Spectroelectrochemical studies of cobalt(II) porphyrins with paracyclophanyl, pyridinium and nucleoside substituents*

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Abstract

This work describes the synthesis of novel cobalt complexes of porphyrins: (meso-tetrakis [2.2]paracyclophanylporphyrinato)cobalt(II) (T(PCP)PCo(II)); (meso-mono[2.2]paracyclophanyltriphenylporphyrinato)cobalt(II) (PCPPCo(II)); (meso-tetrakis(5'-0-p-phenylene-2',3'-0-isopropylideneuridine)porphyrinato)cobalt(II) (TPUPCo(II)), and (meso-5'-0-p-phenylene-2',3'-0-isopropylideneuridinetri(N-methyl-4-pyridinium)porphyrinato)cobalt(II) (PUPCo(II)). The redox properties of these complexes were characterized by voltammetry and UV-visible spectroelectrochemistry. The effects of the electron-donating and electron-withdrawing properties of the substituents on the electrochemical and spectroscopic data obtained are described and discussed. These compounds are the first examples of a linkage of a biomolecule, such as uridine, with the porphyrin system. These porphyrins also undergo electrochemical polymerization with the formation of conductive films.

INTRODUCTION

We have synthesized novel types of porphyrins in which the phenyl groups of *meso*-tetraphenylporphyrin (TPP) are replaced by different substituents. We have found [1-4] that porphyrins with diethylamino, 3-methoxy-4-hydroxyphenyl and [2.2]paracyclophanyl meso-substituents form conductive polymeric films that exhibit good catalytic properties for a number of reactions on electrodes. This work presents and discusses some interesting and unexpected properties using spectroscopic and electro-

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chemical data for *meso*-tetrakis[2.2]paracyclophanylporphyrin (T(PCP)P) [5] and *meso*-[2.2]paracyclophanyltriphenylporphyrin (PCPP) [6], which consists of [2.2]paracyclophane units (PCP) directly attached to the porphyrin core (P). The electron-donating properties of paracyclophane [7] and the unusual electronic structure, which includes transannular interactions, is responsible for some rather intriguing consequences when it joins with the porphyrin core. T(PCP)P and PCPP demonstrate a negative shift in the first oxidation potential compared to TPP, strong bathochromic shifts of the Soret bands and oxidative electropolymerization with subsequent film formation. In addition, the polymeric films are highly conductive and show both catalytic activity and photovoltaic effects, which make them possible candidates for application in electrocatalysis and in energy storage devices [4,8].

A more recent aspect of porphyrin research has arisen from studies into DNA binding and DNA cleavage by porphyrin molecules [9–11]. This work reports the synthesis of a new class of porphyrin derivatives containing one to four nucleosides covalently bound as meso-substituents. One derivative contains four uridines and the other contains uridine and three pyridinium meso-substituents. The effects of the electron-withdrawing properties of these substituents on the electrochemical and spectroscopic data obtained are described and discussed. These porphyrins undergo electrochemical polymerization with the formation of conductive films under certain conditions. They provide the first examples of the linkage of a biomolecule, such as uridine, with the porphyrin system and they can be used to study the interaction of porphyrins with nucleic acids, nucleosides, and purines and pyrimidines.

The effect of large substituents on porphyrin redox reactions yielding Co(I) and Co(I) π -anion radicals or the reactions of Co(II) to Co(III) and Co(III) π -cation radicals and dications have not been reported. The Co(II) \rightleftharpoons Co(I) reactions on the related Vitamin B₁₂ and model B₁₂ systems have been investigated extensively [12].

In this paper we present a spectroelectrochemical study of T(PCP)PCo(II) and PCPPCo(II), as well as of (*meso*-tetrakis(5'-0-*p*-phenylene-2',3'-0isopropylideneuridine)porphyrinato)cobalt(II) (TPUPCo(II)) and (*meso*-5'-0-*p*-phenylene-2',3'-0-isopropylideneuridine-tri(*N*-methyl-4-pyridinium)porphyrinato)cobalt(II) (PUPCo(II)) complexes (Fig. 1).

EXPERIMENTAL

Synthesis of T(PCP)PCo(II)

Free bases of T(PCP)P and PCPP were synthesized according to procedures published previously [5,6]. T(PCP)P (20mg) was added to 10ml



Fig. 1. Structures of the Co(II) porphyrins under consideration: (a) PCPPCo(II); (b) T(PCP)PCo(II); (c) PUPCo(II); (d) TPUPCo(II).

dimethylformamide (DMF) at 150°C and the solution stirred for one minute. A ten-fold excess of $Co(CH_3COO)_2 \cdot 4H_2O(0.081 g)$ was added to the solution and the mixture was refluxed with stirring for 15 min. The heat source was removed from the reaction and 15 ml of water was added directly to the reaction mixture. The reaction flask was placed in an ice bath for 15 minutes to ensure complete precipitation of the desired metal complex. The solution was filtered using a Büchner funnel and the product washed with cold water. T(PCP)PCo(II) was purified on a neutral alumina column using hexane to remove non-polar contamination and chloroform as the mobile phase.

Synthesis of PCPPCo(II)

The synthesis of this product was identical to the synthesis of T(PCP)PCo(II) except that PCPP was used in place of T(PCP)P.

Synthesis of TPUPCo(II)

Meso-tetra(p-hydroxyphenyl)porphyrin (102 mg, 0.15 mmol) and 5'-0-tosyl-2',3'-0-isopropylideneuridine (526 mg, 1.20 mmol) were dissolved in DMF (100 ml) and added dropwise 60% NaH (144 mg, 3.6 mmol), and Cs₂CO₃ (196 mg, 0.60 mmol) was dissolved in DMF (150 ml). The mixture was stirred at 65°C for 48 h, then filtered; the filtrate was added to $4:1 \text{ v/v } \text{H}_2\text{O}/\text{MeOH}$ and extracted with CHCl₃. The extract was washed with 5% aq. NH₃ and water, then dried. Chromatography was carried out on the extract on a silica gel column with CHCl₃/MeOH as eluent, its composition gradually changing from 50:1 to 10:1. The product was obtained in the first fraction; yield 9%. FAB-MS (M + 1)⁺: m/e 1744 (3% base) and 1743 (4.3% base). ¹H NMR (DMSO): 10.00 (s, 4H, H-3), 8.86 (m, 8H, β -pyrrole), 8.11 and 7.39 (dd, 4H_{ar}, 8.2 Hz), 7.99 and 7.20 (dd, 12H_{ar}, 8.2 Hz), 7.83 (d, 4H, 7.7 Hz, H-6), 5.98–5.80 (m, 8H, H-1', H-5); 4.93, 4.90 (dd, 2.6 Hz) and 4.76, 4.73 (dd, 3.2 Hz) (8H, H-2', H-3'); 4.39–4.13 (m, 12H, H-4', H-5'), 1.50 (s, 12H_{ip}), 1.31 (s, 12H_{ip}), -2.88 (s, 2H_{por}), UV-vis(EtOH): 230, 250, 418.5(S), 516, 554, 593, 650.

Analysis for $C_{92}H_{86}N_{12}O_{24}$. Calc.: C, 63.37; H, 4.97; N, 9.64. Found: C, 63.23; H, 4.96; N, 9.81.

The Co(II) complex was obtained by refluxing the aqueous solution of free-base porphyrin with a two-fold excess of $CoCl_2 \cdot 2H_2O$ for 12 h, followed by precipitation from a saturated solution of NaClO₄.

Synthesis of PUPCo(II)

Condensation of *p*-anisaldehyde, 4-pyridine carboxaldehyde and pyrrole in propionic acid gave, besides other porphyrins and polymers, the *meso*tri(4-pyridyl)-*p*-methoxyphenylporphyrin, separated by column chromatography on silica gel using MeOH/CHCl₃ (1:50) as eluent. Demethylation with pyridine hydrochloride at 220°C for 2.5 h gave the *p*-hydroxyphenyl derivative. The condensation of the latter with the 5'-0-tosylate of 2',3'-0isopropylideneuridine was carried out in DMF solution containing Cs₂CO₃ and NaH at 65°C for 24–36 h. The ratio of porphyrin to tosyluridine was 1:2 per OH group in the porphyrin. The ratio of porphyrin to Cs₂CO₃ and NaH was 1:1 and 1:12 respectively. Chromatography on a silica gel column with CHCl₃/MeOH (30:1) gave as the first fraction the respective *meso*-tri(4pyridyl)(5'-0-*p*-phenylene-2',3'-0-isopropylideneuridine)porphyrin with the yield 15–17%. *N*-methylation by refluxing at 70°C for 12 h with a mixture of CH_3I and CH_3NO_2 (4:3 v/v) gave the *meso*-tri(*N*-methyl-4-pyridinium)(5'-0*p*-phenylene-2',3'-0-isopropylideneuridine)porphyrin, with about 90% yield.

¹H NMR (DMSO): 9.48 (d, $6H_{py}$, 6.4 Hz), 9.16 (s, $5H_{py}$), 9.05 (s, $1H_{py}$), 8.99 (m, $8H\beta_{py}$), 8.14 and 7.44 (dd, $4H_{ar}$, 8 Hz), 7.88 (d, 1H, 8 Hz, H-6), 5.96 (s, 1H, H-1'), 5.70 (d, 1H, 8 Hz, H-5), 5.21 (d, 1H, 7.8 Hz, H-3'), 5.09 (m, 1H, H-2'), 4.72 (s, 9H, N–Me), 4.50–4.40 (m) and 3.87 (m) (3H, H-4', H-5'), 1.61 (s, $3H_{ip}$), 1.41 (s, $3H_{ip}$), -3.02 (s, $2H_{por}$). UV–vis: (H₂O) 221, 259, 425(S), 522, 559, 585, 643; (DMSO) 259, 427(S), 520, 554, 590, 646. The Co(II) derivative was obtained by refluxing an aqueous solution of the free base porphyrin with a two-fold excess of $CoCl_2 \cdot 2H_2O$ for 12 h, followed by precipitation with a saturated solution of sodium perchlorate; yield of metallation was 90%.

Electrochemical and spectroelectrochemical methods

Cyclic voltammetric and differential pulse voltammetric measurements were made with an IBM EC225 voltammetric analyzer. An omnigraphic Houston 1000 X-Y recorder was used to record the current voltage output for sweep rates between 0.002 and 0.30 V/s. Current voltage curves were collected on a digital storage oscilloscope with an X-Y recorder attached. Coulometry was performed with a PAR Model 273 potentiostat. A conventional three-electrode system was used. This consisted of a platinum working electrode (diameter 2 mm), a platinum wire counterelectrode and a saturated calomel electrode (SCE) as the reference electrode. The SCE was separated from the solution by a double electrolytic bridge (aqueous/ non-aqueous) and a porous glass frit.

UV-visible spectra were obtained with a Tracor Northern multichannel analyzer. The system comprised a Tracor Northern 6050 spectrometer containing a crossed Czerny-Turner spectrograph and a Tracor Northern 1710 multichannel analyzer. Spectra were recorded by a double-array detector. Spectroelectrochemistry was performed in a thin-layer cell, which followed the design of Lin and Kadish [13] with a calculated path length of 0.5 mm and platinum mesh as a working electrode. Glass plates covered with indium oxide and electrochemically deposited films were used to obtain UV-visible spectra of the polymeric porphyrins. 1,2-Dichloroethane (DCE, Fisher Scientific) was purchased as HPLC grade and was twice distilled from P_2O_5 before use. Dimethylsulfoxide (DMSO, Eastman) was purchased as analytical grade and was vacuum distilled over CaH₂ prior to use. The supporting electrolyte, tetrabutylammonium perchlorate (TBAP, Eastman) was twice recrystallized from ethanol, dried and stored in vacuo at 45°C.



Fig. 2. Cyclic voltammogram of (a) PCPPCo(II); (b) T(PCP)PCo(II) in 1,2-dichloroethane containing 0.1 M TBAP.

RESULTS

Electrochemistry and spectroelectrochemistry of PCPPCo(II) and T(PCP)PCo(II)

A typical cyclic voltammogram obtained for PCPPCo(II) in DCE containing 0.1 M TBAP is shown in Fig. 2a. PCPPCo(II) undergoes two reductions and three oxidations. Half-wave potentials are listed in Table 1. The first reduction (peak I) occurs at -0.90 V and involves a reversible electron transfer. The second reduction (peak II) at -1.26 V is irreversible in that there is no coupled oxidation peak. The shape of this reduction peak, as well as the scan-rate dependence of the peak current, suggests a reaction sequence involving an initial one-electron transfer followed by a chemical reaction. Coulometric measurements, first on the plateau of process I and then on the plateau of process II, show that one faraday of charge per mole is transferred in each process. The first process, at -0.90 V, can be attributed to the reduction of Co(II) to Co(I), which is generally found to occur for Co porphyrins in the range -0.8 to -0.9 V [12]. The second process, at -1.26 V, is the reduction of PCPPCo(I) to the anion radical. This has been

TABLE 1

Compound	Metal				Porphyrin ring			
	Ox.	Red.			Ox.			
	ĪV	I	II	III	v	VI	VII	VIII
PCPP ^a			- 1.24	- 1.53	0.95	1.18	1.42	1.72
T(PCP)P ^a			-1.27	-1.65	0.52	0.88	1.30	1.46
PCPPCo	0.83	-0.90	-1.26		0.96	1.20		
T(PCP)PCo	0.75	-0.93			0.94	1.14		
PUPCo		- 0.67	-0.92	-1.25				
TPUPCo		- 0.88	- 1.38					

Half-wave potentials for reduction and oxidation of Co(II) complexes with PCPP and T(PCP)P in EtCl₂ (0.1 M TBAP), and PUP and TPUP in DMSO (0.1 M TBAP)

*From refs. 3 and 5.

found to occur at -1.24 V for the free base PCPP [3]. The difference in potential from peak II to the second oxidation process (peak VI) is 2.46 V, which is close to the expected value of 2.25 ± 0.15 V for the potential difference between the first ring oxidation and the first ring reduction of porphyrins [14].

The cyclic voltammogram obtained for T(PCP)PCo(II) in DCE containing 0.1 M TBAP is shown in Fig. 2b. The one reduction processes, observed at -0.93 V, can be attributed to the Co(II)/Co(I) couple.

In the cyclic voltammetry of PCPPCo(II), the first two oxidation peaks, observed at 0.83 and 0.95 V respectively, each have $E_{\rm pa} - E_{\rm pc} = 60 \pm 5 \,\mathrm{mV}$ and are both reversible on the cyclic voltammetry time scale up to $100 \,\mathrm{mV \, s^{-1}}$. The first oxidation process, peak IV, is attributed to the Co(II)/Co(II) couple and, unlike the Co(II)/Co(I) couple, is greatly influenced by the solvent system used in analysis. The second reversible couple (peak V) involves one-electron transfer and can be attributed to the formation of a cation radical. In the third oxidation process, peak VI, the potential difference between the anodic and cathodic peak potentials is 150 mV, which indicates that the process is quasi-reversible. The anodic peak current is higher than the cathodic peak current and is also higher than the anodic currents increased at slow potential scan. This indicates that the third oxidation process is followed by deposition of conductive film on the surface of electrode.

A typical cyclic voltammogram of T(PCP)PCo(II) shows three ill-defined peaks at $E_{pa} = 0.75$, 0.92 and 1.14 V (Fig. 2b) and none are reversible on the time scale of either cyclic voltammetry or controlled-potential electrolysis.



Fig. 3. Thin-layer absorption spectra for reduced (a) PCPPCo(II); (b) T(PCP)PCo(II) in 1,2dichloroethane (0.1 M TBAP).

In addition, the peaks do not become better defined at higher concentration, indicating some type of surface effect, i.e. adsorption-desorption is occurring on the electrode surface. The first oxidation in T(PPC)PCo(II) is attributed to the Co(II)/Co(III) couple which, in this case, is irreversible. As with PCPPCo(II), the next two oxidation reactions, peaks V and VI, are ascribed to the formation of the cation radical and dication.

The spectral changes observed during thin-layer UV-visible spectroelectrochemistry of PCPPCo(II) and T(PCP)PCo(II) are shown in Figs. 3 and 4. Wavelengths for the major peaks are listed in Table 2. Electronic absorption spectra were collected before and during the controlled-potential oxidation and reduction of each complex. The original spectrum of PCPPCo(II) in DCE (0.1 M TBAP) shows two distinct bands at 418 and 539 nm (Fig. 3a). During the first oxidation process, the Soret peak at 418 nm decreases and shifts to 426 nm and the Q-band at 539 nm also decreases and shifts bathochromically. A new Soret band at 435 nm appears and grows. As the oxidation proceeds through the processes occurring at peaks V and VI, the Soret band decreases until a broad band emerges at 464 nm and continues to increase. The final spectra obtained during processes V and VI showed two additional broad bands at 679 and 790 nm, which are characteristic of the cation radical and dication [15].

The original spectrum of T(PCP)PCo(II) shows a Soret band at 429 nm and a Q-band at 547 nm (Fig. 3b). During the first oxidation process, the



Fig. 4. Thin-layer absorption spectra for oxidized (a) PCPPCo(II); (b) T(PCP)PCo(II) in 1,2-dichloroethane (0.1 M TBAP).

TABLE 2

Thin-layer	UV-visible a	bsorption data	for: free-base	PCPP and T	(PCP)P, and	metal-contain-
ing PCPP	and T(PCP)P	(in DCE, 0.1 M	[TBAP); PUP	and TPUP	(in DMSO, 0).1 M TBAP)

Compound	λ_{\max} (nm)						
	Soret ba	nds	Q-bands				
PCPPCo(II)							
Neutral	416		539				
Final oxidation	464		679	790			
Final reduction	406	$431 \mathrm{sh}$	541				
Film	443	484 sh					
T(PCP)PCo(II)							
Neutral	429		547				
Final oxidation	450		651	738			
Final reduction	414		547				
PUPCo(II)							
Neutral	429		545	580			
Final reduction	429	479 sh	545	584	815		
Film	443		556	582	620		
TPUPCo(II)							
Neutral	435		557				
Final reduction	447		589	700			

Soret band decreases and shifts bathochromically while the band at 547 nm decreases and disappears. The final spectrum shows a single broad band at 450 nm and two broad bands at 651 and 738 nm. These spectral changes during electrochemical oxidation of PCPPCo(II) and T(PCP)PCo(II) indicate an oxidation of cobalt in the first step and the formation of a cation radical and dication in the second and third step respectively. Time-resolved spectra obtained during the reduction of PCPCo(II) and T(PCP)PCo(II) are shown in Fig. 4. As the reduction of PCPPCo(II) proceeds, there is a slight decrease of the Soret band at 421 nm from $\varepsilon = 4.7 \times 10^4$ to 4.3×10^4 M⁻¹ cm⁻¹. A gradual hypsochromic shift of the Soret band is also observed. At the end of the first step of electrolysis (wave I), the Soret band is observed at 406 nm. This change of absorbance is characteristic of a metal-centered reaction and can be attributed to the reduction of Co(II) to Co(I). The first reduction process is spectrally reversible, and switching the applied potential from -1.1 V to -0.5 V yields a spectrum characteristic of the PCPPCo(II) starting material. This one-electron transfer process was found to be reversible by both macro and microscale electrolysis.

During the second reduction step of PCPPCo(II), only a small shoulder appears next to the Soret band at 431 nm, and no bands characteristic of an anion radical in the region of 600–900 nm were observed. The second reduction, which is irreversible in the cyclic voltammetry time scale, is also irreversible in spectroelectrochemistry and the final spectrum obtained after addition of the second electron can be attributed to the product of decomposition of the unstable radical [PCPP[·]Co(I)]⁻².

Electron absorption spectra monitored during controlled-potential reduction of T(PCP)PCo(II) (Fig. 4b) are similar to those observed for the first reduction of PCPPCo(II), i.e. the Soret band at 429 nm decreased and shifted to 414 nm. The final spectrum can be attributed to stable $[T(PCP)PCo(I)]^{-1}$ which can be reoxidized to the original T(PCP)PCo(II) by switching the applied potential from -1.1 V to -0.5 V.

Electrochemistry and spectroelectrochemistry of PUPCo(II) and TPUPCo(II)

Cyclic voltammograms of PUPCo(II) and TPUPCo(II) in DMSO (0.1 M TBAP) are shown in Fig. 5 and half-wave potentials are listed in Table 1. Three reduction peaks are observed for PUPCo(II) and two for TPUPCo(II). Neither of the complexes show any oxidation processes in the range of potential available in DMSO (up to 1.5 V). The first reduction of PUPCo(II) (peak I) is a reversible one-electron transfer that can be attributed to the reduction of Co(II) to Co(I). This reduction occurs at -0.67 V, which is 230–260 mV more positive than the potential observed for the first reduction of the paracyclophanylporphyrins. This indicates that Co(II) can be



Fig. 5. Cyclic voltammogram of (a) PUPCo(II); (b) TPUPCo(II) in DMSO (0.1 M TBAP).

reduced much more easily when it is coordinated to PUP. Reduction of Co(II) to Co(I) in TPUPCo(II) occurs at -0.88 V, which is similar to the potential observed for complexes of cobalt with paracyclophanylporphyrin (Table 1) and tetraphenylporphyrins [12].

Spectra obtained during the reduction of PUPCo(II) and TPUPCo(II) are shown in Fig. 6. On addition of one electron to the PUPCo(II) complex (Fig. 6a), the Soret band decreases from $\varepsilon = 4.1 \times 10^4$ to 3.8×10^4 M⁻¹ cm⁻¹ and is shifted from 429 to 422 nm, along with a small decrease in the Q-bands at 545 and 584 nm. During the second and third reductions, the Soret band decreases and shifts bathochromically to 435 nm and a new band, characteristic of the anion radical and dianion, appears and grows at 815 nm. This confirms the voltammetric data, which indicate that PUPPCo(II) is further reduced at -0.92 V (peak II, reversible process) and at -1.25 V (peak III, irreversible process) to the anion radical and dianion respectively.

The spectral changes during the first reduction of TPUPCo(II) are quite different from the small changes observed for PUPPCo(II). The original Soret band at 435 nm decreases significantly from $\varepsilon = 4.7 \times 10^4$ to $3.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ with a gradual hypsochromic shift to 420 nm. During the second reduction to the anion radical, a further decrease of the Soret band is observed with a bathochromic shift to 447 nm. In addition, a new broad and low intensity band appears at 700 nm. In cyclic voltammetry,



Fig. 6. Thin-layer absorption spectra of (a) PUPCo(II); (b) TPUPCo(II) in DMSO (0.1 M TBAP).

TPUPCo(II) is further reduced at -1.38 V in a one-electron irreversible process to the anion radical, but no significant changes of spectra were observed in the spectroelectrochemical experiment.

Electrochemical formation of conductive polymeric films

In continuous scan cyclic voltammetry from -0.6 to 1.7 V at 0.1 Vs⁻¹, the growth patterns for PCPPCo(II) on a platinum electrode show that the current of peaks IV-VI grows initially with each scan, which indicates the formation of a conductive film. During polymerization, the anodic current shifts to more positive potentials and the cathodic current shifts to more negative potentials, resulting in less definition of anodic peaks IV and V. Unlike PCPP, which shows the formation of passivating film during electropolymerization by continuous-scan cyclic voltammetry [3], PCPPCo(II) shows a growth pattern in the same electropolymerization process. In addition, the PCPPCo(II) film formed on either a platinum or glassy carbon electrode is stable and conductive, and demonstrates catalytic properties [16]. The UV-visible spectrum of the PCPPCo(II) film deposited on an indium oxide electrode shows a Soret peak at 443 nm and a broad shoulder at 484 nm (Fig. 7a). The growth patterns for T(PCP)PCo(II) during continuous-scan cyclic voltammetry from -0.2 to 1.6 V illustrate film formation quite different from PCPPCo(II). Instead of a voltammogram



Fig. 7. Absorption spectra of dry polymeric film of (a) PCPPCo(II); (b) PUPPCo(II) on an indium oxide electrode.

which shows a continual increase in current with each successive scan, this voltammogram indicates that a passive film is formed after several layers of material are deposited. Film cannot be deposited on the indium oxide electrode; therefore, its spectrum is not reported.

Taking into consideration all of the voltammetric and spectroelectrochemical data from both PCPPCo(II) and T(PCP)PCo(II), the mechanism for film formation can be assumed to follow the pathway via the cation radical and dication. As with the free bases PCPP and T(PCP)P, polymerization may occur by way of the quinone system. Formation of the quinone system can follow internal transfer of electrons from electron-donating paracyclophanyl substituents to the oxidized porphyrin ring [3].

Continuous potential scanning with either PUPCo(II) or TPUPCo(II) in DMSO shows no film formation. However, when PUPCo(II) is dissolved in aqueous 0.1 M NaOH and oxidized at potential 0.42 V, highly conductive film is formed. The UV-visible spectrum of PUPPCo(II) on indium oxide electrode shows a Soret band at 443 nm and a small band at 556 nm (Fig. 7b).

DISCUSSION

The electrochemistry of the complexes studied is significantly influenced by the nature of the meso-substituents on the porphyrin ring. Paracyclophanyl is a strong electron-donating substituent while pyridinium is strongly electron-withdrawing. Uridine is also electron-withdrawing, but not as much so as pyridinium. Electron-donating or electron-withdrawing substituents located on the periphery of the conjugated prophyrin ring system have been shown to affect the basicity of the porphyrin nitrogen atoms. The visible absorption spectra, redox potentials, and axial ligation reaction of the free bases and their respective metalloporphyrin complexes are also affected. The following set of equations summarizes all the reactions that Co-porphyrin complexes PCo(II) might undergo on a platinum electrode. The particular complexes studied in this work exhibit reactions (2)-(5). The Roman numeral gives the charge on the cobalt and the Arabic numeral the total charge of the complex. Porphyrin radicals are shown as P° .

$$[PCo(II)]^{0} + e \rightleftharpoons [PCo(I)]^{-}$$
(1)

$$[PCo(I)]^{-} + e \rightleftharpoons [P^{\cdot}Co(I)]^{2-}$$
⁽²⁾

$$[\mathbf{P}^{\cdot}\mathbf{Co}(\mathbf{I})]^{2^{-}} + \mathbf{e} \rightleftharpoons [\mathbf{P}\mathbf{Co}(\mathbf{I})]^{3^{-}}$$
(3)

$$[PCo(II)]^{0} - e \rightleftharpoons [PCo(III)]^{+}$$
(4)

$$[PCo(III)]^{+} - e \rightleftharpoons [P^{\cdot}Co(III)]^{2+}$$
(5)

$$[P^{\cdot}Co(III)]^{2+} - e \rightleftharpoons [PCo(III)]^{3+}$$
(6)

As expected, some of these redox reactions involve the metal and others include the porphyrin ring system. This discussion will elucidate the relationship between the nature of the meso-substituents and the number and type of reactions observed for the porphyrin–Co complex.

The redox potential of the reduction of $[PCo(II)]^0$ to $[PCo(I)]^-$ (eqn. (1)) is only slightly dependent on the solvent conditions, and has been reported in the literature as occurring at 0.76 V in DMF and -0.82 V in DMSO [12]. In the presence of coordinating ligands, Co(II) is known to be coordinated in one axial position. On reduction to Co(I), the axial ligand may or may not be bound to the metal, depending on the specific solution conditions [17]. For the complex PUPCo(II), the reduction potential for Co(II) to Co(I), -0.67 V, is over 200 mV more positive than that observed for the cobalt tetraphenylporphyrins (-0.8 to -0.9 V) [12]. However, in TPUPCo(II), in which three electron-withdrawing pyridinium substituents are replaced by uridine substituents, the potential is shifted negatively to -0.88 V, the typical potential region for Co(II)/Co(I) reduction in DMSO. Reduction of cobalt which occurs at potentials more negative than -0.9 Vfrom PCPPCo(II) and T(PCP)PCo(II) is more difficult than the reduction from PUPCo(II) and TPUPCo(II). This is due to the electron-donating properties of the paracyclophanyl substituent.

After reduction to Co(I) from PCPCo(II) and T(PCP)PCo(II), a 10–20 nm hypsochromic shift of the Soret band is observed. This indicates a significant stabilization of the porphyrin ring by Co(I) in these complexes. The 5–10 nm hypsochromic shift following the Co(II) reduction for PUPCo(II)

and TPUPCo(II) is less significant but still indicates stabilization of the Co(I) porphyrin complex. Voltammetric and spectroelectrochemical data confirm the relatively high stability of the Co(I) porphyrin for all of the complexes studied. In cyclic voltammetry, the Co(II)/Co(I) couple is reversible or quasi-reversible for all of the complexes studied up to $100 \,\mathrm{mV \, s^{-1}}$ potential scan rate.

Further reduction of $[PCo(I)]^-$ to the porphyrin ring radical anion $[P^{\cdot}Co(I)]^{2-}$ (eqn. (2)), followed by reduction to $[PCo(I)]^{3-}$ (eqn. (3)), was observed only for PUPCo(II). The radical anion $[PUPCo(I)]^{3-}$ is highly unstable.

Generally, it has been assumed that porphyrin ring oxidation to yield π -cations is more sensitive to substituent effects than porphyrin ring reduction to yield π -anions. This seems to be true for both paracyclophanyl as well as uridine- and pyridinium-substituted porphyrins. However, for T(PCP)PCo(II), no π -anion radical formation has been observed, which suggests that four paracyclophanyl substituents significantly influence porphyrin ring reduction. Oxidation of the porphyrin ring was observed for neither PUPCo(II) nor TPUPCo(II) complexes. Clearly, the electron-with-drawing effect of pyridinium substituents make porphyrin ring oxidation so difficult that it is not observed in the potential range available in DMSO.

Cobalt, like nickel and copper, is categorized as a "hypso" central metal in complexes [18]. Ions of these metals shift the spectrum of a complex to shorter wavelengths in comparison with the spectrum of the ligand, in this case, the porphyrin free base. This shift is expected when porphyrins are coordinated with metals in Groups VIII and IB with metal ion configurations d^m, m = 6-9, which have the e_{σ} (d π) orbitals filled. The d⁶-d⁹ ions have two filled $d\pi$ orbitals, d_{xz} and d_{yz} , which have the correct symmetry to overlap with the empty porphyrin π^* orbitals. This raises the energy of the π^* energy levels, due to backbonding from the metal, causing the porphyrin $\pi \rightarrow \pi^*$ transition to be hypsochromically shifted from the free-base porphyrin. Hypsochromic shift spectra reflect stronger metal perturbation on the $\pi \to \pi^*$ transition. Spectroscopic data obtained in these studies (Table 2) indicate that the Co(II) derivatives of the [2.2]paracyclophanylporphyrins show this hypsochromic effect. This shift is 5 nm for PCPPCo(II) and 11 nmfor T(PCP)PCo(II). (The Soret bands for PCPP and T(PCP)P have wavelengths of 416 and 429 nm, respectively.) A strong stabilization of the porphyrin ring by cobalt is also observed in the redox properties of paracyclophanylporphyrins. The oxidation of T(PCP)P to the π -cation radical is observed in DCE at 0.46 V. This same redox reaction is observed for T(PCP)PCo(II) at 0.94 V. The coordination by cobalt makes oxidation of the porphyrin ring more difficult by 480 mV for T(PCP)PCo(II). Based on electrochemical and spectroelectrochemical data, it can be concluded that cobalt stabilizes the porphyrin ring and this stabilization decreases as the oxidation state of cobalt increases Co(I) > Co(II) > Co(III).

Oxidation of Co(II) to Co(III) (eqn. (4)) is markedly dependent on the coordinating ability of the solvent. In strongly coordinating solvents such as DMSO, oxidation of Co(II) to Co(III) is usually observed within the potential range 0.1-0.3 V [12]. However, in the case of PUPCo(II) and TPUPCo(II), no oxidation of Co(II) to Co(III) was observed due to the strong electron-withdrawing effect of the pyridinium substituents.

The formation of a stable, conductive polymeric film was observed only from PCPPCo(II) and PUPCo(II) in solution. Both films show a broad Soret band at 443 nm on indium oxide electrodes. The conductivity of a PUPCo(II) film is significantly higher (about 400 ohm⁻¹ cm⁻¹) than a PCPPCo(II) film (about 20 ohm⁻¹ cm⁻¹). However, a reversible redox reaction of Co(II) is observed in both of the films. The relatively high conductivity and the solid-state redox reaction make these materials suitable for the heterogeneous catalytic oxidation of small organic molecules like methanol, formic acid and hydrazine and the reduction of oxygen directly to water. All of these reactions can find an application in fuel cells and/or air batteries.

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