

Electrochemical, spectroscopic and microscopic studies of new manganese phthalocyanine complexes in solution and as self-assembled monolayers on gold

Megan Coates, Edith Antunes⁶ and Tebello Nyokong*⁶

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

Received 25 March 2010 Accepted 15 May 2010

ABSTRACT: Four new manganese(III) phthalocyanines (**3a–d**), octasubstituted at the peripheral position with pentylthio, decylthio, benzylthio, and phenylthio groups, respectively, were synthesized. Their specific electrochemical, spectroscopic and microscopic properties in solution and as self-assembled monolayers on gold were characterized. The UV-vis spectra confirmed red-shifted Q bands for all the complexes, due to the effect of the central metal and the electron-donating substituents. Three redox couples were visible during cyclic voltammetry studies for the four complexes, and spectroelectrochemistry confirmed the couples as corresponding to Mn^{III}Pc⁻²/Mn^{II}Pc⁻² (**II**) (metal reduction), Mn^{II}Pc⁻³ (**III**) (ring reduction) and Mn^{III}Pc⁻¹/Mn^{III}Pc⁻² (**I**) (ring oxidation). Electrochemistry was also used to determine the blocking characteristics of the MnPc self-assembled monolayers on gold, which proved to be highly dependent on the type of substituent. Other methods of characterization included Raman spectroscopy, atomic force and scanning electrochemical microscopy analyses of the SAMs.

KEYWORDS: manganese thiol-derivatised phthalocyanines, cyclic voltammetry, spectroelectrochemistry, self-assembled monolayer.

INTRODUCTION

Metallophthalocyanines (MPcs) are incredibly diverse and widely studied compounds, as their properties and characteristics can be tailored fairly simply by changing the central metal and/or the nature of the substituents on the ring [1–3]. MPcs are macrocyclic 18 π -electron systems and a variety of substituents can be positioned at four different points on each isoiminoindoline ring, resulting in a large range of products with a common central structure.

Electrodes modified with MPcs have been widely used to facilitate electrocatalysis of many analytes that are otherwise difficult to detect [1]. The substituents on the Pc ring can also be used to link the MPcs to an electrode in order to make a reproducible, stable and uniform sensor surface. Sulfur-containing substituents have been used in this regard to produce a self-assembled monolayer (SAM) on gold [1, 4].

Manganese phthalocyanines (MnPcs) have not been as extensively studied as some MPcs, like those containing cobalt as the central metal. Mn^{III}Pcs have typically redshifted absorbance spectra in the visible region (the Q band), and this can be shifted further to the red by non-peripheral substituents and the electron-donating properties of groups like those containing sulfur [4–8]. Electron-donating substituents can also affect the electrochemical properties of the Pc, making it more easily oxidized but harder to reduce [9]. Mn has a number of oxidation states, ranging from Mn^I to Mn^{IV}, but it is Mn^{II}Pc that has been shown to form a μ -oxo species, PcMn^{III}–O–Mn^{III}Pc, on absorption of oxygen with the possibility of monomeric Mn^{III}Pc also forming [5, 10]. Formation of this dimer is highly dependent on the position, number and type of substituents [5].

MPc derivatives containing alkyl- and aryl-thio groups with different central metals are known [4, 7–9, 11–17]. However, mainly tetrasubstituted derivatives of the MnPcs have been reported [9], with few examples of

⁶SPP full member in good standing

^{\$\$}SPP student member

^{*}Correspondence to: Tebello Nyokong, email: t.nyokong@ ru.ac.za, tel: +27 46-6038260, fax: +27 46-6225109



Scheme 1. Synthetic route for the produced thiol-derivatised metallophthalocyanine complexes. Complex 3a, manganese(III) octa(pentylthio)phthalocyanine, (OAc)MnPc^{β}{S(CH₂)₄CH₃}. Complex 3b, manganese(III) octa(decylthio)phthalocyanine, (OAc)MnPc^{β}{S(CH₂)₉CH₃}. Complex 3c, manganese(III) octa(benzylthio) phthalocyanine, (OAc)MnPc^{β}{SCH₂Ph)₈. Complex 3d, manganese(III) octa(penylthio)phthalocyanine, (OAc)MnPc^{β}{SPh)₈</sub>.

octa-substitution in these complexes [11]. Octa-substitution in MPc complexes has advantages over tetra-substitution due to isomeric purity, and hence ease of purification and characterization. The complexes synthesized in this work are shown in Scheme 1. They are Mn^{III} phthalocyanines octasubstituted at the peripheral positions with pentylthio (3a), decylthio (3b), benzylthio (3c) and phenylthio (3d) groups. Dodecylthio octasubstituted phthalocyanine complexes have been reported for other central metals such as Cu [13] and Ni [12] as well as hexylthio octasubstituted phthalocyanine complexes of Cu and Zn [14] and butylthio octasubstituted ZnPc complex [15], but the ligands of interest in this work have not been reported for MnPc derivatives. Changes in the structure of the MPc and the type of central metal can have substantial effects on the behavior of the complex as an electrocatalyst [9, 18-23] and on the formation of SAMs [4, 9, 21-24]. SAMs of the MnPcs were produced by utilizing the high affinity of sulfur for gold, and their properties were studied in this work using electrochemical, spectroscopic and microscopic techniques to determine the effect of the alkyl and aryl substituents on monolayer formation.

RESULTS AND DISCUSSION

Synthesis and characterization

The syntheses of the aryl- and alkyl-thio substituted phthalonitriles were accomplished by reacting the appropriate thiol with 4,5-dichlorophthalonitrile in the presence of potassium carbonate, which facilitated a base-catalyzed nucleophilic aromatic displacement reaction. The success of the reaction was confirmed by proton NMR analysis, and the clean spectra clearly showed the alkyl or aryl substituents bonded to the phthalonitrile through sulfur and resulting in a highly pure product. Sulfur caused deshielding of the adjacent CH₂ protons on the alkyl substituents, shifting them to 3.01 ppm.

The phthalonitriles were then reacted with manganese(II) acetate by refluxing in ethylene glycol for 4 or 5 h. Yields of complexes 3a to 3d ranged from 32 to 74%. The complexes were purified by column chromatography using Bio-beads, which relies on size-exclusion. The use of a Bio-bead column instead of the commonly used silica column was much more effective and provided higher yields for these complexes. The choice solvent for elution was CHCl₃ as the use of THF as an eluting solvent resulted in the formation of µ-oxo MnPc species, as shown by its typical spectrum [8] in Fig. 1 with a peak at 650 nm. μ-oxo MnPc complexes absorb in the 630 to 650 nm region and hence are highly blue-shifted compared to monomeric Mn^{III}Pc complexes, which commonly have their Q band near 750 nm or above. The observed µ-oxo MnPc formation in THF could be a result of the different amounts of dissolved oxygen in the solvent compared to chloroform.



Fig. 1. UV-visible spectra of **3d** showing spectral changes during elution from Biobeads column with DCM (a) followed by THF (b) and (c) in various subsequent fractions

The mechanism for the formation of the μ -oxo dimer and Mn^{II} species was put forward by Lever *et al.* [10] and is as follows:

$$Mn^{II}Pc + O_2 \leftrightarrows Mn^{III}Pc(O_2)$$
(1)

$$Mn^{III}Pc(O_2) + Mn^{II}Pc \leftrightarrows Mn^{III}Pc - O_2 - PcMn^{III}$$
(2)

$$Mn^{III}Pc-O_2-PcMn^{III} \leftrightarrows 2Mn^{IV}PcO$$
(3)

$$2Mn^{IV}PcO + 2Mn^{II}Pc \leftrightarrows 2Mn^{III}Pc - O - PcMn^{III} \qquad (4)$$

Net:
$$Mn^{II}Pc + O_2 \cong 2Mn^{III}Pc - O - PcMn^{III}$$
 (5)

Complexes 3c and 3d were soluble in CHCl₃, DCM, THF, DMF and DMSO, whereas 3a and 3b were insoluble in DMF and DMSO, likely due to their more non-polar alkyl substituents. Complexes 3a and 3b also showed good stability in the solvents over time, with little to no change in their spectra. However, complexes 3c and 3dexhibited unstable spectra in DMF and THF over time, with the formation of bands typical of the μ -oxo species, similar to that shown in Fig. 1, due to the effects of dissolved oxygen. It can be seen that the spectra and thus the color of these Pcs changes depending on the solvent conditions, and care needs to be taken in their preparation.

The UV-visible spectra of complexes **3a** to **3d** are shown in Fig. 2 in chloroform. Because of the presence of manganese and the electron-donating properties of sulfur, the Q band is highly red-shifted and the complexes are dark red, brown, or dark brown in color. This is typical of Mn^{III}Pc complexes [9, 11, 16]. The synthesis used Mn(II) acetate, however, as purification took place in aerobic conditions the Mn^{III}Pc species was formed, as outlined in Equation 1 above, and there was no indication of residual Mn^{II}Pc.

Complex **3d** was slightly more red-shifted compared to the other Pcs, with a Q band at 773 nm, while the alkylthio-Pcs (**3a** and **3b**) had a Q band at 768 nm and for **3c** it was at 767 nm in DCM (Table 1). The spectra in DCM were identical to that in CHCl₃. This correlates with



Fig. 2. UV-visible spectra of 3a, 3b, 3c and 3d in CHCl₃

previous work and confirms that the alkyl chain length in MPc complexes does not significantly affect the Q band position [12, 16, 25]. The spectral differences between the two arylthio MnPcs could be attributed to the CH_2 group separating the sulfur and the ring for **3c**, and so making it behave more similarly to the alkyl substituents with regard to electron-donating ability. The electron-rich phenyl ring in complex **3d**, however, could directly contribute to the electron-donating properties of the substituents and shift the spectra further to the red. This indicated that although alkyl chain length does not affect the electronic properties of the ring, aryl substituents can play a larger role.

The Pcs also had three bands near 405, 465 and 530 nm. The bands between 400 and 550 nm are due to charge transfer between the metal and the Pc ring [8]. For both **3a** and **3b** the Q band spectra shifted to 755 nm in THF (data not shown). Figure 2 shows that **3d** is less aggregated than the other Pcs, as judged by the narrower Q band. However, Beer's law was observed for all complexes at concentrations less than 9.0×10^{-6} M. Comparisons of Q band maxima between similar complexes (peripherally tetrasubstituted and non-peripherally octasubstituted, Fig. 3) are shown in Table 1.

For compounds **3a** and **7** containing the same chain length but the latter non-peripherally substituted

Table 1. Electronic absorption spectra of $Mn^{III}Pc$ derivatives in DCM

Complex	Q band absorbance	Reference
3a	768	this work
3b	768	this work
3c	767	this work
3d	773	this work
4	764	[4]
5	749	[9]
6	745	[9]
7	893	[11]



Complex	Substituent	Abbreviation	Reference
number			
3a	R1 = R4 =H; R2 = R3 =	$(OAc)MnPc^{\beta}\{S(CH_2)_4CH_3\}_8$	This work
	S(CH ₂) ₄ CH ₃		
3b	R1 = R4 =H; R2 = R3 =	$(OAc)MnPc^{\beta}\{(SCH_2)_9CH_3\}_8$	This work
	(SCH ₂) ₉ CH ₃		
3c	R1 = R4 =H; R2 = R3 =	$(OAc)MnPc^{\beta}(SCH_2Ph)_8$	This work
	SCH ₂ Ph		
3d	R1 = R4 =H; R2 = R3 =	$(OAc)MnPc^{\beta}(SPh)_{8}$	This work
	SPh		
4	R2 = R3 = R4 = H; R1 = SPh	$(OAc)MnPc^{\alpha}(SPh)_4$	4
5	R1 = R3 = R4 =H; R2 =	$(OAc)MnPc^{\beta}\{(SCH_2)_{11}CH_3\}_4$	9
	(SCH ₂) ₁₁ CH ₃		
6	$R1 = R3 = R4 = H; R2 = SCH_2Ph$	$(OAc)MnPc^{\beta}(SCH_2Ph)_4$	9
7	$R2 = R3 = H; R1 = R4 = S(CH_2)_4CH_3$	$(OAc)MnPc^{\alpha} \{S(CH_2)_4 CH_3\}_8$	11
173		1 1.1 1	1

Fig. 3. Molecular structures of the compared manganese phthalocyanine complexes

(structures are shown in Fig. 3), the Q band was observed at 768 nm and 893 nm [11] in DCM, respectively (Table 1), showing that peripheral substitution caused an expected blue shift in the Q band compared to nonperipheral substitution [8].

Looking at the octasubstituted complex **3c** ($\lambda_Q = 767$) and comparing it to its tetrasubstituted counterpart **6** ($\lambda_Q =$ 745), the Q band spectrum was blue-shifted in the tetrasubstituted complex [9]. These results show that the octasubstituted MnPcs exhibited greater electron-donation by the substituents than the equivalent tetra-MnPcs, which can be simply attributed to the greater number of substituents around the ring.

Comparing complexes **3d** ($\lambda_Q = 773$) and **4** ($\lambda_Q = 764$), one is the peripheral octasubstituted version (**3d**) and the

other is the tetrasubstituted non-peripheral (4), the latter has a comparatively blue-shifted Q band despite being non-peripherally substituted [4]. This indicates that the number of substituents could play a larger role than the position of these substituents on the electronic properties of the ring.

Voltammetric and spectroelectrochemical characterization

Figure 4 shows the cyclic (CV) and differential pulse voltammograms (DPV) of complex 3c, representing all the other MnPcs synthesized. All electrochemical analyses were performed in deaerated DCM using TBABF₄ as an electrolyte.



Fig. 4. Cyclic voltammogram for 3c in DCM containing 0.1 M TBABF₄. Scan rate = 50 mV/s. Inset: DPV

The half-wave potentials $(E_{1/2})$ for **3a–d** and other similar compounds are shown in Table 2. Complexes **3a–d** displayed three main redox processes, with ΔE values from 93 to greater than 200 mV. 3a displayed redox processes at: $E_{1/2} = +0.97$ V (I), $E_{1/2} = -0.35$ V (II) and $E_{1/2} = -1.07 \text{ V}$ (III) vs. Ag|AgCl with **3b** displaying redox processes at: $E_{1/2} = +0.94$ V (I), $E_{1/2} = -0.46$ V (II) and $E_{1/2} = -1.08 \text{ V}$ (III) vs. Ag|AgCl. 3c displayed redox processes at: $E_{1/2} = +0.96$ V (I), $E_{1/2} = -0.26$ V (II) and $E_{1/2}$ = -0.94 V (III) vs. Ag|AgCl while 3d displayed redox processes at: $E_{1/2} = +0.88$ V (I), $E_{1/2} = -0.34$ V (II) and $E_{1/2} = -1.15$ V (III) vs. Ag|AgCl. In some of the complexes, a weak process could be observed around -0.1 V. This process was attributed to aggregation of the compounds, as the peaks were observed to decrease with dilution. Plots of peak current (I_p) vs. square root of the scan rate $(v^{1/2})$ were linear, suggesting diffusion control at the electrode surface for all the complexes. Figure 4 shows broad cyclic voltammetry peaks, which are often observed in MnPc complexes, especially those containing long-chain substituents [9]. This was also observed for the tetrasubstituted complexes 5 and 6 (structures in Fig. 3) [9]. However, complex 7 octasubstituted with

pentylthio groups at the non-peripheral positions showed reversible behavior [11], most likely due to the prevention of aggregation by non-peripheral substitution. The assignments of these processes were confirmed with spectroelectrochemistry, as discussed below.

The Mn^{III}Pc⁻²/Mn^{II}Pc⁻² process (**II**) could be clearly observed at similar potentials in all thiol-derivatized MnPcs, Table 2 (except for **6**) [4, 9, 11]. The oxidation of Mn(III) to Mn(IV) could not be conclusively observed in the synthesized Pcs in this work, although the process has been observed before [9, 11, 16]. Process **III** has been assigned in similar complexes to either Mn^{II}Pc⁻²/Mn^IPc⁻² [5, 7] or Mn^{II}Pc⁻²/Mn^{II}Pc⁻³ [7, 9, 11, 16, 22], although the latter has been reported more frequently. In this work, spectroelectrochemistry was used to assign this process to ring reduction.

Process I could be attributed to ring oxidation, and it is in a similar range to that reported in literature [7, 9, 11]. Thiol substituted complexes often decompose during ring oxidation, and this can contribute to the irreversibility of process I [7, 9].

Ease of oxidation and reduction of complexes is related to the electron-donating or electron-withdrawing effects of the substituents. Electron-donating substituents are expected to facilitate easier oxidation and harder reduction, as they should increase the electron density on the ring [26, 27]. As aromatic rings are electron donors, 3d should then be more electron-donating than 3c, which would in turn be more electron-donating than 3a followed by 3b. This behavior was partially confirmed by the absorbance spectra of the compounds (Fig. 2), which showed the Q band positions of **3a-c** at an approximately equivalent position, while 3d was the most red-shifted as its phenyl substituents were the most electron-donating. As expected then, **3a-c** were harder to oxidize with regard to process I when compared to complex 3d. Looking at process III, 3d was the hardest to reduce (as expected) with an $E_{1/2}$ of -1.15 V, with **3a** and **3b** having similar values and **3c** being the easiest to reduce with an $E_{1/2}$ of -0.94 V. The ease in reduction for 3c could be attributed

Table 2. Electrochemical data of thiol-derivatized MnPcs. The compounds were analyzed in DCM containing TBABF₄ and the half-wave potential ($E_{1/2}$) as V against Ag|AgCl, unless otherwise specified

Complex	Mn ^{II} Pc ⁻² /Mn ^{II} Pc ⁻³ (III)	Mn ^{III} Pc ⁻² /Mn ^{II} Pc ⁻² (II)	Mn ^{III} Pc ⁻¹ /Mn ^{III} Pc ⁻² (I)	Reference
3a	-1.07	-0.35	0.97	this work
3b	-1.08	-0.46	0.94	this work
3c	-0.94	-0.26	0.96	this work
3d	-1.15	-0.34	0.88	this work
5	-0.98	-0.26	0.83	[9]
6	-0.84	-0.08	0.87	[9]
7	-1.24	-0.46	_	[11]

to the aromatic ring being separated from the Pc by a CH₂ group, as this has been observed before with complexes **5** and **6** [9]. No particular trend could be observed for process **II** except that again complex **3c** showed the greatest ease in reduction with an $E_{1/2}$ of -0.26 V.

Looking at peripheral (**3a**) *vs.* non-peripheral (**7**) substitution (using the same substituent), complex **3a** showed greater ease in reduction compared to complex **7** [11]. Pc ring oxidation of **7**, although attributed to $Mn^{IV}Pc^{-1}/Mn^{III}Pc^{-2}$ rather than $Mn^{III}Pc^{-1}/Mn^{III}Pc^{-2}$ as in this work, showed that the non-peripheral complex was more easily oxidized with an $E_{1/2}$ of +0.75 V [11]. Octasubstituted **3c** proved to be harder to oxidize compared to the tetrasubstituted complex **6** containing the same substituent. The same was true of complex **3b** compared to the similar tetrasubstituted compound **5** [9], though the chain lengths were slightly different.

Spectroelectrochemical studies allowed a confident assignment of the redox couples to be made. Figure 5 shows the spectral changes that occurred for complex 3a, which were similar to the spectral changes observed for the other complexes in this work. Oxidation at potentials of process I resulted in degradation of the complex, as has



Fig. 5. UV-vis spectral changes for complex **3a** observed using controlled potential electrolysis at: (a) -0.65 V and (b) -1.3 V. Electrolyte = DCM with 0.1 M TBABF₄

been observed during oxidation of thio-substituted MPc complexes [9]. Figure 5(a) illustrates spectral changes observed on application of potentials more negative than process II (-0.65 V), clearly showing the reduction of Mn(III) to Mn(II) as there is a decrease in the Mn(III) Q band and a growing blue-shifted Q band that correlates to Mn(II) [4, 8, 9, 11]. The Q band shifted from 768 nm for the Mn(III) complex to 720 nm for the Mn(II) complex and the color of the complex in the OTTLE cell visibly changed from red-brown to green. There was also a decrease in intensity of two of the charge transfer bands at 465 and 530 nm, with the former disappearing almost completely and the latter shifting to 540 nm. The spectra had three clear isosbestic points at 738, 614 and 407 nm and the value of *n* was calculated using Q = nFCV to be approximately equal to 1. Figure 5(b) shows spectral changes observed on application of potentials more negative than process III (-1.3 V), with the decrease in the Q band and the formation of new features between 500 and 650 nm characteristic of ring-based reduction processes in Pcs [28], leading to the assignment of this as Mn^{II}Pc⁻²/Mn^{II}Pc⁻³. The spectral changes were similar to that reported elsewhere for this process [7, 9, 11]. It has been shown that the nature of ring substituents are responsible for the formation of Mn^{II}Pc⁻³ as opposed to Mn^IPc⁻² [7] and there was no evidence of the broad Q band forming at around 550 nm that is characteristic of Mn^I [7]. confirming process III as ring-based reduction. Based on these results, the processes could be assigned as follows:

$Mn^{m}Pc^{-2} \rightarrow Mn^{m}Pc^{-1} + e^{-1}$ (proc	cess I)	(6)
--	---------	-----

 $Mn^{III}Pc^{-2} + e^{-} \rightarrow Mn^{II}Pc^{-2}$ (process II) (7)

 $Mn^{II}Pc^{-2} + e^{-} \rightarrow Mn^{II}Pc^{-3}$ (process III) (8)

Self-assembled monolayers

SAM films were formed by immersing the bare gold electrode in the desired complex for an average time of 48 h in each case. Formation of SAM films is facilitated by coordination of the sulfur group (using its lone pair of electrons) with gold, with the C-S bond remaining intact as reported previously [18]. Electrochemistry, Raman spectroscopy, atomic force microscopy (AFM) and scanning electrochemical microscopy (SEM) were used to characterize the modified gold electrodes and give further spectroscopic evidence of their formation. For the latter studies (Raman, AFM and SEM), only 3b and 3d were used to identify the effect of the different substituents on the SAM layer as these both showed good blocking characteristics. Gold-coated glass was immersed in the MnPc solution for 10 days for these analyses, to ensure a fullyformed SAM and complete coverage.

Inhibition of faradaic processes. Electrochemical properties of the films are closely related to the extent to which they inhibit common faradaic processes associated with the bare gold surface. Figure 6(a) shows oxidation (at +0.21 V vs. Ag|AgCl) and reduction (gold oxide



Fig. 6. Cyclic voltammograms for bare Au, **3a**-Au, **3b**-Au, **3c**-Au and **3d**-Au in: (a) 1 M Na₂SO₄ in pH 4 buffer solution, (b) 1 mM Fe(NH₄)₂(SO₄)₂ in 1 M HClO₄, (c) 1 mM K₃[Fe(CN)₆] in 0.1 M KCl and (d) 1 mM CuSO₄ in pH 4 buffer solution. Scan rate = 50 mV/s *vs*. Ag|AgCl

stripping peak, at +0.15 V vs. Ag|AgCl) of the bare gold surface in 1 M Na₂SO₄ in pH 4 buffer solution. As seen in this figure, there was appreciable passivation of this process in the presence of all the MPc-SAMs, although the **3c**-SAM was the least effective at blocking the electrode. Gold oxidation was considerably inhibited with a decrease in intensity of the gold oxide stripping peak, suggesting that the electrolyte was no longer accessible to the bare gold surface and confirming SAM formation.

Figure 6(b) shows the cyclic voltammograms obtained for the bare Au electrode and the SAM-modified gold electrodes in 1 mM ferrous ammonium sulfate (Fe(NH₄)₂(SO₄)₂) containing 1 M perchloric acid (HClO₄). The clearly resolved quasi-reversible redox process ([Fe(H₂O)₆]³⁺/[Fe(H₂O)₆]²⁺) on the bare electrode was almost completely inhibited for the **3d**-SAM, and almost completely uninhibited for the **3c**-SAM. The inhibition of this process on the SAM-modified gold electrodes suggests the isolation of the gold surface from the electrolyte, confirming defect-free SAM formation for **3a** and **3b**. For **3d**,

the voltammograms were distorted, but more resolved for **3c**. It is possible that the bulky aryl substituents in **3c** and **3d** were less effective in blocking the redox process, as the SAMs they formed appeared to be more permeable to this analyte.

Figure 6(c) shows the cyclic voltammograms of the bare Au electrode and the SAM-modified electrodes in 1 mM solution of [Fe(CN)₆]³⁻ containing 0.1 M KCl as the supporting electrolyte. Unlike the $[Fe(H_2O)_6]^{3+}/$ $[Fe(H_2O)_6]^{2+}$ redox process in Fig. 6b, the $[Fe(CN)_6]^{3-/4-}$ redox couple was not inhibited on the SAM-modified electrodes because of the fast nature of electron transfer for this process. This observation has been reported previously for adsorbed cobalt tetra-amino phthalocyanine films on a vitreous carbon electrode [19]. However, the cathodic-to-anodic peak difference (ΔE) for this process was larger for SAMs of 3a, 3b and 3d, but the same for 3c. The anodic and cathodic current intensities of the [Fe(CN)₆]^{3-/4-} redox couple on bare gold electrode are larger than that observed on the SAM-modified electrodes, confirming the formation of the SAM films.

Figure 6(d) shows the cyclic voltammograms of the bare Au electrode and the SAM-modified electrodes in 1 mM CuSO₄ in pH 4 buffer solution. The bulk deposition of Cu began at 133 mV (*vs.* Ag|AgCl on the negative scan) and the maximum of the large underpotential deposition stripping peak of the Cu occurred at 101 mV (*vs.* Ag|AgCl) on the bare Au electrode. This process was significantly inhibited on the SAM-modified electrodes, indicating SAM formation for **3a**, **3b** and **3d**. The **3c**-SAM again showed the least inhibition of the redox process, indicating that it was not completely blocked.

In general **3a** and **3b** showed particularly good blocking characteristics in all solutions, suggesting that the benzyl and phenyl groups for **3c** and **3d** prevent the formation of good SAMs.

Surface coverage. Figure 7 shows the cyclic voltammetry profiles obtained for the SAM-modified electrodes in 1 M HClO₄. The redox processes observed in Fig. 7 are associated with Mn³⁺/Mn⁴⁺ ($E_{1/2} = \sim 0.23$ V vs. Ag|AgCl, Table 3) as compared to similar compounds [4, 9, 11]. This process was not observed above in solution, and there were no peaks in this potential range in solution. It has



Fig. 7. Cyclic voltammograms for **3a**-Au, **3b**-Au, **3c**-Au and **3d**-Au in 1 M HClO₄. Scan rate = 50 mV/s *vs*. Ag|AgCl

been reported before for NiPc complexes that some metal processes are observed when the complexes are absorbed but not when in solution [1]. The difference between the free and bound MnPc is associated with the nature of the SAM and the different solution environments.

Surface coverage (Γ) for each SAM was estimated from the relevant redox process in Fig. 7 using Equation 9:

$$\Gamma_{SAM} = \frac{I_{pa}4(RT)}{n^2 F^2 A v} \tag{9}$$

where I_{pa} is the peak current (A) in Fig. 7 for each SAM, A is the real surface area of the gold electrode, n is the number of electron transferred (approximately 1) and the other symbols have their usual meanings. The real surface area of the electrode was estimated using the wellestablished method [29] applying Equation 10 (Randles-Sevcik equation). [Fe(CN)₆]³⁻ was used as the redox active species because it has a known diffusion coefficient.

$$I_{\rm pa} = (2.69 \times 10^5) \ n^{3/2} \ D^{1/2} \ v^{1/2} \ AC \tag{10}$$

where n is the number of electrons transferred (approximately 1), D is the diffusion coefficient of the redox active species $(7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ [29]})$, A is the geometric surface area (0.0201 cm²), v is the scan rate (0.05 V.s⁻¹) and C is the bulk concentration of $[Fe(CN)_6]^{3-}$ (0.001 M). Roughness factor of the electrode was calculated to be 1.02 (ratio of I_{pa} (exptal)/ I_{pa} (theor)), where I_{pa} (exptal) and $I_{\rm pa}$ (theor) are the experimental current and current calculated using Equation 10, respectively. The geometrical area was used in the estimation of I_{pa} (theor). The product of the roughness factor and theoretical surface area gives the real surface area (0.0205 cm^2) . Thus the values of surface coverage obtained on the gold electrode were 0.64×10^{-10} mol.cm⁻² for **3a**, 0.30×10^{-10} mol. cm⁻² for **3b**, 0.42×10^{-10} mol.cm⁻² for **3c** and 1.45×10^{-10} mol.cm⁻² for **3d** (Table 3). Except for **3d**, these values are slightly less than the values obtained for a monolayer coverage of an MPc molecule lying flat on the electrode [30], which is estimated at 1×10^{-10} mol.cm⁻². These values are, however, still within the range for monolayer

MnPc complex	Mn ^{III} /Mn ^{II}	Mn ^{IV} /Mn ^{III}	Surface concentration $(10^{10} \text{ mol.cm}^{-2})$	Reference
3 a		0.22	0.64	this work
3b	_	0.24	0.30	this work
3c	_	0.22	0.42	this work
3d	_	0.23	1.42	this work
4	-0.2	0.30	1.1 (24 h) ^b	[4]
5	_	0.2	0.78 (18 h) ^b	[9] ^a
6	_	0.35	0.69 (18 h) ^b	[9] ^a
7	-0.1	_	1.1	[21] ^a

Table 3. Electrochemical parameters of SAMs of complexes **3a–d** in 1 M HClO₄, (formation time = 48 h)

^a In pH 4 phosphate buffer. ^b Numbers in brackets refer to the time allowed for SAM formation.



Fig. 8. Cyclic voltammograms in 1 mM $CuSO_4$ in pH 4 buffer solution for Au electrode after: (1) 0 h, (2) 24 h and (3) 48 h SAM formation in 1 mM **3d** in CHCl₃. Scan rate = 50 mV/s *vs*. Ag|AgCl

coverage. Complexes **4–6** showed higher (compared to **3a–3c**) surface coverage values in Table 3, even though shorter SAM formation times (18 h and 24 h, compared to 48 h used in this work) were employed, suggesting that the tetra-substitution may enhance SAM formation. The importance of allowing the monolayer to form completely and fully is shown by Fig. 8, where formation times of 0 h, 24 h, and 48 h for the **3d**-SAM on gold are tested by looking at the electrochemistry of the SAM in 1 mM CuSO₄ in pH 4 buffer solution. As seen in this figure, a formation time of 24 h was not enough to block the electrode, while after 48 h the monolayer was almost completely pinhole-free.

Interestingly, the **3c**-SAM had an almost similar surface coverage to the **3b**-SAM despite the former SAM showing less inhibition of electrochemical processes at the electrode. The **3c**-SAM consistently displayed poor blocking of the gold surface in Fig. 6, but the surface coverage value indicates that this is not because of poor monolayer coverage. It is likely that the nature of the substituents, which are bulky and are also able to rotate more freely around the CH_2 group, creates a layer that is more permeable to the small redox ions and so allowing them to reach the gold surface. The long alkyl chains, however, appear to prevent ions from reaching the surface so easily despite having a similar surface coverage value to **3c**. This indicates once again the importance of different substituents in the formation of these layers.

Raman spectroscopy, AFM and SEM. Gold-coated glass was employed, in place of a gold electrode, for probing surface properties of the **3b**- and **3d**-SAM films. The formation time was increased to 10 days to ensure complete coverage of the glass surface with the MnPcs.

The peak characteristic of the Au-S linkage was observed at ~345 cm⁻¹ in the Raman spectra of the SAMs [30]. Surface natures of the SAM films were probed using AFM (in non-contact mode) and SEM. SEM and AFM are used to give information beyond the surface-blocking characteristics (which are easily studied using electrochemical techniques), such as whether the MnPcs are aggregated on the gold surface or whether they form a uniform layer. SEM is also commonly used to look at the surface morphology of thin films formed at different temperatures [31]. These methods should be used in conjunction because although SEM gives a broader view of the surface with regards to larger (micro-scale) aggregated clusters, like transmission electron microscopy (TEM), it does not give an indication of the height of the surface or aggregation on a smaller (nano) scale [32]. AFM, on the other hand, indicates clearly whether there is complete coverage by looking at the difference in the height of the surface before and after modification [33]. Aggregation is an important factor in SAM formation, and it can affect formation of a uniform layer on a surface [32-34] as well as the electrical properties [35] and reaction of the sensor with analytes. It could, for example, play a role in increasing or reducing passivation effects of the electrode, depending on the nature of the layer.

Figure 9(a) shows the AFM 2D and 3D images of the gold-coated glass before the formation of SAMs, indicating that the bare gold surface was fairly smooth and uniform with the small bright areas being attributed previously to imperfections on the surface [24]. Figure 9(b) shows the **3b-SAM** (alkylthio) and Fig. 9(c) shows the **3d-SAM** (arylthio) on gold. The most important data to take away from AFM are the values for mean thickness and roughness, and any clear indications of complete coverage or the formation of aggregates [34-38]. Figure 9 indicates that there are significant differences in the topographies of the surfaces. The mean roughness and thickness of the gold-coated glass before SAM formation are 0.278 nm and 1.643 nm, respectively. The mean roughness and thickness after the 3b-SAM formation are 2.081 nm and 8.738 nm, while the mean roughness and thickness after 3d-SAM formation are 1.870 and 8.666 nm, respectively. This increase in the roughness and thickness of the surface after SAM formation confirms the presence of a layer of the MnPcs on the surface. The images appear to show some nano-scale aggregation of the MnPcs, which can be expected as these peripherally substituted Pcs are more prone to aggregation than their non-peripherally substituted derivatives. The alkylthio-MnPc, 3b, had higher roughness and thickness factors than the arylthio-MnPc, **3d**. This indicates that the layer was more densely packed because of the long chains, and is supported by the better blocking characteristics of the 3b-SAM showed in Fig. 6b with regards to the $[Fe(H_2O)_6]^{3+}/[Fe(H_2O)_6]^{2+}$ redox process. For the non-peripheral tetrasubstituted complex 4, the inverse of the above behavior was observed. AFM showed that the roughness of the surface decreased upon 4-SAM formation, and this was explained to be a result of the complex filling in the grooves in the electrode [24]. In this case the bare gold had an initial roughness of 1.257 nm [24],



Fig. 9. AFM images of (a) bare gold-coated glass, (b) 3b-SAM-modified gold-coated glass and (c) 3d-SAM-modified gold-coated glass

which was far greater than the roughness of 0.278 nm observed in this work. This could explain the difference in the behavior of the SAMs. SAMs of complexes **5**, **6** and **7** were not analyzed using AFM or SEM. However, octa- and tetrasubstituted MPcs containing Sn as a central metal with non-peripherally substituted long alkyl-thio chains were shown to increase the roughness of the gold surface after SAM formation [39], as was observed in this work. Non-peripheral substituents also appeared to decrease the occurrence of surface aggregates.

Figure 10 shows the SEM images of gold-coated glass alone (a), after **3b**-SAM formation (b), and after **3d**-SAM formation (c). Although detailed features are not visible because the scale does not permit resolution of distinct molecules [35], the bare gold-coated glass depicts a smoother surface than the SAM-modified gold-coated glass which showed signs of aggregation. The SEM images indicate that there are areas with large clusters of aggregated MnPc molecules on the surface, as well as the smaller groups



Fig. 10. SEM images of (a) bare gold-coated glass, (b) 3b-SAM-modified gold-coated glass and (c) 3d-SAM-modified gold-coated glass

of aggregated molecules shown by the AFM results. As with the AFM images, the **3b**-SAM appeared to be rougher than the **3d**-SAM. Aggregation is known to be enhanced by the presence of long alkyl chains [12], which could account for the greater roughness of the **3b**-SAM in the AFM and the presence of larger surface clusters in the SEM image. SEM has not been used to analyze SAMs of complexes **4**–**7** on gold, but comparing the difference in topographies of the surfaces is another method that can be used to confirm SAM formation.

EXPERIMENTAL

Materials

Dimethylsulphoxide (DMSO), dichloromethane (DCM), tetrahydrofuran (THF), dimethylformamide (DMF), chloroform (CHCl₃), deuterated chloroform (CDCl₃), methanol and ethanol were purchased from Merck. Manganese(II) acetate, acetone, 1-pentanethiol, 1-decanethiol, thiophenol, tetrabutylammonium tetrafluoroborate (TBABF₄) and ethylene glycol were obtained

from Aldrich. Saarchem provided anhydrous potassium carbonate. Benzyl mercaptan was procured from Fluka, while argon was purchased from Afrox. Bio-beads S-X1 (200–400 mesh) were obtained from Bio-Rad and silica gel 60 (0.04 to 0.063 mm) was purchased from Merck. 4,5-dichlorophthalonitrile was synthesized according to a well-known procedure [40, 41] starting from dichlorophthalic anhydride. Solvents were dried and distilled before use, and all other chemicals and reagents were of analytical grade and were used as received.

Equipment

UV-visible spectra were recorded on a Cary 500 UV/ vis/NIR spectrophotometer. ¹H-nuclear magnetic resonance (NMR, 400 MHz) spectra were recorded using a Bruker AMX 400 MHz NMR spectrometer in CDCl₃ using standard 1D pulse programs. Elemental analysis was done using a Vario-Elementar Microcube ELIII on the purified Pcs. Spectroelectrochemical studies were done using a homemade optically transparent thin-layer electrochemical (OTTLE) cell connected to a Bioanalytical Systems (BAS) CV 27 voltammograph and using a Shimadzu Model UV-2550 UV-vis spectrophotometer. MALDI-TOF mass data was obtained in an α-cyano-4hydroxycinnamic acid matrix, on a ABI Voyager DE-STR MALDI-TOF instrument in positive ion mode, by the University of Stellenbosch in South Africa. AFM images were obtained in non-contact mode in air with a CP-11 Scanning Probe Microscope from Veeco Instruments (Carl Zeiss, South Africa) at a scan rate of 1 Hz. Scanning electrochemical microscopic (SEM) images were recorded using a Tescan Digital Microscope model scanning electron microscope at the Rhodes University Electron Microscopy Unit. A Bruker Vertex 70 spectrometer (fitted with the RAM II module and equipped with a 1064 nm Nd: YAG laser and a liquid nitrogen-cooled germanium detector) was used to collect the Raman spectral data.

Electrochemical studies

Cyclic (CV) and differential pulse (DPV) voltammetry data was obtained using a Bio-Analytical Systems (BAS) B/W 100 Electrochemical Workstation. Differential pulse voltammetric analysis was carried out at a pulse amplitude of 50 mV, sample width of 17 msec, pulse width of 50 msec, pulse period of 200 msec and a scan rate of 20 mV/s. A typical three-electrode system with a silver/ silver chloride (Ag|AgCl) pseudo-reference, platinum auxiliary and glassy carbon (GCE) working electrode was used. The potential response of the Ag AgCl pseudoreference electrode was less than the Ag AgCl (3M KCl) by 0.015 ± 0.003 V. The GCE was cleaned by polishing with 0.5 µm alumina on a Beuhler felt pad before use. DCM containing 0.1 M TBABF₄ as a supporting electrolyte was used for the electrochemical experiments. The concentration of the various MnPcs in solution was in the millimolar (mM) range.

For SAM studies, the gold electrode was rinsed with freshly distilled CHCl₃ and placed in deaerated CHCl₃ containing the MnPc complex for 48 h. Gold-coated glass was used for surface characterization of the SAM films using AFM, SEM and Raman. The glass was immersed in solution of the desired complex in CHCl₃ for 10 days for the latter studies.

Synthesis

As stated above, the synthesis of 4,5-dichlorophthalonitrile (1) has been reported before [40, 41] and so shall not be discussed here. The conversion to the required phthalonitriles followed by formation of the phthalocyanine is illustrated in Scheme 1.

4,5-bis(pentylthio)phthalonitrile(2a). Compound 2a was synthesized as reported in literature [11] with some modifications. Briefly, 1-pentanethiol (30.45 mmol) and 1 (2.0 g, 10.2 mmol) were dissolved in DMSO (15 mL) under argon. The mixture was stirred for 15 min and ground anhydrous potassium carbonate (5.1 g, 36.9 mmol) was added portion-wise over 2 h with stirring. The mixture was stirred under an argon atmosphere for 12 h. Water (100 mL) was then added and the mixture stirred for 30 min. The precipitate was filtered and washed with water, followed by recrystallization from ethanol. Yield: 38%. IR (KBr): v_{max}, cm⁻¹ 3075, 2949, 2930, 2859, 2231 $(C \equiv N)$, 1618, 1563, 1456, 1433, 1350, 1264, 1225, 1112 929, 900, 869, 731, 682, 605, 527. ¹H NMR (400 MHz; CDCl₃; Me₄Si): δ, ppm 7.41 (2H, s, Ar-H), 3.01 (4H, t, S-CH₂), 1.76 (4H, m, -CH₂), 1.49 (4H, m, -CH₂), 1.39 (4H, m, -CH₂), 0.93 (6H, t, -CH₃).

4,5-bis(decylthio)phthalonitrile (2b). Compound **2b** was synthesized as described above for **2a**, using 1-decanethiol (30.5 mmol), DMSO (15 mL) under argon and **1** (2.0 g, 10.2 mmol). Yield: 56%. IR (KBr): v_{max} , cm⁻¹ 3071, 2943, 2921, 2852, 2359, 2340, 2230 (C=N), 1692, 1614, 1580, 1457, 1343, 1224, 1186, 1108, 1004, 929, 899, 870, 831, 761, 735, 668, 609, 528. ¹H NMR (400 MHz; CDCl₃; Me₄Si): δ , ppm 7.41 (2H, s, Ar-*H*), 3.01 (4H, t, S-CH₂), 1.75 (4H, m, -CH₂), 1.49 (4H, m, -CH₂), 1.28 (24H, m, -CH₂), 0.89 (6H, t, -CH₃).

4,5-bis(benzylthio)phthalonitrile (2c). Compound **2c** was synthesized as described above for **2a**, using benzyl mercaptan (30.5 mmol), DMSO (15 mL) under argon and **1** (2.0 g, 10.2 mmol). Yield: 54%. IR (KBr): v_{max} , cm⁻¹ 3060, 3027, 2359, 2336, 2227 (C=N), 1768, 1719, 1565, 1494, 1452, 1331, 1238, 1115, 1029, 933, 889, 873, 778, 712, 694, 633, 530, 483, 465. ¹H NMR (400 MHz; CDCl₃; Me₄Si): δ , ppm 7.40 (2H, s, Ar-*H*), 7.31 (10H, m, Ar-*H*), 4.20 (4H, s, S-CH₂).

4,5-bis(phenylthio)phthalonitrile (2d). Compound **2d** was synthesized as described above for **2a**, using thiophenol (30.5 mmol), DMSO (15 mL) under argon and **1** (2.0 g, 10.2 mmol). Yield: 75%. IR (KBr): v_{max} , cm⁻¹ 3075, 2959, 2921, 2850, 2229 (C=N), 1768, 1714, 1653, 1564, 1473, 1453, 1437, 1384, 1349, 1331, 1259, 1218,

1108, 1022, 924, 883, 799, 758, 693, 528, 489. ¹H NMR (400 MHz; CDCl₃; Me₄Si): δ, ppm 7.53 (10H, m, Ar-*H*), 7.01 (2H, s, Ar-*H*).

2,3,9,10,16,17,23,24-octakis(pentylthio)phthalocyaninatomanganese(III)(Ac), (OAc)MnPc^{β}{S(CH₂)₄-CH₃}₈ (3a). Compound 2a (0.9 g, 2.7 mmol), manganese(II) acetate (0.12 g, 0.71 mmol) and anhydrous ethylene glycol (6 mL) were mixed and refluxed for 4 h at 200 °C under argon. The mixture was allowed to cool before excess methanol was added to precipitate out the crude product, which was then purified using a Bio-Bead S-X1 column eluting with CHCl₃. Yield: 72%. UV-vis (CHCl₃): λ_{max} , nm (log ϵ) 405 (4.2), 465 (4.2), 530 (4.1), 768 (4.5). IR (KBr): v_{max} , cm⁻¹ 2955, 2925, 2856, 2360, 2343, 1701, 1637, 1618, 1551, 1458, 1413, 1376, 1328, 1072, 959, 743, 669, 618, 486. Anal. calcd. for C₇₂H₉₆N₈S₈Mn(Ac): C, 61.55; H, 6.91; N, 7.76; S, 17.76%. Found: C, 61.89; H, 7.05; N, 7.02; S, 17.35%. MS (MALDI-TOF): m/z 1384 (calcd. for [M - Ac]⁺ 1385).

2,3,9,10,16,17,23,24-octakis(decylthio)phthalocyaninatomanganese(III)(Ac), (OAc)MnPc^β{(SCH₂)₉-CH₃}₈ (3b). Complex **3b** (MnODTPc) was synthesized as described above for **3a** using compound **2b** (1.0 g, 2.1 mmol), manganese(II) acetate (0.10 g, 0.55 mmol) and anhydrous ethylene glycol (6 mL). Yield: 32%. UV-vis (CHCl₃): λ_{max} , nm (log ε) 405 (4.2), 465 (4.3), 530 (4.2), 769 (4.6). IR (KBr): v_{max} , cm⁻¹ 2955, 2924, 2853, 2360, 2342, 1701, 1654, 1592, 1458, 1414, 1377, 1328, 1073, 960, 782, 743, 669, 597, 509. Anal. calcd. for C₁₁₂H₁₇₆N₈S₈Mn(Ac) (CHCl₃): C, 65.01; H, 8.54; N, 5.28; S, 12.07%. Found: C, 64.61; H, 8.60; N, 4.59; S, 12.63%. MS (MALDI-TOF): *m/z* 1945 (calcd. for [M -Ac]⁺ 1946).

2,3,9,10,16,17,23,24-octakis(benzylthio)phthalocyaninatomanganese(III)(Ac), (OAc)MnPc^β(SCH₂ Ph)₈ (**3c).** Complex **3c** (MnOBTPc) was synthesized as described above for **3a** using compound **2c** (1.3 g, 3.5 mmol), manganese(II) acetate (0.16 g, 0.92 mmol) and anhydrous ethylene glycol (6 mL). Yield: 74%. UV-vis (CHCl₃): λ_{max} , nm (log ε) 407 (3.9), 472 (3.9), 530 (3.9), 770 (4.0). IR (KBr): v_{max} , cm⁻¹ 2924, 2853, 2360, 2342, 1639, 1617, 1412, 1378, 1327, 1073, 958, 669, 618, 486. Anal. calcd. for C₈₈H₆₄N₈S₈Mn(Ac) (CHCl₃): C, 63.42; H, 3.98; N, 6.50; S, 14.88%. Found: C, 64.78; H, 3.73; N, 6.49; S, 15.08%. MS (MALDI-TOF): *m/z* 1544 (calcd. for [M - Ac]⁺ 1545).

2,3,9,10,16,17,23,24-octakis(phenylthio)phthalocyaninatomanganese(III)(Ac), (OAc)MnPc^β(SPh)₈ (3d). Complex **3d** (MnOPhTPc) was synthesized as described above for **3a** using compound **2d** (1.0 g, 2.9 mmol), manganese(II) acetate (0.13 g, 0.76 mmol) and anhydrous ethylene glycol (6 mL). Yield: 55%. UV-vis (CHCl₃): λ_{max} , nm (log ε) 462 (4.3), 530 (4.1), 694 (3.9), 773 (4.7). IR (KBr): v_{max} , cm⁻¹ 2923, 2852, 2361, 2343, 1701, 1637, 1614, 1555, 1438, 1326, 1064, 955, 743, 669, 618, 486. Anal. calcd. for C₈₀H₄₈N₈S₈Mn(Ac) (CHCl₃): C, 61.87; H, 3.25; N, 6.96; S, 15.92%. Found: C, 62.72; H, 3.49; N, 6.65; S, 15.08%. MS (MALDI-TOF): *m*/*z* 1432 (calcd. for [M - Ac]⁺ 1433).

CONCLUSION

The octakis(pentylthio)-, (decylthio)-, (benzylthio)and (phenylthio)phthalocyaninato manganese(III) acetate complexes (3a-d) showed solvent-dependent conversion to the µ-oxo dimer, as well as a solvent-dependent shift in the Q band. The different substituents did not greatly affect the UV-vis spectra of the compounds, but did appear to have an effect on their electrochemical properties. Three main redox processes for the complexes were identified as Mn^{III}Pc⁻²/Mn^{II}Pc⁻² (II), Mn^{II}Pc⁻²/Mn^{II}Pc⁻³ (III) and Mn^{III}Pc⁻¹/Mn^{III}Pc⁻² (I) and confirmed using spectroelectrochemistry. Self-assembled monolayers (SAMs) of the MnPcs were formed on gold, and showed good surface coverage in all cases. All the MnPc-SAMs except 3c showed good blocking characteristics for gold oxidation, copper UPD and the redox chemistry of $Fe(NH_4)_2(SO_4)_2$, and even some blocking for K_3 [Fe(CN)₆], with **3a** and **3b** being the most effective. Raman, AFM and SEM also confirmed SAM formation and good surface coverage, although the latter two did indicate that there was some aggregation of the Pcs. The specific behavior of the SAM seemed again to be dependent on the nature of the substituents. The successful formation of MnPc-SAMs confirms the potential of these surfaces for use in electrochemical sensors, and the investigation of the use of these SAMs in sensors is currently underway in our laboratories.

Acknowledgements

The authors would like to thank Ms. S. D'Souza and Dr. W. Chidawanyika for the AFM images, and Mr. M. Randall and Ms. S. Pinchuck from the Rhodes University Electron Microscopy Unit for the SEM images.

This work was supported by the Department of Science and Technology (DST) and National Research Foundation (NRF) of South Africa through DST/NRF South African Research Chairs Initiative for Professor of Medicinal Chemistry and Nanotechnology and Rhodes University and by DST/Mintek Nanotechnology Innovation Centre (NIC). MC thanks NIC and Rhodes University Henderson for Scholarships.

REFERENCES

- Nyokong T. In N₄-macrocyclic Metal Complexes, Zagal JH, Bedioui F and Dodelet J-P. (Eds.) Springer: USA, 2006; pp 315–362.
- Ben-Hur E and Chan W. In *The Porphyrin Handbook: Applications of Phthalocyanines*, Vol. 19, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: New York, 2003; pp 1–36.

- Dini D and Hanack M. In *The Porphyrin Handbook: Phthalocyanines: Properties and Materials*, Vol. 17, Kadish KM, Smith KM and Guilard R. (Eds.) Academic Press: New York, 2003; pp 1–36.
- Matemadombo F, Griveau S, Bedioui F and Nyokong T. *Electroanalysis* 2008; 20: 1863–1872.
- Dolotova O, Bundina N, Kaliya O and Lukyanets E. J. Porphyrins Phthalocyanines 1997; 1: 355–366.
- Adebayo AI and Nyokong T. *Polyhedron* 2009; 28: 2831–2838.
- Sehlotho N, Durmuş M, Ahsen V and Nyokong T. Inorg. Chem. Commun. 2008; 11: 479–483.
- Stillman MJ and Nyokong T. In *Phthalocyanines: Properties and Applications*, Vol. 1, Leznoff CC and Lever ABP. (Eds.) VCH: New York, 1989; Chapter 3.
- Agboola B, Ozoemena K, Westbroek P and Nyokong T. *Electrochim. Acta* 2007; **52**: 2520–2526.
- Lever ABP, Wilshire J and Quan S. *Inorg. Chem.* 1981; 20: 761–768.
- Mbambisa G, Tau P, Antunes E and Nyokong T. Polyhedron 2007; 26: 5355–5364.
- Ogunbayo TB, Ogunsipe A and Nyokong T. Dyes Pigm. 2009; 82: 422–426.
- Ooi K, Maeda F, Ohta K, Takizawa T and Matsuse T. J. Porphyrins Phthalocyanines 2005; 9: 544–553.
- Özkaya A, Gürek A, Gül A and Bekaroğlu Ö. *Polyhedron* 1997; 16: 1877–1883.
- 15. Takahashi K, Kawashima M, Tomita Y and Itoh M. *Inorg. Chim. Acta* 1995; **232**: 69–73.
- Leznoff CC, Black L, Hiebert A, Causey P, Christendat D and Lever ABP. *Inorg. Chim. Acta* 2006; 359: 2690–2699.
- 17. Tau P and Nyokong T. *Dalton Trans.* 2006; 4482–4490.
- Ozoemena K, Westbroek P and Nyokong T. *Electrochem. Commun.* 2001; 3: 529–534.
- Griveau S, Pavez J, Zagal J and Bedioui F. J. Electroanal. Chem. 2001; 497: 75–83.
- Marcuccio SM, Svirskaya PI, Greenberg S, Lever ABP, Leznoff CC and Tomer KB. *Can. J. Chem.* 1985; 63: 3057–3069.
- 21. Mbambisa G, Nombona N and Nyokong T. *Microchem. J.* 2009; **93**: 60–66.
- Obirai J and Nyokong T. *Electrochim. Acta* 2005; 50: 5427–5434.

- 23. Sivanesan A and John SA. *Langmuir* 2008; **24**: 2186–2190.
- 24. Matemadombo F, Durmuş M, Togo C, Limson J and Nyokong T. *Electrochim. Acta* 2009; **54**: 5557–5565.
- 25. Khene S, Cammidge AN, Cook MJ and Nyokong T. *J. Porphyrins Phthalocyanines* 2007; **11**: 761–770.
- 26. Wöhrle D and Schmidt V. J. Chem. Soc., Dalton Trans. 1988; 549–551.
- Louati A, El Meray M, Andre JJ, Simon J, Kadish KM, Gross M and Giraudeau A. *Inorg. Chem.* 1985; 24: 1175–1179.
- Stillman M. In *Phthalocyanines: Properties and Applications*, Vol. 3, Leznoff CC and Lever ABP. (Eds.) VCH: New York, 1993; chapter 5.
- Finklea H. In *Electroanalytical Chemistry: A Series* of Advances, Bard AJ and Rubenstein I. (Eds.) Marcel Dekker: New York, 1996; pp 109–335.
- Li Z, Lieberman M and Hill W. *Langmuir* 2001; 17: 4887–4894.
- EJ, Kim S, Lim E, Lee K, Cha D and Friedman B. *Appl. Surf. Sci.* 2003; 205: 274–279.
- Ottaviano L, Di Nardo S, Lozzi L, Passacantando M, Picozzi P and Santucci S. *Surf. Sci.* 1997; **373**: 318–332.
- Sánchez Vergara M, Islas Bernal I, Rivera M, Ortíz Rebollo A and Alvarez Bada J. *Thin Solid Films* 2007; **515**: 5374–5380.
- 34. Lee Y, Wu H, Chang C and Yang Y. *Thin Solid Films* 2003; **423**: 169–177.
- Caminiti R, Capobianchi A, Marovino P, Paoletti A, Padeletti G, Pennesi G and Rossi G. *Thin Solid Films* 2001; **382**: 74–80.
- Lee Y, Chen Y, Chang C, Yang Y and Maa J. *Thin* Solid Films 2000; **370**: 278–284.
- Kment S, Kluson P, Drobek M, Kuzel R, Gregora I, Kohout M and Hubicka Z. *Thin Solid Films* 2009; 517: 5274–5279.
- Cao Jr. R, Díaz-García AM and Cao R. Coord. Chem. Rev. 2009; 253: 1262–1275.
- 39. Khene S, Geraldo D, Togo C, Limson J and Nyokong T. *Electrochim. Acta* 2008; **54**: 183–191.
- 40. Gürek A and Bekaroğlu Ö. J. Chem. Soc., Dalton Trans. 1994; 1419–1423.
- 41. Young J and Onyebuagu W. J. Org. Chem. 1990; **55**: 2155–2159.