# Electrochemical Studies of Corrphycenes and Metallocorrphycenes

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Corrphycene **3** (Cn) is a structural isomer of porphyrin **1** that was synthesized for the first time 5 years ago. This paper reports on the redox properties of free-base octaethylcorrphycene $H_2OECn$ and 16 metal complexes derived therefrom. In $CH_2Cl_2$ solution, the free base and the metallo(II) octaethylcorrphycenes, $M^{II}OECn$, typically undergo four distinct one-electron redox steps involving the tetrapyrrolic macrocycle, of which two are reduction steps and two are oxidations. One exception to this general pattern is displayed by the $Co^{II}OECn$ complex. In this instance, the first one-electron reduction is metal-centered and produces $Co^{I}OECn$. A comparison of the redox potentials of corrphycenes with those of porphyrins and porphycenes indicates that the first reduction potentials of the free base and of the metallo-octaethylcorrphycenes are between those of the porphycenes—the easiest to reduce molecules in this set of isomeric tetrapyrrolic systems—and those of the porphyrins. The oxidation potentials of corrphycenes and porphyrins are found to be quite similar. On the other hand, porphycenes are oxidized at less positive potentials. The redox gap $\Delta E_{1/2} = E_{1/2}^{\mathrm{Ox}}1 - E_{1/2}^{\mathrm{Red}}1$ is equal to 2.15 ± 0.08 V for the free base corrphycene and the various metallocorrphycenes that were subjected to study. This redox gap is not much different from that observed in porphyrins ($\Delta E_{1/2} = 2.25 \pm 0.1$ V), whereas if differs significantly from that observed in porphycenes ($\Delta E_{1/2} = 1.85 \pm 0.15$ V). The sequence of these $\Delta E_{1/2}$ values parallels the lowest energy absorption maxima observed in the UV−vis spectra of these three isomers.

## 1. Introduction

Although porphyrins, being molecules attracting interdisciplinary interest, have been the subject of intense research,[1,2] it was only fairly recently (1986)[3] that a constitutional isomer of porphyrin **1** ([18]porphyrin-(1.1.1.1))[4] was synthesized. This isomer, termed porphycene **2** ([18]porphyrin-(2.0.2.0))[4] (Figure 1), contains a rectangular, inward-pointing[3] $N_4$ coordinating core and, like porphyrin, may be regarded as a hetero [18]annulene. Porphycene and its derivatives form stable complexes with quite a variety of di- and trivalent metal cations and display well-defined Soret and Q-like bands in the visible spectrum.

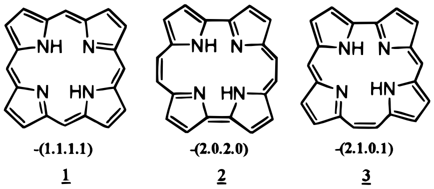

**Figure 1.** Free-base porphyrin **1** ([18]-porphyrin-(1.1.1.1.)) and its isomers porphycene **2** ([18]-porphyrin-(2.0.2.0.)) and corrphycene **3** ([18]-porphyrin-(2.1.0.1.)). The three isomers are reported here as [18]-porphyrins-(...).

In addition to porphycene, several other porphyrin isomers have become known during the past few years.[5] Among these, corrphycene **3** ([18]porphyrin-(2.1.0.1), Figure 1) has been prepared by no less than four groups as its $\beta$-octamethyl-,[6] $\beta$-tetramethyltetraethyl-,[7,8] $\beta$-octaethyl-,[7] and $\beta$-hexamethylbisethoxycarbonyl[9] derivatives. Corrphycene contains a trapezoidal $N_4$ coordinating core but, like porphyrin and porphycene, is capable of stabilizing complexes from a wide range of di- and trivalent metal cations.[9] To date, corrphycene has been characterized structurally in both its free-base[7] and protonated forms[11] as well as in the form of numerous metal complexes. However, it has yet to be subjected to detailed electrochemical analysis. In this paper we report the redox properties of free-base octaethylcorrphycene ($H_2OECn$; Cn = corrphycene) and 16 metal complexes derived therefrom. We also report the results of spectroelectrochemical analyses involving several representative complexes. These studies, like those carried out previously

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with porphyrins[1,2,12−15] and porphycenes,[16−23] were intended to increase our understanding of structure−activity relationships in porphyrinoid systems. In this context, the fact that porphyrin, porphycene, and corrphycene defined a congruent, matched set of $N_4$ metal coordinating isomers was considered particularly important; it was expected to allow detailed comparisons to be made.

## 2. Experimental Section

The metallocorrphycenes used in this study were synthesized according to the generalized metal insertion procedures described previously.[7,24,25] In all cases, $\beta$-substituted octaethyl derivatives (i.e., 2,3,6,7,11,12,17,18-functionalized systems), abbreviated as X(OECn) ($X = H_2$ or M) for the purpose of this report, were employed. Electrochemical measurements were carried out at room temperature (20 ± 2 °C) in DMF or $CH_2Cl_2$ containing 0.1 M $Bu_4NPF_6$ as the electrolyte in a classic three-electrode cell. Relevant solvent purification protocols and experimental electrochemical procedures are described elsewhere[20,26] and are available as Supporting Information. Briefly, the working electrode was a glassy carbon disk, the auxiliary electrode was a platinum wire, and all potentials were measured versus a silver wire used as a pseudo-reference electrode. Throughout the present series of experiments, either the ferrocene/ferrocinium ($Fc/Fc^+$) or cobaltocene/cobalticinium couples were used as internal standards. However, measured potentials are reported versus SCE (saturated calomel electrode), allowing for comparison with literature data that is often given versus SCE. Under the conditions employed herein, ferrocene was oxidized at +0.48 V vs SCE and cobalticinium reduced at −0.86 V vs SCE

## 3. Results

The free base form of corrphycene $H_2OECn$ was found to exhibit four one-electron redox steps: two oxidations and two reductions. In dichloromethane, the first oxidation was irreversible at sweep rates lower than 1 V $s^{-1}$, whereas it became reversible at higher sweep rates (Figure 2). Even under the latter conditions, however, the second oxidation process remained irreversible. On the other hand, the first reduction process was reversible whereas the second reduction step was found to be irreversible at all sweep rates.

In DMF (Table 1) only the two reduction waves were observed over the available potential range. The first reduction was a reversible electron transfer, whereas the second was irreversible even at high sweep rates. Further, even when a Hg electrode was used and potentials as negative as −2.80 V vs SCE were applied to the working electrode, no further (i.e., tertiary) reduction process could be detected. This stands in marked contrast to what is seen in the case of free-base porphyrins where additional[27] reduction events may often be observed. This dichotomy thus serves to highlight, at least on a purely empirical level, one of the important electrochemical differences between corrphycenes and porphyrins.

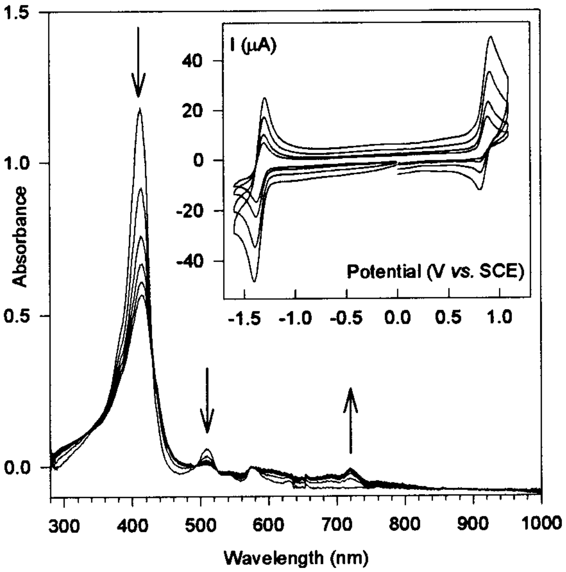

**Figure 2.** Time-resolved UV−vis spectroelectrochemistry of $H_2OECn$ in $CH_2Cl_2$ + 0.1 M $Bu_4NPF_6$ corresponding to the first reduction, with electrolysis at −1.5 V vs SCE. Inset: cyclic voltammetry of the free-base $H_2OECn$ in $CH_2Cl_2$ + 0.1 M $Bu_4NPF_6$. The first reduction and first oxidation are at sweep rates of 0.1, 0.2, 0.5, and 1 V $s^{-1}$.

Optically transparent thin-layer electrode (OTTLE) UV−vis spectroelectrochemical studies were carried out in order to characterize the spectral changes associated with the above-mentioned redox reactions. In $CH_2Cl_2$, no study of the oxidation processes could be carried out owing to the irreversibility of the reactions. By contrast, as illustrated in Figure 2, clean spectral evolutions were found to be associated with the first reduction step of $H_2OECn$. The initial spectrum (i.e., that of the starting free base) could be regenerated by reoxidation of the corresponding one-electron reduced species. The spectrum of the one-electron reduced species is typical of a radical anion with a low-energy band at 719 nm and is quite similar to the spectrum of $H_2OECn^{\bullet -}$ observed elsewhere by radiolytic reduction.[10] As in the case of free-base porphyrins, chlorins, bacteriochlorins,[27] and porphycenes,[18,19] the broad absorption feature in the 650−800 nm spectral region was considered characteristic of a $\pi$-radical anion; it was thus used to identify putative $\pi$-radical anions obtained from metallocorrphycenes.

Like the free base form, the metallocorrphycenes $M^{II}OECn$ (M = Mg, Co, Ni, Cu, Zn, Pd, Ag, Cd, Pt, Pb) could be reduced in both DMF and $CH_2Cl_2$ (Table 1). As a general rule, two reversible reduction steps were observed by cyclic voltammetry in DMF when sweep rates greater than 5 V $s^{-1}$ were employed. In $CH_2Cl_2$, however, divalent metallocorrphycenes generally displayed one reversible reduction and two one-electron reversible oxidations under conditions of cyclic voltammetry as

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**Table 1.** Reduction and Oxidation Potentials (in V vs SCE) of Corrphycenes in DMF and $CH_2Cl_2$ + 0.1 M $Bu_4NPF_6$ (Ferrocene, Used as Internal Standard, Is Oxidized at +0.48 V vs SCE)

| | in DMF, on Hg | | | in $CH_2Cl_2$, on GC | | | | HOMO−LUMO gap |
|---|---|---|---|---|---|---|---|---|
| | $Red_2$ | $Red_1$ | $Red_2$ | $Red_1$ | metal | $Ox_1$ | $Ox_2$ | |
| $H_2OECn$ | −1.62[a] | −1.27 | −1.73[a] | −1.32 | | +0.90 | +1.37[a] | 2.22 |
| NiOECn | −1.86 | −1.34 | | −1.39 | | +0.71 | +1.09 | 2.10 |
| CuOECn | −1.94 | −1.29 | | −1.38 | | $+0.74_5$ | +1.11 | 2.13 |
| PtOECn | −1.83 | −1.28 | | −1.34 | | $+0.72_5$ | +1.23 | 2.07 |
| PdOECn | −1.86 | −1.29 | | −1.37 | | $+0.77_5$ | $+1.21_5$ | 2.15 |
| ZnOECn | −1.95 | −1.54 | | −1.54[a] | | +0.64 | +0.93 | 2.18 |
| $SnCl_2OECn$ | −1.27 | −0.85 | | −0.97 | | +1.34 | | 2.31 |
| MgPyOECn | −2.06 | −1.58 | | −1.58[a] | | +0.56 | +0.83 | 2.14 |
| MnClOECn | −2.05 | −1.51 | | | −0.39[b] | +1.06 | +1.45 | |
| FeClOECn | −1.85 | −1.39[e] | | −1.36 | −0.40[b] | +1.00 | $+1.32_5$ | 2.36 |
| FeOAcOECn | | | | −1.43 | −0.48[b] | +0.98 | | 2.41 |
| CoOECn | −2.00 | −1.15 | (−1.47)[d] | −1.26[a] | +0.41[c] | +0.86 | +1.12 | |
| PbOECn | −1.81 | −1.32 | | −1.39 | | +0.73 | +0.99 | 2.12 |
| AgOECn | | *f* | | −0.82 | | +1.48 | | 2.30 |
| CdPyOECn | −1.95 | −1.50 | | −1.60[a] | | +0.49 | | 2.09 |
| $Al(OAc)_2OECn$ | | | | −1.31 | | +0.84 | +1.04 | 2.15 |
| $Rh_2(CO)_4OECn$ | | | | −1.32 | | +0.83 | +1.21 | 2.13 |

[a] Irreversible electron transfer. [b] M(III) → (M(II) reduction step. [c] M(II) → (M(III) oxidation step. [d] Reduction of species from chemical reaction of one-electron reduced $Co^{II}$ (OECn). [e] The reduction of iron(III) to iron(II) occurs at − 0.30 V vs SCE. [f] Badly resolved because of adsorption.

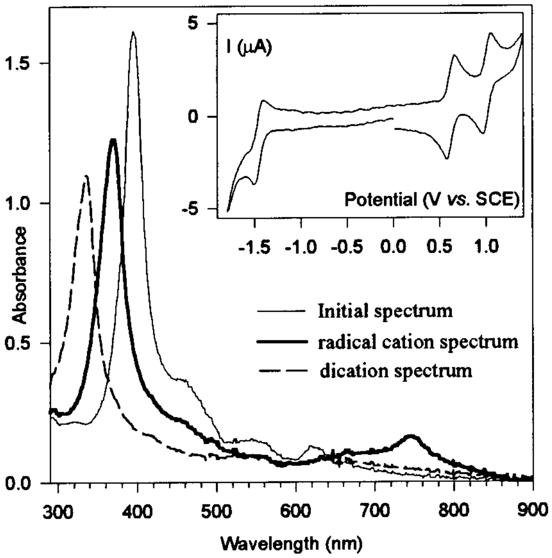

**Figure 3.** UV−vis spectra of NiOECn, $[NiOECn]^{\bullet+}$, and $[NiOECn]^{2+}$ recorded during spectroelectrochemical oxidation at +0.8 (first oxidation) and +1.2 V vs SCE (second oxidation) of NiOECn in $CH_2Cl_2$ + 0.1 M $Bu_4NPF_6$. Inset: cyclic voltammetry of NiOECn in $CH_2Cl_2$ + 0.1 M $Bu_4NPF_6$ at 0.2 V $s^{-1}$.

illustrated in Figure 3 for NiOECn. For this latter complex, OTTLE UV−vis spectroelectrochemical studies were carried out in an effort to identify the sites of electron transfers. Under conditions of electrochemical oxidation, a clean evolution in spectral characteristics, with well-defined isosbestic points, was observed. Further, it was found that the initial spectrum could be recovered by stepwise reduction. The spectrum of the one-electron and two one-electron oxidized species are reproduced in Figure 3. The spectrum of the one-electron oxidized species, with a blue-shifted Soret-like band at 373 nm and a Q-type band at 745 nm, is typical of a radical cation. The latter band, considered particularly diagnostic of a radical cation, was seen to vanish during the second oxidation step. Such behavior demonstrates, at least in this instance, that oxidation occurs on the tetrapyrrolic ligand and serves to generate the corresponding corrphycene radical cation and dication. Reductive spectroelectrochemistry could not be carried out for NiOECn because of electrode inhibition during electrolysis.

Any deviations in electrochemical behavior relative to the free-base form, if actually observed, might be considered as reflecting the electrostatic effect the bound cation has on the ring reduction (or oxidation) chemistry. As can be inferred from an inspection of Table 1, in $CH_2Cl_2$, the first reduction wave of $Zn^{II}OECn$ was irreversible. This irreversibility is ascribed to a partial overlapping between the complex-centered reduction and the reduction process involving the solvent ($CH_2Cl_2$) or the supporting electrolyte (0.1 M $Bu_4NPF_6$).

Similar irreversible behavior was also observed in the case of the cadmium(II) and magnesium(II) complexes, which also were harder to reduce. In these two complexes, however, the more negative reduction potential probably results, at least in part, from coordination of a pyridine to the metal center. Such a shift to negative potential, compared to the free base and to other metallocorrphycenes, is rationalized in terms of the low electronegativity of the complexed metal. Indeed, a plot of the reduction (or oxidation) potential of the complexes versus the electronegativity of the divalent cation proved to be linear. Such effects were seen previously in the case of metalloporphyrins.

In the case of cobalt(II) porphyrinoid complexes, special consideration has to be given to the fact that the metal center might be both easier to reduce and easier to oxidize than the tetrapyrrolic ligand to which it is bound. Such complexes thus occupy a place of special importance within the lexicon of porphyrin-focused electrochemistry. In the context of the present study, it was found that oxidation of the octaethylcorrphycene-bound $Co^{II}$ center (to $Co^{III}$) does indeed occur prior to oxidation of the ligand, as inferred from spectroelectrochemical analyses carried out in DMF. Indeed, spectral evolutions observed during the first oxidation wave (Figure 4) are typical of a metal-centered electron-transfer event. Also, the lack of an observable band at 745 nm, a spectral feature characteristic of a radical cation, is in agreement with a metal-centered oxidation step.

In contrast to the oxidation chemistry, which proved straightforward to interpret, electroreduction of $Co^{II}OECn$ in $CH_2Cl_2$ gave rise to a more complex behavior. In particular, cyclic voltammetry revealed two irreversible reduction waves with peak potentials at −1.26 and −1.47 V vs SCE at $v = 0.1$ V $s^{-1}$. With increasing sweep rates, the second reduction peak amplitude decreased and vanished once a scan rate of $v = 10$ V $s^{-1}$ was obtained. Likewise, the first reduction step, corre-

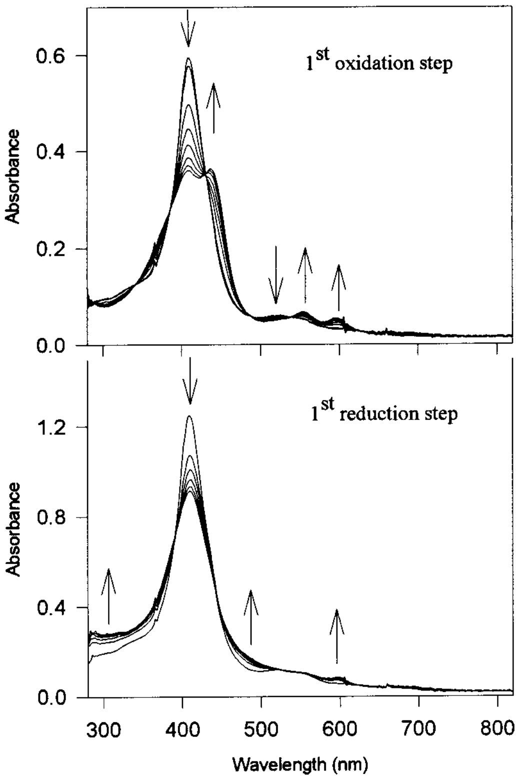

**Figure 4.** Time-resolved spectroelectrochemistry of $Co^{II}OECn$ in DMF (+0.1 M $Bu_4NPF_6$) corresponding to the first oxidation (electrolysis at +0.4V vs SCE) (a) and the first reduction (electrolysis at −1.25 V vs SCE) (b) steps, both one-electron events.

sponding to a one-electron reduction process with an $E_{1/2}$ of −1.27 V vs SCE, became reversible. Analysis of the specific characteristics of this latter reduction event led to the conclusion that this first step corresponds to an $E_{rev}C_{irrev}$ mechanism. Here, the chemical step is ascribed to an irreversible chemical reaction involving the first one-electron reduced species that serves to produce a daughter species that, in turn, becomes reduced at −1.47 V vs SCE. Such a behavior has been observed previously for cobalt porphyrins,[28] wherein the reaction was ascribed to an attack of Co(I) on $CH_2Cl_2$.

In marked contrast to what was observed in $CH_2Cl_2$, cyclic voltammetric reduction of $Co^{II}OECn$ in DMF gave rise to two well-defined reversible one-electron waves at −1.15 and −2.00 V vs SCE. A comparison of these two potential values with those for other divalent metallocorrphycenes (Table 1) led to the conclusion that the first reduction potential of $Co^{II}OECn$ is less negative and that the potential difference between the two first reductions of $Co^{II}OECn$ observed in DMF is rather high (0.85 V) compared to the average $\Delta E_{1/2}$ of 0.51 V observed in other $M^{II}OECn$ complexes. Such a discrepancy is consistent with the first reduction of $Co^{II}OECn$ involving a metal-centered electron-transfer reaction. Support for this conclusion came from OTTLE UV−vis spectroelectrochemistry, also carried out in DMF. These studies revealed, inter alia, that the one-electron reduced species derived from $Co^{II}OECn$ gives rise to spectral features in the UV−vis spectrum that are characteristic of an unmodified tetrapyrrolic ring; in particular, this reduced species displayed a spectrum with an unshifted Soret band and Q bands that would be expected for a $(Co^{I}OECn)^{-}$ complex (Figure 4). In addition, the lack of absorption bands centered around 720 nm, as would be expected for a macrocycle-centered radical anion, provided important further support for the conclusion that the reduction is indeed metal-centered.

**Table 2.** Reduction and Oxidation Potentials (in V vs SCE) of Octaethylporphycenes (OEPn) and Octaethylporphyrins (OEP) in $CH_2Cl_2$

| | $Red_2$ | $Red_1$ | $Ox_1$ | $Ox_2$ | HOMO−LUMO gap |
|---|---|---|---|---|---|
| $H_2OEPn^a$ | −1.26 | −0.94 | +0.87 | +1.10 | 1.82 |
| $NiOEPn^a$ | −1.41 | −1.06 | +0.81 | +1.12 | 1.87 |
| $ZnOEPn^a$ | −1.38 | −1.09 | +0.64 | +0.78 | 1.73 |
| $H_2OEP^b$ | | −1.41 | +0.81 | +1.36 | 2.22 |
| $CuOEP^b$ | | −1.59 | +0.70 | | 2.29 |
| $NiOEP^b$ | | −1.44 | +0.75 | +1.28 | 2.19 |

[a] Values in $CH_2Cl_2$ + 0.1 M $Bu_4NClO_4$ on a platinum working electrode (taken from ref 17). [b] Values in $CH_2Cl_2$ + 0.1 M $Bu_4PF_6$ on a glassy carbon working electrode.

In the chemistry of porphyrins, complexes containing coordinated tri- and tetravalent cations are often of special interest. This is because initial electrochemical reductions can occur either at the ligand or at the metal center. In the case of the higher valent corrphycene complexes studied here, namely, the $Al^{III}$, $Fe^{III}$, $Mn^{III}$, and $Sn^{IV}$ adducts, only those with $Fe^{III}$ and $Mn^{III}$ were found to be more easy to reduce at the metal than at the ring; in the latter complexes, initial electrochemical reduction produced the corresponding divalent $Fe^{II}$ and $Mn^{II}$ corrphycene complexes. In preliminary work, it has also been found that, at least in the case of $Fe^{III}$, these reduction potentials are sensitive to the type of axial ligand X employed (Table 1). Further studies of these effects are currently under way.

## 4. Discussion

As noted in the Introduction, the corrphycenes bear considerable structural analogy to porphyrin and porphycene, two well-studied $N_4$ porphyrinoids. However, they differ in the size and shape of the central ligating cavity. One of the key objectives of the present study was thus to determine how, if at all, these key differences in structure are reflected in terms of changes in electrochemical characteristics. Because the redox potential depends on the experimental conditions, only data from octaethyl derivatives, whose redox characteristics were determined under the same experimental conditions, are compared. Because of the lack of prior experimental results for OEP in $CH_2Cl_2$, we studied again some of the MOEP derivatives under our experimental conditions. The results we obtained are summarized in Table 2.

One of the most critical and obvious ways in which free-base corrphycenes differ from porphyrins is that they exhibit only two one-electron reduction steps. The electrochemical behavior of corrphycenes thus parallels closely what is observed for porphycenes, species for which the reduction process also occurs in two steps.[16−19] By contrast, free-base porphyrins and their metal complexes generally undergo reduction via processes that involve more than two distinct redox steps.[27,29−31] Another major difference in redox behavior is the instability of the electrogenerated radical cation of $H_2OECn$ compared to that produced from porphyrins and porphycenes, at least on the time scale of cyclic voltammetry.

In terms of their electrochemical behavior in DMF, metallocorrphycenes containing coordinated divalent cations bear

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some passing resemblance to porphycenes in terms of the number of reduction waves normally observed, namely, two. On the other hand, corrphycenes differ from porphycenes in that they are significantly harder to reduce by one electron. For instance in $CH_2Cl_2$, the first reduction wave for corrphycenes appears about 0.3 to 0.4 V more negative than that measured for porphycenes[16−19] (Table 2). In contrast, metallocorrphycenes ($M^{II}$OECn) are generally slightly easier to reduce than porphyrins by about 100 mV (i.e., reduced at less negative potentials). Interestingly, the redox potentials differences among corrphycene, porphycene, and porphyrin are much less apparent under conditions of electrochemical oxidation. Indeed, the first oxidation wave for corrphycenes (Table 1) occurs at potentials close to those of porphyrins.

The difference between the first oxidation and the first reduction potentials ($\Delta E_{1/2} = E_{1/2}{}^{Ox}1 - E_{1/2}{}^{Red}1$) of the corrphycene ligand, taken from Table 1, is nearly constant for all metals investigated and equal to 2.15 (±0.08) V. This difference is not much different from that observed in porphyrins ($\Delta E_{1/2} = 2.25 \pm 0.10$ V),[32] whereas it differs significantly from that observed in porphycenes ($\Delta E_{1/2} = 1.85 \pm 0.15$ V).[17] If this energy difference parallels the energy gap between the frontier orbitals HOMO and LUMO, the sequence of these three $\Delta E_{1/2}$ values is consistent with the decrease in energy associated with the lowest energy (i.e., highest wavelength) absorption maxima of these three isomers. This energy decreases from porphyrin to corrphycene to porphycene, with the smaller gap (i.e., $\Delta\lambda_{max}$) lying between porphyrin and corrphycene.[7]

The difference between the first and the second reduction potentials of the ligand is higher in corrphycene and its complexes ($\Delta E_{1/2} = 0.50 \pm 0.15$ V) than in the corresponding octaethylporphyrin systems ($\Delta E_{1/2} = 0.42 \pm 0.05$ V)[32] or porphycene analogues ($\Delta E_{1/2} = 0.35 \pm 0.07$ V).[17] Remarkably, and at variance with what is generally observed for porphyrins and porphycenes, in the case of the corrphycenes containing divalent metal cations, this critical difference in the first and second reduction potential seems dependent, at least to a certain extent, on the nature of coordinated metal.

The special case of the cobalt(II) complex $Co^{II}$OECn, wherein the first reduction process occurs preferentially at the metal center, provides another opportunity to compare the electrochemical behavior of corrphycene with that of porphyrin and porphycene. Interestingly, an appropriate comparison in this instance reveals that again corrphycene more closely resembles porphyrin than porphycene. Indeed, whereas the first reduction of Co(II) octaethylporphyrin generates the corresponding anionic Co(I) complex,[28] it is a ligand-centered radical anion that is produced[19] in the first reduction of Co(II)porphycene.

In summary, the redox properties of octaethylcorrphycene and its metal complexes resemble much more closely those of the corresponding porphyrins than those of the seemingly more analogous porphycenes. This serves to underscore the fact that subtle changes in size, shape, and electronic character, rather than just simple issues involving reduction in symmetry, serve to define the electrochemical properties, and presumably other key characteristics, of $N_4$ in porphyrinoids.

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**Supporting Information Available:** Electrochemical experimental section and discussion of the correlation between the observed redox potential and the central metal electronegativity. This material is available free of charge via the Internet at http://pubs.acs.org.

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