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Effect of Peripheral Substitution and Extended Conjugation on the Redox Potentials of Nickel Porphycenes

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Introduction

Several reports[1] have appeared in the literature describing the spectral and electrochemical behavior of porphycenes, the most widely investigated of the porphyrin structural isomers.[2] The redox properties of metalloporphycenes are similar to those of metalloporphyrins upon oxidation but not upon reduction where reduction at the metal is more difficult to achieve and ring-centered reactions predominate in the case of the porphycenes. The ring-centered reductions of metalloporphycenes such as octaethylporphycene (OEPc) and tetrapropylporphycene (TPrPc) occur at potentials which are shifted positively by up to 300 mV with respect to $E_{1/2}$ of the corresponding metalloporphyrins containing octaethylporphyrin (OEP) or tetraphenylporphyrin (TPP) macrocycles.[1a,b] The more facile reduction of the metalloporphycenes leads to a smaller HOMO-LUMO energy gap as compared to the metalloporphyrins with the same central metal ion and this value, given by $\Delta E_{1/2} = E_{1/2}(\mathrm{ox}) - E_{1/2}(\mathrm{red})$, has been proposed to average 1.85 ± 0.15 V for a variety of porphycenes,[1a,b,e] as compared to the well-quoted value of 2.25 ± 0.15 V for porphyrins containing OEP or TPP type macrocycles.[3,4]

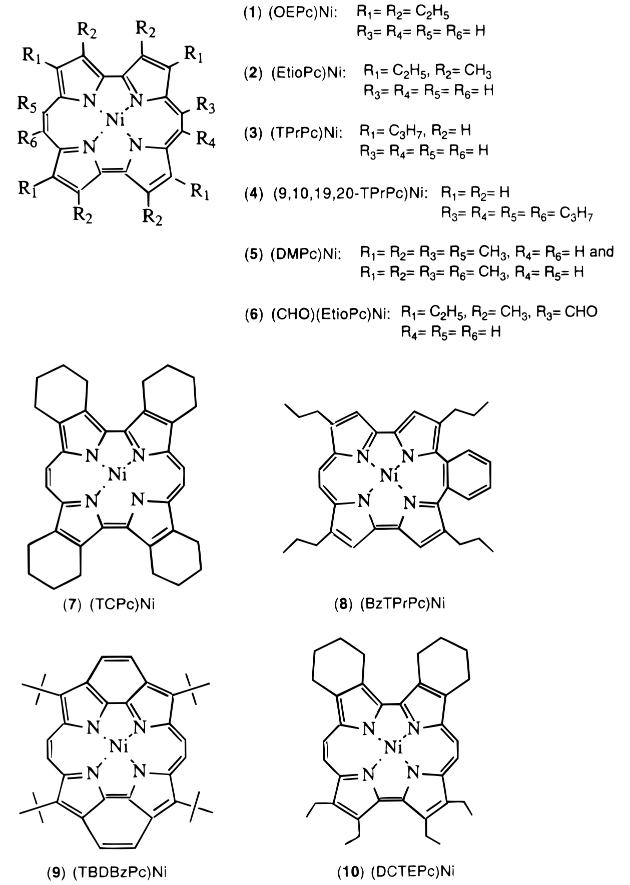

Figure 1. Structures of nickel porphycenes employed in the present study.

It is now well known that the HOMO−LUMO separation of 2.25 V in the case of metalloporphyrins will depend in large part on the type and position of substituents on the macrocycle,[5,6] and this is also the case for the porphycenes as will be shown in the present paper which reports the electrochemistry of eight different nickel porphycenes bearing substituents on the pyrrole β and/or the ethylenic carbons of the macrocycle.

Structural formulas of the investigated porphycenes are shown in Figure 1. Two of the compounds, (BzTPrPc)Ni (**8**) and (TBDBzPc)Ni (**9**), have an increased π-conjugation. Compound **8** possesses a fused six membered ring on one set of the ethylenic carbons while compound **9** has two conjugated six membered rings which are formed by bridging the pyrrole β carbons of adjacent pyrrole rings.

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Experimental Section

Chemicals. Benzonitrile (PhCN), obtained from Aldrich Chemicals was distilled over P_2O_5 under reduced pressure. Tetra-*n*-butylammonium perchlorate (TBAP), obtained from Eastman Chemicals, was recrystallized from ethanol and then dried in vacuo at 40 °C.

Synthesis of Compounds. The synthesis of (OEPc)Ni, **1**, is described in ref 1b while the syntheses of (TPrPc)Ni, **3**, and (TPrPc-(9,10,19,20))Ni, **4**, are described in ref 1a. The synthetic procedures for the other compounds are given below.

(EtioPc)Ni, 2. A mixture of 48 mg (0.1 mmol) of $(EtioPc)H_2$ and 124 mg (0.5 mmol) of nickel(II) acetate tetrahydrate in 30 mL of acetic acid was refluxed for 2 h. The complex was precipitated on cooling the reaction mixture. The solid was collected by filtration and washed several times with water. Further crystallization was carried out in toluene, and the product was recovered in 90% yield (48.6 mg) as violet cubes. ^{1}H NMR ($CDCl_3$): δ 9.36 (s, 4H, H-9,10,19,20), 3.85 (q, 8H, H-2a,7a,12a,17a), 3.53 (s, 12H, H-3a,6a,13a,16a), 1.70 (t, 12H, H-2b, 7b,12b,17b). UV/vis (CH_2Cl_2), λ_{max}, nm (ϵ): 368 (45 000), 389 (138 000), 560 (13 900), 600 (43 000). MS: *m*/*z* 540.

(DMPc)Ni, **5.** A mixture of 45 mg (0.1 mmol) of $(DMPc)H_2$ and 124 mg (0.5 mmol) of nickel(II) acetate tetrahydrate in 30 mL of acetic acid was refluxed for 2 h. The complex was precipitated on cooling the reaction mixture. The solid was collected by filtration and washed several times with water. Further crystallization was carried out in toluene, and the product was recovered in 90% yield (45.5 mg). ^{1}H NMR ($CDCl_3$): δ 8.80 (s, 2H-9,19 trans), 8.75 (s, 2H, H-10,19 cis), 3.74 and 3.71 (2s, 6H, CH_3-R_3, R_6), 3.31−3.17 (8s, 24H, CH_3-R_1, R_2). UV/vis (CH_2Cl_2), λ_{max}, nm: 398, 585, 630. MS: *m*/*z* 506.

(CHO)(EtioPc)Ni, 6. The Vielsmeier Haack reagent was prepared according to the classical procedure: $POCl_3$ (6.8 mL) was added dropwise in 5 mL of dry DMF at 0 °C under nitrogen. The reaction mixture was maintained at room temperature for 30 min. A solution of (EtioPc)Ni (50 mg) in 1,2-dichloroethane (40 mL) was added dropwise under vigorous stirring with 1.5 mL of the Vielsmeier Haack solution at 50 °C. The reaction mixture was refluxed for 30 min and poured into a saturated sodium acetate solution (100 mL). Sodium hydroxide solution was added to the reaction mixture to increase the pH to 12, after which the mixture was heated for another 30 min. The desired compound was recovered by solvent extraction using CH_2Cl_2 and recrystallized in CH_2Cl_2-CH_3OH (yield = 40%). ^{1}H NMR ($CDCl_3$): δ 11.60 (s, 1H, −CHO), 9.70 (s, 1H, H-10), 9.73−9.42 (dd, 2H, H-19,20), 1.8-4.0 (m, 32H, alkyl groups). UV/vis (CH_2Cl_2), λ_{max}, nm (ϵ): 416 (13 400), 617 (4200), 643 (3500).

(TCPc)Ni, 7. A mixture of 53.3 mg (0.1 mmol) of $(TCPc)H_2$ and 124 mg (0.5 mmol) of nickel(II) acetate tetrahydrate in 30 mL of acetic acid was refluxed for 2 h. The complex was precipitated on cooling the reaction mixture. The solid was collected by filtration and washed several times with water. Further crystallization was carried out in toluene, and the product was recovered in 90% yield (53 mg). ^{1}H NMR ($CDCl_3$) δ, 9.30 (s, 4H, H-9,10,19,20), 3.95−2.30 (m, 32H, alkyl groups). UV/vis (CH_2Cl_2), λ_{max}, nm (ϵ): 368 (46 200), 390 (139 600), 560 (15 000), 608 (44 200). MS: *m*/*z* 589.

(BzTPrPc)Ni, **8.** A 53 mg (0.1 mmol) sample of $(BzTPrPc)H_2$ was dissolved in 10 mL of dichloromethane and 50 mL of acetic acid. Then 177 mg (1 mmol) of nickel(II) acetate was added, and the mixture was refluxed for 4 h. The complex was precipitated on cooling the solvent to room temperature. The solid was collected by filtration and washed with hexane. Crystallization from hexane yielded 85% (50 mg) of **8** as violet needles. ^{1}H NMR ($CDCl_3$): δ 8.89 (m, 2H, H-9a,10a), 7.89 (s, 2H, H-6,13) 7.75 (s, 2H, H-19,20), 7.66 (s, 2H, H-3,16), 7.48 (m, 2H, H-9b,10b), 3.38 (t, 4H, H-7a,12a), 3.20 (t, 4H, H-2a,17a), 1.98 (m, 4H, H-2b,17b), 1.87 (m, 4H, H-7b,12b), 1.14 (t, 6H, H-2c,17c), 1.02 (t, 6H, H-7c,12c). UV/vis (CH_2Cl_2), λ_{max}, nm (ϵ): 279 (35 200), 333 (17 500), 406 (67 600), 605 (12 900), 740 (9800), 817 (22 200). MS: *m*/*z* 584.

(TBDBzPc)Ni, 9. A mixture of 116 mg (0.2 mmol) of $(TBDBzPc)H_2$ and 514 mg (2 mmol) of nickel(II) acetylacetonate in 15 mL of freshly distilled phenol was refluxed for 4 h under a blanket of nitrogen. The solvent was removed under vacuum, and the residue was purified over a silica gel column using CS_2 as eluent. The first fraction was found to contain the desired compound. Further crystallization of the compound was carried out in chloroform/ethanol (3/1) and the product was recovered in a 40% yield (51 mg) as violet cubes. ^{1}H NMR ($CDCl_3$): δ 8.75 (s, 4H, H-9,10,19,20), 7.08 (s, 4H, H-3a,6a,13a,16a), 1.92 (s, 36H, H-2b,7b,12b,17b). UV/vis (CH_2Cl_2), λ_{max}, nm (ϵ): 258 (41 900), 287sh (26 100), 359 (42 400), 372 sh (35 800), 406 sh (28 200), 538 sh (8500), 580 (10 200), 676 sh (12 900), 739 (28 500). MS: *m*/*z* 638.

Table 1. Half-Wave Potentials, V vs. SCE, for Nickel(II) Porphycenes in PhCN Containing 0.1 M TBAP

compd	macrocycle	$E_{1/2}$, V vs SCE					
		oxidation			reduction		
		third	second	first	first	second	$\Delta E_{1/2}$[b]
1	OEPc	1.74	1.09	0.81	−1.11	−1.47	1.92
2	EtioPc	1.76	1.16	0.82	−1.06	−1.47	1.88
3	TPrPc[a]		1.34	0.90	−0.99	−1.36	1.89
4	TPrPc (9,10,19,20)[a]		1.05	0.81	−0.81	−1.05	1.62
5	DMPc	1.83	0.90	0.67	−1.02	−1.29	1.69
6	(CHO)EtioPc	1.82	1.12	0.91	−0.86	−1.17	1.77
7	TCPc	1.90	1.15	0.81	−1.20	−1.53	2.01
8	BzTPrPc	1.90	0.94	0.64	−0.69	−1.02	1.33
9	TBDBzPc			1.06	−0.58	−0.91	1.64
10	DCTEPc	1.77	1.15	0.83	−1.14	−1.50	1.97

[a] Measured in CH_2Cl_2. Data from ref 1a. [b] HOMO−LUMO gap given by $\Delta E_{1/2} = E_{1/2}$(first oxidation) − $E_{1/2}$(first reduction).

(DCTEPc)Ni, **10.** A mixture of 53 mg (0.1 mmol) of $(DCTEPc)H_2$ and 124 mg (0.5 mmol) of nickel(II) acetate tetrahydrate in 30 mL of acetic acid was refluxed for 2 h. The complex was precipitated on cooling the reaction mixture. The solid was collected by filtration and washed several times with water. Further crystallization was carried out in toluene, and the product was recovered in 90% yield (52.7 mg). ^{1}H NMR ($CDCl_3$): δ 9.42−9.20 (2d, 4H, H-9,10,19,20), 3.98 (m, 4H, α,α'-cyclohexyl), 3.89 (m, 8H, H-12a,13a,16a,17a), 2.32 (broad s, 8H, β,β'-cyclohexyl), 1.70 (m, 12H, H-12b,13b,16b,17b). UV/vis (CH_2Cl_2), λ_{max}, nm (ϵ): 372 (43 200), 390 (122 500), 562 (12 900), 596 (38 400), 609 (32 100). MS: *m*/*z* 586.

Instrumentation and Methods. Cyclic voltammetry was carried out with an EG&G Model 173 potentiostat or an IBM Instruments Model EC 225 voltammetric analyzer. Current-voltage curves were recorded on a Houston Instruments Model 2000 X-Y recorder. A three-electrode system was used and consisted of a platinum or glassy-carbon button working electrode, a platinum-wire counter electrode, and a saturated calomel electrode (SCE) as reference. The reference electrode was separated from the bulk of the solution by a fritted-glass bridge filled with the solvent and supporting electrolyte. Solutions containing the supporting electrolyte and the metalloporphycene were first deoxygenated by a stream of nitrogen for at least 10 min and then protected by a blanket of nitrogen which was passed over the solution during the experiment. All potentials are referenced to the SCE.

Spectroelectrochemical experiments and thin-layer coulometry were performed at a platinum thin-layer electrode whose design is described in the literature.[7] Potentials were monitored with an IBM Instruments Model EC 225 voltammetric analyzer. Time-resolved UV−visible spectra were recorded with a Tracor Northern Model 6500 rapid spectrophotometer/multichannel analyzer.

Results and Discussion

In agreement with earlier studies,[1g] seven of the eight Ni(II) porphycenes whose potentials were measured in this study undergo three one-electron oxidations and two one-electron reductions within the potential window of benzonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP) (see Table 1). The third oxidation of compounds **3** and **4** was not reported in the literature[1a] and the only clear exception to the three oxidations is compound **9** which has a substantially increased

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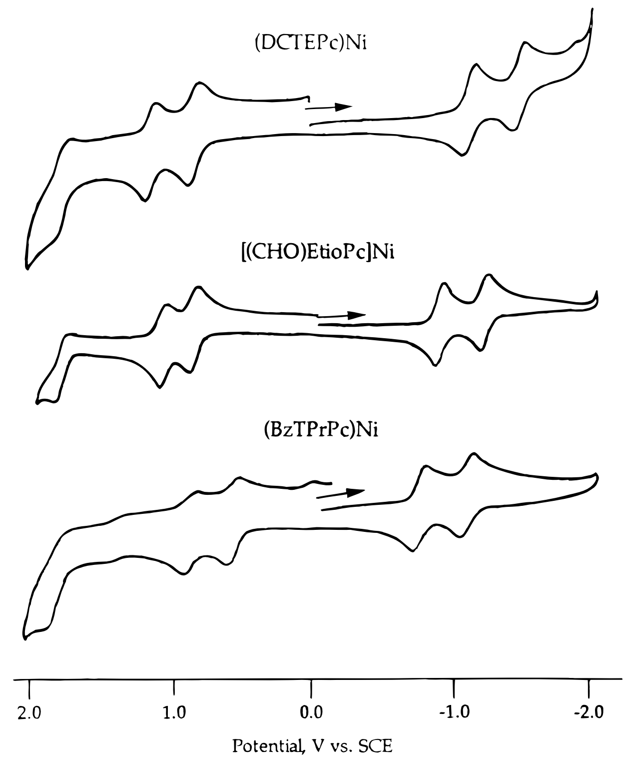

Figure 2. Cyclic voltammograms of a few representative nickel porphycenes in PhCN containing 0.1 M TBAP.

degree of conjugation as compared to the other nine porphycenes shown in Figure 1. Selected cyclic voltammograms are shown in Figure 2. The first two reductions and first two oxidations of each compound involve the macrocycle and the third oxidation is proposed to involve the nickel center and a metal centered Ni(II)/Ni(III) transition. Half-wave potentials for the oxidations and reductions of each compound are listed in Table 1.

The $\Delta E_{1/2}$ values vary from 2.01 V for (TCPc)Ni (**7**) to 1.33 V for (BzTPrPc)Ni (**8**), thus accounting for a difference of nearly 700 mV as a result of changes in the type and positions of substituents and/or degree of ring conjugation. Among the pyrrole β-substituted porphycenes, the octasubstituted derivatives (**1**, **2**, **7** and **10**) are easier to oxidize and more difficult to reduce as compared to the tetrasubstituted porphycene, **3**. This is consistent with the electron-donating nature of the alkyl groups. The potential difference between the first oxidation and the first reduction, $\Delta E_{1/2}$, corresponding to the electrochemically measured HOMO−LUMO energy gap, does not vary appreciably with the number of alkyl substituents on the pyrrole β positions and averages 1.94 ± 0.07 V for **1**, **2**, **3**, **7** and **10** (see Table 1). In contrast, noticeable changes in both the half-wave potentials and the HOMO−LUMO energy gap are observed for the compounds which have alkyl groups on the ethylenic carbons (**4**, **5**, and **6**) or those with an extended macrocycle conjugation (**8** and **9**).

Table 2. UV−visible Data for Nickel(II) Porphycenes in PhCN

compd	macrocycle	λ_{max},[c] nm					
1	OEPc	370 sh	394	606	621 sh		
2	EtioPc	370 sh	393	565 sh	606		
3	TPrPc[a]	366 sh	387	558 sh	600	614	
4	TPrPc (9,10,19,20)[b]	393		600 sh	643		
5	DMPc	380 sh	402	590 sh	632		
6	(CHO)EtioPc		418	619	646 sh		
7	TCPc	370 sh	395	596	610		
8	BzTPrPc	410	500 sh	610	622 sh	740 sh	819
9	TBDBzPc	361	414 sh	542	582	680	744
10	DCTEPc	370 sh	393	602	612		

[a] Measured in CH_2Cl_2. Data from ref 2g. [b] Measured in CH_2Cl_2. Data from ref 2h. [c] sh: shoulder.

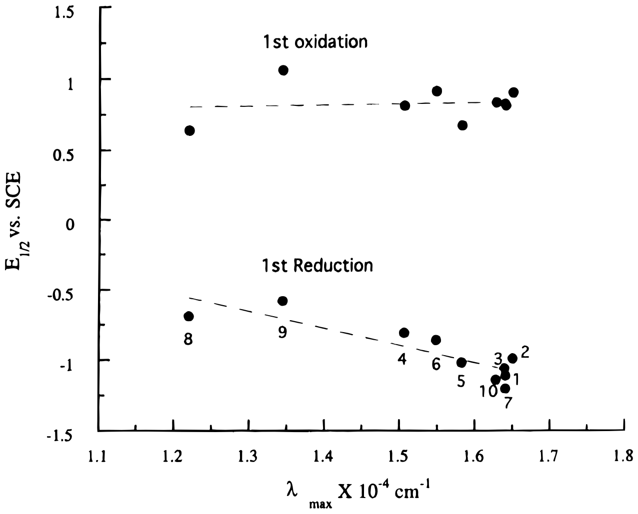

Figure 3. Correlation between the first oxidation and first reduction potentials of the complexes and the wavelength maximum of their lowest energy absorption.

A summary of the UV−visible spectra for each compound is given in Table 2 while Figure 3 shows the correlation which exists between redox potentials, in V *vs.* SCE, for the first oxidation or first reduction of the 10 compounds and the absorption maxima, in cm^{-1}, for the lowest energy transition of the same porphycenes. This plot quantitatively illustrates how the HOMO and LUMO energy levels are perturbed as a result of substituents on the macrocycle. The data in Table 1 and Figure 3 clearly indicate that the HOMO level is relatively invariant with changes in the type and position of substituents and the degree of ring conjugation (see $E_{1/2}$ values for compounds **1**, **2**, **3**, **4**, **7** and **10**) as opposed to the LUMO level which shifts substantially for the same series of compounds.

The macrocyclic ring of (9,10,19,20-TPrPc)Ni, **4**, is moderately nonplanar due to the twisting deformation around the ethylenic carbons as a result of steric effects caused by the four propyl entities[2h] as compared to that of (2,7,12,17-TPrPc)Ni, **3**. Furthermore, EPR studies on the electrochemically generated π-anion radical of (OEPc)Ni (**1**) have demonstrated that the unpaired electron in this B_{2g} type radical is localized on the four nitrogens and four hydrogens of the ethylenic bridges of the porphycene macrocycle.[1b,d] Thus, a substitution at the ethylenic carbons or any variation in geometry of the macrocycle at the same position is expected to perturb the LUMO energy level more than substitution at the pyrrole β positions. This would explain the large, 620 mV, variation in reduction potentials as opposed to the smaller, 390 mV, range in $E_{1/2}$ values for oxidation of the same series of compounds. Similar effects may also be applicable but, to a lesser extent, for the two HOMO orbitals of the compounds (a_u and b_{1u}) which are almost degenerate[1b,c,h] and these different effects on the HOMO and LUMO orbitals lead to a smaller gap (as quantitated by $\Delta E_{1/2}$) for (9,10,19,20-TPrPc)Ni (**4**) where the alkyl groups are on the ethylenic bridges, as compared to (2,7,12,17-TPrPc)Ni (**3**) which has the four alkyl groups attached directly at the pyrrole β positions of the macrocycle. In a similar manner, (DMPc)Ni (**5**), which has a methyl group on each of the ethylenic carbons and (CHOEtioPc)Ni (**6**), which has an electron withdrawing aldehyde group on one of the ethylenic carbons, both have smaller values of $\Delta E_{1/2}$ (see Table 1).

Extending the π-conjugation of the compounds also results in a further lowering of the HOMO-LUMO energy gap and this is in agreement with the general trend observed in the case of polyaromatic hydrocarbons.[7] The magnitude of this effect is larger for (BzTPrPc)Ni (**8**) which possesses only one fused six-membered ring on the ethylenic carbons than for (TBDBzPc)-Ni (**9**) which has two fused six-membered rings through the pyrrole β carbons. This, once again, agrees with the trend that substituents at the ethylenic carbons of the porphycene have more of an effect on $E_{1/2}$ than do those at the pyrrole β carbons.

In summary, the investigated nickel porphycenes are the first examples where the HOMO−LUMO energy gap of tetrapyrrole macrocycles can be varied by over 700 mV as a result of "simple" changes in the macrocycle substitution or an extended conjugation of the macrocycle. These studies also show that substitution at the ethylenic carbons of a porphycene macrocycle perturbs the energy levels more than does substitution at the pyrrole β positions. Finally, extending the conjugation of the porphycene ring leads to a smaller $\Delta E_{1/2}$ although, in the case of **9**, the effects are more complicated as evidenced by the lack of a third metal centered oxidation and the much more positive than expected value for the first oxidation potential.

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