Electrochemically controlled ligand shuttling between zinc porphyrin and *meso*-phenylenediamine substituent[†]

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Received (in Cambridge, UK) 17th February 2009, Accepted 13th March 2009 First published as an Advance Article on the web 6th April 2009 DOI: 10.1039/b903374m

ZnTMP-PD was synthesized and fully characterized; by using electrochemical and spectroelectrochemical methods, ligand shuttling between the zinc porphyrin and the *meso*phenylenediamine substituent could be monitored; EPR results indicated that the charge was delocalized on ZnTMP-PD.

Metalloporphyrins have been used to mimic biological systems.¹ The understanding of metalloporphyrin properties in relation to biological processes is of great importance. A great number of experimental results have been reported over the past three decades concerning the axial ligation properties of metalloporphyrins with S, O, P and N bases.¹ Recently, many efforts have been focussed on the molecular recognition of bio-interest by zinc porphyrins.^{2,3} A binding mode of the pyridine group of the nicotine guest coordinated to the Zn ion of the host was found.⁴ Detailed studies on the solvation and axial ligation properties of ZnTPP have been reported.^{5–8} Addition of imidazole and 2-methylimidazole to zinc porphyrins caused a cathodic shift of the oxidation potentials.^{8*b*,9}

Hydrogen bonds are one of the most important types of inter- and intramolecular interactions in biological systems.¹⁰ Recently, chemists have studied hydrogen bonds in similar systems, such as multimolecular assemblies¹¹ or engineering structures.¹² Hydrogen bonds are electrostatic in nature.¹³ In 1962, the effect of hydrogen bonds on redox potential had been investigated by Peover.¹⁴ In the presence of hydrogen bonding to flavin in flavinproteins, one redox state would be stabilized relative to another based on the potential shift.15 Rotello and co-workers also reported hydrogen bonding for diimide and triimide.¹⁶ Using an electrochemical method, reduced quinone derivatives or arylimides formed hydrogen bonds with different ureas and diamines as investigated by Smith and co-workers.¹⁷ They also demonstrated a reversible, redox dependent interaction between nitrobenzene derivatives and arylureas.

We have synthesized a novel zinc porphyrin substituted with phenylenediamine, ZnTMP-PD (Fig. 1). By electrochemical oxidation, the oxidized ZnTMP-PD will form hydrogen and coordinate bonding in the presence of *N*-methylimidazole (MeIm). This study should be helpful in providing insight of the intermediate of heme-dependent enzymatic reactions. PD has two redox couples at $E_{1/2} = +0.59$ and +1.01 V (Fig. S2A, ESI[†]). As for oxidation, ZnTMP has two redox couples at $E_{1/2} = +0.79$ and +1.11 V (Fig. S3A, ESI[†]).^{8b} In the oxidation of ZnTMP-PD (Fig. 2A), three reversible redox couples could be observed at $E_{1/2} = +0.58$, +0.81 and +1.13 V, respectively (Scheme S2, ESI[†]). These three redox couples contained those of the metalloporphyrin ring and *para*-phenylenediamine (PD) substituent. Besides, differential pulse voltammetry (DPV) (Fig. S1B, ESI[†]) was used to identify the number of electrons oxidized by calculating each integration area. Thus, it could be inferred that in ZnTMP-PD the first redox reaction was at the PD substituent, the second on the zinc porphyrin, and the third redox couple on both parts.

After 0.5 equivalent of MeIm was added to PD solution, the current of the first redox couple increased while that of the second decreased to about half (Fig. S2, ESI[†]). After PD was oxidized to PD^{+•}, HN^{+•} in the PD would quickly form hydrogen bonding with MeIm. When 1.0 equivalent of MeIm was added, the second redox couple of PD disappeared, while the current value of the first redox couple became twice as high. Scheme S3 is proposed (see ESI[†]).¹⁸ For ZnTMP in the presence of MeIm, the first oxidation potential shifted cathodically while the second one shifted anodically (Scheme S4, ESI[†]).

When MeIm was added to ZnTMP-PD solution, the first two oxidation waves moved towards more negative potentials, while the third oxidation wave shifted to a more positive potential (Fig. 2B–D). When MeIm reached 1.5 equivalent, the oxidation waves no longer shifted. Three oxidation waves were at $E_{1/2} = +0.51$, +0.70 and +1.17 V (Table 1), with their shifted potentials of -0.07, -0.11 and +0.04 V, respectively. Based on the results of the cyclic voltammograms in Fig. S2 and S3 (ESI†), the first redox couple in Fig. 2 was assigned to PD substituent oxidation in ZnTMP-PD (PD^{+•} and then PD²⁺-MeIm formation), and the second and third redox couples were on the zinc porphyrin.

The absorption peak of ZnTMP-PD at 308 nm, a characteristic absorption of the PD substituent, had a molar



Fig. 1 Structure of zinc porphyrin linked with meso-phenylenediamine.

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[†] Electronic supplementary information (ESI) available: Details on synthesis, electrochemical and spectral studies of PD, ZnTMP and ZnTMP-PD. See DOI: 10.1039/b903374m



Fig. 2 Cyclic voltammetry of 1.0×10^{-3} M ZnTMP-PD in the presence of *N*-methylimidazole in CH₂Cl₂ containing 0.1 M TBAP: [MeIm] = (A) 0.00, (B) 0.50, (C) 1.00, (D) 1.50 equiv. of ZnTMP-PD. Working electrode: glassy carbon. Scan rate: 0.1 V s⁻¹.

 Table 1
 Oxidation potential of PD, ZnTMP and ZnTMP-PD in the absence and presence of *N*-methylimidazole

	$E_{1/2}/\mathrm{V}$		
	1st	2nd	3rd
PD	+0.59	+1.01	
PD^a	$+0.62^{b}$		
ZnTMP	+0.79	+1.11	
$ZnTMP^{a}$	+0.67	+1.32	
ZnTMP-PD	+0.58	+0.81	$+1.13^{b}$
ZnTMP-PD ^a	$+0.51^{b}$	+0.70	+1.17

^{*a*} In the presence of 1.0 equiv. *N*-methylimidazole. ^{*b*} Two-electron transfer.

extinction coefficient of $2.21 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, and the Soret band at 421 nm had a value of $2.52 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. In the potential range $E_{appl.} = +0.00 + 0.59$ V, the spectra at potential increments were obtained by using an optically transparent thin-layer electrode (OTTLE). (Fig. S7A, ESI⁺). As the potential shifted positively, it was observed that the 308 nm peak gradually decreased with an isosbestic point at 340 nm. The Soret band (421 nm), on the other hand, grew slightly. In the wavelength range 600-1000 nm, there was a small rising in background, which is ascribed to PD^{+•} absorption (Fig. S5A, ESI[†]). In another potential range at $E_{\text{appl.}} = +0.67 + 0.93 \text{ V}$ (Fig. S7B, ESI[†]), the Soret band (421 nm) and the Q band (550 nm) absorbances decreased dramatically. A new peak at 415 nm with much smaller absorbance and broad band at 550-800 nm, conceivably due to porphyrin ring radical cation, were observed. The spectra change is consistent with the previous inference from CV that



Fig. 3 Spectral changes of 2.0×10^{-5} M ZnTMP-PD in the presence of 0.75 equiv. *N*-methylimidazole in CH₂Cl₂ containing 0.1 M TBAP at various applied potentials.

the first oxidation occurred at the PD substituent with the second at the zinc porphyrin.

In the presence of MeIm (Fig. S8, ESI⁺), MeIm coordinated with a portion of ZnTMP-PD ($\lambda_{max} = 421$ nm) and formed (MeIm)ZnTMP-PD (λ_{max} = 430 nm). Fig. 3 shows the spectroelectrochemical results for ZnTMP-PD oxidation in the presence of 0.75 equivalent MeIm. In the potential range $E_{\text{appl.}} = +0.00 + 0.59$ V, corresponding to PD substituent oxidation, the absorbance at 308 nm gradually decreased, and a new peak at 288 nm was formed. The absorbance at 430 nm decreased and that at 421 nm increased significantly. The base lines of the spectra increased in the same way as for without imidazole. It is noteworthy that the absorption at 430 nm of (MeIm)ZnTMP-PD disappeared upon PD oxidation and the 421 nm absorbance increased, indicating the removal of MeIm from ZnTMP. In the potential range of $E_{appl.}$ = +0.67-+0.93 V, the absorption peaks of the Soret band (421 nm) and Q band (550 nm) gradually decreased. The absorbance at 288 nm also decreased, while a broad band at 570-1000 nm grew.

The change of spectra and absorption peaks in the absence (Fig. S7A, ESI†) and presence (Fig. 3A) of MeIm for ZnTMP-PD is discussed as follows (Scheme 1). The coordination constant of MeIm and ZnTMP-PD is about $10^4 \text{ M}^{-1.8b,9}$ When (MeIm)ZnTMP-PD was oxidized starting at $E_{appl.} = +0.38 \text{ V}$, the absorbance at 430 nm gradually decreased while that at 421 nm rose. For (MeIm)ZnTMP-PD, MeIm moved to form

$$I \qquad \underbrace{\mathbb{Z}_n}_{R} \xrightarrow{H} \underbrace{-e^{-}}_{R} \underbrace{\mathbb{Z}_n}_{R} \xrightarrow{H} \underbrace{-e^{-}}_{R} \underbrace{\mathbb{Z}_n}_{R} \xrightarrow{H} \underbrace{-e^{-}}_{R} \underbrace{\mathbb{Z}_n}_{R} \xrightarrow{H} \underbrace{\mathbb{Z}_n} \xrightarrow{H} \underbrace{\mathbb{Z}_n}_{R} \xrightarrow{H} \underbrace{\mathbb{Z}_n} \xrightarrow$$



hydrogen bonding with $\text{HN}^{+\bullet}$ after PD oxidation to $\text{PD}^{+\bullet}$. The formation constant $(\sim 10^5 \text{ M}^{-1})^{17,19}$ of the hydrogen bonding was larger than the coordination constant $(\sim 10^4 \text{ M}^{-1})^{8b,9}$ of MeIm with zinc porphyrin. After MeIm moved over, the center of zinc porphyrin was restored to a four-coordinated state, causing the original zinc porphyrin absorption peak (421 nm) to increase upon PD moiety oxidation.

Fig. S7B (ESI[†]) shows a change in the spectrum when ZnTMP-PD was oxidized, and the spectral change was similar to ZnTMP cation radical formation. In the absence of MeIm, those of the Soret band and the Q band decreased. A broad band at 500–800 nm characteristic for the porphyrin cation radical grew. However, in the presence of MeIm (Fig. 3B), the absorption peak at 288 nm decreased. In the applied potential range, $[ZnTMP^{+\bullet}-PD^{2+}]^{3+\bullet}$ was formed; ZnTMP^{+•} and MeIm have a very large coordination constant of about $10^{6}-10^{7}$ M⁻¹,^{8b,9} larger than the constant for MeIm and PD^{+•}. At this point, MeIm would move back to the zinc ion center of the metalloporphyrin.

Cation radicals PD^{+•}, ZnTMP^{+•} and ZnTMP-PD^{+•} were obtained by the electrochemical oxidation at 298 K in CH₂Cl₂ and were stable at room temperature. The EPR spectrum of PD^{+•} at room temperature exhibited a broad six-line pattern (Fig. S9A, ESI[†]) with g = 2.0030. A number of hydrogen nuclei in PD^{+•} had various hyperfine coupling (hfc) constants resulting in broad line width.¹⁸ Fig. S9B (ESI[†]) shows the ZnTMP^{+•} EPR spectrum, which could be distinguished as a nine-line pattern. ZnTMP was oxidized at the a_{2u} orbital with g = 2.0030. The ZnTMP^{+•}, and gave a twelve-line pattern (Fig. S9C, ESI[†]) with g = 2.0033. The results indicated that in ZnTMP-PD^{+•}, the radical did not rest on the PD substituent, but delocalized across the *meso*-position to the zinc porphyrin.

In summary, ZnTMP-PD in the neutral state was ligated by MeIm to the zinc ion center to form a five-coordinate species. MeIm then moved to form hydrogen bonding with oxidized PD and the characteristic absorption spectrum of four-coordinate ZnTMP was restored. When the electrode potential was shifted anodically and ZnTMP moiety was also oxidized, MeIm further moved back to ligate onto the ZnTMP. The shuttling of MeIm has been determined by the electrode potential and the formation constant for MeIm with different moieties of ZnTMP-PD at various oxidation states.

The authors thank the National Science Council of the Republic of China for support of this work.

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