MPH<sub>2</sub>), formed by adding two H<sup>+</sup> at the  $\beta$ -pyrrole positions of the dianions, are characterized by a narrow peak at 600–650 nm and are stable in the presence of O<sub>2</sub>. Phlorins (H<sub>3</sub>PH), formed by protonation at a *meso* position and at a pyrrolic nitrogen, and phlorin anions ( $H_2PH^-$  or MPH<sup>-</sup>), where one proton is added at the *meso* position, are characterized by very broad absorptions at 600–900 nm and are oxidized rapidly by  $O_2$  to recover the original porphyrin. Radiolytic and photochemical reduction of various porphyrins and metalloporphyrins in aqueous solutions has been found to yield chlorins or phlorins, or both, depending on the porphyrin structure, the metal centre and the reduction conditions.<sup>10–13</sup> Increasing the electronegativity of the metal centre enhanced the ratio of phlorin to chlorin production. This effect appears to be related to inhibition of protonation but the exact mechanism remains vague. In the present study we find that steric effects play a major role in determining the final site of protonation, *i.e.* in the production of chlorin vs. phlorin.

#### Experimental<sup>†</sup>

The free-base porphyrins and *N*-methylporphyrins were obtained from Mid-Century (Posen, IL), and were sulfonated using either concentrated sulfuric acid or 20% oleum. There is no optimal set of conditions to sulfonate all the porphyrins, and the original literature<sup>14–16</sup> should be consulted for specific derivatives. Nevertheless, the general work-up procedure

<sup>&</sup>lt;sup>†</sup> The identification of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

was similar in all cases. For example, tetrakis(4-sulfonatophenyl)prophyrin<sup>14,17-19</sup> was made by heating ca. 5 g of tetraphenylporphyrin ( $H_2TPP$ ) in 100 cm<sup>3</sup> of  $H_2SO_4$  overnight at 100 °C. Ice was added to the green mixture, the acid neutralized by careful addition of 50% NaOH solution and ice until the colour turned red, and after adjustment to ca. pH 7, the liquid was evaporated in an oven at 100 °C. The resulting solid was pulverized and the sulfonated porphyrin extracted into methanol with a Soxhlet apparatus. Evaporation of the methanol yielded the crude sulfonated compound. To remove traces of salts, o-phenanthroline added to a pH 3 aqueous solution of the porphyrin leads to the precipitation of the (H-Phen)<sup>+</sup> salt of TPP(SO<sub>3</sub>)<sub>4</sub>, which is washed with water and passed through an ion-exchange column in the Na<sup>+</sup> form and then lyophilized.<sup>20</sup> This precipitation method worked well for the para-substituted porphyrins, whereas the ortho derivatives often formed tarry oils with phenanthroline, which could not be solidified.

The mixtures of compounds, H<sub>2</sub>TPPS<sub>4</sub>, H<sub>2</sub>TPPS<sub>3</sub>, 5, 10-bis(4sulfonatophenyl)-15,20-diphenylporphyrin (cis-H<sub>2</sub>TPPS<sub>2</sub>), 5,15-bis(4-sulfonatophenyl)-10,20-diphenylporphyrin (trans- $H_2TPPS_2$ ) and mono(4-sulfonatophenyl)triphenylporphyrin  $(H_2TPPS_1)$  could be prepared by stirring  $H_2TPP$  in  $H_2SO_4$ at room temperature for periods from 15 to 180 min, depending on the major fraction desired. Larger amounts of porphyrin and shorter times favour the production of the lower sulfonated derivatives. Following work-up, the mixture of porphyrins was separated using low-pressure liquid chromatography columns packed with LiChroprep RP-18 silica gel.<sup>21</sup> The packing material was soaked in methanol, washed thoroughly with deionized water and equilibrated with a 0.01 mol dm<sup>-3</sup> sodium phosphate buffer at ca. pH 7.4. The porphyrin mixture applied in this buffer remained at the top of the column. The  $H_2TPPS_4$  and  $H_2TPPS_3$  fractions were eluted with 25% MeOH, the cis- and trans-H<sub>2</sub>TPPS<sub>2</sub> with 50% MeOH, and ultimately  $H_2TPPS_1$  was collected with pure MeOH. The fractions usually had to be rechromatographed to produce uncontaminated products. The solvent was evaporated and the pure porphyrins added to a small C-18 column, washed with water to remove any remaining salt and collected by elution with MeOH-H<sub>2</sub>O. The  $R_{\rm f}$ values on Whatman KC-18 plates in 80:20 MeOH-H<sub>2</sub>O  $(0.01 \text{ mol } \text{dm}^{-3} \text{ phosphate buffer, } ca. \text{ pH } 7.4)$  were 0.94 for H<sub>2</sub>TPPS<sub>4</sub>, 0.88 for H<sub>2</sub>TPPS<sub>3</sub>, 0.74 for trans-H<sub>2</sub>TPPS<sub>2</sub>, 0.59 for cis-H<sub>2</sub>TPPS<sub>2</sub>, and 0.12 for H<sub>2</sub>TPPS<sub>1</sub>. Since H<sub>2</sub>TPPS<sub>4</sub><sup>17</sup> and H<sub>2</sub>TPPS<sub>3</sub><sup>22</sup> are known compounds, only the cis-H<sub>2</sub>TPPS<sub>2</sub> was analysed. Calculated for Na<sub>2</sub>(H<sub>2</sub>TPPS<sub>2</sub>) · 7H<sub>2</sub>O: C, 55.04%; H, 4.41%; N, 5.83%; S, 6.68%. Found: C, 55.07%; H, 4.26%; N, 5.92%; S, 6.59%.

All the ortho and di-ortho substituted phenylporphyrins were sulfonated overnight at room temperature in 20% oleum. After work-up, spotting a given porphyrin on the reverse-phase TLC plates in 80:20 MeOH-H<sub>2</sub>O (0.01 mol  $dm^{-3}$  phosphate buffer, ca. pH 7.4) produced two or three bands. Radically different results were found using 60:40 MeOH-ammonium acetate (1 mol dm<sup>-3</sup>) as the developing agent. For example, the 2,6-dichloro mixture, which showed three spots in 80 : 20, gave 8-10 bands with the 60 : 40 eluent. In general, all of the porphyrins, both para and ortho substituted, gave multiple and distinct spots with this more powerful 60:40 solvent, and thus many sulfonated products are formed from the ortho and para compounds. As outlined above, the porphyrins were separated by C-18 column chromatography using 5-40% MeOH-0.1 mol dm<sup>-3</sup> sodium phosphate (pH 7.4) for the initial stages, followed by 25-100% MeOH-0.01 mol dm<sup>-3</sup> sodium phosphate (pH 7.4) mixtures at later times. The higher the salt and the lower the methanol concentration, the slower the elution. For the J. CHEM. SOC. FARADAY TRANS., 1993, VOL. 89

Another method of determining the number of sulfonic acids involved adding different amounts of  $Co(NH_3)_6^{3+}$  to fixed amounts of porphyrin, removing the precipitate with a 0.45 µm Millipore filter, and plotting the resulting observed absorbance vs. the ratio  $[Co(NH_3)_6^{\bar{3}+} : H_2TPPS]$ . A sharp break in the curve indicated the stoichiometry of the precipitate. The results were excellent for H<sub>2</sub>TPPS<sub>4</sub>, but suggestive rather than definitive for the other porphyrins. We also attempted to use a series of porphyrins, containing  $2-8 \text{ CO}_2^$ groups at the  $\beta$ -pyrrole positions, as charge markers with the 60:40 solvent, for a given mixture of sulfonated porphyrins. The  $H_2$ TPPS<sub>2</sub> and  $H_2$ TPPS<sub>4</sub> ran faster than the di- and tetra-carboxy porphyrins, and the results were never unequivocal. Electrophoresis, NMR and FAB-MS experiments were also relatively unproductive. The present studies were done with a single band from the centre of each porphyrin mixture, which could be the tetra- or penta-sulfonated species. The solubility of the porphyrin from the fraction used was similar to that of H<sub>2</sub>TPPS<sub>4</sub>, in comparison with the order  $H_2TPPS_4$  (very soluble) >  $H_2TPPS_3$  (soluble) >  $cis-H_2TPPS_2$  (slightly soluble) >  $trans-H_2TPPS_2$  (very slightly soluble)  $\gg$  H<sub>2</sub>TPPS<sub>1</sub> (fairly insoluble).

When the number of sulfonic acid groups is uncertain the compound is termed TPPS [*e.g.*  $H_2T(4-OMe)PPS$ ] whereas  $H_2TPPS_2$  indicates the actual composition. For simplicity, the ionic charges on the porphyrins are omitted from the abbreviations and the species produced by one- and two-electron reduction of the ligand are referred to as the  $\pi$ -radical anion and the dianion.

The metal complexes MTPPS<sub>4</sub> were obtained from Mid-Century. Propan-2-ol and the inorganic compounds were analytical-grade reagents from Mallinckrodt. Water was purified with a Millipore Super-Q system. Fresh solutions were prepared before each experiment and were irradiated after bubbling with the required gas. y-Radiolysis was carried out in a Gammacell 220 <sup>60</sup>Co source with a dose rate of 1.5 Gy  $s^{-1}$ . Pulse radiolysis was carried out with the apparatus described before,<sup>23</sup> which utilizes 50 ns pulses of 2 MeV electrons from a Febetron model 705 accelerator. The dose per pulse was varied between 4 and 40 Gy and was determined by dosimetry with N<sub>2</sub>O saturated aqueous KSCN solutions.<sup>24</sup> All radiolysis experiments were carried out at room temperature,  $21 \pm 2$  °C. The equilibrium studies were performed using a Beckman DU-70 recording spectrophotometer and the capacitor discharge temperature-jump apparatus was described before.25

### **Results and Discussion**

### Synthesis of Sulfonated Porphyrins

Based on the initial work of Winkelman *et al.*,<sup>26</sup> a number of groups have explored the synthesis and properties of the water-soluble ligands tetrakis(4-sulfonatophenyl)porphyrin,  $H_2TPPS_4^{7,14,18}$  and tris(4-sulfonatophenyl)monophenyl-porphyrin,  $H_2TPPS_3$ .<sup>6,9</sup> Although it was not possible to grow single crystals of Fe<sup>III</sup>TPPS<sub>4</sub> for X-ray studies,<sup>27</sup> NMR indicates that sulfonation occurs in the *para* position of  $H_2TPPS_4$ .<sup>7</sup> As outlined in the Experimental section, while moderate temperatures, low porphyrin concentrations and long reaction times lead uniquely to  $H_2TPPS_4$ , the lower members of the phenyl/(4-sulfonatophenyl)porphyrin series are readily prepared with lower temperatures and shorter

reaction periods, and can be separated from one another by reverse-phase column chromatography techniques.

tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrin The  $[H_2T(2,6-Cl)PPS_4]$  was synthesized by Dolphin et al.<sup>28</sup> in oleum (7 h, 165 °C). The Soret band shifted from 418 to 423 nm upon sulfonation, and it was noted that no method was found to remove the excess of  $Na_2SO_4$  from the product. Bruice and co-workers<sup>29</sup> prepared tetrakis(2,6-dimethyl-3sulfonatophenyl)porphyrin in concentrated sulfuric acid (4 h, 100 °C), and indicated that the NMR was more consistent with sulfonation at the 3- rather than the 4-position as suggested by others<sup>30</sup> for the same compound. The reported N:S ratio for this sulfonated dimethyl compound was 4.0:4.3 as compared to the expected 4.0:4.0, and the three reverse-phase TLC bands observed were explained as due to the presence of three of the four expected atropisomers. Three TLC bands were also noted by Panicucci and Bruice<sup>31</sup> for the  $H_2T(2,6-Cl)PPS_4$  prepared by Dolphin's method,<sup>28</sup> and the N: S ratio of 4.0: 6.12 was rationalized by including 0.5  $SO_4^{2-}$  and  $Na_2SO_4$  in the molecular formula. After sulfonation of the tetrakis(2,6-difluorophenyl)- and tetrakis(2,6dichlorophenyl)-porphyrins in sulfuric acid (5 h, 135 °C), the Zn<sup>II</sup> complexes of the presumed 3-sulfonatophenylporphyrins showed 3.9 and 3.2 sulfonate groups per porphyrin, respectively.<sup>32</sup> Turk and Ford<sup>33</sup> sulfonated the 2,6-dichlorophenylporphyrin in sulfuric acid (5 h, 185 °C), and their NMR and analytical data (N : S = 4.0 : 3.4) indicated ca. 3.4-3.5  $SO_3^-$  groups per porphyrin ring, with 75% sulfonation at the 3 (meta) and 25% at the 4 (para) positions. Meunier and coworkers<sup>34</sup> sulfonated the 2,4,6-trimethylphenylporphyrin in 20% oleum (4-5 h, 120°C), with the formation of the 3,5disulfonated derivative. Using sulfuric acid at room temperature for short time periods, Stinson and co-workers<sup>19</sup> isolated and characterized the 3-sulfonatophenyl derivatives of the tetra(4-OH) and tetra(4-OMe)phenyl porphyrins.

From our reverse-phase TLC data using the 60:40 MeOH-ammonium acetate (1 mol  $dm^{-3}$ ) solvent, the conclusion is that a mixture of sulfonation products is often produced from the ortho, di-ortho and para substituted phenylporphyrins, just as a mixture of products is formed from tetraphenylporphyrin and sulfuric acid under mild conditions. Such a conclusion is not inconsistent with the results outlined above from other laboratories. The observation that the tetramesitylporphyrin and its 3,5-disulfonated product have essentially the same Soret maxima<sup>34</sup> (419 and 418 nm, respectively), might indicate that in addition to the phenyl ring reaction, sulfonation is also occurring at the  $\beta$ -pyrrole positions when the sulfonated porphyrins show bands shifted >6 nm above that of the parent porphyrin peak. It is our experience that sulfonation of deuteroporphyrin-IX dimethyl ester<sup>35</sup> in sulfur trioxide-pyridine melts produces the 2- and 4-monosulfonated and the 2,4-disulfonated deuteroporphyrins, as well as compounds with hydrolysed ester groups. In general, porphyrins with one, two or no sulfonic acids on a given phenyl ring, as well as mono-sulfonation in the 4 and 3 positions on the same ring, and perhaps  $\beta$ -pyrrole sulfonated species, in addition to the various numbers of atropisomers could all be present in the water-soluble sulfonation mixture.

At the ionic strength studied, the equilibrium and kinetic properties of the mixtures of porphyrins are essentially the same as found for several of the central isolated fractions. Before we realized just how many sulfonated species could be present for a given porphyrin,  $pK_a$  data were obtained for seven of the *ortho* and di-*ortho* porphyrin mixtures. The  $pK_a$  values of the mixtures were essentially the same ( $\pm 0.2 \text{ pK}$  units) as that observed for individual spots from the centre fractions. The absorption spectra during such pK titrations

gave no indication that a mixture of porphyrins was present, and the same was true for kinetic ( $Zn^{II}P$  acid solvolysis) and equilibrium (CdP formation) results reported elsewhere.<sup>15</sup> Such centre fractions were chosen because they were better resolved than the higher  $R_f$  compounds, which often had Soret bands shifted to higher wavelengths and could involve  $\beta$ -pyrrole/phenyl sulfonic acid mixtures.

#### Monomer-Dimer Equilibria

The majority of negatively charged metal-free porphyrins and certain metalloporphyrins<sup>5,6,21,36,37</sup> undergo monomerdimer equilibria in aqueous solution.

$$2\mathbf{H}_2\mathbf{P} \rightleftharpoons (\mathbf{H}_2\mathbf{P})_2; \qquad K_{\mathbf{D}}, \, k_{\mathbf{f}}, \, k_{\mathbf{r}} \tag{1}$$

In order to know the species present at any given total porphyrin concentration, the dimerization constants,  $K_{\rm D}$ , were determined. Spectrophotometric Beer's law studies were done at constant wavelength and ionic strength at ca.  $10^{-4}$ - $10^{-7}$  mol dm<sup>-3</sup> porphyrin levels. Deviations from Beer's law allow the determination of  $K_D$  by standard curve-fitting techniques.<sup>22,35</sup> In the present work, the ionic strength was 0.10 mol dm<sup>-3</sup> (NaNO<sub>3</sub>) and the pH maintained at 7.4 with  $1 \times 10^{-3}$  mol dm<sup>-3</sup> HEPES buffer [4-(2-hydroxyethyl)-1piperazineethanesulfonic acid,  $pK_a = 7.4$ ]. Weighed amounts of each purified porphyrin were dissolved in and diluted with this medium and the spectra recorded in the Soret region. Fig. 1 shows a typical absorbance vs. concentration plot for  $H_2T(4-Cl)PPS$  and the excellent fit of the data with  $K_p = (1.7)$  $\pm$  0.3) × 10<sup>4</sup> dm<sup>3</sup> mol<sup>-1</sup>. The dimerization constants for many of the other compounds are comparable: H<sub>2</sub>T(4-F)PPS,  $(2.7 \pm 0.8) \times 10^4$ ; (4-Me),  $(1.6 \pm 0.3) \times 10^4$ ; and (4-OMe),  $(3.3 \pm 0.2) \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup>. In the H<sub>2</sub>TPPS<sub>x</sub> series,  $K_{\rm D}$  increases with a decrease in porphyrin charge and solubility: H,TPPS₄,  $(2.1 \pm 0.4) \times 10^4;$ H<sub>2</sub>TPPS<sub>3</sub>,  $(7.3 \pm 0.5) \times 10^4$ ; cis-H<sub>2</sub>TPPS<sub>2</sub>,  $(1.4 \pm 0.7) \times 10^7$  and trans-H<sub>2</sub>TPPS<sub>2</sub>,  $> 10^7$  dm<sup>3</sup> mol<sup>-1</sup>. The same trend is shown by the S<sub>1</sub>-S<sub>4</sub> sulfonated Al<sup>III</sup>-phthalocyanines.<sup>21</sup>

Under the same conditions, the ortho-substituted derivatives, (2-F), (2-Cl), (2-Me) and H<sub>2</sub>T(2-OMe)PPS and the diortho-substituted (2,6-F), (2,6-Cl) and H<sub>2</sub>T(2,6-OMe)PPS showed no substantial deviations from Beer's law, and are considered to be monomeric, with  $K_D < 10^3$  dm<sup>3</sup> mol<sup>-1</sup>.  $K_D$ increases with ionic strength, and porphyrins in their dimeric forms have lower molar absorptivities than the corresponding monomers.<sup>36</sup> For a given porphyrin at a fixed concentration, overlay spectra show sharp high-absorbance peaks in the 480–700 nm range at low ionic strength that begin to



Fig. 1 Plot of absorbance vs. total porphyrin concentration for  $H_2T(4-Cl)PPS$ . The upper line is the absorbance expected if the porphyrin were always monomeric and the dots indicate the observed behaviour. The theoretical curve through the dots is based on  $K_D = (1.7 \pm 0.3) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ 

broaden, decrease and shift slightly to shorter wavelengths as the salt concentration is increased. This was found to be the case for all the *para*-substituted porphyrins mentioned above. With the *ortho*- and di-*ortho* derivatives which followed Beer's law, the spectra were virtually superimposable when the ionic strength was changed from *ca*. 0 to 0.8 mol dm<sup>-3</sup>. In addition, temperature-jump relaxation studies<sup>5,6,21</sup> at  $I = 0.10 \text{ mol dm}^{-3}$  with the *para*-substituted porphyrins gave dimer formation rate constants,  $k_f$ , in the range (6–16) × 10<sup>7</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, where  $K_D = k_f/k_r$ . For the *ortho* and di*ortho* porphyrins under the same conditions, no relaxations were observed.

Very few water-soluble, meso-substituted, negatively charged porphyrins have been probed in detail for their monomer-dimer characteristics. Tetrakis(4-sulfonatophenyl) porphyrin,<sup>5</sup> tris(4-sulfonatophenyl)monophenylporphyrin<sup>6,21</sup> and tetrakis(4-carboxyphenyl)porphyrin<sup>22</sup> show similar monomer-dimer behaviour, while tetrakis(3-carboxyphenyl) porphyrin and its 2-isomer<sup>37</sup> were monomeric in solution at 0.1 mol dm<sup>-3</sup> ionic strength. The 2,4-disubstituted deutero-porphyrin dicarboxylic acids<sup>37</sup> and various ethylenediamine-substituted protoporphyrins<sup>36</sup> generally have  $K_{\rm D}$  values one or two orders of magnitude larger than shown by the mesophenyl compounds, indicating that phenyl groups inhibit dimerization. Although such phenyl porphyrins have lower  $K_{\rm D}$  values, their  $k_{\rm f}$  values are similar to those of the  $\beta$ -pyrrole macrocycles, showing that  $K_{\rm D}$  is mainly determined by  $k_{\rm r}$ , the rate constant for dimer dissociation.<sup>36</sup> Based on PMR studies<sup>38</sup> on the Fe<sup>III</sup> halide derivatives of tetrakis(4-methylphenyl)porphyrin, these phenylporphyrin dimers are formed by the  $\pi$ - $\pi$  van der Waals interactions between two adjacent pairs of pyrrole groups on each porphyrin, with the phenyl rings tilted ca. 20-30° from the mean porphyrin planes, allowing a ca. 5 Å porphyrin-porphyrin separation. In the present work, we find that the sulfonated porphyrins with OCH<sub>3</sub>, CH<sub>3</sub>, Cl or F groups in the 4-phenyl positions show monomer-dimer interactions similar to  $H_2TPPS_4$ . On the other hand, the sulfonated 2-substituted Cl, F, CH<sub>3</sub> and OCH<sub>3</sub>, and the 2,6-disubstituted Cl, OCH<sub>3</sub> and F compounds, show no evidence of dimerization, either by Beer's law studies or from kinetic relaxation experiments. The steric interactions between the ortho substituents on the phenyl rings and the hydrogen atoms on the  $\beta$ -pyrrole positions tend to make the phenyl rings more perpendicular and less able to twist toward planarity with the porphyrin nucleus than in the case of the para-substituted compounds. This 'ortho effect' inhibits dimerization by preventing the phenyl rings from rotating sufficiently to facilitate the  $\pi$ - $\pi$  interaction of the adjacent  $\beta$ -pyrrole groups. In addition, only the most ringelectron-rich basic porphyrins having  $pK_3$  values > ca. 4.8 show dimerization. Such electron-density arguments have been used to explain why the less basic tetrakis(N-methyl-4pyridyl)porphyrin is monomeric, as opposed to the dimeric behaviour of the more basic H<sub>2</sub>TPPS<sub>4</sub> compounds.<sup>6</sup>

## **Acid Aggregation**

Fleischer et al.<sup>7</sup> found that  $H_4TPPS_4$ , which has a typical di-acid porphyrin spectrum with bands at 435, 593 and 645 nm at ca. pH 4, changes more or less rapidly into an unexplained form with peaks at 435, 491, 645 and 707 nm below pH 2, as in Fig. 2 (insert). Pasternack<sup>6</sup> noted the same phenomenon with  $H_2TPPS_3$ , and showed that the formation of this new species was favoured by high porphyrin and ionic strength levels, with the extent depending on the identity of the cation used to produce the ionic media. We find that the same behaviour occurs with other TPPS<sub>x</sub> derivatives in 0.1 mol dm<sup>-3</sup> HCl, where the extent of aggregation is in the



**Fig. 2** pH profile of the protonation reactions of  $H_2T(2,6-F)PPS$  at  $I = 0.1 \text{ mol } dm^{-3}$  (NaNO<sub>3</sub>). The solid theoretical curve is based on eqn. (4) with  $pK_3 = 2.5$  and  $pK_4 = 1.8$ . Insert: the four-band spectrum of aggregated TPPS<sub>4</sub> in 0.1 mol dm<sup>-3</sup> HCl (upper curve) and the spectrum of  $H_4TPPS_4$  after passage through a 0.45 µm Millipore filter

approximate order of solubility, trans-TPPS<sub>2</sub> (fully aggregated)  $\gg$  cis-TPPS<sub>2</sub> > TPPS<sub>3</sub> ~ TPPS<sub>4</sub>. If the TPPS<sub>4</sub> in 0.1 mol dm<sup>-3</sup> HCl is filtered through a 0.45 µm Millipore filter, the aggregate is removed, leaving the di-acid in solution (Fig. 2). After allowing this to stand in  $1.5 \times 10^{-2}$  to 0.94 mol dm<sup>-3</sup> HCl solutions overnight, ca.  $1 \times 10^{-6}$  mol dm<sup>-3</sup>  $H_4TPPS_4$  is left after filtration in all cases from solutions that were initially  $4 \times 10^{-6}$  mol dm<sup>-3</sup> in porphyrin. A green powder precipitates from 0.1 mol  $dm^{-3}$  HCl after 5 days. The same phenomenon, peak shift to higher wavelengths and ultimate precipitation is found with both chlorophyll a and b, which apparently produce metastable solutions of microcrystals with different solvent mixtures.<sup>39</sup> This aggregation is rather specific to the  $TPPS_x$  series, as such behaviour is not noted with any of the sulfonated ortho, di-ortho or para substituted porphyrins examined in this study. The  $H_4TPPS_x$ compounds, where the sulfonate groups are partially in the SO<sub>3</sub>H form, could multiply overlap in an edge to edge stairstep fashion, forming aggregates larger than 0.45 µm. This leads to delocalization of the porphyrin  $\pi$  clouds, as evidenced by the absorption maxima shifting towards the red.

#### Acid-Base Equilibria

Many free-base porphyrin molecules,  $H_2P$ , can protonate at the central nitrogen atoms to form the mono-  $(H_3P^+)$  or dications  $(H_4P^{2+})$  in the pH range 0–10.<sup>3</sup> The equilibrium constants are defined as:

$$H_4 P^{2+} \rightleftharpoons H_3 P^+ + H^+; \qquad K_4 \tag{2}$$

$$\mathbf{H}_{3}\mathbf{P}^{+} \rightleftharpoons \mathbf{H}_{2}\mathbf{P} + \mathbf{H}^{+}; \qquad K_{3} \tag{3}$$

The porphyrins were dissolved in 500 cm<sup>3</sup> of a 0.10 mol dm<sup>-3</sup> NaNO<sub>3</sub> solution buffered with  $1 \times 10^{-3}$  mol dm<sup>-3</sup> MES (4-morpholineethane sulfonic acid,  $pK_a = 6.18$ ) for the high pH work, or unbuffered for porphyrins that had  $pK_a$  values below *ca*. 3. The total porphyrin concentrations were near  $10^{-7}$  mol dm<sup>-3</sup> to minimize the presence of dimers. Small volumes of HNO<sub>3</sub> or NaOH solutions were added to change the pH 0.1–0.2 units for each addition, and the absorption spectra were monitored as a function of pH. The relationship between the observed absorbance  $A_x$ , the total

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porphyrin concentration,  $[P]_T$ , and  $[H^+]$  is of the form:

$$\frac{A_x}{[P]_{\rm T}} = \frac{(\varepsilon_2 K_3 K_4 + \varepsilon_3 K_4 [{\rm H}^+] + \varepsilon_4 [{\rm H}^+]^2)}{(K_3 K_4 + K_4 [{\rm H}^+] + [{\rm H}^+]^2)} \tag{4}$$

where  $\varepsilon_2$ ,  $\varepsilon_3$  and  $\varepsilon_4$  are the molar absorptivities of the free base, mono- and di-cations, respectively.  $\varepsilon_2$  and  $\varepsilon_4$  are readily obtained from the absorbance plateau values at high and low pH, and a non-linear least-squares program was used to calculate the best values for  $\varepsilon_3$ ,  $K_3$  and  $K_4$ . Fig. 2 shows a plot of  $A_x/[P]_T vs.$  pH for H<sub>2</sub>T(2,6-F)PPS and the excellent fit to the experimental data with the values of  $pK_3 = 2.5$ ,  $pK_4 =$ 1.8 and  $\varepsilon_3 = (4.0 \pm 0.4) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The  $pK_a$ results for the sulfonated porphyrins, along with the absorption spectra of the free bases and dications are given in Table 1.

Porphyrin  $pK_a$  data are valuable in understanding the relative reactivities of porphyrins and metalloporphyrins. For example,  $pK_3$  values parallel the one-electron reduction potentials of porphyrins to their radical anions<sup>40</sup> and are proportional to the rate constants for acid-catalysed demetallation and to the equilibrium constants for metalloporphyrin formation reactions.<sup>41</sup> The  $pK_3$  values range from 7.1 for T(4-OMe)PPS to 1.8 for T(2,6-Cl)PPS, a factor of over 10<sup>5</sup> in proton affinity. As noted earlier, the number of sulfonic acid groups on the porphyrin has little effect on the proton basicities found at an ionic strength of 0.1 mol dm<sup>-3</sup>. The full mixtures, and compounds isolated from the bands at the centre of the mixture had pK values within  $\pm 0.2$  units of one another. Fig. 3 shows the proportionality between  $pK_3$  and  $pK_4$ , where  $pK_3 = 0.51 + 0.98 pK_4$ .

While the ortho derivatives are less basic, the para compounds are equally basic or more so than  $H_2TPPS_4$ . The high basicity of the 4-OMe and 4-F compounds is due to electron-donating resonance effects between the 4-substituent, the phenyl group(s), and the porphyrin ring, where the overlap is maximum when the rings are coplanar. The ortho substituents provide a steric barrier to such coplanar conformations. Since four protons cannot fit into the central porphyrin cavity, the  $H_4P^{2+}$  and  $H_3P^+$  species are relatively non-planar<sup>42</sup> as compared to  $H_2P$ , and thus deformation accompanies protonation. The flexibility of the porphyrin nucleus is of the order 4 > 2 > (2,6)-substituted, and this is the order of basicities found. Similar results were noted for the positively charged water soluble tetrakis(N-methyl-Xpyridyl)porphyrins,<sup>15</sup> where  $pK_3 = -0.9$  for the ortho (X = 2) derivative, and 1.4 for the para (X = 4) compound. In addition, titrations in non-aqueous solvents also indicate that



Fig. 3 Correlation between  $pK_3$  and  $pK_4$  for a series of water soluble sulfonated porphyrins

uncharged ortho substituted porphyrins are more basic than their para counterparts.<sup>43</sup>

#### Reduction

The porphyrins  $(H_2P)$  and metalloporphyrins (MP) were reduced by radiolysis in deoxygenated aqueous solutions containing  $Pr^iOH$ , as discussed previously.<sup>44</sup>

$$H_2O \rightsquigarrow e_{aq}^-, H^{\bullet}, OH^{\bullet}, H^+, H_2, H_2O_2$$
(5)

$$(CH_3)_2CHOH + OH^{\bullet}(H^{\bullet}) \rightarrow (CH_3)_2COH + H_2O(H_2)$$
(6)

$$H_2P + e_{aq} \rightarrow H_2P^{-} \tag{7}$$

$$H_2P + (CH_3)_2COH \to H_2P^{*-} + (CH_3)_2CO + H^+$$
 (8)

Differential absorption spectra of short-lived  $\pi$ -radical anions (H<sub>2</sub>P<sup>-</sup> and MP<sup>-</sup>) were examined by pulse radiolysis and the spectra of stable products were monitored following  $\gamma$ -radiolysis. The  $\pi$ -radical anions exhibit a broad absorption in the region 600–800 nm, which is independent of pH for MP<sup>-</sup>. The spectra of the  $\pi$ -radical anions of the metal-free porphyrins, however, change with pH due to protonation at a pyrrolic nitrogen.

$$H_2 P^{*-} + H^+ \rightleftharpoons H_3 P^* \tag{9}$$

For  $H_2$ TPPS<sub>4</sub>, the peak shifted from 700 to 840 nm upon increasing the acid concentration. The  $pK_a$  value for the protonation, determined from the dependence of the transient absorbance at 820 nm upon pH, was found to be 9.5, very

Table 1 Protonation equilibrium constants and absorption spectra of substituted H<sub>2</sub>TPPS (25 °C, 0.1 mol dm<sup>-3</sup> ionic strength)

substituents on phenyl <sup>a</sup>		pK4 <sup>b</sup>	$\lambda_{max}/nm$ (relative absorbance)		
	pK3 <sup>b</sup>		free-base porphyrin	diacid porphyrin	
4-OMe	7.1	6.3	418 (78), 520 (2.6), 560 (1.9), 580 (1.7), 640 (1.0)	445 (75), 614 (1.8), 671 (11.6)	
4-F	6.5	5.3	413 (95), 516 (3.8), 553 (1.7), 579 (1.8), 634 (1.0)	433 (99), 547 (0.8), 595 (2.2), 647 (10.3)	
4-Me	4.9	4.9	414 (115), 516 (4.1), 554 (1.8), 579 (1.7), 634 (1.0)	436 (104), 547 (0.8), 593 (2.3), 645 (9.9)	
4-Cl	4.9	4.8	415 (79), 516 (3.1), 557 (1.4), 578 (1.4), 634 (1.0)	437 (77), 597 (2.1), 648 (7.9)	
Н	4.7	4.8	413 (105), 515 (4.0), 552 (1.8), 579 (1.7), 663 (1.0)	435 (101), 546 (0.95), 593 (2.5), 645 (10.0)	
2-OMe	4.1	3.8	418 (54), 517 (3.2), 548 (1.3), 585 (1.5), 641 (1.0)	444 (29.4), 592 (1.8), 648 (3.5)	
2-Me	3.4	2.1	418 (75), 520 (3.4), 551 (1.1), 587 (1.4), 642 (1.0)	437 (62), 548 (0.9), 589 (2.2), 642 (2.2)	
2-Cl	3.3	2.7	417 (75), 518 (4.3), 552 (1.6), 586 (1.9), 639 (1.0)	433 (58), 580 (2.6), 628 (3.3)	
2-F	3.3	3.1	411 (133), 511 (6.5), 545 (1.9), 577 (3.0), 630 (1.0)	428 (143), 540 (1.7), 579 (5.0), 628 (8.7)	
2,6-OMe	3.0	2.6	419 (93), 519 (5.8), 552 (2.1), 586 (2.8), 639 (1.0)	439 (88), 550 (2.0), 583 (4.4), 633 (4.0)	
2,6-F	2.5	1.8	413 (172), 514 (7.8), 547 (2.0), 580 (2.8), 633 (1.0)	431 (145), 579 (5.8), 628 (5.1)	
2,6-Cl	1.8	1.7	417 (165), 518 (8.1), 552 (1.7), 586 (3.4), 639 (1.0)	433 (142), 580 (6.5), 628 (4.0)	

<sup>a</sup> From the literature,  $pK_3$  and  $pK_4$  are 3.4 and 3.2 for T(2,6-Me)PPS,<sup>30</sup> 5.0 and 4.8 for TPPS<sub>4</sub>,<sup>8</sup> and 5.0 and 4.9 for TPPS<sub>3</sub>.<sup>9</sup> <sup>b</sup> Accurate to  $\pm 0.1$ .

similar to that determined previously for the tetra(4-carboxyphenyl)porphyrin.<sup>45</sup> These  $pK_a$  values for the  $\pi$ -radical anions are *ca*. 5 units higher than the corresponding  $pK_3$  for protonation of the third nitrogen in the parent porphyrins. Such enhanced basicity upon electron addition is expected and has been observed for radical anions of various organic molecules.<sup>46</sup>

Stable products are formed by disproportionation of  $MP^{*-}$ ,  $H_2P^{*-}$  or  $H_3P^{*}$ , to yield the porphyrin and the protonated two-electron-reduced species, either chlorin or phlorin. Disproportionation of  $H_3P^{*}$  is likely to result in a phlorin ( $H_3PH$ ).

$$H_3P' + H_3P' \rightarrow H_2P + H_3PH \tag{10}$$

Disproportionation of  $H_2P^{-}$  may produce a phlorin, a phlorin anion ( $H_2PH^-$ ), or a chlorin ( $H_2PH_2$ ). The decay of  $MP^{-}$  may lead to phlorin anion or chlorin.

$$MP^{-} + MP^{-} \rightarrow MP + MP^{2-}$$
(11)

$$MP^{2^{-}} + H^{+}(2H^{+}) \rightarrow MPH^{-}(MPH_{2})$$
(12)

Some metallophlorin anions were unstable in neutral solutions and disproportionated to species absorbing at lower wavelengths which may be the four-electron-reduction product.<sup>13</sup> Generally, these products were also oxidized by  $O_2$  back to the porphyrins.

The spectral changes upon  $\gamma$ -radiolytic reduction of  $H_2TPPS_4$  [Fig. 4(*a*)] show bleaching of the porphyrin peaks and formation of the phlorin absorption near 700 nm. From



Fig. 4 Spectral changes observed upon radiolytic reduction of  $H_2TPPS_4$  to the phlorin (a) and  $ZnTPPS_4$  to the chlorin (b). The porphyrins were irradiated in deoxygenated aqueous solutions containing 1% Pr'OH and borate buffer at pH 9. The solid lines are the spectra before irradiation and the dotted and the dashed lines after consecutive irradiations for 21 (a) or 25 s (b). When the irradiation was continued beyond these points, secondary products began to appear

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the known yield of radicals produced by the radiolysis it is indicated that this product results from a two electron reduction process. Exposure of the phlorin to  $O_2$  recovers the original porphyrin quantitatively within several minutes. The spectrum of the phlorin changes with pH; the peak shifts from 753 nm at low pH to 685 nm at high pH. From the pH dependence of the absorbance at the peak we estimate  $pK_a \approx 6.0$  for the acid-base equilibrium between the phlorin and its anion.

$$H_3PH \rightleftharpoons H_2PH^- + H^+$$
 (13)

The same 685 nm phlorin absorption was also formed when the reduction was performed in 95% MeOH with 0.1 mol dm<sup>-3</sup> Na<sub>2</sub>CO<sub>3</sub>. Similar results were obtained upon reduction of H<sub>2</sub>TPPS<sub>3</sub> and *cis*- and *trans*-H<sub>2</sub>TPPS<sub>2</sub>. At pH 3 the phlorins were produced ( $\lambda_{max} = 750-755$  nm) and at pH 6.7 the phlorin anions were observed ( $\lambda_{max} = 690$  nm).

In contrast with the behaviour of the metal-free porphyrin, ZnTPPS<sub>4</sub> produced mainly the chlorin [Fig. 4(b)] at pH 7–10. Only at a higher pH did the phlorin peak appear, and at pH > 12 the product consisted of the phlorin anion with no detectable chlorin (Table 2). Pd<sup>II</sup>TPPS<sub>4</sub> also yielded mainly the chlorin in neutral solution and the phlorin at high pH. Al<sup>III</sup> and In<sup>III</sup>TPPS<sub>4</sub> were reduced to the chlorin in acidic solutions but at pH  $\ge$  7 the phlorin was the predominant product. Sn<sup>IV</sup> TPPS<sub>4</sub> produced some phlorin even at pH 2. The latter two metalloporphyrins also formed long-lived  $\pi$ radical anions at high pH (Table 2).

It is clear from these results that a major difference exists between the behaviour of porphyrins and metalloporphyrins. Since the  $\pi$ -radical anions of the free base porphyrins can protonate at the nitrogen, their decay is likely to take place via  $H_3P^{\bullet} + H_3P^{\bullet}$  or  $H_3P^{\bullet} + H_2P^{\bullet-}$ , which are expected to be more rapid reactions than  $H_2P^{\bullet-} + H_2P^{\bullet-}$ . Even when the fraction of  $H_3P^{\bullet}$  in equilibrium eqn. (9) is very small, its contribution to the decay may be substantial. As a result, the reduced product is likely to be the phlorin.  $MP^{\bullet-}$  cannot protonate at the pyrrole nitrogens (under mild conditions) and thus the decay leads to the dianion,  $MP^{2-}$ , which subsequently protonates. The results indicate that protonation at the  $\beta$ -pyrrole positions to give chlorin is more likely in acidic

Table 2 Radiolytic reduction of H<sub>2</sub>TPPS<sub>4</sub> and its metal complexes

metal centre	pH	major (minor) products <sup>a</sup>	
(H <sub>4</sub> )	3	753, ph	
$(H_2)$	5-6	753, ph	
-	7-11	685, ph <sup>-</sup>	
Zn <sup>II</sup>	7–10	620, ch	
	11	795, ph <sup>-</sup> (620, ch)	
	12.3	795, ph <sup>-</sup>	
Pd <sup>II</sup>	6.6	600, ch	
	11.2	775, ph <sup>-</sup> (600, ch)	
Cu <sup>II</sup>	10-11	620, ch; 760, ph <sup>-</sup>	
	12.3	760, ph <sup></sup>	
Al <sup>m</sup>	2.8	605, ch	
	7–11	790, ph <sup>-</sup>	
In <sup>m</sup>	1.8-3	606, ch	
	6.6–7	805, ph <sup>-</sup> (ca. 606, ch)	
	10-12.7	785, ph <sup>-b</sup>	
	13.3 (80% PrOH)	726, <i>ca.</i> 860, $InP^{-} \rightarrow 790$ , $ph^{-}$	
Sn <sup>IV</sup>	2–3	610, ch (790, ph <sup>-</sup> )	
	6.6	610, ch, 790, ph <sup>-</sup>	
	10–13	725, 840, SnP <sup>•–</sup>	
	13.3 (80% PrOH)	725, 850, $\text{SnP}^- \rightarrow 825$ , $\text{ph}^-$	

<sup>*a*</sup> The main peaks at 600–900 nm are given, along with their assignment to chlorin (ch), phlorin (ph), phlorin anion ( $ph^-$ ) or  $\pi$ -radical anion (**MP**<sup>-</sup>). <sup>*b*</sup> The change in peak position of the phlorin anion with pH is due to change in axial ligation from water to OH<sup>-</sup>.

solutions, while at high pH the phlorin anion is produced. Furthermore, at any particular pH, the formation of phlorin anion is enhanced by increased electronegativity of the metal centre (which retards protonation). With high metal centre electronegativity and high pH, such as seen with In<sup>III</sup> and Sn<sup>IV</sup> TPPS<sub>4</sub> (Table 2), the  $\pi$ -radical anions are found to be long-lived due to inhibition of protonation, as discussed previously for the corresponding tetrakis(*N*-methyl-4-pyridyl)porphyrins.<sup>11</sup>

Substituents on the phenyl groups of H<sub>2</sub>TPPS<sub>4</sub> also may exert a considerable effect on the site of protonation in the reduced products (Table 3). The (4-Cl), (2-F) and  $H_2(2-OMe)PPS$  are reduced to phlorins, as is  $H_2TPPS_4$ . The (2-Me) and (2-Br) derivatives also are reduced to phlorins, although the peaks of these phlorins are shifted to longer wavelengths. A striking effect is, however, seen with the 2,6disubstituted derivatives, particularly the Me and Cl derivatives, where the predominant product at low pH is the chlorin. Clearly, this product is formed because protonation at the meso position is retarded by the steric effect of the bulky ortho substituents. This steric effect is exerted not only by inhibiting the protons from reaching the meso position but more importantly by preventing the bending necessary for converting the meso carbon into an sp<sup>3</sup> configuration. Such a steric effect probably plays a role also in causing the difference in behaviour between free-base and metal complexes; the latter are less likely to deform because the nitrogens are held in place by the metal centre and thus are more likely to yield chlorins.

Table 4 summarizes the absorption peaks of  $(N-Me)TPPS_4$ in its various acid-base forms and of its Zn complex as well

 Table 3
 Radiolytic reduction of phenyl-substituted H<sub>2</sub>TPPS

substituent	рН	major (minor) products <sup>a</sup>
4-Cl	1.1	760, ph
2-F	1.5	740, ph
2-OMe	1.1	760, ph
2-Me	1.1	ca. 810, pH
2-Cl	$(1 \text{ mol } dm^{-3} \text{ HClO}_4)$	ca. 640, ch
	1.1	640, ch (740, ph)
	6.6, 11	4e; 650, ch
	13	780, ph <sup>-</sup> (650, ch)
2-Br	1.1	ca. 810, ph
2,6-F	1.6	810, ph
	6.6, 11.2	4e (645, ch)
2,6-OMe	1.5	790, ph; 640, ch
	6.6	ca. 790, ph (640, ch)
	11.4	<i>ca.</i> 790, ph
2,4,6-Me	1.7	640, ch
	6.6	820, ph (645, ch)
	11.4	730, ph <sup>-</sup> (645, ch)
2,6-Cl	0.8	640, ch
	2–3	640, ch; 820, ph
	6.6, 11.2	4e (640, ch)
	12.7	705, $P^{-} \rightarrow 820$ , ph (640, ch)

<sup>a</sup> Footnotes as in Table 2.

as their one-electron and two-electron reduction products. Pulse radiolysis results show  $\lambda_{max} = 820$  nm for the  $\pi$ -radical anion at all pH values examined, similar to that of the protonated radical H<sub>3</sub>TPPS<sub>4</sub>, *i.e.* N-protonation and Nmethylation exert similar effects on the spectrum. The peak for the  $\pi$ -radical anion of  $Zn(N-Me)TPPS_4$ , however, is similar to that observed with  $ZnTPPS_4$ .<sup>47</sup> Two-electron reduction of (N-Me)TPPS<sub>4</sub> yields the phlorin in acid solutions and the phlorin anion in basic solution, as in the case of  $TPPS_4$ . The Zn complex also yields the phlorin, in contrast with ZnTPPS<sub>4</sub> which forms the chlorin at the same pH. [It is not possible to test for chlorin formation at a lower pH because Zn(N-Me)TPPS<sub>4</sub> demetallates.] This greater tendency of the  $Zn(N-Me)TPPS_4$  to be reduced to the phlorin may be due to the fact that this macrocycle is already deformed since the Zn and the N-Me groups are located on opposite sides of the mean porphyrin plane.48

In summary, di-ortho substitution on the phenyl rings attached at the meso positions of porphyrins exert a strong steric effect that changes the behaviour of these porphyrins in various ways. Steric crowding inhibits deformation of the porphyrin macrocycle around the meso position and as a result retards protonation of the dianions at this position, thus leading to preferential formation of chlorin rather than phlorin upon reduction. It also inhibits protonation at the central nitrogens, thus decreasing the  $pK_3$  and  $pK_4$  values. Steric crowding forces the phenyl rings into a plane nearly perpendicular to the mean porphyrin plane and thus prevents dimerization and aggregation of the porphyrins.

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<b>Table 4</b> Radiolytic reduction of (N-)	Me)TPPS
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		peaks/nm		
porphyrin	pH	porphyrin	$\pi$ -radical anion	products
$H_3(N-Me)TPPS_4^{2+}$	1.8ª	445, 610 sh 665,	820	750, 850, ph
$H_2(N-Me)TPPS_4^+$	5.4 <sup>a</sup>	440, 570 sh, 616, 662	820	750, 850, ph
H(N-Me)TPPS₄	11.2	434, 544 sh, 587, 666	820	680, ph <sup>-</sup>
Zn(N-Me)TPPS <sub>4</sub>	8.5	430, 440, 552, 600, 650	730	755, ph <sup>-</sup>

<sup>a</sup> From ref. (16),  $pK_3 = 3.0 \pm 0.1$  and  $pK_2 = 9.1 \pm 0.1$  in 0.1 mol dm<sup>-3</sup> NaNO<sub>3</sub>.

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