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Spectroscopic and electrochemical characterization of solutions and films of a new redox couple: Co(II)/Co(III) N-confused porphyrin

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Abstract

Co(II) ion was introduced in N-confused tetraphenylporphyrin (NCTPP) as evidenced by ESR and UV–Vis spectroscopy as well as electrochemical methods. The Co(II)NCTPP complex shows a typical ESR spectrum of a high spin $3d^7$ Co(II) ion, Soret bands at 460 and 445 nm in CH_2Cl_2 and CH_3CN, respectively, and oxidation potential of +0.55 V vs. Ag/AgCl/KCl (satd.). Adsorbed films of Co(II)NCTPP on glassy carbon electrodes are stable and show reversible redox waves in aqueous basic solutions attributed to the Co(II)/Co(III)NCTPP couple with $E_{1/2}$ = +0.025 V at pH 14. It is also shown that NCTPP can be electropolymerized and the films readily metallate with Co(II) ions.

Keywords: N-confused porphyrins; Co(II) complex; Spectroscopy; Redox; Electropolymerization

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N-confused porphyrins (NCP) are porphyrin isomers where one of the pyrrole rings is inverted [1,2]. These porphyrins possess three nitrogens and one carbon atom which display N–H and C–H tautomerism [3,4] and act as chelating donor atoms. They can behave both as dianionic and trianionic ligands when complexing with metal ions [5] and have been shown to form complexes with transition metal ions such as iron [6], manganese [7,8], copper [9,10], nickel [11–13], silver [5] and palladium [14]. The N-confused pyrrole can play different roles depending on the metal ion and oxidation state as well as the synthesis method [15,16]. The internal carbon can be bonded to a metal ion in different ways [2,6,8,9,17] and the external nitrogen can be free [3,5,18], proton bearing [2,3,6,8,9,14,17] or involed in coordination [14–16,19]. The coordination of N-confused porphyrins has been recently reviewed by Harvey and Ziegler [20].

The B_{12} coenzymes contain a corrin ring with a low-spin Co(III) ion in an octahedral configuration. In one group of enzymes, the cobalt ion coordinates to the imidazole side chain of a histidine residue and in another group the cobalt ion binds to the pendant dimethylbenzimidazole group of the coenzyme. The second axial site is coordinated to a methyl or 5′-deoxyadenosyl groups and these form an organometallic Co–C bond. In view of the possible involvement of this bond in enzymatic reactions and in the chemistry of the different oxidation states of cobalt ion, we have explored the complexation

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M = Co(II)
R = Phenyl

Scheme 1. Schematic structure of Co(II)NCTPP.

of N-confused tetraphenylporphyrin with cobalt ions (CoNCTPP). Very recently, X-ray crystal data of Co(III)NCTPP with H_2O, triphenylphosphine and pyridine were reported [21]. Here we present the preparation [1] of the Co(II) derivative (Scheme 1) and spectroscopic as well as electrochemical properties of the Co(II)/Co(III)NCTPP couple which has not yet been reported in the literature. Moreover, we show for the first time that NCTPP can be electropolymerized on electrode surfaces and metal ions can be readily introduced into these films.

Room temperature X-band EPR spectra of polycrystalline Co(II)NCTPP showed a poorly resolved signal at a g value of approximately 3.3. The spectrum is typical of a high spin ($S = 3/2$) $3d^7$ Co(II) ion, similar to that reported for Co(II) texaphyrin [22] and unlike other Co(II) porphyrins which generally exist as low spin ($S = 1/2$) complexes [23].

UV–Vis spectroscopy showed that the Co(II)NCTPP complex dissolved and was stable in CH_2Cl_2, even when exposed to air (Fig. 1A, curve a: Soret band at 460 nm and Q bands at 652 and 804 nm). However, the spectrum after imidazole addition was similar to that obtained for non-metallated NCTPP dissolved in CH_2Cl_2 in the absence as well as presence of imidazole (Fig. 1B, curve a: Soret band 439 nm and Q bands at 539, 582 and 727 nm). The spectrum of Co(II)NCTPP in CH_3CN showed a Soret band at 445 nm and Q bands at 550, 600, 719 and 793 nm (Fig. 1A, curve b) and differed from that of NCTPP (Fig. 1B, curve b: Soret at 434 and Q bands at 538, 580, 645, 695 and 722 nm). However, as in the case of addition of imidazole to Co(II)NCTPP, the spectrum of Co(II)NCTPP in DMF (Fig. 1A, curve c) showed similar features to those of the non-metallated NCTPP in this solvent (Fig. 1B, curve c: Soret at 438 and Q bands at 537, 581 and 731 nm). These results indicate that the Co(II)-carbon bond, unlike the Co(III)–C bond [21], is not stable in the presence of nitrogenous bases such as imidazole and DMF which ligate the Co(II) ion and demetallate the complex.

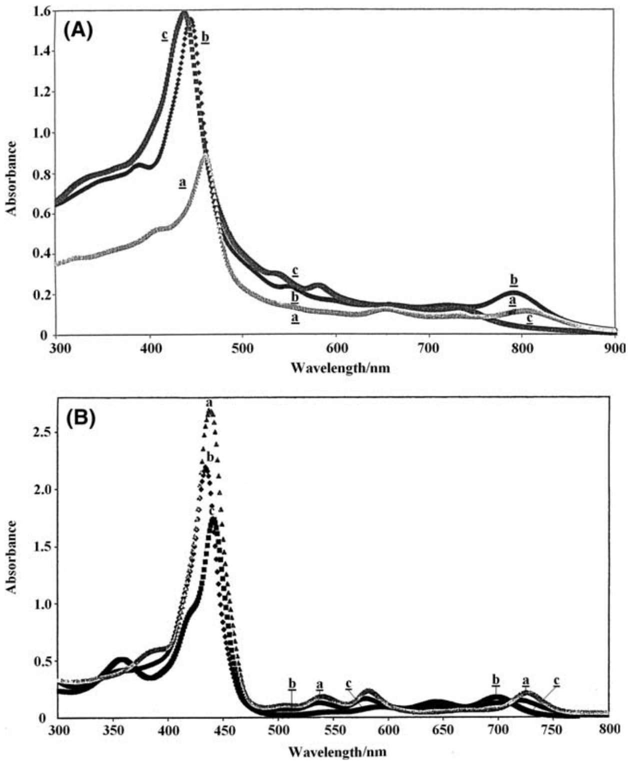

Fig. 1. Optical absorption spectra in CH_2Cl_2 (a), CH_3CN (b) and DMF (c) of Co(II)NCTPP (A) and non-metallated NCTPP (B). Absorbance is in arbitrary scale.

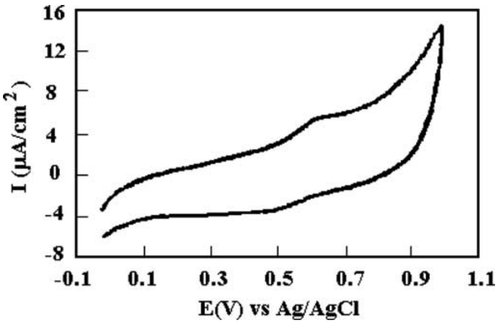

Fig. 2. Cyclic voltammogram (20 mV/s) obtained at a GC electrode for a CH_2Cl_2 solution containing 0.5 mM Co(II)NCTPP and 0.1 M Bu_4NClO_4.

Cyclic voltammetry of Co(II)NCTPP complex in CH_2Cl_2 at a glassy carbon (GC) electrode (Fig. 2) showed a quasi-reversible peak ($\Delta E_p = 0.11$ V) with $E_{1/2} = 0.55$ V vs. Ag/AgCl/KCl (satd.) and current peaks which increased linearly with the concentration of Co(II)NCTPP in solution. Although this peak differs from the oxidation peaks obtained for the non-metallated porphyrin (0.65 and 1.0 V), it is not possible in this stage to ascribe it as metal- or ligand-centered oxidation.

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[1] In a typical synthesis, insertion of Co(II) ions in NCTPP (Midcentury, Posen, IL) was achieved by mixing a solution of 15 mM $Co(ClO_4)_2$ in methanol with a solution of 1 mM of NCTPP in 10 ml CH_2Cl_2 and stirring for 72 h at room temperature. The vessel was then opened to air until the solvents totally evaporated. In order to dissolve excess of the Co(II) salt, 20 ml of water were added and the solution was stirred for a few hours. Collection of the non-crystalline solid product was made after decantation, drying in air overnight and precipitation from a CH_2Cl_2 solution.

Electrochemical experiments for adsorbed Co(II)NCTPP films on GC electrodes [2] were conducted in aqueous electrolyte solutions. Fig. 3A shows cyclic voltammograms for such a film in a NaOH solution at various pH's. A well defined and reversible wave $E_{1/2} = 0.025$ V and $\Delta E_p = 0.05$ V was observed at pH 14 (curve a). Since it is improbable that a radical cation would yield a reversible wave in aqueous solution, it is attributed to the Co(II)/Co(III)NCTPP couple. The redox potential of this couple is relatively high compared to other cobalt porphyrins which have been examined (dissolved or as films) in basic solutions (for example, $E_{1/2} = -0.16$ V) for Co(III/Co(II) tetrakis(*o*-aminophenyl)porphyrin in 1 M NaOH [23]). Moreover, the wave shifts to more anodic potentials and becomes quasi-reversible as the pH decreases and at pH lower than 11, it is almost undetectable. The slope of $E_{1/2}$ vs. log [OH^-] is linear (inset of Fig. 2) with a slope of 36 mV per decade, indicating an electrochemical process involving one electron per two hydroxyl ions:

$$\mathrm{Co(III)NCTPP(OH^-)_2 + e \rightarrow Co(II)NCTPP + 2OH^-} \qquad (1)$$

The formation constant of Co(III) NCTPP(OH^-)$_2$ as estimated from the intercept is 1.07×10^9 M^{-2}.

Repetitive potential scanning in the range 0 to +1.1 V for a CH_2Cl_2 solution of NCTPP at a GC electrode revealed growth of oxidation peaks at ~+0.4, +0.6 and +1 V. Similar processes have also been observed for 1-phenylpyrrole and "non-confused" porphyrins with N-substituted pyrroles [24] and have been attributed to the electropolymerization of the pyrrole derivative. Electropolymerized films of NCTPP (poly(NCTPP)) when transferred to a deaerated 0.1 M NaOH solution did not show any cyclic voltammetric peaks (Fig. 3B, curve a). However, after dipping these films overnight in an aqueous solution of $CoCl_2$, rinsed and transferred to 0.1 M NaOH, a redox couple with $E_{1/2} = 0.11$ V was detected (Fig. 3B, curve b). This clearly indicates that Co(II) ions have been introduced in the poly(NCTPP) films. Attempts to directly electropolymerize Co(II)NCTPP were unsuccessful. This result differs from that obtained with "non-confused" amino-, pyrrole, and hydroxy-substituted tetraphenylporphyrins which have been electropolymerized in their non-metallated as well as metallated forms [24]. This is attributed to the oxidation of Co(II) to the Co(III) state and as suggested for the oxidation of Cu(II) to Cu(III)NCTPP [10] as well as for Co(III)NCTPP with pyridine axial ligands [21], the peripheral N–H is converted to non-protonated nitrogen. This nitrogen is less prone to oxidation since in contrast to the N–H form, it has a pair of electrons which are in resonance with the whole porphyrin π electrons system.

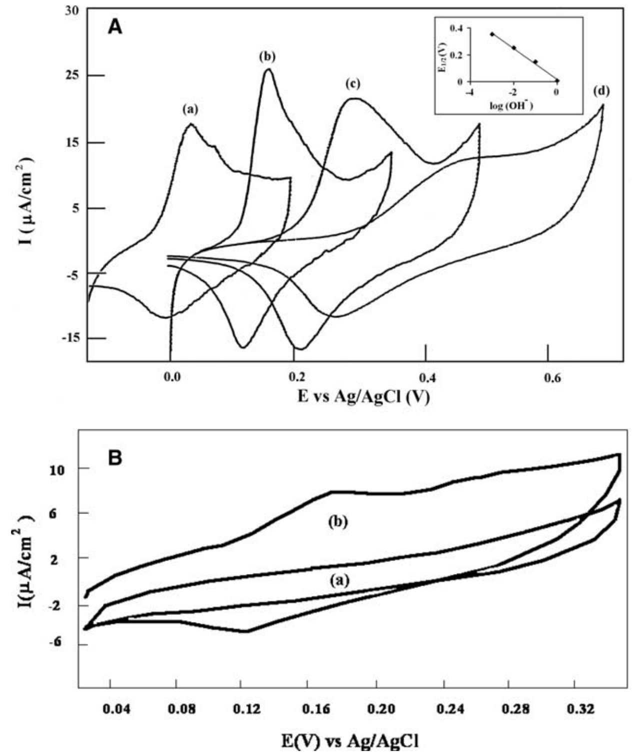

Fig. 3. (A) Cyclic voltammograms (5 mV/s) for adsorbed films of Co(II)NCTPP on GC electrodes in NaOH solutions at pH: (a) 14; (b)13; (c) 12 and (d) 11. Inset: $E_{1/2}$ of Co(II)/Co(III)NCTPP vs. log [OH^-]. (B) Cyclic voltammograms (20 mV/s) at pH 13 for electropolymerized films of NCTPP before (a) and after (b) being contacted with a 1 mM $CoCl_2$ aqueous solution.

To conclude, Co(II) ion was introduced in N-confused tetraphenylporphyrin as evidenced by ESR and UV–Vis. spectroscopy as well as electrochemical methods. The Co(II)NCTPP is stable in aprotic non-coordinating solvents. While nitrogenous bases decompose the Co(II)–carbon bond, films of Co(II)NCTPP are stable in aqueous base. Since the metal–carbon bond in Co(II)NCTPP is part of the macrocyclic compound, it differs from that found in B_{12} coenzymes in which it involves an axial ligand. However, this bond and the transition from high spin Co(II) to low spin Co(III) seem to be responsible for the high redox potential found for the Co(II)/Co(III)NCTPP couple. The Co(II)NCTPP complex is insensitive to air so that use of the Co(II)/Co(III) couple to catalyze oxygen reduction can be excluded but it can be considered for possible application in electrocatalytic oxidation processes. It has been demonstrated that NCTPP electropolymerizes and readily metallates with Co(II) and probably with a variety of other metal ions. This offers the possibility of future research related to these films in various fields, such as electron transfer, biomimetic catalysis and sensors.

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[2] Adsorbed films of Co(II)NCTPP on GC electrodes (Metrohm, 0.07 cm^2) were prepared by placing 20 μl of a CH_2Cl_2 solution containing 2×10^{-4} Co(II)NCTPP on the surface and allowing to dry for ~1/2 h.

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