Aggregation and axial ligand exchange behavior of water-soluble pyrrole-β brominated porphyrins

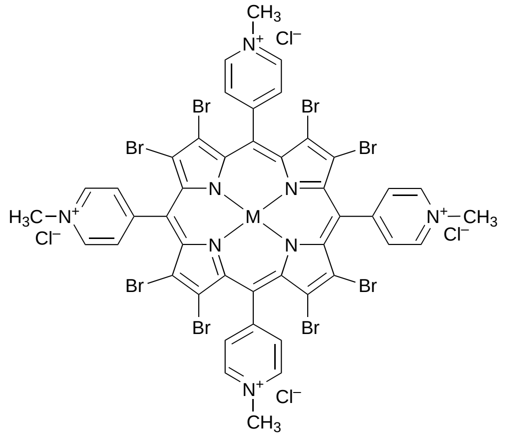
Francis D'Souza,*,† Gollapalli R. Deviprasad and Melvin E. Zandler

Department of Chemistry, The Wichita State University, 1845 Fairmount, Wichita, KS 67260-0051, USA

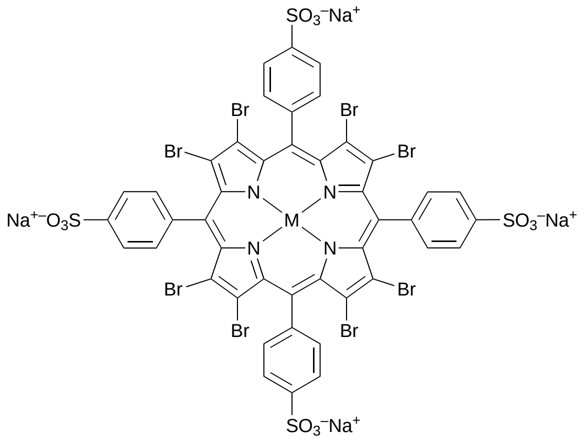
Synthesis of two water-soluble pyrrole-β brominated porphyrins, the tetrachloro salt of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(*N*-methyl-4-pyridinio)porphyrin [tetrakis(*N*-methyl pyridyl)-β-octabromoporphyrin, $(Br_8TMpyP)H_2$] and the tetrasodium salt of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis-(phenyl sulfonate)porphyrin [tetrakis(4-sulfonatophenyl)-β-octabromoporphyrin, $(Br_8TPPS)H_2$] and their zinc(II) derivatives have been reported. The investigated porphyrins are highly non-planar due to the presence of eight bromo substituents at the pyrrole-β positions and four aryl groups at the meso positions. At $I = 0.1$ M and $T = 23$ °C, the two sulfonated derivatives, $(Br_8TPPS)H_2$ and $(Br_8TPPS)Zn$ show a small tendency to aggregate while such behavior is almost negligible for the *N*-methyl pyridyl derivatives. Like the unbrominated water-soluble zinc(II) porphyrin derivatives, the pyrrole-β brominated zinc(II) porphyrins, with one or two water molecules as axial ligand(s) in aqueous solution, undergo ligand exchange reactions with nitrogeneous bases. The calculated equilibrium constant, *K*, for this reaction is found to be smaller in magnitude when compared to that obtained for the corresponding unbrominated zinc(II) porphyrin derivatives. The equilibrium constant values parallel the basicity of the axial ligands.

The rational design of molecular systems comprising of metalloporphyrins to perform specific catalytic functions is an area of active research[1] and porphyrins bearing halogens at the pyrrole-β positions or on the meso aryl groups are found to be effective catalysts. An immediate consequence of β-halogenation is that the porphyrin macrocycle experiences a severe distortion and a great deal of effort has been directed towards understanding how the non-planarity of porphyrins can be related to their chemical and physical properties,[2] in particular, their redox potentials.[3] It was found that the pyrrole-β substituted porphyrins are comparatively easier to oxidize as a result of an extreme non-planar conformation of the porphyrin macrocycle resulting from peripheral steric crowding, and this has indicated that non-planar conformational distortions of tetrapyrroles may play an important role in biological and non-biological systems.[4,5]

To date, several porphyrins with non-planar rings have been synthesized and studied.[4,5] However, studies on water-soluble porphyrins containing non-planar rings are very few.[6–8] Investigations along this line are important not only because of their catalytic applications but also for probing their interactions with DNA and other biological substrates.[9] To promote such chemical reactivities of metalloporphyrins, one of the key factors is to have a better understanding of their aggregation and ligand exchange behavior with axial ligands in solution. Though several studies have reported the aggregation behavior of water-soluble porphyrins with planar rings,[10] no such study on non-planar water-soluble porphyrins has been carried out. Here, we have performed such a study and report the effect of pyrrole-β bromination on the aggregation of water-soluble porphyrins and axial ligand exchange properties of their zinc(II) derivatives with nitrogeneous bases.



$(Br_8TMpyP)M$: M = 2H, Zn^{II}



$(Br_8TPPS)M$: M = 2H, Zn^{II}

Fig. 1 Structural formula of the investigated water-soluble pyrrole-β brominated porphyrins

Towards this, two water-soluble pyrrole-β brominated porphyrins, *viz.*, the tetrachloro salt of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(*N*-methyl-4-pyridinio)porphyrin [tetrakis-(*N*-methylpyridyl)-β-octabromoporphyrin, $(Br_8TMpyP)H_2$] and the tetrasodium salt of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(phenylsulfonate)porphyrin [tetrakis(4-sulfonatophenyl)-β-octabromoporphyrin, $(Br_8TPPS)H_2$] and their zinc(II) derivatives have been synthesized (Fig. 1). These porphyrins are highly non-planar due to the presence of eight bromo

---

† E-Mail: dsouza@wsuhub.uc.twsu.edu

Table 1 Protonation constants for the free-base porphyrins and the optical absorption data for the water-soluble pyrrole-β brominated porphyrins

Porphyrin	pK_2	pK_1	λ/nm (log ε)
$(Br_8TPPS)H_2$	4.83[a]	1.96[a]	356.4 (4.65), 468.0 (5.35), 655.5 (4.09), 740.0 (3.65)
$(TPPS)H_2$	4.99[a]	4.76[a]	418.0 (5.63), 514.0 (4.22), 550.0 (3.85), 587.0 (3.73), 642.0 (3.54)
$(Br_8TMpyP)H_2$[b]	≈2[c]	<1[c]	316.5 (3.14), 498.0 (3.78), 670.8 (2.82), 752.3 (2.44)
$(TMpyP)H_2$	1.8[d]	0.7[d]	424.0 (5.35), 520.0 (4.16), 559.0 (3.96), 587.0 (3.87), 643.0 (3.39)
$(Br_8TPPS)Zn$	—	—	365.0 (4.59), 471.5 (5.37), 652.5 (4.17), 748.5 (4.59)
$(TPPS)Zn$	—	—	422.0 (5.45), 556.0 (4.00), 595.0 (3.63)
$(Br_8TMpyP)Zn$	—	—	333.5 (4.91), 489.0 (5.47), 667.0 (4.43), 760.0 (3.76)
$(TMpyP)Zn$	—	—	436.0 (5.28), 564.0 (4.03), 604.0 (3.53)

[a] From ref. 8. [b] The optical data is for $(Br_8TMpyP)H_3^+$. See text for details. [c] pK_a values of $(Br_8TMpyP)H_2$ are taken from ref. 7. [d] From ref. 11.

substituents at the pyrrole-β positions and four aryl groups at the meso positions. They are also water soluble due to the presence of positive charges at the *N*-methyl pyridyl groups in the case of $(Br_8TMpyP)H_2$ and $(Br_8TMpyP)Zn$ and due to the negative charges of the phenylsulfonato groups in the case of $(Br_8TPPS)H_2$ and $(Br_8TPPS)Zn$.

Experimental

The sodium salt of tetrakis(4-sulfonatophenyl)porphyrin, $(TPPS)H_2$ and tetrakis(*N*-methylpyridyl)porphyrin chloride, $(TMpyP)H_2$ and their zinc(II) derivatives were procured from Mid-Century Chemicals Co. The synthesis of $(Br_8TMpyP)Zn$ and $(Br_8TPPS)Zn$ was achieved by direct bromination of zinc(II) porphyrins in methanol–chloroform using liquid bromine in chloroform followed by purification on a Sephadex LH-20 column.[8] The tetrakis(*N*-methyl pyridyl)-β-octabromoporphyrin derivative was isolated in its protonated form, $(Br_8TMpyP)H_3^+$ while the tetrakis(4-sulfonatophenyl)-β-octabromoporphyrin, $(Br_8TPPS)H_2$ was isolated in the free base form.

Synthesis of $(Br_8TMpyP)H_3^+$

The compound $(Br_8TMpyP)H_3^+$ was synthesized by demetallation of $(Br_8TMpyP)Zn$ according to a literature method.[6] The compound $(Br_8TMpyP)Zn$[8a] (100 mg) was dissolved in 50 cm^3 of concentrated sulfuric acid and stirred for an hour at 0 °C. At the end, 2 equivalents of ammonium hexafluorophosphate were added to precipitate $(Br_8TMpyP)H_3^+$ from the solution as the hexafluorophosphate salt. The crude product was dissolved in acetone and converted to the chloride by a metathesis reaction using tetraethylammonium chloride. Further purification was achieved by gel filtration on a Sephadex LH-20 column using methanol as the eluent. The second fraction was found to contain the desired product. $\lambda_{max}(H_2O)$/nm (log ε): 316.5 (3.14), 498.0 (3.78), 670.8 (2.82) and 752.3 (2.44). ^{1}H NMR in [$^2H_6$]dimethyl sulfoxide (dmso): δ 9.53 (d, 8 H, *o*-H), 9.21 (d, 8 H, *m*-H), 4.66 (s, 12 H, $^+NCH_3$), 1.41 (broad band, ≈3 H, imino-H).

Synthesis of $(Br_8TPPS)H_2$

This was prepared using a procedure different to that reported in the literature[7] but quite similar to that adopted for the synthesis of $(Br_8TMpyP)H_3^+$. About 100 mg of $(Br_8TPPS)Zn$[8b] was demetallated by dissolving it in an excess of sulfuric acid at 0 °C for about 2 h. The solution was then cooled to about −5 °C followed by slow addition of NaOH (1 M), taking all precautions to maintain the temperature below 0 °C. The addition of base was continued until the pH of the solution was around 8. The reaction mixture was evaporated under reduced pressure to yield the compound adsorbed onto sodium sulfate which was recovered as the tetrasodium salt, by Soxhlet extraction of the solid using methanol. The compound was further purified on a Sephadex LH-20 column using methanol as eluent. λ_{max}/nm (log ε), 356.4 (4.65), 468.0 (5.35), 655.5 (4.09), 740.0 (3.65). ^{1}H NMR in [$^2H_6$]dmso: δ 8.86 (d, 8 H, *o*-H), 8.77 (m, 8 H, *m*-H), −1.73 (broad band, ≈2 H, imino-H). The ^{1}H NMR spectra of $(Br_8TPPS)H_2$ and $(Br_8TMpyP)H_3^+$ revealed no peak corresponding to the pyrrole-β protons, indicating a complete conversion of the pyrrole-β protons to bromides. The fast atom bombardment (FAB) mass spectra of both compounds revealed the molecular ion peak corresponding to the octabrominated derivatives.

The presently developed method for the synthesis of $(Br_8TPPS)H_2$ is found to be efficient compared to that reported by Tabata *et al.*[7] which involved bromination of free-base tetraphenylporphyrin by the reaction of *N*-bromosuccinamide, followed by sulfonation using concentrated sulfuric acid at 90 °C for 2 d. Here, the product was isolated in the tetrasulfonic acid form.

The UV/VIS spectral measurements were carried out with a Shimadzu Model 1600 UV/VIS spectrophotometer. A matched pair of quartz cuvettes were used for the spectral measurements. All the spectral measurements were carried out at a temperature of 23 °C, at a constant ionic strength of $I = 0.1$ M in NaCl (0.1 M). Solutions were freshly prepared using deionized water for spectral analysis and were protected from direct light. Proton NMR spectra were recorded on a Bruker 270 MHz spectrometer.

Results and Discussion

The investigated compounds show optical absorption spectra characteristic of pyrrole-β brominated porphyrins,[5b] *i.e.* a red-shifted Soret band and less intense visible bands which are also red-shifted. Table 1 lists the absorption maxima for both the brominated and the corresponding unbrominated porphyrin derivatives along with their pK_a values from the literature. Due to the presence of electron-withdrawing bromines on the pyrrole-β positions, the protonation of the brominated porphyrins is generally more difficult than the corresponding unbrominated porphyrin derivatives. Likewise, porphyrins bearing negative charges on the ring periphery, *i.e.* sulfonato phenyl groups at the meso positions, are easier to protonate due to the induced electronic effects of the negative charges when compared with those bearing positive charges, *i.e.* *N*-methylpyridyl groups at the meso positions.

Aggregation behavior

It is well known that the properties of water-soluble porphyrins of the meso-substituted variety are dependent on the type of charges present at the periphery of the molecule.[10] Porphyrins having negative charges at the periphery (*e.g.* meso-tetrasulfonatophenyl porphyrin) are considerably more basic and have much greater tendency to aggregate than those with positive charges at the periphery [*e.g.* meso-tetrakis(*N*-methylpyridyl)porphyrin]. The aggregation behavior is often monitored by optical absorption, fluorescence (steady-state and time-resolved), temperature jump and more recently by resonance-Raman methods.[10] Evidence for the π–π stabilization of the aggregated form have been obtained from these studies. In the present study, we have employed an optical absorption

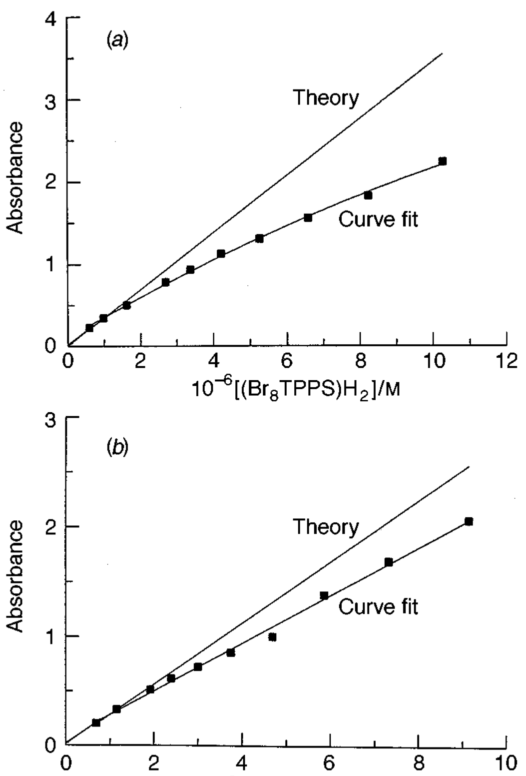


Fig. 2 Beer's law experiment for (*a*) $(Br_8TPPS)H_2$ and (*b*) (Br$_8$TPPS)-Zn in aqueous solution, pH 7.0 at the Soret band. The theoretical plots were constructed from the ε values obtained for the individual species from the lowest concentrated solution

technique to investigate the aggregation behavior of the water-soluble non-planar porphyrins. Spectral measurements in aqueous solution in the range 350–800 nm have been carried out for all the four porphyrin derivatives at a constant ionic strength of 0.1 M.

The aggregation behavior of all four non-planar pyrrole-β brominated porphyrins have been investigated in aqueous solution containing KNO_3 (0.1 M). Beer's law experiments are conducted in the concentration range 5×10^{-7} to 1.8×10^{-5} M while monitoring the intensity of the Soret band. It is found that for three of the four investigated porphyrins, *viz*., (Br$_8$TPPS)Zn, $(Br_8TMpyP)H_3{}^+$ and (Br$_8$TMpyP)Zn, the absorbance is directly proportional to concentration, with no appreciable changes in the position of the Soret band. However, for $(Br_8TPPS)H_2$, this behavior is different as revealed by a deviation of the plot at higher concentrations [Fig. 2(*a*)]. Theoretical Beer's plots for each of these investigated porphyrins have also been constructed by using the ε values calculated for the solutions at their lowest concentration, assuming that at this concentration only the monomeric species is the dominant one. Thus, a comparison between the theoretical and experimental plots could be used to monitor the aggregation behavior with increase in concentration. A greater deviation of the experimental plot from the theoretical plot is suggestive of the formation of aggregated species at higher concentration. It is found that in the case of $(Br_8TMpyP)H_3{}^+$ and (Br$_8$TMpyP)Zn, the experimental plots do not deviate appreciably from the theoretical plots indicating negligible amounts of aggregation. Interestingly, the investigated (Br$_8$TPPS)Zn and $(Br_8TPPS)H_2$ porphyrins show a greater deviation between theoretical and experimental plots (Fig. 2) indicating the formation of considerable amounts of aggregated species at higher concentrations. A comparison of these results with that reported for the unbrominated porphyrins in the literature[10] and also by comparing the plots constructed for the unbrominated porphyrins using a procedure similar to that adopted in the present study (plots not shown) suggests that the overall tendency to form the aggregated species is relatively smaller for the investigated non-planar porphyrins. By neglecting any adsorption of porphyrin on the inner walls of the cell, two effects could be mainly visualized to explain these observations: (*i*) charges on the periphery of the porphyrin macrocycle and (*ii*) the non-planarity of the porphyrin ring.

As evident from the protonation constant values, $(Br_8TPPS)H_2$ is considerably more basic due to the negative charges at the ring periphery compared to $(Br_8TMpyP)H_2$ which has positive charges on the ring periphery. A similar argument could be used for their respective zinc(II) derivatives. An immediate consequence of the negative charges on the porphyrin periphery and the higher basicity is the greater tendency of aggregation in these porphyrins than in those having positive charges at the ring periphery.[10b] In addition to this, the non-planar nature of the porphyrin ring could also influence the aggregation behavior of these porphyrins.

X-Ray structural studies of the octabrominated porphyrins have shown a saddle-shaped non-planarity of the porphyrin ring.[3a,5c] In these structures the pyrrole rings are approximately co-planar with bromo substituents tilted alternatively up and down relative to the mean porphyrin plane defined by the 24-atom core, as well as being twisted relative to this plane. The meso-phenyl rings show similar alternating vertical displacements and their mean planes are rotated toward the 24-atom core mean plane of the porphyrins in order to minimize the intramolecular steric interactions between the bromines and the *ortho* and *ortho'* carbon atoms of the meso-phenyl rings. As a result of these ring perturbations, one would expect a greater intermolecular distance between the two porphyrins in the aggregated form, a direct consequence of which is a smaller π–π stabilization of the aggregated species in solution, and hence formation of such a species is not a favoured process for non-planar porphyrins. However, the sulfonated porphyrins, especially the free-base derivative shows a higher tendency to aggregate which could be due to the higher basicity of the porphyrin ring. For this one may argue that the effects induced by the negative charges on the ring periphery are higher than that caused by the non-planarity of the porphyrin ring.

Axial ligation

A number of studies have reported the Lewis acid–base interaction between metalloporphyrin and nitrogeneous bases in non-aqueous media,[5c,12] and in a few cases in aqueous media by using water-soluble porphyrins.[13] Of these studies, several have employed a zinc(II) porphyrin since this metalloporphyrin is known to co-ordinate to a single axial ligand to form a five-co-ordinated complex with 1 : 1 stoichiometry in solution.[12,14] Due to this simplicity of the zinc(II) porphyrin, we have, in the present study chosen zinc(II) porphyrins to probe the effects induced by the bromine substituents at the porphyrin macrocycle on the axial ligand exchange properties.

It is known that water-soluble zinc(II) porphyrins with relatively planar rings, exist as five-co-ordinated species in aqueous solution with water as the fifth axial ligand.[14] This might also be the case for the investigated non-planar zinc(II) porphyrins, though the presence of another weakly co-ordinated water molecule, as a sixth ligand cannot be excluded. A control experiment involving addition of water to methanolic solutions of zinc(II) derivatives revealed a systematic spectral shift indicating co-ordination of water to zinc(II) porphyrins. Hence, in aqueous solutions, addition of stronger axial ligands such as nitrogeneous bases (B) would replace the co-ordinated water molecule as shown in equation (1). The equilibrium constant,

$$(P)Zn:H_2O + B \rightleftharpoons (P)Zn:B + H_2O$$

$$K = \frac{[(P)Zn:B]}{[(P)Zn:H_2O][B]} \quad (1)$$

K, determined using the method of Scatchard[15] for the ligand exchange reactions [equation (1)] of the zinc(II) porphyrins with six water-soluble bases with varying pK_a of the conjugate acids have been measured. Typical absorption spectra of (Br$_8$TMpyP)Zn in aqueous solution on addition of increasing amounts or pyridine are shown in Fig. 3. Addition of bases leads to a small blue shift with an increase in intensity of the Soret band and new absorption bands in the visible region. The decrease in the absorbance at 664 nm and increase at 617 nm are monitored for the evaluation of the equilibrium constant. The calculated equilibrium constant for the ligand exchange is given in Table 2 for the investigated zinc(II) porphyrin derivatives. For a given axial ligand, the equilibrium constant, K, follows the order: (Br$_8$TMpyP)Zn < (TMpyP)Zn < (Br$_8$TPPS)Zn < (TPPS)Zn, *i.e.* smaller K values for a brominated porphyrin compared to that of the related unbrominated porphyrin.

The observed trends in the K values in the present study contradict those reported for the ligand addition reactions of pyrrole-β brominated zinc(II) tetraphenylporphyrin in toluene for which the K value for base-binding was an order of magnitude higher than that of the corresponding unbrominated zinc(II) porphyrin.[5f] This could be rationalized using the equilibrium process according to equation (1). Under the present solution conditions, the water-soluble porphyrin which exists as a five-co-ordinated complex undergoes a ligand exchange reaction with the added base unlike the ligand addition reaction of pyrrole-β brominated zinc(II) tetraphenylporphyrin. Porphyrins with a less basic ring bind the water molecule more strongly than those with a more basic ring. As a result, replacing the strongly bound water molecule of less basic porphyrins with added base is relatively more difficult and hence a smaller equilibrium constant could be expected for this process. In order to verify this, a control experiment involving (Br$_8$TMpyP)Zn and pyridine in acetonitrile was carried out. The equilibrium constant, K, for the five-co-ordinated complex was found to be 7940 M^{-1} indicating stronger complex formation between (Br$_8$TmPyP)Zn and pyridine.

Fig. 4 shows the relationship that exists between log K and the pK_a values of the conjugate acids of the nitrogeneous bases. Linear plots obtained for the investigated porphyrins indicate the occurrence of ligand exchange reactions with the added base. The slope of the straight line is indicative of the ability of a given porphyrin to undergo the equilibrium reaction described in equation (1) with respect to the basicity of the axial ligands. The calculated slope follows the order: (Br$_8$TMpyP)Zn > (TPPS)Zn ≈ (Br$_8$TPPS)Zn ≈ (TMpyP)Zn indicating comparatively higher effects for the porphyrin with the least basic ring, (Br$_8$TMpyP)Zn.

Conclusion

In summary, the synthesized water-soluble brominated porphyrins are less basic compared to the corresponding unbrominated porphyrin derivatives as a consequence of the pyrrole-β bromination. The investigated non-planar porphyrins show a small tendency to aggregate when compared with the corresponding unbrominated derivatives due to the reduced ring basicity and non-planarity of the macrocycle which would make the π–π stabilization of the porphyrin rings in the aggregated form less favorable. The smaller values of the equilibrium constant, K, calculated for the ligand exchange reaction with nitrogeneous bases also reflect on the low basicity of the porphyrin ring for which the calculated K values parallel the basicity of the axial ligands.

Acknowledgements

The authors are thankful to the National Science Foundation under Grant No. EPS-9550487 and matching support from the State of Kansas for supporting this work.

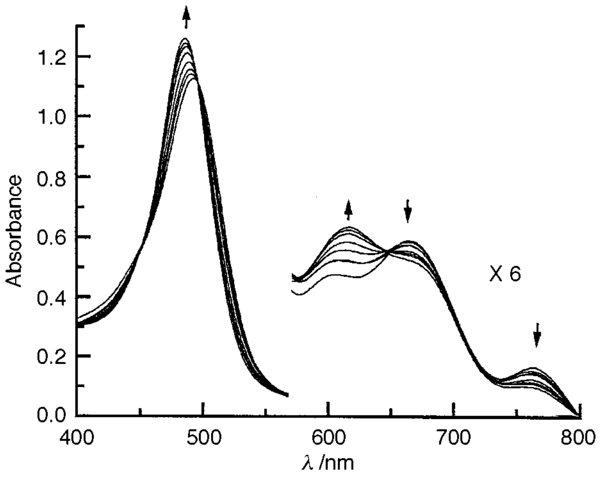


Fig. 3 Optical absorption spectrum of (Br$_8$TMpyP)Zn (1 μM) in water on successive additions of pyridine at 25 °C

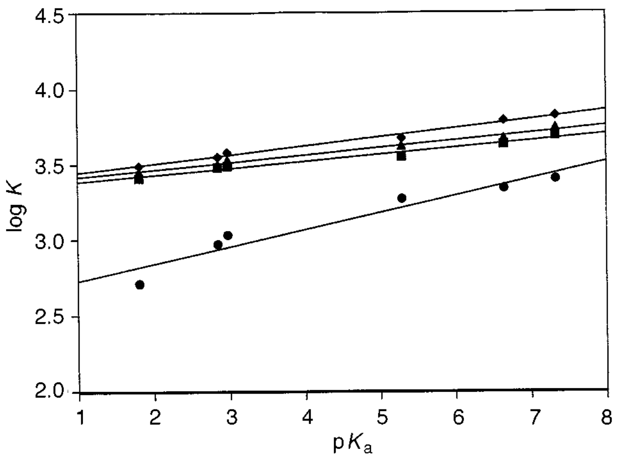


Fig. 4 Relationship between the ligand basicity (σ donor strength) and log K for (◆) (TPPS)Zn, (▲) (Br$_8$TPPS)Zn, (■) (TMpyP)Zn and (●) (Br$_8$TMpyP)Zn in aqueous solution, pH 7.0, I = 0.1 M

Table 2 Equilibrium constants* for the axial ligand exchange reactions of water-soluble zinc(II) porphyrins with nitrogeneous bases

		$10^3\ K/\text{M}^{-1}$			
Axial ligand	pK_a	(TMpyP)Zn	(TPPS)Zn	(Br$_8$TMpyP)Zn	(Br$_8$TPPS)Zn
4-Cyanopyridine	1.81	2.60	3.07	0.51	2.85
3-Chloropyridine	2.84	3.06	3.59	0.93	3.20
3-Fluoropyridine	2.97	3.10	3.80	1.08	3.40
Pyridine	5.29	3.80	4.67	1.87	4.20
Imidazole	6.65	4.30	6.13	2.19	4.70
1-Methylimidazole	7.33	4.90	6.67	2.52	5.56

* The estimated uncertainty in the K values is ± 5%.

References

1 *Metalloporphyrins in Catalytic Oxidations*, ed. R. A. Sheldon, Marcel Dekker, New York, 1994; M. W. Grinstaff, M. G. Hill, J. A. Labinger and H. B. Gray, *Science*, 1994, **264**, 1311; A. R. Battersby, C. J. R. Fookes, G. W. J. Matcham and E. McDonald, *Nature* (*London*), 1980, **285**, 17.

2 K. M. Barkigia, L. Chantranupong, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1988, **110**, 7566; J. Fajer, K. M. Barkigia, K. M. Smith, E. Zhong, E. Gudowska-Nowak and M. Newton, in *Reaction Centers of Photosynthetic Bacteria*, ed. M. E. Micheal Beyerle, Springer-Verlag, Berlin, 1990, p. 367.

3 (*a*) P. Ochsenbein, K. Ayougou, D. Mondon, J. Fischer, R. Weiss, R. N. Austin, K. Jayaraj, A. Gold, J. Terner and J. Fajer, *Angew. Chem.*, 1994, **33**, 348; (*b*) K. M. Kadish, F. D'Souza, A. Villard, M. Autret, E. V. Caemelbecke, A. Bianco and P. Tagliatesta, *Inorg. Chem.*, 1994, **33**, 5169; (*c*) M. Ravikanth and T. K. Chandrashekar, *Struct. Bonding* (*Berlin*), 1995, **82**, 105.

4 K. M. Barkigia, M. D. Berber, J. Fajer, C. J. Medforth, R. W. Renner and K. M. Smith, *J. Am. Chem. Soc.*, 1990, **112**, 8851; J. A. Shelnutt, C. J. Medforth, M. D. Berber, K. M. Barkigia and K. M. Smith, *J. Am. Chem. Soc.*, 1991, **113**, 4077; K. M. Barkigia, R. W. Renner, L. R. Furenlid, C. J. Medforth, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1993, **115**, 3627; S. Gentemann, C. J. Medforth, T. P. Forsyth, D. J. Nurco, K. M. Smith, J. Fajer and D. Holten, *J. Am. Chem. Soc.*, 1994, **116**, 7363; M. W. Renner, K. M. Barkigia, Y. Zhang, C. J. Medforth, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1994, **116**, 8582; W. Jentzen, J. D. Hobbs, M. C. Simpson, K. K. Taylor, T. Ema, N. Y. Nelson, C. J. Medforth, K. M. Smith, M. Veyrat, M. Mazzanti, R. Ramasseul, J.-C. Marchon, T. Takeuchi, W. A. Goddard III and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1995, **117**, 11 085; S. Tsuchiya, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 716; J. Takeda, T. Ohya and M. Sato, *Chem. Phys. Lett.*, 1991, **183**, 384; C. J. Medforth, M. O. Senge, K. M. Smith, L. D. Sparks and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1992, **114**, 9859; S. Tsuchiya, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1475; J. Takeda, T. Ohya and M. Sato, *Inorg. Chem.*, 1992, **31**, 2877; J. D. Hobbs, S. A. Majumder, L. Luo, G. A. Sickelsmith, J. M. E. Quirke, C. J. Medforth, K. M. Smith and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1994, **116**, 3261; M. O. Senge and K. M. Smith, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 923.

5 (*a*) T. G. Traylor and S. Tsuchiya, *Inorg. Chem.*, 1987, **26**, 1338; (*b*) P. Bhyrappa and V. Krishnan, *Inorg. Chem.*, 1991, **30**, 239; (*c*) D. Mandon, P. Ochsenbein, J. Fischer, R. Weiss, K. Jayaraj, A. Gold, P. S. White, O. Brigaud, P. Battioni and D. Mansuy, *Inorg. Chem.*, 1992, **31**, 2044; (*d*) F. D'Souza, A. Villard, E. V. Caemelbecke, M. M. Franzen, T. Boschi, P. Tagliatesta and K. M. Kadish, *Inorg. Chem.*, 1993, **32**, 4142; (*e*) P. Bhyrappa, M. Nethaji and V. Krishnan, *Chem. Lett.*, 1993, 869; (*f*) P. Bhyrappa, V. Krishnan and M. Nethaji, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1901; (*g*) E. Watanabe, S. Nishimura, H. Ogoshi and Z. Yoshida, *Tetrahedron*, 1975, **31**, 1385; (*h*) L.-G. Gong and D. Dolphin, *Can. J. Chem.*, 1985, **63**, 401; (*i*) L.-C. Gong and D. Dolphin, *Can. J. Chem.*, 1985, **63**, 406; (*j*) G.-Z. Wu, W.-X. Gan and H.-K. Leung, *J. Chem. Soc.*, *Faraday Trans.*, 1991, **87**, 2933; (*k*) M. O. Senge, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 3539.

6 R. A. Richards, K. Hannons, M. Joe and G. M. Miskelly, *Inorg. Chem.*, 1996, **35**, 1940.

7 M. Tabata, J. Nishimoto, A. Ogata, T. Kusano and N. Nahar, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 673.

8 (*a*) F. D'Souza, G. R. Deviprasad and Y.-Y. Hsieh, *J. Electroanal. Chem.*, 1996, **411**, 167; (*b*) F. D'Souza, Y.-Y. Hsieh and G. R. Deviprasad, *J. Electroanal. Chem.*, 1997, **426**, 17.

9 R. F. Pasternack, C. Bustamane, P. J. Collings, A. Giannetto and E. J. Gibbs, *J. Am. Chem. Soc.*, 1993, **115**, 5393 and refs. therein; D. R. McMillin, F. Liu, K. A. Meadows, T. K. Aldridge and B. P. Hudson, *Coord. Chem. Rev.*, 1994, **132**, 105 and refs. therein.

10 (*a*) L. L. Shipman, T. M. Cotton, J. R. Norris and J. J. Katz, *J. Am. Chem. Soc.*, 1976, **98**, 8222; (*b*) R. F. Pasternack, P. R. Huber, P. Boyd, G. Engasser, L. Francesconi, E. Gibbs, P. Fasella, G. C. Venturo and L. deC. Hinds, *J. Am. Chem. Soc.*, 1972, **94**, 4511; (*c*) R. F. Pasternack, L. Francesconi, D. Raff and E. Spiro, *Inorg. Chem.*, 1973, **12**, 2606; (*d*) K. Kano, T. Nakajima, M. Takei and S. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1281; (*e*) D. L. Akins, H.-R. Zhu and C. Guo, *J. Phys. Chem.*, 1996, **100**, 5420; (*f*) F. J. Vergeldt, R. B. M. Koehort, A. van Hoek and T. J. Schaafsma, *J. Phys. Chem.*, 1995, **99**, 4397.

11 R. F. Pasternack, N. Sutin and D. H. Turner, *J. Am. Chem. Soc.*, 1976, **98**, 1908.

12 M. Nappa and J. S. Valentine, *J. Am. Chem. Soc.*, 1978, **100**, 5075; G. C. Vogel and J. R. Stahlbush, *Inorg. Chem.*, 1977, **16**, 950; O. W. Kolling, *Inorg. Chem.*, 1979, **18**, 1175; R. S. Drago, M. K. Kroeger and J. R. Stahlbush, *Inorg. Chem.*, 1981, **20**, 307; J. Cole, G. C. Curthoys, E. A. Magnusson and N. J. Phillips, *Inorg. Chem.*, 1977, **11**, 1024.

13 R. F. Pasternack and M. A. Cobb, *J. Inorg. Nucl. Chem.*, 1973, **35**, 4327; R. F. Pasternack, M. A. Cobb and N. Sutin, *Inorg. Chem.*, 1975, **14**, 866; R. F. Pasternack, E. Spiro and M. Teach, *J. Inorg. Nucl. Chem.*, 1974, **36**, 599; H. J. Schneider and M. X. Wang, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 413; H.-J. Schneider and M. X. Wang, *J. Org. Chem.*, 1994, **59**, 7464 and refs. therein.

14 B. Shah and P. Hambright, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3420.

15 (*a*) G. Scatchard, *Ann. N.Y. Acad. Sci.*, 1949, **51**, 661; (*b*) W. R. Carper, C. M. Buess and G. R. Hipp, *J. Phys. Chem.*, 1970, **74**, 4229.

Received 10*th April* 1997; *Paper* 7/02456H