Spectral and Electrochemical Investigations on the "Tail-On" and "Tail-Off" Mechanism in Pyridine Covalently Bound Zinc(II) Porphyrins

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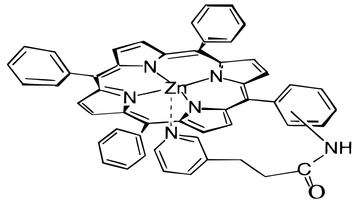
Introduction

Over the years, a number of studies have reported porphyrins with covalently attached axial ligand(s) as model compounds for the study of the mechanism of various biological reactions, viz., hemoxygenation, cytochrome oxidase and peroxidase, and others.[1−3] Various spectroscopic studies have revealed the existence of stable five- and six-coordinate metalloporphyrins,[4−24] thus mimicking the active site of various heme proteins in which axial ligands are provided to the heme by side chains of the protein entity.

In the present study, we are particularly interested in examining the effect of the appended pyridine on coordinating the metal center with respect to the position of the linkage. For this reason, we have synthesized both the *ortho* and *meta* substituted zinc(II) porphyrin derivatives (Chart 1) and report their spectral and electrochemical behavior. It is observed that the ortho substituted derivative exists as a stable pentacoordinated complex an observation similar to that reported by Walker and Benson.[14] Interestingly, for the *meta* derivative, a temperature dependent "tail-on" and "tail-off" type of binding mechanism is operative. Either a tetra- or pentacoordinated zinc(II) complex could be generated depending on the solution conditions for this model system in which the chain length of the side arm is just enough to coordinate the central metal ion.

Chart 1



ortho: ZnP*o*~Py
meta: ZnP*m*~Py

Furthermore, while the redox behavior of zinc(II) porphyrin in presence of externally added pyridine is well-known,[25−27] nothing is known about systems in which the pyridine is covalently attached to the porphyrin entity. Also, a two-electron oxidation process leading directly to the formation of a porphyrin dication has been reported for porphyrins possessing four amide bonds located in the immediate vicinity of the porphyrin ring, such as "picket fence" porphyrin (TpivPP)Cu, where TpivPP is the dianion of *meso*-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphyrin and "basket handle" porphyrins of Cu, Zn, and Mg central metal ions.[28−32] One might expect a similar redox behavior for a porphyrin bearing a single amide bond. Therefore, it would be of interest to examine the electrochemical properties of porphyrins possessing covalently attached pyridine through an amide bond such as those shown in Chart 1. The present investigation deals with these aspects.

Experimental Section

Benzonitrile (Aldrich) for electrochemical experiments was distilled over P_2O_5 under vacuum. Toluene and CH_2Cl_2 were purified according to the standard methods.[33] Pyridine (Aldrich) was used without further purification. Tetra-*n*-butylammonium perchlorate (TBAP) (Kodak) was recrystallized from ethyl alcohol. All other reagents were of analytical grade and used without further purification unless otherwise indicated.

Synthesis of Pyridine-Appended Zinc(II) Tetraphenylporphyrins. The synthesis of (5,10,15-triphenyl-20-(*o*-(((3′-pyridyl propoxy)carbonyl)amino)phenyl)porphyrinatozinc(II), ZnP*o*~Py, was carried out using methods described in the literature.[14] ^1H NMR in $CDCl_3$, δ in ppm: 8.73−8.92 (m, 8H, β-pyrrole protons), 6.16, 5.42, 2.40, 2.18 (d, m, d, s, 4H, pyridyl protons), 7.66−7.83 (m, 9H, meta and para protons of the triphenyl entity), 8.20−8.26 (m, 6H, ortho protons of the triphenyl entity), 8.37, 8.11, 7.94 (4H, substituted phenyl protons).

The free base 5,10,15-triphenyl-20-(*m*-amionophenyl)porphyrin was synthesized using earlier published methods.[34] 3-Pyridyl propionic acid was prepared by dichromate oxidation of 3-pyridinepropanol (Aldrich). The acid chloride of 3-pyridylpropionic acid (100 mg), obtained by treating the acid with thionylchloride, was condensed with 5,10,15-triphenyl-20-(*m*-amionophenyl)porphyrin (30 mg) in dichloromethane

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(50 mL) containing pyridine (2 mL) for 30 min. The reaction mixture was dried under vacuum and the desired compound, 5,10,15-triphenyl-20-(*m*-(((3′-pyridylpropoxy)carbonyl)amino)phenyl) porphyrin, H$_2$P*m*∼Py was obtained by purification over basic alumina using chloroform as eluent. Zinc(II) insertion was carried out using zinc(II) acetate tetrahydrate by literature methods.[35] **H$_2$P*m*∼Py**: ^{1}H NMR in CDCl$_3$, δ in ppm, 8.90 (8H, m, β-pyrrole protons), 7.82 (m, 9H, meta and para protons of the tripheyl entity), 8.15 (m, 6H, ortho protons of the triphenyl entity), 7.17, 7.45, 8.02, 8.20, 8,41 (8H, pyridyl and substituted phenyl protons), 2.61, 3.05 (d, 4H, CH$_2$ H). The ^{1}H NMR spectrum of **ZnP*m*∼Py** exhibited a complex peak pattern for the appended pyridyl and CH$_2$ protons at room temperature due to the presence of an equilibrium between the tetra and penta coordinated species.

Instrumentation. The UV−visible spectral measurements were carried out with a Shimadzu Model 1600 UV−visible spectrophotometer. ^{1}H NMR studies were carried out on a Bruker 270 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Cyclic voltammograms were obtained with an IBM Model EC 225 voltammetric analyzer or on a EG&G Model 263A potentiostat using a three-electrode system. A platinum button or glassy carbon electrode was used as the working electrode. A platinum wire served as the counter electrode and a saturated calomel electrode (SCE) separated from the test solution by a fritted supporting electrolyte/solvent bridge, was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard and in benzonitrile, containing 0.1 M TBAP, its $E_{1/2}$ is found to be 0.41 V. Bulk electrolysis was carried out using a EG&G PAR Model 377A coulometry cell system.

Results and Discussion

It is now well-known that the (tetraphenylporphyrinato)zinc(II), ZnTPP, forms pentacoordinated complexes with coordinating ligands.[36−40] On complexing ZnTPP with an axial ligand, two effects are often seen in the UV−visible spectrum *viz.*, a red shift of the entire spectrum relative to that of ZnTPP and an increase in the $\epsilon_\alpha/\epsilon_\beta$ ratio of the two visible bands. Thus, one could use the wavelength shift and intensity ratio of the visible bands as a measure of the degree of complexation. This property of zinc(II) porphyrin has been utilized in the present study to examine the complexation behavior of the pyridine-appended porphyrins.

The absorption spectrum of the synthesized compounds along with ZnTPP as a reference compound is shown in Figure 1a. ZnTPP in chloroform exhibits bands in the visible region at 549 nm (β band) and 588 nm (α band), with an intensity ratio $\epsilon_\alpha/\epsilon_\beta$ equal to 0.16. Upon intermolecular complexation with pyridine (2 mol), the absorption bands experience a red shift of ∼15 nm. In accordance with the literature results,[36] the intensity ratio of these bands increases from 0.16 to 0.42. Similarly, the absorption spectrum of ZnP*o*∼Py, in which the appended pyridine is intramolecularly coordinated to the metal,[14,23] also experiences a red shift with peak maxima located at 562 and 603 nm. The intensity ratio $\epsilon_\alpha/\epsilon_\beta$ for this complex is found to be equal to 0.41. It may be mentioned here that varying the temperature of the solution containing ZnP*o*∼Py did not result in any appreciable change in the spectrum with regard to the absorption wavelength and the intensity ratio.

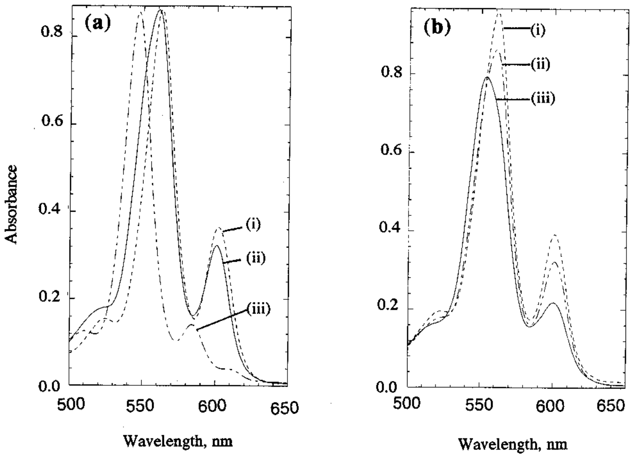
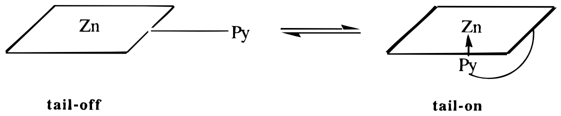


Figure 1. Optical absorption spectra of (a) (i) ZnP*o*∼Py, (ii) ZnP*m*∼Py and (iii) ZnTPP in chloroform at room temperature and (b) ZnP*m*∼Py at different temperatures, (i) 10 °C, (ii) 25 °C, and (iii) 60 °C, in toluene.

Scheme 1



Interestingly, the spectrum of the *meta* derivative, ZnP*m*∼Py reveals spectral features intermediate between the tetracoordinated ZnTPP and pyridine ligated pentacoordinated ZnTPP. ZnP*m*∼Py exhibits peaks at 558 and 600 nm at 22 °C with an intensity ratio of 0.36 indicating the presence of both tetra- and pentacoordinated species in solution (Scheme 1). Further studies reveal that the equilibrium shifts to the left or right with variation in the temperature (Figure 1b). At 60 °C, ZnP*m*∼Py exhibits absorption bands at 550 and 598 nm with an intensity ratio of 0.28. As the temperature is lowered, the formation of pentacoordinated complex is favored and a complete conversion is achieved at 10 °C. At this temperature, the absorption bands of ZnP*m*∼Py are located at 561 and 603 nm with an intensity ratio of 0.41. The equilibrium constant K, calculated for this process (Scheme 1) is found to be 2.99 ± 0.20 at 22 °C with a $\Delta H = -10.8$ kcal/mol and $\Delta S = 33$ cal/(deg·mol) The calculated K value for the *meta* derivative is nearly 3 orders of magnitude smaller than that reported for the *ortho* derivative, ZnP*o*∼Py.[14] It may be mentioned here that the K values do not change appreciably in the concentration range of 2×10^{-5} to 9×10^{-5} M, indicating the absence of any significant intermolecular type of complexation.

Electrochemistry. Cyclic voltammograms for the oxidation of the investigated complexes are shown in Figure 2, and the data are summarized in Table 1. ZnTPP undergoes two one-electron reversible oxidations in non-aqueous solvents.[27] In benzonitrile, containing 0.1 M TBAP, these two reversible processes are located at $E_{1/2} = 0.71$ and 1.07 V vs SCE. On complexing ZnTPP with pyridine, the first oxidation process gets negatively shifted and is located at $E_{1/2} = 0.69$ V vs SCE. However, the second oxidation process becomes irreversible and shows a new peak at $E_{pc} \sim 0.30$ V during the cathodic scan of the potential (Figure 1b). This new electrode process at $E_{pc} = 0.30$ V has been ascribed to the reduction of the chemical species generated at the electrode surface, and this chemical species has been spectrally identified to be an isoporphyrin, a chemical product in which a pyridine is attached to the porphyrin macrocycle either at the *meso* position[25] or at the pyrrole β-position.[41,42] Similar to the results of pyridine-bound ZnTPP, the oxidation potentials of ZnP*o*∼Py are also negatively shifted (see Table 1). The first oxidation is a reversible, one-electron

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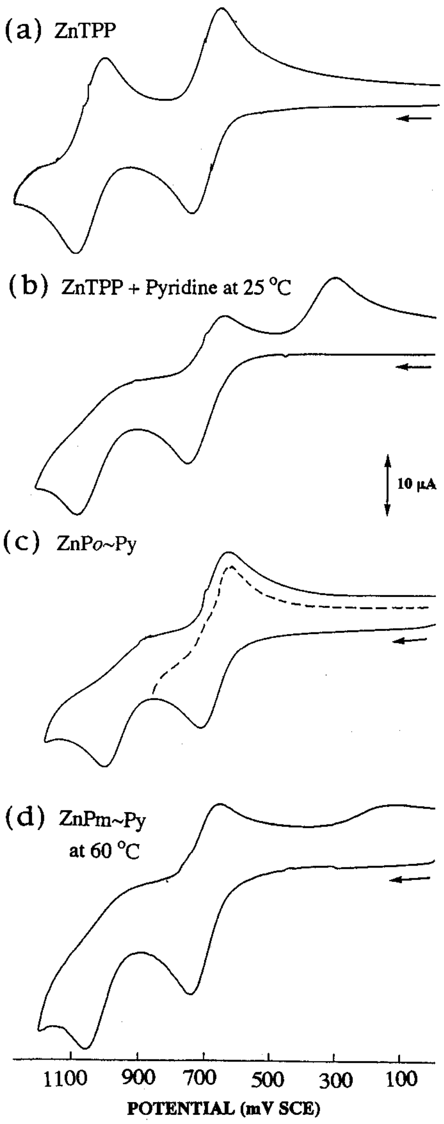

Figure 2. Cyclic voltammograms illustrating the oxidation of (a) ZnTPP, (b) ZnTPP + pyridine (5 equiv), (c) ZnP*o*∼Py and (d) ZnP*m*∼Py (at 60 °C) in benzonitrile containing 0.1 M TBAP. Scan rate = 100 mV/s.

Table 1. Half-Wave Potentials for Oxidation and Reduction of the Investigated Zinc(II) Porphyrins[a]

compound	2nd oxidn	1st oxidn	1st redn
ZnTPP	1.07	0.71	−1.44
ZnTPP + Py	1.07[b]	0.69	−1.52
ZnP*o*∼Py	1.02[b]	0.68	−1.50
ZnP*m*∼Py	1.06[b]	0.70	−1.50

[a] In benzonitrile containing 0.1 M TBAP. [b] E_{pa} at 0.1 V/s.

process and occurs at $E_{1/2} = 0.68$ V while the second oxidation process is quasireversible and is located at $E_{pa} = 1.02$ V at a scan rate of 0.1 V/s (Figure 2c). No new electrode processes corresponding to the formation of a secondary chemical reaction product have been observed during the cathodic scan of the potential.

Earlier, for porphyrins possessing four amide groups at the ortho positions of the tetraphenylporphyrin, such as in case of “picket-fence” or “basket handle” porphyrins, a one-step two-electron transfer giving directly a dicationic species has been reported.[28−32] This unique behavior was ascribed to the presence of four amide groups in the immediate vicinity of the porphyrin ring.[28] The electrooxidation behavior of the presently investigated compound which possesses a single amide group is rather similar to the “normal” porphyrins where a stepwise one-electron oxidation occurs.[27] These results indicate that the electrochemical oxidation of porphyrins having one amide group in the vicinity of the porphyrin is similar to that of the “normal” porphyrins and that only higher number of amide groups might cause the one-step two-electron oxidation process.

Interestingly, ZnP*m*∼Py upon the second electron abstraction undergoes a chemical reaction leading to the formation of an isoporphyrin. The first oxidation process of ZnP*m*∼Py is reversible and occurs at $E_{1/2} = 0.70$ V. The second oxidation process is irreversible with a peak potential $E_{pa} = 1.06$ V and generates a new wave at $E_{pc} = 0.27$ V during the cathodic scan of the potential. This process can be best illustrated by a cyclic voltammogram recorded at 60 °C (Figure 2d). At this temperature, the electrooxidation behavior of ZnP*m*∼Py is similar to that of pyridine coordinated ZnTPP (Figure 2b) and suggests that the wave at $E_{pc} = 0.27$ V could be due to the reduction of the isoporphyrin generated at the surface of the electrode by the reaction of porphyrin dication with appended pyridine. In order to further characterize the reaction product, as to whether it is a pyrrole β-substituted or *meso*-substituted isoporphyrin, bulk electrolysis of ZnP*m*∼Py was carried out in dry dichloromethane at an applied potential of 1.30 V. The product obtained after separating the starting material and further purification on a basic alumina column using chloroform/acetone as eluent revealed absorption bands at 425, 517(sh), 556, and 597 nm respectively which is characteristic of a pyrrole β-substituted isoporphyrin.[41−43] However, the isolated product is found to be unstable in solution on longer time-scale and decomposes to the starting ZnP*m*∼Py.

In summary, the present investigation demonstrates the presence of a stable pentacoordinated complex for ZnP*o*∼Py in which the coordinated pyridine does not readily participate in any chemical reaction during the electrochemical oxidation of the porphyrin. A temperature dependent “tail-on” and “tail-off” type of binding is operative in case of ZnP*m*∼Py. Additional chemical reactions leading to a pyrrole β-substituted isoporphyrin occurs during the electrochemical oxidation of the *meta*-substituted derivative.

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Supporting Information Available: UV−visible spectrum of the zinc β-pyridiniumylporphyrin (1 page). Ordering information is given on any current masthead page.

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(43) The presence of water in the solvent produces small amounts of *meso*-substituted isoporphyrin. However, this can be avoided using very dry solvents.