

# The synthesis and electrochemical behaviour of water soluble manganese phthalocyanines: Anion radical versus Mn(I) species

Nthapo Sehlotho, Mahmut Durmuş, Vefa Ahsen and Tebello Nyokong\*

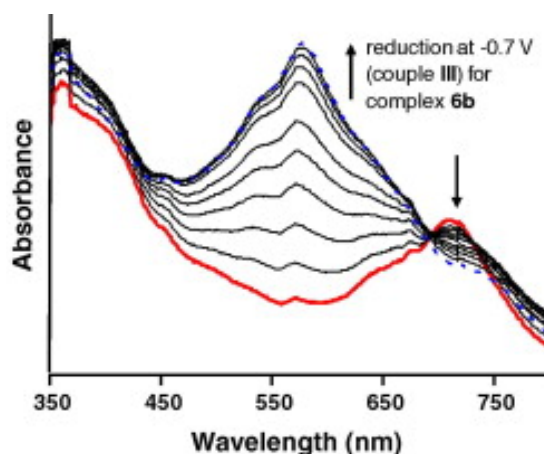
\*Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

## Abstract

The following MnPc derivatives were synthesized: 1,(4)-tetra-(2-mercaptopyridine) phthalocyaninato manganese(III)(OH) (5a), quaternized 1,(4)-tetra-(2-mercaptopyridine) phthalocyaninato manganese(III)(OH) (5b), 2,(3)-tetra-(2-mercaptopyridine) phthalocyaninato manganese(III)(OH) (6a) and quaternized 2,(3)-tetra-(2-mercaptopyridine) phthalocyaninato manganese(III)(OH)(6b). Spectro-electrochemistry shows that the reduction of Mn(II)Pc to Mn(I)Pc occurs only when the complexes are in their quaternized form (5b and 6b). The reduction (to Mn(I)Pc(-2)) of the quaternized form occurs at a lower potential than that (to Mn(II)Pc(-3)) of the unquaternized form. This observation suggests that metal reduction (to Mn(I)Pc(-2)) versus ligand reduction (to Mn(II)Pc(-3)) in Mn(II)Pc complexes depends on the nature of the ring substituents.

## Graphical abstract

The reduction of Mn(II)Pc to Mn(I)Pc occurs only when the complexes are in their quaternized form, suggesting that metal vs. ligand reduction in Mn(II)Pc complexes depends on the nature of the ring substituents.



Phthalocyanines (Pcs) have attracted a lot of interest in research because of their diverse properties that are harnessed in applications, ranging from photodynamic therapy treatment of cancer (PDT) [1], non-linear optical devices [2], [3] and [4], to the security printing industry [5]. For many applications such as in PDT, Pcs have to be water-soluble. The solubility of phthalocyanines can be

improved by introduction of substituents on the periphery of the molecule, which increase the  $\pi$ -electron density and make solvation easier. The water solubility of these photosensitizers is an advantage despite the fact that the aggregation tendency in such polar medium, in particular, is very high. Substitution of MPcs at the non-peripheral ( $\ast$ ) position causes red shifting of the Q-band [6] and [7] and also reduces aggregation tendencies to a greater extent than substitution at the peripheral ( $\beta$ ) position. The presence of electron donating sulfur groups in addition to substitution at the non-peripheral position, will result in the shift of the Q-band to even longer wavelengths. Pc complexes containing Mn as a central metal, in particular, show a highly red-shifted Q-band [7]. Hence in this work we present the synthesis and electrochemistry of new sulphur substituted MnPc complexes (complexes 5a, 5b, 6a, 6b, Fig. 1). The study of the electrochemistry of Mn macrocycles is important for their potential use as superoxide dismutase (SOD) mimics [8] and [9]. SODs are enzymes which provide protection against oxidative stress by catalysing the dismutation of superoxide radical to molecular oxygen and hydrogen peroxide. For this application it is important to understand the oxidation states of the central Mn ion in MnPc complexes.

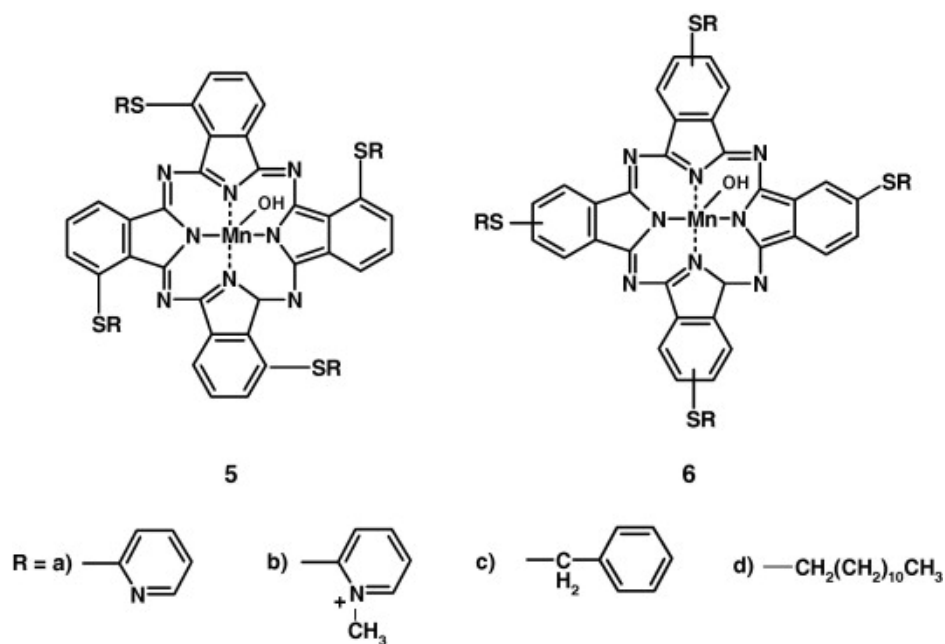


Fig. 1. Molecular structures of tetra-substituted 2-mercaptopyridine (phthalocyaninato) Mn(III)(OH) substituted at the  $\ast$ (5a) and  $\beta$  (6a) positions. The corresponding quaternized derivatives are represented as 5b and 6b.

The first reduction in  $\text{Mn}^{\text{II}}\text{Pc}^{-2}$  complexes has been a subject of some controversy, with some reports proposing ring reduction to the  $\text{Mn}^{\text{II}}\text{Pc}^{-3}$  species and others suggesting metal reduction to the  $\text{Mn}^{\text{I}}\text{Pc}^{-2}$  species. The former species has been reported by us and other authors [10], [11] and [12], and the latter has rarely been observed [13]. In this communication, we report on the formation of a  $\text{Mn}(\text{I})\text{Pc}$  species depending on the nature of substituents for the new  $\text{MnPc}$  complexes (Fig. 1).

The metallophthalocyanine complexes (5a, b and 6a, b) were prepared by the template reaction of thiol-substituted phthalonitrile precursors with manganese(II) chloride in the presence of DBU. The details are supplied as supplementary material. The complexes were characterized by spectroscopic methods and elemental analyses. The latter gave acceptable percent carbon values which differed by less than 1% from the calculated values. The mass spectra of the water soluble complexes 5b and 6b proved difficult to obtain, however, elemental analyses gave satisfactory results. The quaternized  $\text{MnPc}$  derivatives were water soluble. The quaternized complexes 5b and 6b, were blue shifted compared to the corresponding unquaternized derivatives (5a and 6a), Fig. 2. This is due to the lowering of the electron donating ability of the nitrogen groups on quaternization.

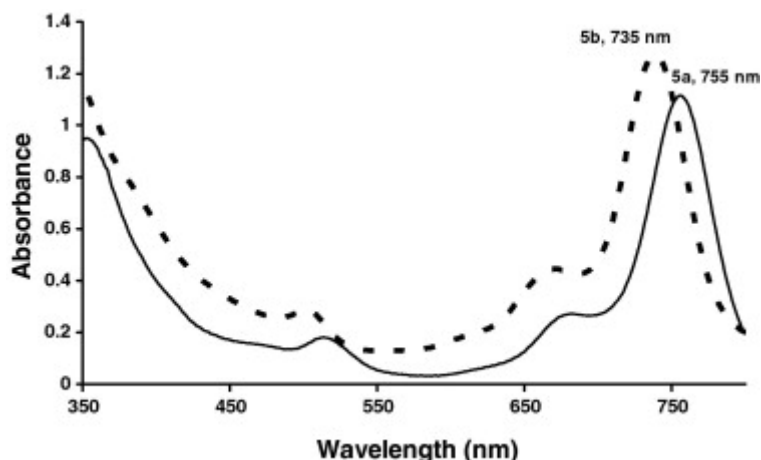


Fig. 2. UV-visible absorption spectra of 5a and 5b in DMF. Concentration  $\approx 10^{-5}$  mol  $\text{dm}^{-3}$ .

The cyclic (CV) and square wave voltammetries (SWV) of the complexes 5a, b and 6a, b were performed in de-aerated DMF containing  $\text{TBABF}_4$  as electrolyte, Fig. 3. The half-wave potentials ( $E_{1/2}$ ) for the complexes are summarised in Table 1 and compared to those of other  $\text{MnPc}$  complexes tetra-substituted with thiol groups, Fig. 1 (complexes 6c and 6d). All complexes exhibited three reduction processes labelled I, II and III, Table 1. Couples II and III are quasi-reversible with peak separations larger than the expected 60 mV, suggesting slow electron transfer. The cathodic to anodic peak separation ( $\Delta E$ ) ranged from 100 to 130 mV and a  $\Delta E$  value of 90 mV was obtained for ferrocene, at a scan rate of 100 mV/sec. The cathodic to anodic peak current ratio ( $I_{pc}/I_{pa}$ ) were

near unity for couples II and III. Process I was totally irreversible. Chronocoulometry showed that the ratio of currents for processes II and III were equal, and were one-third those of process I. The latter is most probably due to the combination of Pc ring oxidation and the oxidation of thiol substituents. Single step (irreversible) multi-electron oxidation accompanied by decomposition has been reported in thiol substituted MPc complexes [14]. Plots of square root of scan rate versus current were linear for all the processes I to III, confirming diffusion control. No new peaks (or changes in peak shape) were obtained on changing the scan rate. Compared to other peripherally thiol substituted derivatives (6c and 6d), complexes 5a and 6a are easier to reduce, the differences in the electron-donating or -withdrawing nature of the ring substituent will affect the ease of oxidation.

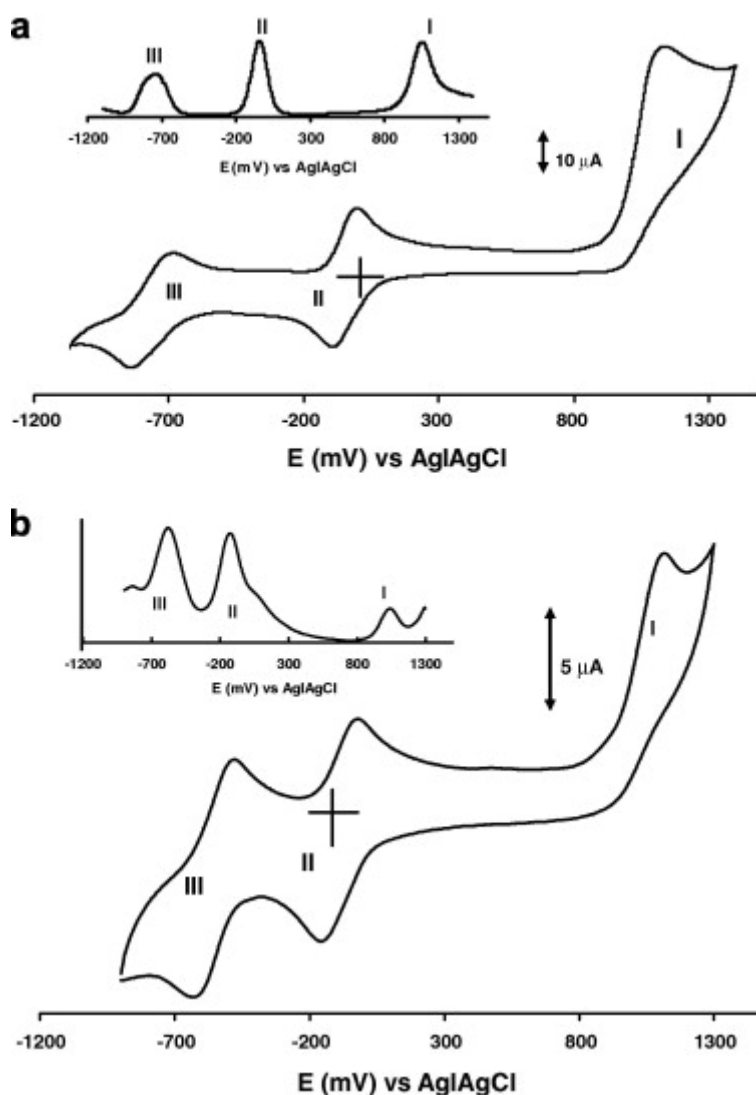


Fig. 3. Cyclic and square wave (inset) voltammograms of (a) complex 5a and (b) complex 6b in DMF containing TBABF<sub>4</sub>.

Table 1.

Electrochemical data for MnPc derivatives (5a, 5b, 6a, 6b) in DMF containing TBABF<sub>4</sub> Potentials vs. Ag|AgCl

Complex	Mn <sup>II</sup> Pc <sup>-2</sup> /Mn <sup>II</sup> Pc <sup>-3</sup>	Mn <sup>II</sup> Pc <sup>-2</sup> /Mn <sup>I</sup> Pc <sup>-2</sup>	Mn <sup>III</sup> Pc <sup>-2</sup> /Mn <sup>II</sup> Pc <sup>-2</sup>	Oxidation processes	Reference
5a	-0.76	–	-0.051	1.18	This work
5b		-0.59	-0.056	1.10	This work
6a	-0.71		-0.057	1.34	This work
6b		-0.56	-0.063	1.13	This work
6c	-0.84		-0.08	~0.3, 0.87	[8]
6d	-0.98		-0.26	~0.3, 0.83	[8]

Spectroelectrochemistry using optically transparent thin layer electrode (OTTLE) cell was employed to characterise the redox processes. Fig. 4a shows the spectral changes observed during the reduction of unquaternized non-peripherally substituted complex 5a at potentials of process II. Upon reduction, there was a blue shift in the Q-band from 750 nm to 694 nm, with an additional peak at 639 nm, and a concurrent decrease of the charge transfer band at 506 nm. These spectral changes occurred with clear isosbestic points at 716 and 533 nm. The blue shift in the Q-band upon reduction is typical of Mn<sup>III</sup>Pc<sup>-2</sup> to Mn<sup>II</sup>Pc<sup>-2</sup> reduction [7].

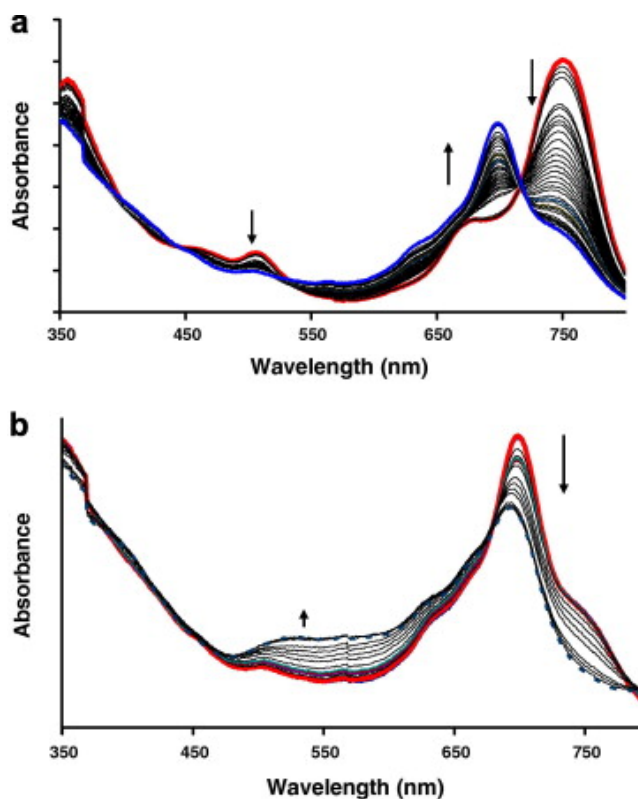


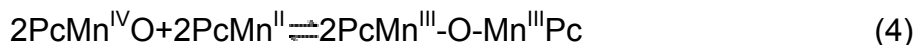
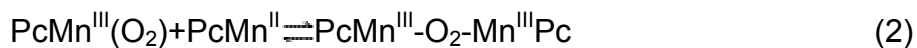
Fig. 4. UV-vis spectral changes for 5a observed using controlled potential electrolysis at potential of (a) process II (-200 mV) and (b) process III (-1.0 V). First spectrum in (b) is the same as the last spectrum in (a). Electrolyte = DMF containing 0.1 M TBABF<sub>4</sub>. Electrolysis time was 30 min for each redox process.

Fig. 4b shows spectral changes observed on application of potentials of process III for 5a. A drastic decrease in the intensity of the Q-band and the formation of a new weak band at 570 nm is typical [15] of ring based processes in MPc complexes. Hence the spectral changes are assigned to Mn<sup>II</sup>Pc<sup>-2</sup>/Mn<sup>II</sup>Pc<sup>-3</sup>.

No further spectral changes were observed in Fig. 4b. The original spectra (in Fig. 4a) could be regenerated (to >75%) by application of a positive potential, after the formation of the Mn<sup>II</sup>Pc<sup>-3</sup> species in Fig. 3b. The lack of complete regeneration of the spectra was due to the formation of MnPc  $\mu$ -oxo species with a typical [7] broad feature around 639 nm. Spectral changes similar to those shown in Fig. 4a and b were also observed for unquaternized peripherally substituted complex 6a. Oxidation at potentials of process I resulted in decomposition of the complexes confirming the irreversible nature of this process.

As stated above, the first reduction in  $\text{Mn}^{\text{II}}\text{Pc}^{-2}$  complexes has been reported to occur either at the metal to form  $\text{Mn}^{\text{I}}\text{Pc}^{-2}$  species or at the ring to form  $\text{Mn}^{\text{II}}\text{Pc}^{-3}$  species. The latter is observed in this work for complexes 5a and 6a, and has been reported by our group [10] and others [11].

For the quaternized derivatives (5b and 6b), spectral changes shown in Fig. 5 were observed on reduction at potentials of couple II. Spectral changes showed a shift in the Q-band from 735 to 705 nm, Fig. 5a, typical of the formation of  $\text{Mn}^{\text{II}}\text{Pc}$  species as explained above. The broad feature around 639 nm is typical of  $\text{MnPc}$   $\mu$ -oxo complexes [7]. Thus reduction of 6b (Fig. 5a) results in the formation of both the  $\text{Mn}^{\text{II}}\text{Pc}$  and the  $\mu$ -oxo complexes. In  $\text{MnPc}$  complexes, the spectrum may consist of three bands corresponding to three different species in solution. This is typical of  $\text{MnPc}$  species in equilibrium in DMF and in the presence of oxygen, as suggested by Lever et al. [16].



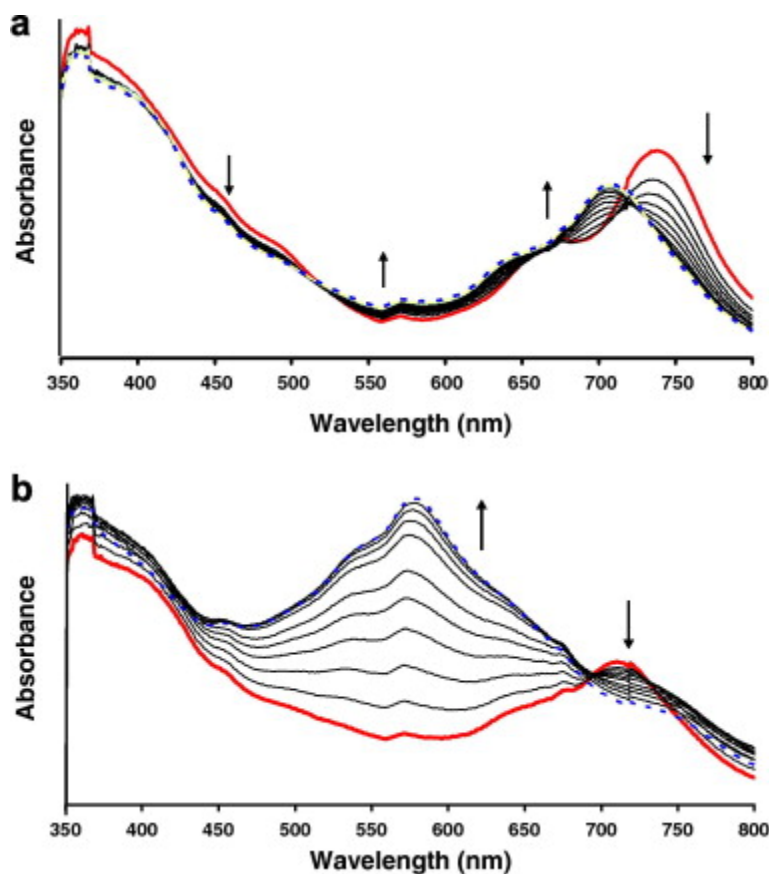


Fig. 5. UV-vis spectral changes for 6b observed using controlled potential electrolysis at potential of (a) process II (-200 mV) and (b) process III (-700 mV). First spectrum in (b) is the same as the last spectrum in (a). Electrolyte = DMF containing 0.1 M TBABF<sub>4</sub>. Electrolysis time was 30 min for each redox process.

In this work, the starting spectrum was Mn(III)Pc species, however oxygen may have entered the OTTLE cell during the reduction process, hence the formation of the MnPc  $\mu$ -oxo species. The formation of this species is less evident in Fig. 4a for 5a.

Reduction at potentials of process III, resulted in spectral changes that were very different from those reported above for unquaternized processes 5a and 6a. These consisted of the formation of a large peak at 575 nm, typical [13] of Mn(I)Pc species. Thus the species observed on reduction at potentials of process III is due to metal reduction and the formation of the Mn(I)Pc(-2) species. The extinction coefficient of the new peak is slightly larger (with  $\log \epsilon = 5.15$ , assuming complete conversion) than that of the original complex before electrolysis ( $\log \epsilon = 5.02$ ). This also goes to prove that the reduction is metal based, since ring reduction results in much lower  $\log \epsilon$  values compared to the starting complex. Thus it seems the formation of the Mn(I)Pc species depends on the substituents.



Reduction of the quaternized 5b and 6b which are positively charged, is expected to occur more readily than for the unquaternized 5a and 6a. However, this is observed only for the reduction of the Mn(II)Pc species in Table 1. Oxidation or reduction of the Mn(III)Pc species seems to be unaffected by the quaternization of the complexes. This implies that reduction of Mn(II)Pc complexes at the central metal is dependent on the substituents and hence on the redox potential values.

In conclusion, this work has shown that in Mn(II)Pc complexes, it is the nature of the ring substituents that control the redox potential of the Mn(II)/Mn(I) couple versus that of the Pc(2-)/Pc(3-). The redox potentials reported in this work are in organic media. For applications as SOD mimics the redox potentials for MnPc complexes should lie between  $\approx +0.4$  V and  $-0.9$  V vs. Ag|AgCl in aqueous media. Work is currently underway to study the electrochemistry and SOD activity of the quaternized 5b and 6b in aqueous media.

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