Synthesis and electrochemical studies of a covalently linked cobalt(II) phthalocyanine–cobalt(II) porphyrin conjugate[†]

Zhixin Zhao, Kenneth I. Ozoemena, David M. Maree and Tebello Nyokong*

Department of Chemistry, Rhodes University, Grahamstown, 6140, South Africa. E-mail: t.nyokong@ru.ac.za; Fax: + 27 46 6225109; Tel: + 27 46 6038260

Received 10th December 2004, Accepted 23rd February 2005 First published as an Advance Article on the web 7th March 2005 Dalton

The synthesis of a cobalt phthalocyanine–cobalt porphyrin heteropentamer (cobalt(II) phthalocyanine– tetrakis(cobalt(II) tetrakis(5-phenoxy-10,15,20-triphenylporphyrin))), (CoPc–(CoTPP)₄), containing four units of cobalt tetraphenylporphyrin linked to a central cobalt phthalocyanine macrocycle *via* ether linkages is reported. Cyclic voltammetry and spectroelectrochemistry were employed to characterize the complexes. Cyclic voltammetry and square wave voltammetry revealed nine processes. Spectroelectrochemistry of the pentamer confirmed that reduction occurs on the individual components in an alternating manner; the first reduction occurring on the CoTPP moieties, the second on the CoPc moiety, the third on the CoTPP moieties and so on. Oxidation occurred first on the CoPc moiety of the pentamer.

Introduction

Published on 07 March 2005. Downloaded by University of Aberdeen on 27/08/2013 19:11:11

Porphyrins and phthalocyanines represent two related classes of very versatile macrocyclic organic molecules. Conjugates of porphyrins and phthalocyanines have attracted some attention but generally very little is known about them. The first synthesis of a porphyrin-phthalocyanine conjugate, a zinc porphyrin-zinc phthalocyanine dimer, was reported about two decades ago by Gaspard et al.1 with the aim of investigating some photochemical properties. Peripherally linked dimers as well as sandwich type dimers and trimers have been reported and have apparent applications as electrochromic materials, molecular and liquid crystals, semiconductors, gas sensors, nonlinear optical materials, molecular magnets and as materials in ionoelectronics.²⁻⁸ Metalloporphyrins are widely studied as biomimetic models for several biological redox processes,⁹ and have been extensively used in chemical and electrochemical analyses according to a recent review.¹⁰ Metallophthalocyanines are well recognised as efficient electrocatalysts.¹¹⁻¹³ Multiporphyrin-phthalocyanine arrays can serve as useful candidates for applications such as in light harvesting and molecular photonics, and catalysis. Porphyrin and phthalocyanine complexes of cobalt(II), in particular, have been intensively studied and found to be excellent electrocatalysts, for example, in the electrocatalytic oxidation of several industrially and biologically important molecules such as thiols,13-17 nitric oxide,18 as well as for the reduction of oxygen¹⁹⁻²² for potential application in fuel cell technology. A possible synergistic means by which the full catalytic activities of cobalt porphyrin and phthalocyanine complexes may be fully harnessed for use in biomimetic reactions or in the design for multi-electron redox catalysts/mediators for biomedical and electrochemical sensing is, for example, by smart synthesis of covalently linked cobalt porphyrin-cobalt phthalocyanine molecules. In this work, we present a synthetic strategy for the preparation of a cobalt phthalocyanine-cobalt tetraphenylporphyrin heteropentamer complex in which four units of cobalt tetraphenylporphyrin are covalently linked to a central cobalt phthalocyanine macrocycle (CoPc-(CoTPP)₄) (Fig. 1). Since certain potential applications (e.g., in the design of an efficient catalyst) of this molecule will require an understanding of the nature of its redox processes, this work also investigates the

Fig. 1 The molecular structure of a cobalt phthalocyanine–cobalt porphyrin $CoPc-(CoTPP)_4$ pentamer.

electrochemical and spectroelectrochemical properties of CoPc-(CoTPP)₄.

Experimental

Equipment

UV-vis spectra were recorded on a Varian 500 UV-Visible/NIR spectrophotometer. IR (KBr pellets) were recorded on a Perkin-Elmer Spectrum 200 FTIR spectrometer. ¹H NMR spectra were recorded using a Bruker EMX 400 NMR spectrometer. MALDI TOF spectra were recorded with Perseptive Biosystems Voyager DE-PRO Biospectrometry Workstation and possessing Delayed Extraction Technology at the University of Cape Town.

Electrochemical data were obtained under purified nitrogen gas with BioAnalytical System (BAS) 100 B/W Electrochemical Workstation. Cyclic voltammograms (CVs) and Osteryoung square wave voltammograms (OSWV) were collected using a conventional three-electrode set-up with a glassy carbon electrode (GCE, 3.00 mm diameter) as a working electrode, platinum wire as a counter electrode and Ag|AgCl wire as a

† Electronic supplementary information (ESI) available: Fig. S1: ¹H NMR of CoCNOTPP in DMSO-d₆. Fig. S2: Mass spectrum of CoCNOTPP. Fig. S3. Mass spectrum of CoPc–(CoTPP)₄ pentamer. See http://www.rsc.org/suppdata/dt/b4/b418611g/

pseudo-reference electrode. The optimised parameters for the OSWV were: step potential 4 mV; square-wave amplitude 25 mV at a frequency of 15 Hz. For voltammetry studies, concentrations of the porphyrin, phthalocyanine and the pophyrin–phthalocyanine pentamer complexes were maintained at *ca*. 10^{-3} M in dry dimethyl sulfoxide (DMSO) containing TBAP (tetrabutylammonium perchlorate) as supporting electrolyte. Spectroelectrochemical data were obtained with a home-made optically transparent thin-layer electrochemical (OTTLE) cell, with a similar design to that previously reported by Krejčik *et al.*²³ The working and counter electrodes of the cell were platinum grits while a piece of silver wire served as a pseudo-reference electrode. The OTTLE cell was connected to a BAS CV 27 voltammograph. All experiments were performed at 25 ± 1 °C.

Materials

4-Nitrophthalonitrile,²⁴ 5-hydroxy-10,15,20-triphenylporphyrin²⁵ and 5-[4-(3,4-dicyanophenoxy)phenyl]-10,15,20-triphenylporphyrin (H₂CNOTPP, **2**)¹ were synthesized as in literature. 4-Hydroxybenzaldehyde, benzaldehyde, pyrrole, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), *n*-octanol, sodium methoxide, potassium carbonate, hydrous cobalt acetate, tetraphenylporphyrin (H₂TPP), cobalt phthalocyanine (CoPc) were purchased from Sigma–Aldrich and used without further purification. DMSO was dried over alumina before use. TBAP used as supporting electrolyte was purified by recrystallization from ethanol. All other solvents were dried by standard methods prior to use. Silica gel 60 (0.04–0.063 mm) for chromatography was purchased from Merck.

Synthesis

{5-[4-(3,4-Dicyanophenoxy)phenyl]-10,15,20-triphenylporphyrinato}cobalt(II) (CoCNOTPP, 3, Scheme 1). A mixture of H₂CNOTPP (2) (0.12 g, 0.16 mmol) and hydrous cobalt acetate (0.186 g, 0.75 mmol) in DMF (10 ml) was heated at 70 °C for 2 h with stirring under nitrogen atmosphere. After cooling to room temperature, the mixture was added to 40 ml dichloromethane and washed with 100 ml water three times to remove excess cobalt acetate, acetic acid and DMF. Column chromatography on silica gel with dichloromethane as eluent gave one band. Removal of dichloromethane by evaporation gave 0.112 g (86.5%) of a purple-red solid. The purple-red crude product was recrystallized from dichloromethane using absolute methanol. IR [(KBr) v_{max}/cm⁻¹]: 2231 (CN), 1247 (C–O–C); UV-Vis [DMSO, λ_{max}/nm (log ε)]: 415 (5.26), 528 (4.06); ¹H NMR (400 MHz, CDCl₃), δ 15.82 (br s, 8H, pyrrole-H), 13.09 (br s, 8H, phenyl H), 9.56-9.92 (d, 11H, phenyl-H), 8.91 (s, 1H, phthalonitrile H), 8.80 (d, 1H, phthalonitrile H), 8.51 (d, 1H, phthalonitrile H); MALDI-TOF-MS m/z: calc. 813.75; found 812.98 [M]+.

Tetrakis[tetrakis(5-phenoxy-10,15,20-triphenylporphyrinato)cobalt(II)]–(phthalocyaninato)cobalt(II) (CoPc–(CoTPP)₄, 5). A mixture of CoCNOTPP (3, 20.3 mg, 0.025 mmol) and sodium methoxide (5 mg) was added to distilled methanol (5 ml). Anhydrous ammonia gas was bubbled through the stirred suspension for 1 h. The suspension was then refluxed for 6 h with continued addition of ammonia gas, affording complex **4** as an intermediate which was not isolated. The methanol was removed, then hydrous cobalt acetate (12.45 mg, 0.05 mmol), DBU (2 drops) and *n*-octanol (5 ml) were added. The mixture was heated at 160 °C for 6 h with stirring under a



Scheme 1 Synthetic route for the pentamer CoPc-(CoTPP)₄.

nitrogen atmosphere. The reaction was monitored with UV-vis spectroscopy. After cooling to room temperature, the blue– purple solution was poured into 20 ml dichloromethane and washed three times with 100 ml water. The dichloromethane layer was collected, evaporated and the solid applied to a silica gel column. A series of purple bands were eluted by dichloromethane. The desired compound (blue band) was eluted using DMF. Removal of DMF by water afforded 2.8 mg (13.5%) of a green solid (complex **5**). IR [(KBr) ν_{max}/cm^{-1}]: 1234 (C–O–C); UV-Vis [DMSO, $\lambda_{max}/nm (log \varepsilon)$]: 331 (4.74), 419 (5.15), 540 (4.19), 594 (4.16), 659 (4.62); ¹H NMR (400 MHz, DMSO-d₆), δ 9.18 (br s, 8H, phthalocyanine H), δ 8.96 (br s, 4H, phthalocyanine H), 8.23 (br s, 32H, pyrrole H), 7.84 (br s, 32H, phenyl-2,6H), 7.68 (br s, 44H, phenyl-3,4,5H); MALDI-TOF-MS *m/z*: calc. 3314.37; found 3318.37 [M + 4]⁺.

Results and discussion

Synthesis and characterization

The synthetic route to the compounds presented in this work is shown in Scheme 1. The compounds are abbreviated as indicated in the Experimental section. H₂CNOTPP (2) was synthesized as in literature¹ and in our hands we obtained a slightly higher yield of 72%. This compound was metallated using cobalt acetate to give CoCNOTPP, which was then characterized by IR (CN stretch at 2231 cm⁻¹ and aromatic ether at 1247 cm⁻¹), UVvis spectroscopy as well as ¹H NMR spectroscopy. The proton resonances are broad due to the presence of the paramagnetic cobalt.26 Another remarkable characteristic of the ¹H NMR spectrum of this compound is the extremely deshielded pyrrole protons which is witnessed by their resonance at 15.82 ppm. The ¹H NMR resonances for CoPc-(CoTPP)₄ were generally broad due to the complex mixture of isomers formed, typical of a tetrasubstituted phthalocyanine species, in addition to the presence of paramagnetic Co central metal. Useful information is still obtained despite the broad peaks as the number of protons in the molecule could be accurately accounted for. Further proof of this structure being correct is obtained from the mass spectrum of both the precursor CoCNOTPP and the product CoPc-(CoTPP)₄. The mass spectrum of CoCNOTPP had a molecular ion peak at m/z 812.98 [M]⁺ and a molecular ion peak was observed for CoPc-(CoTPP)₄ at m/z 3318.37 [M + 4]⁺.

CoPc-(CoTPP)₄ could only be synthesized in satisfactory yields by conversion of the phthalonitrile into a diiminoisoindoline precursor (4) then synthesising the phthalocyanine. This procedure gave a 13% yield of CoPc-(CoTPP)₄. The product is difficult to elute out on a silica column and it is necessary to use a polar solvent such as dimethylformamide (DMF) to elute the blue phthalocyanine band. After the DMF was removed by addition of water, the product was separated and found not to be soluble in chlorinated solvents such as dichloromethane, it does however dissolve well in DMF or DMSO. The UV-vis spectrum confirms the formation of a phthalocyanine ring by the appearance of a phthalocyanine Q-band at 659 nm (Fig. 2). This figure shows the electronic absorption spectra of CoTPP (Fig. 2(a)), CoCNOTPP (Fig. 2(b)), CoPc (Fig. 2(c)) and the covalently linked compound CoPc-(CoTPP)₄ in DMSO (Fig. 2(d)). The spectra are typical of these complexes in solution. The presence of a phthalonitrile substituent at a ring position of the CoTPP in CoCNOTPP resulted in a slight shift of the high (B, from 409 to 417 nm) and low (Q, from 523 to 528 nm) energy bands of the CoTPP. This shift to longer wavelengths are usually observed for CoTPP to which electron-withdrawing substituents have been attached,^{27,28} thus indicating that phthalonitrile confers some electron-withdrawing effect on the CoTPP. As observed for the zinc phthalocyanine-porphyrin dimer,¹ the UV-vis spectrum of a metallophthalocyanine-metalloporphyrin conjugate should represent the spectrum of each of the component MPc and MP species. Thus, the UV-vis spectrum of the CoPc-(CoTPP)₄



Fig. 2 UV-vis spectrum of $\sim 2 \times 10^{-5}$ M solutions of (a) CoTPP, (b) CoCNOTPP, (c) CoPc and (d) the pentamer CoPc–(CoTPP)₄ in DMSO.

(Fig. 2(d)) is a combination of the respective spectrum of CoTPP (Fig. 2(a)) and CoPc (Fig. 2(c)). Fig. 2(d) shows a slight red shift for both the B and Q bands of CoTPP (from 409 and 523 nm for CoTPP alone (Fig. 2a) to 419 and 540 nm for CoTPP in CoPc-(CoTPP)₄). The Q band of CoPc (from 654 nm for CoPc alone to 659 nm for CoPc in CoPc-CoTPP) is also found to be shifted. The observation of shifting of the CoTPP bands in the pentamer to longer wavelength compared to CoTPP alone suggests that CoPc exerts some electron-withdrawing effects on the CoTPP. CoTPP, on the other hand, confers electrondonating effects on the CoPc since electron-donating peripheral substituents on the MPc complexes gives rise to red shifts in the Q absorption wavelengths.²⁹⁻³² The Q and B band positions for the CoTPP moieties in CoPc-(CoTPP)₄ are typical for Co^{II}TPP species in Fig. 2. However this spectrum was observed when the CoPc-(CoTPP)₄ complex was freshly prepared. With time following preparation of the solid complex, the spectrum changed to that shown in Fig. 3(b). The spectrum (Fig. 3(b)) confirms that the CoTPP moieties of CoPc-(CoTPP)₄ oxidize to Co^{III}TPP with time, and the B band shifts to longer wavelengths. It is well known³³ that the B band of Co^{III}TPP is more red-shifted than that of Co^{II}TPP.



Fig. 3 UV-vis spectra of $\sim 1 \times 10^{-5}$ M solutions of CoPc-(CoTPP)₄ in DMSO: (a) freshly prepared and (b) of the solid complex four weeks after preparation.

Voltammetric and spectroelectrochemical characterisation

The redox properties of $CoPc-(CoTPP)_4$ (5) were studied using cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) and compared with those of its component molecules, H₂TPP, CoTPP and CoPc, and of the



Fig. 4 Cyclic voltammograms of (a) H_2 TPP, (b) CoTPP, (c) H_2 CNOTPP and (d) CoPc (inset: OSWV) on a glassy carbon electrode in DMSO solution containing 0.1 M TBAP. Scan rate = 100 mV s⁻¹.

parent molecules H₂CNOTPP (**2**) and CoCNOTPP (**3**), using similar experimental conditions. Fig. 4 shows typical CVs for (a) H₂TPP, (b) CoTPP, (c) H₂CNOTPP and (d) CoPc in DMSO containing 0.1 M TBAP. Figs. 5 and 6 present the cyclic voltammograms for the precursor CoCNOTPP and the pentamer CoPc–(CoTPP)₄, respectively. The values for the halfwave potential ($E_{1/2}$) are summarised in Table 1. The neutral forms of the porphyrin and phthalocyanine exist as a dianion designated as P⁻² or Pc⁻² for porphyrin or phthalocyanine, respectively.³⁴⁻³⁶ Oxidation at the porphyrin and phthalocyanine rings occurs by successive loss of one or two electrons from



Fig. 5 Cyclic voltammograms of CoCNOTPP on a glassy carbon electrode in DMSO solution containing 0.1 M TBAP. Scan rate = 100 mV s^{-1} .



Fig. 6 Cyclic voltammograms of CoPc–(CoTPPc)₄ pentamer on a glassy carbon electrode in DMSO solution containing 0.1 M TBAP. Scan rate = 100 mV s^{-1} ; inset: OSWV.

the highest occupied molecular orbital (HOMO) resulting in the formation of $[P^{-1}]^{++}$ or $[Pc^{-1}]^{++}$ and $[P^{0}]^{+2+}$ or $[Pc^{0}]^{+2+}$ cation radicals. Reduction, on the hand, occurs by successive gain of electrons by the lowest unoccupied molecular orbital (LUMO) of the porphyrin and phthalocyanine complexes resulting in the formation of $P^{(-2-R)}$ or $Pc^{(-2-R)}$ species (where n = number of electrons). The cyclic voltammogram for H₂TPP shown in Fig. 4(a) is well known and consists of two reversible one-electron reductions. Under our experimental conditions no oxidation couples were observed for this molecule. The cyclic voltammogram for CoTPP is also very well known, and the first reduction and oxidation occur on the central metal. For H₂CNOTPP (Fig. 4(c)), only reduction processes were observed.

Table 1 Half-wave potentials $(E_{1/2}/V)$ of porphyrin and phthalocyanine precursor complexes for CoPc-(CoTPP)₄ in dry DMSO containing 0.1 M TBAP

	Oxidation processes $(E_{1/2}/V)$		Reduction processes $(E_{1/2}/V)$			
Macrocycle	$I(P^{-1}/P^{-2})$	II (Co^{III}/Co^{II})	III (Co ^{II} /Co ^I)	$IV (P^{-2}/P^{-3})$	$V(P^{-3}/P^{-4})$	$VI (P^{-4}/P^{-5})$
H ₂ TPP				-0.77	-1.20	
H ₂ CNOTPP				-0.74	-1.15	-1.29
CoTPP	1.47	0.35	-0.64	-1.68		
CoCNOTPP	1.06	0.44	-0.55	-1.30	-1.62	
CoPc	1.11 (1st)	0.37	-0.31	-1.20	~ -1.70	
	1.30 (2nd)					

Couples IV and V for H₂CNOTPP (Table 1) are similar to those of H₂TPP and are assigned to ring-based processes given by eqns. (1) and (2). These couples are well-recognised and are characteristic of ring-based electrode processes for metalfree porphyrin complexes.³⁷ A third reduction process (VI) was observed in H₂CNOTPP even though it was not observed for H₂TPP. Although it is rare to observe more than two ringbased reduction processes in porphyrin complexes, Campbell *et al.*³⁸ observed three reduction processes for a nickel porphyrin complex with electron-withdrawing formyl substituents.

 $H_2 CNOTPP^{-2} + e^{-} \rightleftharpoons [H_2 CNOTPP^{-3}]^{-}: IV$ (1)

$$[H_2 CNOTPP^{-3}]^- + e^- \rightleftharpoons [H_2 CNOTPP^{-4}]^{2-}: V$$
(2)

$$[H_2CNOTPP^{-4}]^{2-} + e^{-} \rightleftharpoons [H_2CNOTPP^{-5}]^{3-}: VI$$
(3)

However, to check if any of the reduction processes observed in our work might be due to the phthalonitrile substituent, a CV of phthalonitrile alone was recorded. An irreversible anodic peak at ca. -0.80 V was obtained for the phthalonitrile in DMSO containing TBAP. There is no irreversible wave in this region in Fig. 4(c) suggesting that the phthalonitrile peak is not observed when the molecule is bound to porphyrin. Thus all the three reduction processes (IV-VI) are due to H₂CNOTPP. The result also indicates that the phthalonitrile substituent exerts an electron-withdrawing effect on the redox behaviour of the porphyrin molecule, which is apparent in the slight shifts of the reduction potentials to more positive (easier to reduce) potentials as compared to the H₂TPP, thus corroborating the spectroscopic observation. Couple VI was separated from couple V by 0.14 V. The separation between ringbased redox process is affected by the nature of electrolyte, with smaller separations being observed when TBAP is employed compared to TBAPF₆.³⁸ Process (VI) is represented by eqn. (3). The reduction processes for H_2 CNOTPP were reversible to quasi-reversible with anodic to cathodic peak currents being near unity.

Displacement of the two protons in the inner porphyrin or phthalocyanine core with a metal ion usually leads to a shift of the first ring-based reduction potential to a more negative value as a result of the π -back donation of the filled d_{π} of the metal ion into the empty porphyrin or phthalocyanine π^* orbitals.^{36,39} Thus, as expected, the introduction of cobalt ion (*i.e.*, the formation of CoCNOTPP) resulted in the shift of the ring processes to more negative values (compare H₂CNOTPP and CoCNOTPP, Table 1). Comparison with the well-known assignments for CoTPP complexes,28,33,35,37,40-43 nicely corroborated with the $E_{1/2}$ values for CoTPP obtained in this work (Table 1). The first oxidation ($E_{1/2} = 0.44$, II) and reduction $(E_{1/2} = -0.55 \text{ V}, \text{III})$ waves for CoCNOTPP, Fig. 5, are assigned to Co^{III}/Co^{II} and Co^{II}/Co^I processes, respectively. The second oxidation for CoCNOTPP (labelled I) and the remainder of the reduction couples (IV and V) are due to the ring processes. Eqns. (4)-(8) describe redox processes I-V for CoCNOTPP, respectively.

 $[\mathrm{Co}^{\mathrm{III}}(\mathrm{CNOTPP}^{-2})]^{\bullet+} \rightleftharpoons [\mathrm{Co}^{\mathrm{III}}(\mathrm{CNOTPP}^{(-1)})]^{2+} + e^{-}: I \qquad (4)$

 $\operatorname{Co}^{II}(\operatorname{CNOTPP}^{-2}) \rightleftharpoons [\operatorname{Co}^{III}(\operatorname{CNOTPP}^{-2})]^{+} + e^{-}: \operatorname{II}$ (5)

 $\operatorname{Co}^{II}(\operatorname{CNOTPP}^{-2}) + e^{-} \rightleftharpoons [\operatorname{Co}^{I}(\operatorname{CNOTPP}^{-2})]^{-}: \operatorname{III}$ (6)

 $[\operatorname{Co}^{I}(\operatorname{CNOTPP}^{-2})]^{-} + e^{-} \rightleftharpoons [\operatorname{Co}^{I}(\operatorname{CNOTPP}^{-3})]^{2-}: \mathrm{IV}$ (7)

$$[\operatorname{Co}^{I}(\operatorname{CNOTPP^{-3}})]^{2-} + e^{-} \rightleftharpoons [\operatorname{Co}^{I}(\operatorname{CNOTPP^{-4}})]^{3-}: V \qquad (8)$$

Electron-withdrawing substituents on the peripheral positions of phthalocyanine or porphyrin rings lead to a decrease on the average electron density of the total conjugated phthalocyanine or porphyrin system thereby leading to easier reduction and more difficult oxidation.^{16,27-29,44} As observed above for H₂TPP (Fig. 4(a)) and H₂CNOTPP (Fig. 4(c)), the oxo-phthalonitrile confers electron-withdrawing properties on the metallated porphyrin complexes. Comparing the $E_{1/2}$ value of CoTPP with that of CoCNOTPP, shows that the latter is easier to reduce.

Couples II and III for CoPc (Fig. 4(d)) are assigned to metal-centered oxidation (Co^{II}/Co^{I}) and reduction (Co^{II}/Co^{I}), respectively, in comparison with the literature.³⁶ The remainder of the couples are ring-based, see Table 1. The observation of weak currents for the Co^{II}/Co^{I} process is a common phenomenon for CoPc complexes.³⁶ The inset of Fig. 4(d) is the more sensitive OSWV depicting this Co^{II}/Co^{I} process and other ill-defined redox couples.

The pentamer, CoPc-(CoTPP)4 (Fig. 6), showed nine identifiable redox processes (I-VIII), characteristic of a multi-electron redox species. The voltammograms were recorded after the oxidation of the Co^{II} to Co^{III} in CoTPP moieties, as judged by the spectra. As stated above, the CoTPP moieties of the solid oxidized with time to form Co^{III}TPP. The processes in Fig. 6 are easier to observe on the OSWV (inset). All the processes showed quasi-reversible (with large $\Delta E_{\rm p}$, ≥ 100 mV) to irreversible behaviour. The lack of total reversibility in some of the redox couples is most likely due to overlapping of the individual parent monomers that make up the pentamer. The peak currents increased linearly with the square root of the scan rates, for scan rates ranging from 25 to 800 mV s⁻¹, suggesting diffusion-controlled reactions. Repetitive scanning (20 scans) of the DMSO solution of CoPc-(CoTPP)₄ containing TBAP did not show any change in the positions of the peaks except for the process VII that shifted considerably towards negative potential (by 0.2 V) and then broadened leading to the loss of process VIII. However, using a freshly cleaned working electrode surface, a scan similar to the first one in Fig. 6 was reproduced. Aromatic systems physisorb onto glassy carbon surfaces, indicating that this change in peak shapes on continuous scans may be attributed to the adsorption and formation of different products on the electrode surface.

The redox processes (I–VIII) of CoPc–(CoTPP)₄ should involve both the central cobalt ion and the π -ring systems of the porphyrin and the phthalocyanine subunits. Their assignments (as detailed in Table 2) were based on spectroelectrochemistry

Table 2 Half-wave potentials $(E_{1/2}/V)$ or peak potential (E_P/V) , and redox assignments for the electrogenerated species from CoPc-(CoTPP)₄ in dry DMSO containing 0.1 M TBAP

	Redox process ^a	$E_{1/2}$ (or $E_{\rm p}$)/V	Assignment
	I II' III IV V VI VI VII VIII	$ \begin{array}{r} 1.10\\ 0.72\\ 0.40\\ -0.30\\ -0.52\\ -0.73\\ -1.13\\ -1.36\\ -1.70\\ \end{array} $	$\begin{array}{l} Co^{III}Pc^{-1}(TPP^{-1}Co^{III})_4/Co^{III}Pc^{-2}(TPP^{-1}Co^{III})_4\\ Co^{III}Pc^{-2}(TPP^{-1}Co^{III})_4/Co^{III}Pc^{-2}(TPP^{-2}Co^{III})_4\\ Co^{II}Pc^{-2}(TPP^{-2}Co^{III})_4/Co^{II}Pc^{-2}(TPP^{-2}Co^{III})_4\\ Co^{II}Pc^{-2}(TPP^{-2}Co^{II})_4/Co^{II}Pc^{-2}(TPP^{-2}Co^{II})_4\\ Co^{II}Pc^{-2}(TPP^{-2}Co^{II})_4/Co^{I}Pc^{-2}(TPP^{-2}Co^{II})_4\\ Co^{II}Pc^{-2}(TPP^{-2}Co^{II})_4/Co^{I}Pc^{-3}(TPP^{-2}Co^{I})_4\\ Co^{II}Pc^{-3}(TPP^{-2}Co^{II})_4/Co^{I}Pc^{-3}(TPP^{-2}Co^{I})_4\\ Co^{II}Pc^{-3}(TPP^{-2}Co^{II})_4/Co^{II}Pc^{-3}(TPP^{-3}Co^{I})_4\\ Co^{II}Pc^{-3}(TPP^{-3}Co^{I})_4/Co^{II}Pc^{-4}(TPP^{-3}Co^{I})_4\\ \end{array}$
^a See Fig. 6 for the processe	s.		

and on an established⁴³ strategy of comparing the $E_{1/2}$ values of the parent monomeric (CoTPP and CoPc) units (Table 1). Spectroelectrochemistry has successfully been employed to provide an unequivocal identification of the nature of the redox species formed for mono- and hetero-nuclear cobalt phthalocyanine^{28,40,45-48} and porphyrin^{28,40} complexes, hence the technique was used to confirm our cyclic voltammetry assignments.

Thin layer UV-vis spectra of the CoTPP moieties of CoPc– (CoTPP)₄ in DMSO containing TBAP, before application of potential shows the presence of Co^{III}TPP (at 430 nm), with small amounts of Co^{II}TPP at shorter wavelengths, Fig. 7(a)(i). Fig. 7(a) shows UV-vis spectral changes observed during controlled potential reduction of CoPc–(CoTPP)₄ in DMSO solution containing TBAP in OTTLE cell, at potential more negative (*ca.* -0.5 V) than process III in Fig. 6. The B band of the CoTPP moieties of the pentamer shifted from 430 nm of the Co^{III}TPP species to 415 nm due to Co^{III}TPP. Note the slight difference in the B band maximum in Fig. 2(d) compared to Fig. 7(a) probably due to the presence of the electrolyte for the spectrum recorded for spectroelectrochemistry. Thus process III is due Co^{III}Pc⁻²(TPP⁻²Co^{III})₄/Co^{II}Pc⁻²(TPP⁻²Co^{III})₄, Table 2. The reduction occurred with clear isosbestic points at 355, 427, 457, 437 and 700 nm. It can be seen in Fig. 7(a) that during the



Fig. 7 Typical UV-vis spectral changes observed using OTTLE cell during reduction processes of $CoPc-(CoTPP)_4$. The spectra were recorded continuosly during the electrolysis: (a) -0.5 V before (i) and after (ii) electrolysis; (b) -0.75 V: (i) same as (ii) in (a); (ii) after electrolysis; (c) -1.0 V: (i) same as (ii) in (b), (ii) after electrolysis; (d) -1.40 V: (i) same as (ii) in (c), (II) after electrolysis.

controlled electrolysis at potentials of process III, the Q band of the CoPc moiety (at 659 nm) decreased in intensity without any shift in wavelength. Thus no reduction occurred on the CoPc moiety of the pentamer, only some possible degradation.

Fig. 7(b) shows spectroscopic changes when the potential was switched to potentials more negative (-0.75 V) than process IV, following the last spectral change shown in Fig. 7(a). A dramatic shift of the CoPc band at 659 nm to 702 nm was observed, accompanied with formation of a new band 474 nm. These spectral changes are typical of the reduction of Co^{II}Pc to Co^IPc,⁴⁵⁻⁴⁸ which consists of the red shifting of the Q band and the formation of a relatively strong band in the 450 nm region. The intense band in this region is associated with the metal-to-ligand charge transfer (MLCT): $Co^{I}Pc^{-2} [d_{XZ,VX}] \rightarrow \pi^{*}(1b_{1u})(Pc(-2)).^{45-48}$ The B band of the Co^{II}TPP moieties of the pentamer increased in intensity without any shifting in Fig. 7(b). The spectral changes occurred with isosbestic points at 683 and 542 nm. Thus at potentials of process IV, no significant changes occurred on the CoTPP moieties of the pentamer and this process is assigned to $Co^{II}Pc^{-2}(TPP^{-2}Co^{II})_4/Co^{I}Pc^{-2}(TPP^{-2}Co^{II})_4$ (Table 2).

Increasing the reduction potential to values more negative (-1.0 V) of process V, resulted in spectral changes shown in Fig. 7(c). No changes were observed on the CoPc moiety of the pentamer. The spectral changes observed on the CoTPP moieties of the pentamer are typical of Co¹TPP, with a split Soret band.³³ The formation of the new peak at 358 nm is similar to that observed by Zheng *et al.*³³ in the 300–350 nm region for the mononuclear CoTPP and which was attributed to the Co¹TPP. Thus, process V is assigned to Co¹Pc⁻²(TPP⁻²Co^{II})₄/Co¹Pc⁻²(TPP⁻²Co^{II})₄. In Fig. 7(b) the peak at 358 nm began to be formed but complete spectral changes to the Co¹TPP species were only observed in Fig. 7(c).

When the reduction potential was increased to a more negative value (-1.40 V) (Fig. 7(d)) than process VI, the bands due to Co^IPc (703 nm) decreased in intensity and new bands were formed between 480 and 600 nm, in addition to the MLCT band. The bands in the 500-600 nm region are typical⁴⁸ of ring reduction in MPc complexes and the formation of Pc⁻³ species. The bands due to the Co^ITPP remained stable, hence confirming that at potentials of process VI, CoTPP moieties of the pentamer are not involved. Thus, process VI is assigned to $Co^{1}Pc^{-2}(TPP^{-2}Co^{1})_{4}/Co^{1}Pc^{-3}(TPP^{-2}Co^{1})_{4}$, Table 2. There were no further spectral changes when the potential was increased to more negative values. The remaining reduction processes (VII and VIII) are all ring-based and are assigned in comparison with reduction potentials of the precursors and monomer components (Table 1). Process VII is at potentials for ring reduction (to P^{-3}) in the CoCNOTPP precursor (-1.30 V). Thus, this process is assigned to Co¹Pc⁻³(TPP⁻²Co¹)₄/Co¹Pc⁻³(TPP⁻³Co¹)₄, and the last reduction process is at the potential for the second ring reduction in CoPc, hence is assigned to $Co^{I}Pc^{-3}(TPP^{-2}Co^{I})_{4}/Co^{I}Pc^{-4}(TPP^{-3}Co^{I})_{4}$. Table 3 summarizes the spectral data of the complexes.

Table 3 Spectral data for the starting $CoPc(TPPCo)_4$ and its oxidationor reduction products. Data in DMSO containing TBAP. Only Q bands(and other identifying bands) are shown for the CoPc moiety. Wherepossible, both Q and Soret (B) bands are shown for the CoTPP moieties

	λ/nm			
Complex	СоТРР	CoPc		
$\begin{array}{l} Co^{II}Pc^{-2}(TPP^{-2}Co^{III})_4\\ Co^{II}Pc^{-2}(TPP^{-2}Co^{II})_4\\ Co^{I}Pc^{-2}(TPP^{-2}Co^{II})_4\\ Co^{I}Pc^{-2}(TPP^{-2}Co^{II})_4\\ Co^{I}Pc^{-3}(TPP^{-2}Co^{II})_4\\ Co^{III}Pc^{-2}(TPP^{-2}Co^{III})_4 \end{array}$	430 (B), 543 (Q) 415 (B), 532 (Q) 415 (B), 532 (Q) 425 and 358 (split B) 425 and 358 (split B) 430 (B), 543 (Q)	659 (Q) 659 (Q) 703 (Q), 474 703 (Q), 474 482, 533 670		

After the spectroelectrochemical processes shown in Fig. 7(d), the potential was changed to more positive values, to check the reversibilities of the reduction processes. Fig. 8(a) shows that on application of -0.3 V, following changes in Fig. 7(d), the reduction processes on the CoTPP moiety of the pentamer could be reversed with the disappearance in the peaks due to Co¹TPP and the regeneration first of the Co¹¹TPP Soret band at 415 nm, together with the decrease of the Pc⁻³ peaks in the 480–600 nm region (Fig. 8(a)). The peak due to Co¹²PC increased in intensity.

Increasing the potential to 0.4 V (Fig. 8(b)) following the spectral changes shown in Fig. 8(a), resulted in the oxidation of Co^IPc and regeneration of the Co^{II}Pc moiety of the pentamer. There is also a shift of the Soret band of the CoTPP moieties of the pentamer towards longer wavelengths, as Co^{II}TPP is oxidized back to Co^{III}TPP in the pentamer. The complete regeneration of the Co^{III}TPP is only observed when a more positive potential is



Fig. 8 Typical UV-vis spectral changes observed using OTTLE cell during re-oxidation or oxidation of CoPc–(CoTPP)₄ The spectra were recorded continuosly during the electrolysis; (a) -0.3 V: (i) same as (ii) in Fig. 7(d); (ii) after electrolysis; (b) 0.4 V: (i) same as (ii) in (a); (ii) after electrolysis; (c) 1.0 V: (i) same as (ii) in (b), (ii) after electrolysis.

Published on 07 March 2005. Downloaded by University of Aberdeen on 27/08/2013 19:11.11.

applied (1.0 V), Fig. 8(c). Application of this potential resulted in the shift of the Q band of the Co^{II}Pc moiety of the pentamer from 659 nm (of Co^{II}Pc) to 670 nm. The spectral changes are typical of the oxidation of Co^{II}Pc to Co^{III}Pc. Thus the first oxidation of the pentamer occurs at the CoPc moiety. Hence we assign the first oxidation process (II) in Fig. 6, to $Co^{III}Pc^{-2}(TPP^{-2}Co^{III})_4/Co^{II}Pc^{-2}(TPP^{-2}Co^{III})_4$ (Table 2). No further spectral changes were observed on increasing the potential. Processes II' and I are due to ring based processes and are assigned to $Co^{III}Pc^{-2}(TPP^{-1}Co^{III})_4/Co^{III}Pc^{-2}(TPP^{-2}Co^{III})_4$ and $Co^{III}Pc^{-1}(TPP^{-1}Co^{III})_4/Co^{II}Pc^{-2}(TPP^{-1}Co^{III})_4$, respectively. The latter is assigned based on similarities between its redox process and that of the parent CoPc (Fig. 4(d)).

In conclusion, we have shown in this work that the newly synthesized pentamer (CoPc-(CoTPP)₄) has electronic absorption spectral behaviour, which closely resembles that of the parent (CoPc and CoTPP) complexes. The complex showed complicated cyclic voltammetry data, which was interpreted using spectroelectrochemistry. Using the latter technique, the voltammograms were assigned to metal and ring-based processes on both the CoPc and the CoTPP moieties of the pentamer. The processes seemed to alternate between the CoPc and CoTPP species in that the first reduction was on the CoTPP moieties, the second reduction on the CoPc moiety, the third on CoTPP and so on. Each of the redox processes showed distinct spectral changes. This work has thus presented a molecule which absorbs in both the visible and UV region and whose reduction or oxidation gives new spectra, with potential for applications where a wide range of absorption characteristics and/or multielectron transfer reactions are required.

Acknowledgements

This work was supported by Rhodes University and the National Research Foundation (NRF) in South Africa. K. I. O. thanks Andrew Mellon Foundation for sponsorship as an Accelerated Development fellow/lecturer.

References

- 1 S. Gaspard, C. Giannotti, P. Maillard, C. Schaeffer and T. H. Tran-Thi, *Chem. Commun.*, 1986, 16, 1239.
- 2 M. O. Liu and A. T. Hu, J. Organomet. Chem, 2004, 689, 2450.
- 3 M. Lachkar, A. De Cian, J. Fischer and R. Weiss, *New J. Chem*, 1988, **16**, 729.
- 4 J. Jiang, K. Kasuga and D. P. Arnold, in *Supramolecular Photosen-sitive and Electroactive Materials*, ed. H. S. Nalwa, Academic Press, New York, 2001, p. 113.
- 5 D. Chabach, M. Lachkar, A. De Cian, J. Fischer and R. Weiss, *New J. Chem*, 1992, **16**, 431.
- 6 D. Chabach, A. De Cian, J. Fischer, R. Weiss and M. M. Bibout, Angew. Chem., Int. Ed., 1996, 35, 898.
- 7 D. Chabach, M. Tahiri, A. De Cian, J. Fischer, R. Weiss and M. M. Bibout, J. Am. Chem. Soc., 1995, 117, 8548.
- 8 T. H. Tran-Thi, J. F. Lipskier, M. Simoes and S. Palacin, *Thin Solid Films*, 1992, 210–211, 150.
- 9 L. R. Milgrom, The Colours of Life: An Introduction to the Chemistry of Poprhyrins and Related Compounds, Oxford Univ. Press, Oxford, 1997.
- 10 M. Biesaga, K. Pyrzynska and M. Trojanowicz, *Talanta*, 2000, 51, 209.
- 11 J. Obirai and T. Nyokong, J. Electroanal. Chem., 2004, 573, 77.
- 12 J. H. Zagal, Coord. Chem. Rev., 1992, 119, 89.

- 13 N. Phougat, P. Vasudevan and S. A. K. Shukla, J. Power Sources, 1993, 46, 61.
- 14 J. Zagal, M. A. Gulppi, C. A. Caro and G. I. Cárdenas-Jirón, *Electrochem. Commun.*, 1999, 1, 389.
- 15 S. Griveau, M. Gulppi, F. Bedioui and J. H. Zagal, *Solid State Ionics*, 2004, **169**, 59.
- 16 S. Maree and T. Nyokong, J. Electroanal. Chem., 2000, 492, 120.
- 17 K. I. Ozoemena, T. Nyokong and P. Westbroek, *Electroanalysis*, 2003, **15**, 1762.
- 18 T. Nyokong and S. Vilakazi, Talanta, 2003, 61, 27.
- 19 J. P. Collman, M. S. Ennis, D. A. Offord, L. L. Chng and J. H. Griffin, *Inorg. Chem.*, 1996, **35**, 1751.
- 20 F. D'Souza, Y. Y. Hsieh, H. Wickman and W. Kutner, *Chem. Commun.*, 1997, 1191.
- 21 F. D'Souza, Y. Y. Hsieh and G. R. Deviprasad, *Chem. Commun.*, 1998, 1027.
- 22 Y.-H. Tse, P. Janda, H. Lam, J. Zhang, W. Pietro and A. B. P. Lever, *J. Porphyrins Phthalocyanines*, 1997, **1**, 3.
- 23 M. Krejčik M, M. Daněk and F. Hartl, J. Electroanal. Chem., 1991, 317, 179.
- 24 J. G. Young and W. J. Onyebuagu, J. Org. Chem., 1990, 55, 2155.
- 25 M. J. Crossley, L. G. King and S. M. Pyke, *Tetrahedron*, 1987, 43, 4569.
- 26 G. N. La Mar and F. A. Walker, J. Am. Chem. Soc., 1973, 95, 1790.
- 27 C.-L. Lin, M.-Y. Fang and S.-H. Cheng, J. Electroanal. Chem., 2002, 531, 155.
- 28 F. D'Souza, A. Villard, E. V. Caemelbecke, M. Franzen, T. Boschi, P. Tagliatesta and K. M. Kadish, *Inorg. Chem.*, 1993, **32**, 4042.
- 29 J. Metz, O. Schneider and M. Hanack, Inorg. Chem., 1984, 23, 1065.
- 30 D. Dini, M. Barthel and M. Hanack, Eur. J. Org. Chem, 2001, 3759.
- 31 K. Ozoemena and T. Nyokong, J. Chem. Soc., Dalton Trans., 2002, 1806.
- 32 A. Ogunsipe, J.-Y Chen and T. Nyokong, *New J. Chem.*, 2004, **28**, 822.
- 33 G. D. Zheng, Y. Yan, S. Gao, S. L. Tong, D. Gao and K. J. Zhen, *Electrochim. Acta*, 1996, **41**, 177.
- 34 J. F. Myers, R. G. W. Canham and A. B. P. Lever, *Inorg. Chem.*, 1975, 14, 461.
- 35 K. M. Kadish, X. Q. Lin and B. C. Han, Inorg. Chem, 1987, 26, 4161.
- 36 A. B. P. Lever, E. R. Milaeva and G. Speier, in *Phthalocyanines: Properties and Applications*, ed. A. B. P. Lever and C. C. Leznoff, VCH Publishers, New York, 1993, vol. 3, ch. 1, pp. 1–69.
- 37 F. A. Walker, D. Beroiz and K. M. Kadish, J. Am. Chem. Soc., 1976, 98, 3484.
- 38 C. J. Campbell, J. F. Rusling and C. Brückner, J. Am. Chem. Soc., 2000, 122, 6679.
- 39 A. R. Özkaya, A. G. Gürek, A. Gül and Ö. Bekaroğu, *Polyhedron*, 1997, 16, 1877.
- 40 A. Wolberg and J. Manassen, J. Am. Chem. Soc., 1970, 2982.
- 41 C. Araullo-McAdams and K. M. Kadish, *Inorg. Chem.*, 1990, **29**, 2749.
- 42 A. D. Kini, J. Washington, C. P. Kubiak and B. H. Morimoto, *Inorg. Chem.*, 1996, 35, 6904.
- 43 M. Kadish, N. Guo, E. V. Caemelbecke, R. Paolesse, D. Monti and P. Tagliatesta, J. Porphyrins Phthalocyanines, 1998, 2, 439.
- 44 A. G. Hysop, M. Orphanide, U. Javed and E. G. Megehee, *Inorg. Chim. Acta*, 2003, 355, 272.
- 45 W. A. Nevin, M. R. Hempetead, W. Liu, C. C. Leznoff and A. B. P. Lever, *Inorg. Chem.*, 1987, 26, 570.
- 46 W. A. Nevin, W. Liu, S. Greenberg, M. R. Hempstead, S. M. Marcuccio, M. Melnik, C. C. Leznoff and A. B. P. Lever, *Inorg. Chem.*, 1987, 26, 891.
- 47 M. J. Stilman and T. Nyokong, in *Phthalocyanines: Properties and Applications*, ed. A. B. P. Lever and C. C. Leznoff, VCH Publishers, New York, 1989, vol. 1, ch. 3, pp. 133–289.
- 48 M. J. Stilman, in *Phthalocyanines: Properties and Applications*, ed. A. B. P. Lever and C. C. Leznoff, VCH Publishers, New York, 1993, Vol. 3, Ch. 5, pp. 227–296.