

Novel Diporphyrins Containing N₄ and N₃S Cores: Synthesis, Characterization, and Electrochemical Properties

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Novel diporphyrins containing a *meso*-tetraphenylporphyrin (TPPH₂) with an N₄ core and a core-modified monothiaporphyrin (STPPH) with an N₃S core covalently joined through a short alkyl chain at the *para* positions of *meso* phenyl rings have been synthesized and characterized. ¹H NMR and optical spectral data indicate a weak interaction between the two porphyrin subunits for H₂–H and Zn–H diporphyrins. However, in the Zn–Cu and Ni–Ni diporphyrins there is substantial interaction between the two subunits induced by the structural change caused by introduction of metal to the thiaporphyrin subunit. This is reflected in the optical absorption band and redox potential shifts. Furthermore, the geometries around the two metals in these diporphyrins are different because of the difference in the electronic structures of the two porphyrin rings. Electrochemical studies on Zn–Cu and Ni–Ni diporphyrins indicate the reduction of the metal center present in the thiaporphyrin subunit at very low potentials (–0.0885 V for Cu(II)/Cu(I) and –0.28 V for Ni(II)/Ni(I)) suggesting that the metal d_{xy} orbital is lower in energy relative to the e_g(π*) orbital of the thiaporphyrin ring. This observation suggests the possibility of stabilization of different oxidation states of the same metal in homobimetallic and different metals in heterobimetallic diporphyrins.

Introduction

Covalently linked metalloporphyrin dimers have been extensively studied as models for the photosynthetic reaction center,¹ as electrocatalysts for activation of small molecules,² and as photodynamic antitumor agents.³ A variety of porphyrin dimers have been described depending on the orientation of the two porphyrin rings with respect to each other and the nature of the linking groups. For example, in the μ -oxo dimers,⁴ the oxygen atom bridges the two porphyrin rings via the central metal atoms while, in the cofacial dimers⁵ or cyclophanes, the porphyrins are held by a double linkage such that the two rings are oriented in a face to face geometry. Cofacial dimers without the covalent links are also known, and in these the dimerization is induced in solution.⁶ In the side by side or noncofacial dimers, the porphyrins

are joined by a single flexible hydrocarbon chain and in most cases the two porphyrin rings behave as two independent monomeric units.⁷ In oblique porphyrin dimers,^{1e,s,8} a spacer group has been used to link the two porphyrin rings in an oblique manner similar to those found in the reaction center of photosynthetic bacteria.⁹ The efforts of studies on these dimeric systems have provided valuable information on chromophore–

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chromophore interactions^{1f} and photoinduced electron-^{1e,7a,f} and energy-transfer^{7e,10} processes which are useful in assembling artificial supramolecular entities to mimic natural systems.

A common feature among the various porphyrin dimers described above is that they all have similar donor atoms (pyrrole nitrogens) in the porphyrin cores. One area of porphyrin chemistry that has received almost no attention but may lead to systems of interesting structural and electronic properties is characterization of porphyrin dimers with dissimilar cores. Recent studies from this laboratory¹¹ and from others¹² on core modified porphyrins have indicated that the chemical and physical characteristics of the porphyrin skeleton can be significantly altered by replacing one or more pyrrole nitrogen(s) by thiophene sulfur(s). Thus, an assembly containing a thiaporphyrin with an N₃S core and a normal porphyrin with an N₄ core offers a unique diporphyrin with an unusual electronic structure. In this paper, we wish to report the first synthesis, spectral characterization, and electrochemical properties of such a diporphyrin and the metal-free base (Zn-H), homobimetallic (Ni-Ni), and heterobimetallic (Zn-Cu) derivatives (Figure 1).

Experimental Section

All the chemicals used for the synthesis were reagent grade unless otherwise specified. Solvents for spectroscopic measurements were purified and dried according to the standard methods.

I. Syntheses. (a) 2,5-(*p*-tolylhydroxymethyl)thiophene. This was synthesized as reported earlier.^{11a}

¹H NMR in CDCl₃ (ppm): 1.94 (br, 2H), 2.35 (s, 6H), 5.90 (s, 2H), 6.68 (s, 2H), 7.2 (q, 8H).

(b) 5-(4-(5-Bromo-1-pentoxy)phenyl)-10,15,20-tritolylporphyrin (1). This was synthesized by the literature method.^{7b,c}

(c) 5,20-Bis(*p*-tolyl)-10,15-bis(*p*-hydroxyphenyl)-21-thiaporphyrin (2). A mixture of 2 equiv of *p*-hydroxybenzaldehyde (6.785 g, 0.0555 mol) and 1 equiv of 2,5-bis(*p*-tolylhydroxymethyl)thiophene (9 g, 0.0277 mol) and 3 equiv of pyrrole (5.58 g, 0.0833 mol) was dissolved in freshly distilled propionic acid (1000 mL). The reaction mixture was refluxed for ~2 h and was left overnight at room temperature. The solvent was completely removed under reduced pressure. The black residue obtained was washed several times with hot water and was kept in oven at 100 °C for 1 h. Then the crude product was dissolved in CHCl₃, and the mixture was filtered. The crude product was purified by column chromatography over silica gel using chloroform as the eluent. The first yellow fraction obtained was identified as (CH₃)₄S₂TPP (tetrakis(*p*-tolyl)-21,23-dithiaporphyrin). Elution with a mixture of chloroform and methanol (100:2) produced a yellow-brown band identified as 2. Elution and removal of the solvent afforded 2 (0.777 g) in 4.03% yield.

Anal. Calcd for C₄₆H₃₃N₃O₂S: C, 79.859; H, 4.807; N, 6.074. Found: C, 79.951; H, 4.75; N, 6.03. FAB MS: *m/z* 692 (calcd for C₄₆H₃₃N₃O₂S, *m/z* 691.845).

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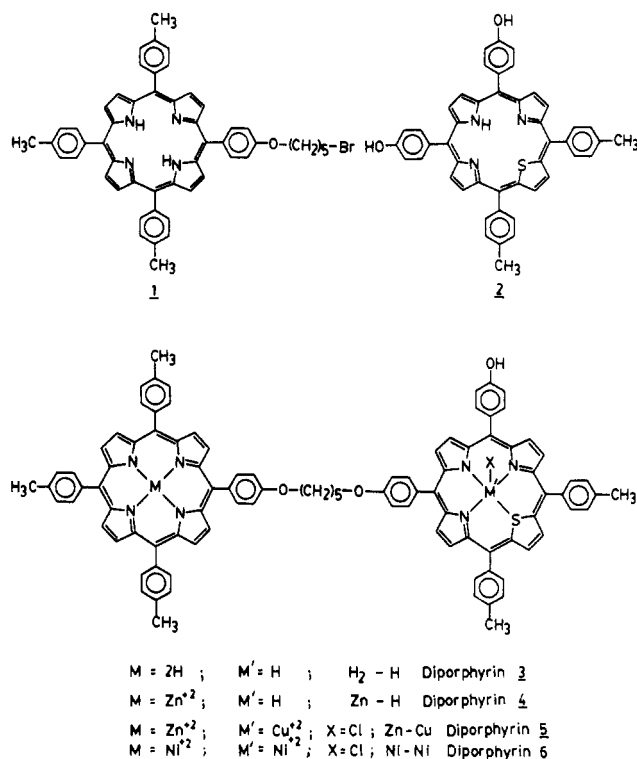


Figure 1. Molecular structures of various diporphyrins and their corresponding monomers.

(d) H₂-H Diporphyrin (3). A mixture of 1 (0.150 g, 0.1824 mmol), 2 (0.403 g, 0.585 mmol), and anhydrous K₂CO₃ (2.0 g) was stirred in 30 mL of dry DMF for 2 weeks at room temperature. The DMF was removed under reduced pressure. The residual solid was washed thoroughly with hot water and dried. It was dissolved in CHCl₃ and chromatographed on a silica gel column. Unreacted 1 was eluted with chloroform as the first pink fraction. Further elution with a mixture of CHCl₃ and methanol (100:0.5) produced a yellow pink fraction identified as 3 and was recovered as a solid after evaporation of solvent under vacuum. It was again chromatographed over a silica gel column. Yield: 0.071 g (27%).

Anal. Calcd for C₉₈H₇₇N₇O₃S: C, 82.153; H, 5.417; N, 6.843. Found: C, 82.27; H, 5.45; N, 6.89. FAB MS: *m/z* 1433 (calcd for C₉₈H₇₇N₇O₃S: 1432.791).

(e) Zn-H Diporphyrin (4). Selective metalation of the "normal" porphyrin subunit in 3 was achieved as follows. A solution of 0.050 g of zinc acetate in 25 mL of methanol was added to a solution of 3 (0.030 g, 0.021 mmol) in 125 mL of chloroform. The solution was heated under reflux for 2 h. It was cooled, and then the solvent was removed under reduced pressure. The residue was dissolved in chloroform and washed several times with water. It was dried over anhydrous Na₂SO₄. Then it was chromatographed over a silica gel column using a mixture of chloroform and methanol (100:1) as the eluent. The yellowish pink fraction of 4 was recovered as a solid after evaporation of solvent under vacuum. It was twice chromatographed over a silica gel column. Yield: 0.027 g (86%).

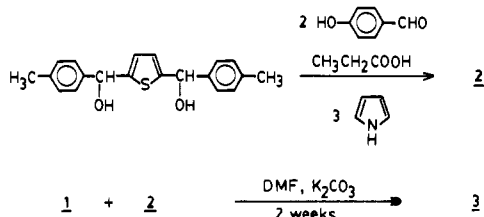
Anal. Calcd for C₉₈H₇₅N₇O₃SZn: C, 78.674; H, 5.052; N, 6.553. Found: C, 78.63; H, 5.01; N, 6.51. FAB MS: *m/z* 1496 (calcd for C₉₅H₇₅N₇O₃SZn, *m/z* 1496.155).

(f) Zn-Cu Diporphyrin (5). A solution of CuCl₂·2H₂O (0.050 g) in 20 mL of methanol was added to a solution of 4 (0.030 g, 0.02 mmol) in 60 mL of chloroform, and the new solution was then refluxed for 6 h. It was cooled, and then the solvent was removed under reduced pressure. The solid was dissolved in chloroform and washed several times with water. It was dried over anhydrous Na₂SO₄ and chromatographed over a silica gel column using a mixture of chloroform:methanol (100:1) as eluent to get unreacted 4. The second greenish pink fraction of 5 (chloroform:methanol, 100:5) was recovered as a solid after evaporation of solvent under vacuum. It was twice chromatographed over a silica gel column. Yield: 0.022 g (70%).

Anal. Calcd for C₉₈H₇₄N₇O₃SZnCuCl: C, 73.838; H, 4.67; N, 6.15. Found: C, 73.65; H, 4.53; N, 6.03. FAB MS (FAB mass data corresponds

Table 1. ¹H NMR Chemical Shift (ppm) Values of Diporphyrins and Their Corresponding Monomers in CDCl₃ at 25 °C

porphyrin	thiophene	pyrrole	phenyl protons		-OCH ₂	-CH ₂ Br	<i>p</i> -CH ₃	-(CH ₂) ₃ -
			<i>ortho</i>	<i>meta</i>				
1		8.75 (s)	8.11 (d)	7.55 (d) 7.22 (d)	4.20 (t)	3.5 (t)	2.65 (s)	1.43 (m)
2	9.75 (s)	8.94 (s) 8.65 (q)	8.14 (d) 8.05 (d)	7.62 (d) 7.18 (d)			2.7 (s)	
3	9.77 (q)	8.95 (q) 8.86 (s) 8.7 (q) 8.66 (q)	8.15–6.95 (m)		4.23 (m)		2.7 (s) 2.67 (s) 2.49 (s) 2.42 (s)	1.5 (m)
4	9.71 (q)	8.96 (q) 8.87 (s) 8.69 (q) 8.65 (q)	8.18–6.98 (m)		4.16 (m)		2.71 (s) 2.69 (s) 2.45 (s) 2.43 (s)	1.54 (m)

Scheme 1

to ionization of apical chloride):¹³ *m/z* 1558 (*M*⁺ - Cl) (calcd for C₉₈H₇₄N₇O₃SZnCuCl, *m/z* 1594.146).

(g) **Ni-Ni Diporphyrin (6).** A solution of NiCl₂·6H₂O (0.125 g) in 50 mL of methanol was added to a solution of 3 (0.020 g) in 125 mL of chloroform, and the mixture was refluxed for 24 h. It was cooled to room temperature. The solvents were evaporated under reduced pressure. Then the solid was dissolved in 50 mL of chloroform and washed several times with water and dried over anhydrous Na₂SO₄. The solvent was reduced to 15 mL and chromatographed over silica gel. Elution with chloroform:methanol (99:1) gave unreacted 3 followed by Ni-H diporphyrin. Further elution with chloroform:methanol (92:8) afforded 6 (0.0088 g) in 35% yield. It was again chromatographed over silica gel column.

Anal. Calcd for C₉₈H₇₄N₇O₃SNi₂Cl: C, 74.375; H, 4.713; N, 6.195. Found: C, 74.23; H, 4.53; N, 6.09. FAB MS: *m/z* 1547 (*M*⁺ - Cl) (calcd for C₉₈H₇₄N₇O₃SNi₂Cl, *m/z* 1582.62) (FAB mass corresponds to ionization of apical chloride).¹³

II. Physical Measurements. The electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer. ESR measurements were done on a Varian E-109 X-band spectrometer at room temperature. The ¹H NMR spectra were recorded on Bruker WM-400 FT NMR spectrometer. The FAB mass spectra were recorded using a Jeol SX-120/DA-6000 mass spectrometer using argon as the FAB gas. Cyclic voltammetric and differential pulse voltammetric studies were conducted on a PAR Model 370 polarographic analyzer utilizing the three-electrode configuration of a Pt (BAS) working electrode, a Pt mesh counter electrode, and a commercially available saturated calomel electrode (SCE) as the reference electrode. A RE 0074 X-Y recorder was used to record the current-voltage output. Half-wave potentials were measured as the average of the cathodic and anodic peak potentials.

Results and Discussion

(a) **Synthesis.** The synthesis of diporphyrins involved the preparation of monomer precursors by condensation of pyrrole and/or 2,5-bis(*p*-tolylhydroxymethyl)thiophene with mixed aldehydes containing suitable functionalities followed by the coupling reaction of two monomer precursors as shown in Scheme 1.

(b) **¹H NMR Spectra.** ¹H NMR spectroscopy has been used to characterize the diporphyrins. The resonances of the diporphyrins were assigned on the basis of the spectra observed for the two monomers taken independently and with consideration of the lower symmetry of the thiaporphyrin subunit in the dipor-

phyrins. Figure 2 shows a comparison of the ¹H NMR spectra of 2 and 3, and data for other porphyrins are listed in Table 1.

The spectrum of 3 obviously should consist of signals attributable to both 1 and 2 and the linking groups. Considering the lower symmetry of the thiaporphyrin subunit in 3 relative to 2, one would expect four separate AB quartets for thiophene and pyrrole protons. The peak marked H_i(T) at 9.77 ppm in Figure 2b is assigned to the two thiophene protons of the thiaporphyrin subunit. The pyrrole protons are assigned as follows: There are fourteen pyrrole protons, eight belonging to the normal porphyrin subunit and six belonging to the thiaporphyrin subunit. The spectrum of Figure 2b (inset) shows four sets of pyrrole protons at 8.95 ppm (quartet), 8.86 ppm (broad singlet), 8.70 ppm (quartet), and 8.66 ppm (quartet). An analysis of integrated peak intensities indicates two protons can be assigned to the quartet at 8.95 ppm, eight protons to the peak at 8.86 ppm, and two protons each to the peaks at 8.66 and 8.7 ppm. The peak at 8.86 ppm is assigned to pyrrole protons at the normal porphyrin subunit (H_P(N)), while the three quartets of 8.95, 8.66, and 8.7 ppm are assigned to the pyrrole protons of the thiaporphyrin subunit (H_P(T)).

The *meso* phenyl *ortho* and *meta* protons appear as a complex multiplet in the region 8.15–6.95 ppm, and it is difficult to make individual assignments without the specific deuteration experiments. No attempts were made in this direction. The linking pentoxy chain protons appear as two multiplets at 4.21 and 1.50 ppm. The multiplet at 4.21 ppm is assigned to -OCH₂ protons on the basis of the electronegativity and closeness to the porphyrin π-system,^{7b,c} while the multiplet at 1.50 ppm is assigned to the -(CH₂)₃- protons. The -OCH₂ protons are expected to appear as a triplet if both the porphyrin units have similar aromaticity.^{12b} However, the observed multiplet structure in the diporphyrin indicates a small difference in the aromaticity of the two individual subunits. This is also supported by the appearance of four closely spaced singlets for *p*-methyl substituents on the *meso* phenyl groups.

The inset in Figure 2 shows two singlets at -2.63 and -2.73 ppm assigned to the inner NH protons of the porphyrin rings. Insertion of Zn²⁺ into the normal porphyrin subunit results in the disappearance of the -2.73 ppm signal. Thus, the -2.63 ppm signal corresponds to the thiaporphyrin subunit NH proton. A comparison of chemical shifts of the various protons of the diporphyrin 3 with those of individual monomeric units indicates only minor differences suggesting that the two porphyrin subunits in the dimer interact very weakly. This is consistent with the earlier reports on the covalently linked tetraphenylporphyrin dimers.^{7a,b,e,14}

The conformation of the two porphyrin rings in covalently linked TPP type dimers can be "folded" or "unfolded" depending on the position of the linkage on the *meso* phenyl rings (*o*, *m*, or

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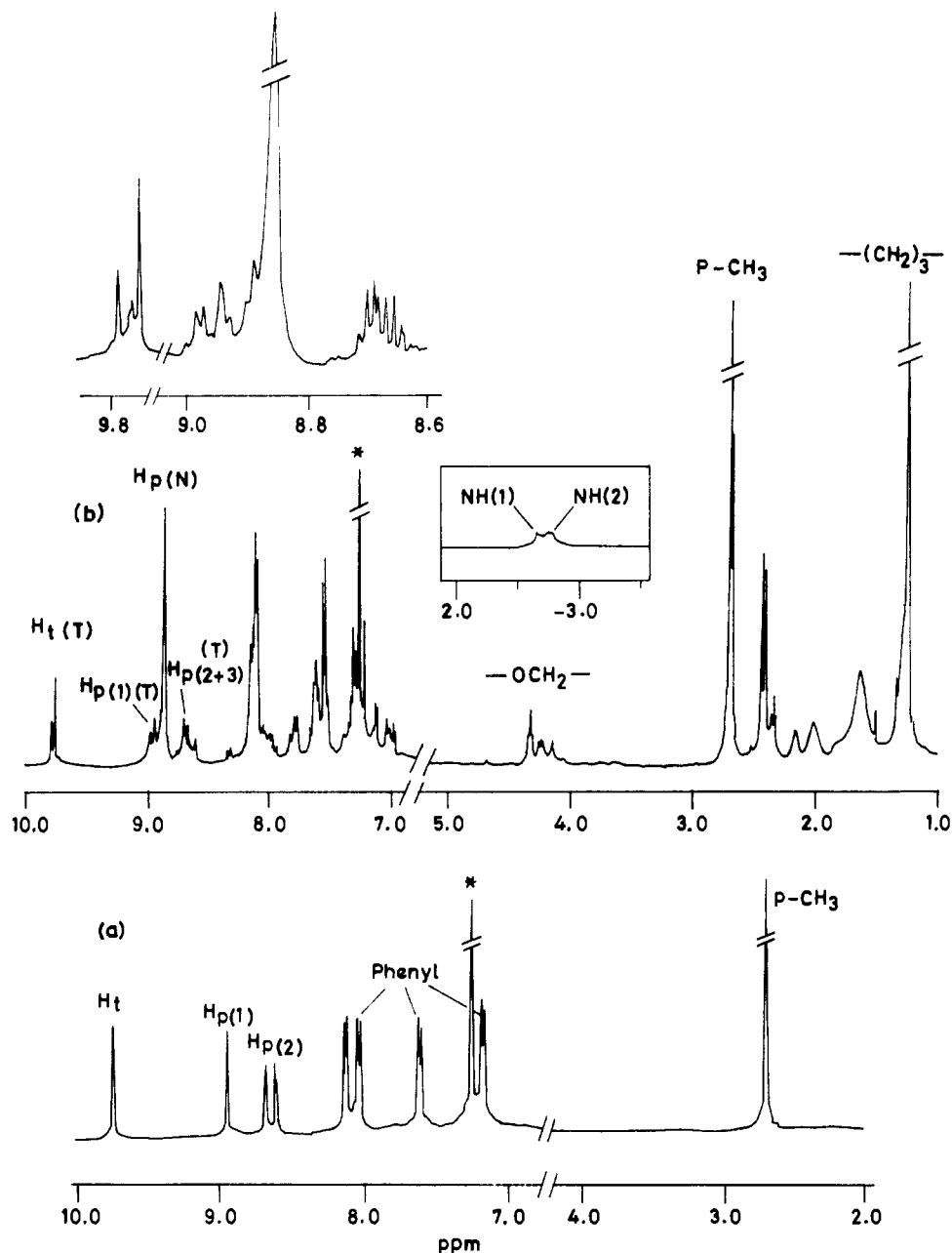


Figure 2. ^1H NMR spectra of (a) **2** and (b) **3** in CDCl_3 . The inset shows the expansion in the region 9.85–8.6 ppm and the $-\text{NH}$ resonances. $\text{H}_t(\text{T})$, $\text{H}_{p(1)}(\text{T})$, $\text{H}_{(2)}(\text{T})$, and $\text{H}_p(\text{N})$ corresponds to thiophene protons, pyrrole protons of the thiaporphyrin subunit, and pyrrole protons of the normal porphyrin subunit, respectively. The asterisk corresponds to CDCl_3 .

p) and the solvent polarity. It has been shown by earlier NMR studies that the *p,p*- and *o,o*-linked TPP dimers predominantly assume an unfolded conformation in CDCl_3 due to restricted rotation along the linking axis by the *meso* phenyl rings.¹⁴ The position of the link (*p,p*) in the present diporphyrins and the similarity of the chemical shifts of protons of **3** to its constitutive monomer units in CDCl_3 suggests an unfolded conformation for **3**. Optical spectra data also support this conclusion (vide infra).

Introduction of Zn^{2+} ion to the normal porphyrin subunit in **3** should not significantly affect the chemical shifts of the pyrrole and thiophene protons of the thiaporphyrin subunit while pyrrole protons of the normal porphyrin subunit are expected to show small deshielding effects.¹³ This is clearly reflected in the ^1H NMR spectra of **4** (Table 1). Thus the proton NMR spectra clearly support the proposed structure of the diporphyrin in solution.

(c) Optical Spectra. Figure 3 shows the absorption spectra of **3–5** in CHCl_3 in the Soret and Q band regions, and the absorption data are tabulated in Table 2. The absorption spectra of **3** appear

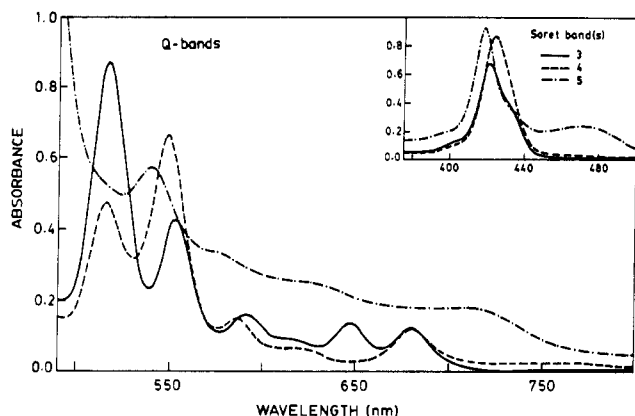
to be simply the sum of the two free base monomers. A comparison of this with a 1:1 mixture of **1** and **2** in CHCl_3 indicates only small shifts (1–2 nm) in the λ_{max} values. However, the molar absorption coefficients of the diporphyrins are only about 70–75% of the corresponding bands, probably suggesting a weak interaction between the two chromophores. Literature reports^{10,14} on covalently linked dimers of TPPH_2 with varying lengths have shown two bands in the Soret region. This has been accounted in terms of presence of folded and unfolded conformers. However the optical spectrum of **3** in different solvents of varying polarity did not show any significant shifts of Soret bands¹⁵ suggesting the presence of predominantly of one conformer in solution.

Metalation of the porphyrin ring results in merging of Q_x and Q_y components thus showing only two Q bands. Introduction of Zn^{2+} ion to the normal porphyrin subunit increases the absorption

(15) The Soret band splits into two bands one to the "red" and other to the "blue" due to exciton coupling. The "red" band is ascribed to the "unfolded" conformer, and the "blue", to the "folded" conformer. See ref 10a for details.

Table 2. Absorption Spectral Data for Diporphyrins and Their Corresponding Monomers in CHCl₃

porphyrin	Soret band(s): λ_{\max} , nm ($10^{-4}\epsilon$, dm ³ mol ⁻¹ cm ⁻¹)	Q bands: λ_{\max} , nm ($10^{-3}\epsilon$, dm ³ mol ⁻¹ cm ⁻¹)					
		VI	V	IV	III	II	I
1	420 (47.5)			517 (18.71)	553 (10.45)	592 (5.52)	6.49 (6.22)
2	430 (17.7)			516 (15.24)	551 (6.93)	618 (3.31)	677 (5.23)
3	421 (47.89)	517 (31.03)	553 (15.07)	591 (5.7)	616 (3.15)	647 (4.98)	680 (4.37)
4	430 (30.28)		516 (16.47)	550 (23.56)	587 (5.62)	617 (2.78)	680 (4.54)
5	423 (43.0)		540 (4.51)	573 (2.65)	617 (2.04)	675 (1.48)	707 (1.45)
6	433 (24.42)						
	418 (5.82)						
	434 (2.08)						
	469 (1.46)						
	419 (17.38)			529 (14.57)	558 (9.84)	614 (4.22)	685 (2.74)
	440 (6.33)						
	472 (5.26)						

**Figure 3.** Absorption spectra of **3** (—), **4** (---), and **5** (-·-) in the Q and Soret band region in CHCl₃ (concentration for Q bands $\approx 1 \times 10^{-5}$ M and for Soret band $\approx 1 \times 10^{-6}$ M).

at the 550- and 587-nm bands while the other Q bands belonging to the thiaporphyrin subunit remain unaltered in intensity. Also the peak positions in **4** match well with a 1:1 mixture of the zinc derivatives of **1** and the free base of **2**. The observation of two well-defined Q bands and a sharp Soret band for the zinc porphyrin subunit in **4** suggests an approximate *D*_{4h} symmetry around Zn²⁺ ion.¹⁶

The absorption spectrum of **5** is quite revealing. Specifically, the absorption bands belonging to the zinc porphyrin part are substantially quenched (Table 2) with a blue shift of both Soret and Q bands. Furthermore the Q band region of the copper thiaporphyrin subunit shows more than two ill-defined bands with reduced molar absorption values. The Soret band splits into two bands at 434 and 469 nm with substantially quenched molar extinction coefficients relative to Zn-H or H₂-H diporphyrin. This clearly suggests the distorted geometry around the copper thiaporphyrin subunit. Furthermore, this also rules out the possibility of metal coordination to the hydroxyl group present on the *meso* phenyl ring of thiaporphyrin unit. Justification for such a conclusion comes from the X-ray structure^{12f,g} and the optical absorption spectrum^{11d} of monomeric Cu(STPP)Cl. The X-ray structure indicates that the thiophene ring is bent out of the porphyrin plane due to coordination needs of the thiophene ring and the Cu²⁺ ion is in a distorted square pyramidal geometry with an apical chloride ligand. The optical spectrum of Cu(STPP)Cl shows a complex pattern of Q bands and the split Soret band as observed for **5** suggesting a distorted structure around the copper thiaporphyrin subunit in **5**.¹⁷ This change in structure around the copper thiaporphyrin subunit induces shifts in the optical absorption bands of the zinc porphyrin subunit implying that the two porphyrin subunits interact substantially in the bimetallic diporphyrin. Electrochemical data also support this conclusion (vide infra).

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The absorption spectrum of **6** also shows feature similar to those observed for **5**. The data in Table 2 clearly indicate quenching of intensity and small blue shifts of absorption bands of normal Ni²⁺ porphyrin subunit suggesting an interaction between the two subunits. The similarity of the absorption spectra of the Ni²⁺ thiaporphyrin subunit (split Soret band and complex pattern Q bands) with that of Ni(STPP)Cl^{11d,12g} again suggests a distorted square pyramidal geometry around Ni²⁺ in the thiaporphyrin subunit in **6**. Thus, Ni²⁺ is five coordinate in the thiaporphyrin subunit while it is four coordinate in the normal porphyrin subunit. FAB mass data also are consistent with this composition.

(d) Electrochemistry. The redox chemistry of various diporphyrins was followed by cyclic voltammetry. All the cyclic voltammograms were recorded in CH₂Cl₂ using 0.1 M TBAP as the supporting electrolyte at a scan rate of 100 mV/s. Differential pulse voltammograms (*V* = 10 mV/s) have also been recorded for a precise measurement of redox potentials. The redox potential data for the diporphyrins and some of the monomeric derivatives are tabulated in Table 3.

The cyclic voltammogram of **3** is displayed in Figure 4. It is apparent from the figure that there are three oxidation processes at 0.942, 1.046, and 1.288 V. The first two oxidations are irreversible, while the third oxidation is quasireversible ($\Delta E_p = 100$ mV). The oxidation wave at 0.942 V is assigned to the oxidation of the thiaporphyrin subunit on the basis of the fact that this value is close to that observed for the first oxidation of **2** (Table 3). The oxidation waves at 1.046 and 1.288 V are assigned to the first and second oxidations of the normal porphyrin subunit on the basis of the following: (a) These potentials are closer to those observed first and second oxidations of **1** (Table 3). (b) The difference in potentials between the two oxidations is in the range (0.29 ± 0.05 V) expected for two successive oxidations.¹⁸ When scanning to negative potentials is undertaken, **3** shows three reduction processes at -1.10, -1.15, and -1.57 V (Figure 4). The first reduction at -1.10 V (seen clearly in the differential pulse voltammogram) is assigned to the first reduction of the thiaporphyrin subunit on the basis of the fact that thiaporphyrins are easier to reduce relative to normal porphyrins.^{12i,19} The two reduction waves at -1.15 V ($\Delta E_p = 169$ mV) and -1.57 V ($\Delta E_p = 181$ mV) are assigned to the first and second reductions of the normal porphyrin unit since the potential

(17) This was further confirmed by recording the EPR spectrum of **5** in CHCl₃:toluene solution at room temperature. The observed EPR parameters for **5** ($g_0 = 2.09$, $A_0^{\text{Cu}} = 71.8 \times 10^{-4}$ cm⁻¹, and $A_0^{\text{N}} = 14.9 \times 10^{-4}$ cm⁻¹) are closer to those observed for Cu(STPP)Cl ($g_0 = 2.14$, $A_0^{\text{Cu}} = 70 \times 10^{-4}$ cm⁻¹, $A_0^{\text{N}} = 14.8 \times 10^{-4}$ cm⁻¹) rather than to CuTPP ($g_0 = 2.107$, $A_0^{\text{Cu}} = 97.7 \times 10^{-4}$ cm⁻¹, $A_0^{\text{N}} = 15.9 \times 10^{-4}$ cm⁻¹) and at -140 °C, $g_{\perp} = 2.192$, $g_{\parallel} = 2.05$, $A_{\perp}^{\text{Cu}} = 163.15 \times 10^{-4}$ cm⁻¹ and $A_{\perp}^{\text{N}} = 14.01 \times 10^{-4}$ cm⁻¹.

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Table 3. Redox Potentials^a (V) of Diporphyrins and Their Corresponding Monomers

porphyrin	oxidn $E_{1/2}^{ox}$			$E_{1/2}$ (M^{2+}/M^+)	redn $E_{1/2}^{red}$		
	I	II	III		I	II	III
1	0.992 ^b	1.254 ^b			-1.181	-1.59 ^b	
Zn deriv of 1	0.735	1.029			-1.315		
2	0.93 ^b	1.376 ^b			-1.092	-1.57 ^b	
3	0.942 ^b	1.046 ^b	1.288		-1.10 ^b	-1.15	-1.57
4	0.735	1.02	1.231		-1.1	-1.312	-1.576 ^b
5	0.919	1.173	1.362	-0.0885	-0.854 ^b	-1.046 ^b	
6	0.98	1.121 ^b	1.4 ^b	-0.280	-0.885		

^a In CH_2Cl_2 containing 0.1 M TBAP. ^b Peak potentials for an irreversible process.

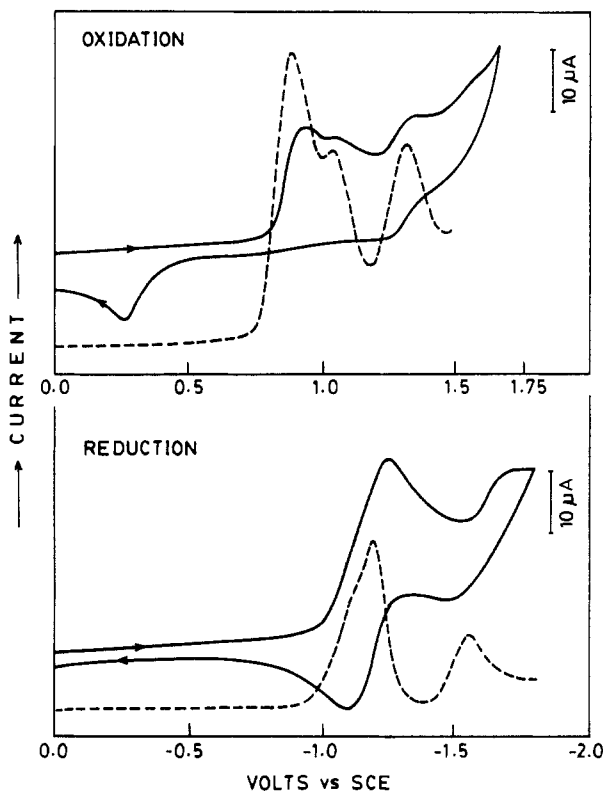


Figure 4. Cyclic voltammogram ($v = 100$ mV/s) and differential pulse voltammogram ($v = 10$ mV/s) (---) of **3** in CH_2Cl_2 .

difference between the two reductions is in the expected range of 0.42 ± 0.05 V.¹⁸ A comparison of redox potential data for **3** with those of **1** and **2** suggests little interaction between the two porphyrin subunits as concluded from the ¹H NMR data. A similar conclusion was arrived at by Becker²⁰ and co-workers for the covalently monolinked zinc porphyrin dimers.

The cyclic voltammogram of **4** shown in Figure 5 indicates three oxidation waves at 0.735, 1.02, and 1.23 V. All the three oxidations are quasireversible. The oxidation waves at 0.735 and 1.02 V correspond to the first and second oxidations of the zinc porphyrin subunit. These assignments were confirmed by synthesizing Zn^{2+} derivatives of **1** (Table 3). Furthermore, the potential difference between two oxidations also lies in the range 0.29 ± 0.05 V. The small shoulder at 1.023 V in the differential pulse voltammogram is unassigned. The oxidation wave at 1.231 V was assigned to the first oxidation of the thiaporphyrin unit in **3** indicating a harder oxidation. Upon reduction, **4** shows three waves at potentials -1.1, -1.312, and -1.576 V. The reduction waves at -1.1 and -1.576 V are assigned to the first and second reductions of the thiaporphyrin subunit on the basis of the closeness of these values to those observed for **3** and **2**. The reduction wave at -1.312 V is reversible and is attributed to the

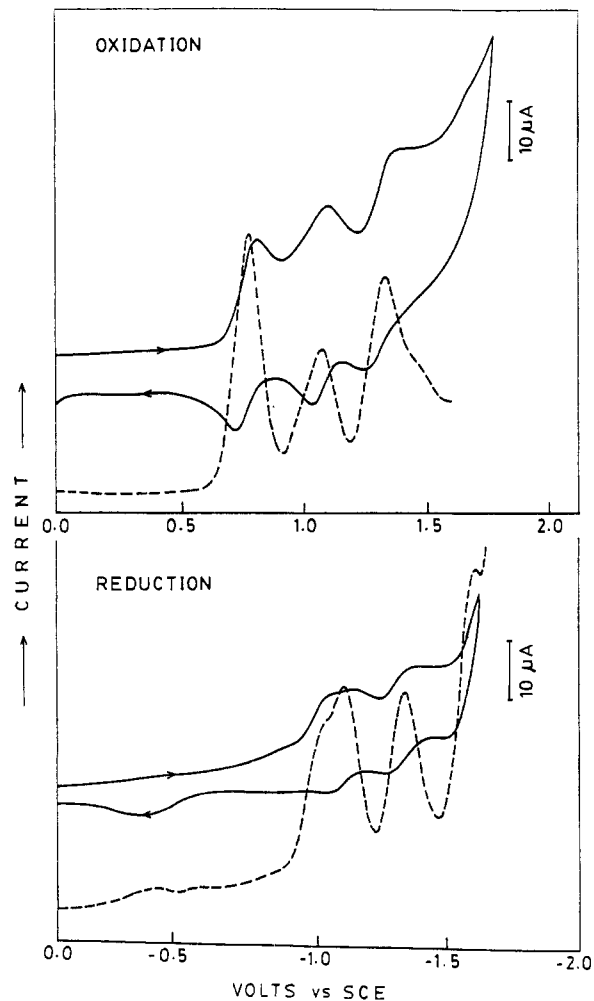


Figure 5. Cyclic voltammogram ($v = 100$ mV/s) and differential pulse voltammogram ($v = 10$ mV/s) (---) of **4** in CH_2Cl_2 .

first ring reduction of the zinc porphyrin unit. The zinc derivative of **1** also shows this reduction at the same potential.

The cyclic voltammogram of **5** is shown in Figure 6. The oxidation at 1.173 V is assigned to the oxidation of the copper thiaporphyrin ring since this value is close to that observed for $Cu(STPP)Cl$ in CH_2Cl_2 .¹²ⁱ The oxidation waves at 0.919 and 1.362 V are assigned to the first and second oxidations of the zinc porphyrin unit. These two oxidation potentials are shifted to more positive values by 184 and 342 mV, respectively, relative to the same oxidations in **4** suggesting harder oxidations. This must be attributed to the structural change accompanying the Cu^{2+} insertion which in turn induces the interaction between the two subunits as found in the optical absorption data.

Three reduction waves are seen upon reduction of **5** at potentials -0.0885, -0.854, and -1.046 V. The first reduction wave is reversible when scanned separately (Figure 6 inset), and this potential is completely away from the range of ring reduction potentials of either the zinc porphyrin subunit or copper

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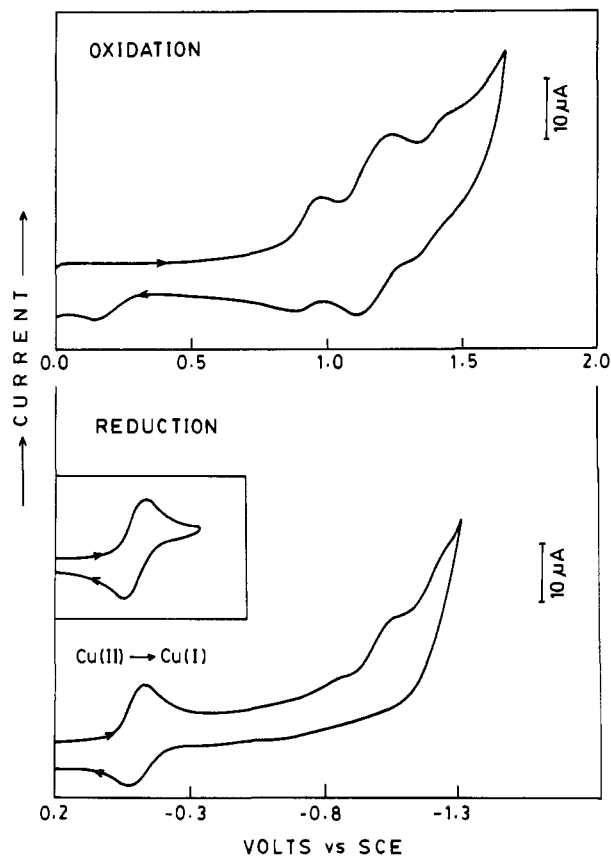


Figure 6. Cyclic voltammogram ($v = 100$ mV/s) of **5** in CH_2Cl_2 . [The inset shows the reversible nature of the Cu(II)/Cu(I) reduction.]

monothiaporphyrin subunit. On the basis of earlier results^{11d,12i} on copper(II) derivatives of monothiaporphyrins, this reduction is attributed to a metal-centered reduction corresponding to the reduction of Cu(II)/Cu(I) in the thiaporphyrin subunit. The second reduction at -0.854 V is assigned to the ring reduction of the thiaporphyrin subunit. Again this potential is close to that observed for Cu(STPP)Cl . The reduction wave at -1.046 V is assigned to the ring reduction of the zinc porphyrin subunit. A comparison of this value with that in **4** indicates a 266-mV positive shift suggesting easier reduction again due to the structural change accompanying the Cu^{2+} insertion into the thiaporphyrin subunit.

The cyclic voltammogram of **6** in Figure 7 indicates three oxidation waves at 0.98 ($\Delta E_p = 69$ mV), 1.12, and 1.4 V (irreversible oxidations). The oxidations at 0.98 and 1.4 V are assigned to the first and second oxidations of the Ni(II) normal porphyrin subunit on the basis of similarities of these potentials with that of NiTPP .²¹ The small shifts suggests the effect of introduction of Ni^{2+} to the thiaporphyrin unit. The oxidation at 1.12 V is assigned to the first ring oxidation of the nickel(II) thiaporphyrin subunit. When scanning to negative potentials is undertaken, two reductions at -0.28 ($\Delta E_p = 64$ mV) and -0.885 V ($\Delta E_p = 77$ mV) are observed. The potential for the first reduction is not in the range expected for the ring reduction of either the thiaporphyrin subunit or the normal porphyrin subunit. On the basis of our earlier work on the water-soluble Ni(II) monothiaporphyrin,^{11d} this first reduction at -0.28 V has been assigned to the reduction of nickel present in the thiaporphyrin subunit. This potential is close to (-0.23 V) that observed for the reduction of nickel in Ni(STPP)Cl in THF.^{12b} The second reduction at -0.885 V is assigned to the first ring reduction of the thiaporphyrin subunit. This is based on the following two observations: (i) The ring reduction in Ni(STPP)Cl thiaporphyrin

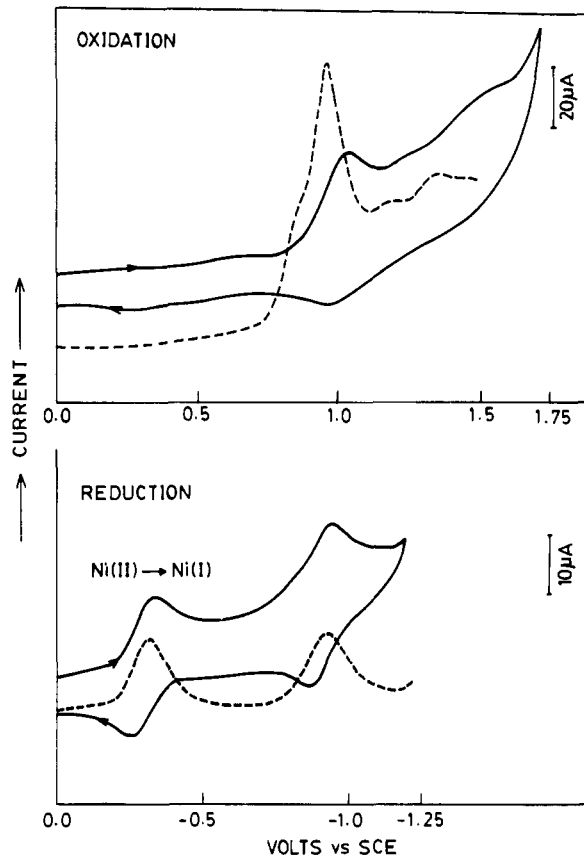


Figure 7. Cyclic voltammogram ($v = 100$ mV/s) and differential pulse voltammogram ($v = 20$ mV/s) (---) of **6** in CH_2Cl_2 .

is at -0.82 V and (ii) normal nickel(II) porphyrins exhibit a first ring reduction at -1.2 V.²¹ Further scanning above -1.0 V results in the decomposition of the sample probably suggesting a coupled chemical reaction. Thus, the Ni(II)-Ni(I) diporphyrin can be at least observed electrochemically.

Literature data reveal that the electronic interaction between the two porphyrin rings in the dimeric porphyrins significantly alters the redox potentials and light absorption and emission energies.^{2b,22-24} The strength of such an interaction depends on a number of factors such as interplanar distance,^{22a} orientation of one porphyrin ring with respect to the other,²⁴ shape of the porphyrin cavity,^{22b} extent of ruffling of the porphyrin ring upon metal insertion,^{2b} and the nature of the bridging group.^{22a,c} Bruce and co-workers from their studies on a series of aza-bridged bis(porphyrins) have accounted for the altered redox potentials in the dimers in terms of a decreased center to center distance because of the steric bulk of the bridging group.^{22a} Chang and co-workers have related the electrocatalytic activity of anthracene pillared bis(porphyrins) to the slip of the porphyrin ring with respect to each other, which in turn controls the metal-metal distance.^{2b} In these systems, the X-ray structure reveals the porphyrin ring ruffling upon insertion of the metal. Thus the observed changes in the redox potentials and the transition energies in Zn-Cu and Ni-Ni diporphyrins described here are ascribed to $\pi-\pi$ interaction between the two dimeric subunits. It is proposed that the structural change required for thiophene coordination to the metal in the thiaporphyrin subunit facilitates such an interaction between the two subunits probably due to the decreased center to center or interplanar distance. Only the X-ray structure of the one of the diporphyrins can confirm such a conclusion.

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(e) Conclusions. Synthesis of a unique diporphyrin containing N_4 and N_3S cores have been achieved. Metal ions such as Zn^{2+} , Cu^{2+} , and Ni^{2+} present in the porphyrin cores yield both homo- and heterobimetallic diporphyrins. 1H NMR, FAB mass, EPR, and optical absorption spectroscopy and cyclic voltammetry have been used to characterize these diporphyrins. The spectral studies reveal only weak interaction between the two subunits in the free base diporphyrin **3** and Zn-H diporphyrin **4**. However, introduction of a metal to the thiaporphyrin subunit results in a substantial interaction between normal and thiaporphyrin subunits. A blue shift and quenching of the absorbance of Q and Soret bands and a positive shift of oxidation and reduction potentials of the zinc normal porphyrin subunit in **5** justifies such a conclusion. Furthermore, in bimetallic diporphyrins the geometries around the two metals are different due to the differing electronic structure of the two porphyrin subunits. In **5** and **6** the observation that the first reduction is metal centered (the

metal present in the thiaporphyrin subunit) indicates the reversal of order of energy levels of the metal $d_{x^2-y^2}$ and the porphyrin $e_g(\pi^*)$ similar to that observed for individual metallot-hiaporphyrins.^{11d,12b} The possibility of stabilization of different oxidation states of the metals in homo- and heterobimetallic diporphyrins is interesting, and the preliminary studies on chemical reduction of **6** and **5** using mild reducing agents (sodium dithionite in water-ethyl acetate) reveal the presence of Ni(II)-Ni(I) and Zn(II)-Cu(I) in the N_4 and N_3S cores, respectively. We think the easy synthetic accessibility and stability of this unique diporphyrin merit further investigation.

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