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# The effects of point of substitution on the electrochemical behavior of new manganese phthalocyanines, tetra-substituted with diethylaminoethanethiol

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#### ABSTRACT

The syntheses and comparative studies of the spectral, voltammetry and spectroelectrochemical properties of new manganese phthalocyanine complexes, tetra-substituted with diethylaminoethanethio at the peripheral (complex **3a**) and non-peripheral positions (complex **3b**) are reported. Solution electrochemistry of complex **3a** showed quasi-reversible metal-based ( $Mn^{IIP}C^{-2}/Mn^{IP}C^{-2}$ ,  $E_{1/2} = -0.07$  V vs. Ag|AgCl) and ring-based ( $Mn^{IIP}C^{-2}/Mn^{IP}C^{-3}$ ,  $E_{1/2} = -0.78$  V vs. Ag|AgCl) reductions, but no ring-based oxidation. However, complex **3b** showed weak irreversible ring-oxidation signal ( $E_p = +0.86$  vs. Ag|AgCl). Reversible metal-based ( $Mn^{IIP}C^{-2}/Mn^{IIP}C^{-2}$ ,  $E_{1/2} = -0.04$  V vs. Ag|AgCl) and ring-based ( $Mn^{IIP}C^{-2}/Mn^{IIP}C^{-3}$ ,  $E_{1/2} = -0.68$  V vs. Ag|AgCl) reductions were also observed for complex **3b**. Spectroelectrochemistry was used to confirm these processes. Reduction process involving the metal ( $Mn^{IIP}C^{-2}/Mn^{IIP}C^{-2}$ ) was associated with the formation of manganese  $\mu$ -oxo complex in complex **3a**.

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#### 1. Introduction

The present and potential applications of metallophthalocyanine (MPc) complexes have attracted unprecedented research interest in these macrocycles. Their uses in electronic devices, as gas sensors, as photosensitizers, in non-linear optics, in electrochromic devices and in Langmuir–Blodgett films have been reported [1,2]. Incorporation of different metals into the phthalocyanine cavity and changes in the nature and position of substituent (peripheral and non-peripheral), give MPc complexes with different chemical, physical, electrochemical, spectroscopic, electrocatalytic, photophysical and photocatalytic properties. The possibility of tuning these properties, to form MPc complexes with specific requirements, needed for different applications, promotes the versatility of these macrocycles.

The electrochemical properties of manganese phthalocyanine (MnPc) complexes have attracted attention [3–5]. MnPc complexes show interesting electrochemical behavior with oxidation states of the central Mn ion ranging from Mn<sup>I</sup> to Mn<sup>IV</sup> [6–16]. Mn<sup>IV</sup>Pc species rarely occurs, but has been reported recently [11,12]. The reduction of Mn<sup>II</sup>Pc<sup>-2</sup> species has been extensively contested, with some authors proposing metal reduction to Mn<sup>IP</sup>c<sup>-2</sup> species and others ring reduction forming Mn<sup>II</sup>Pc<sup>-3</sup> species. The latter was ob-

served in this work. The formation of  $\mu$ -oxo complex in DMF and in the presence of oxygen is common for MnPc complexes, hence in this work the effects of changing the substituent position on the formation of  $\mu$ -oxo MnPc species is discussed.

In the present work, we report on the syntheses and the effects of the point of substitution on the spectral, voltammetric and spectroelectrochemical properties of new MnPc complexes containing diethylaminoethanethio, tetra-substituted at the peripheral (complex **3a**) and non-peripheral (complex **3b**) positions (Scheme 1). The electrochemical behavior of complexes **3a** and **3b** is compared with that of the octa-substituted derivatives {manganese(III) (acetate) octakis-(2-diethylaminoethanethio) phthalocyanine, OAcMnODEAETPc( $\beta$ )}, reported before [17]. The formation of different redox products is highly influenced by the nature of substituents in MnPc complexes [18]; hence it is important to increase the range of substituted MnPc complexes.

The choice of the substituent employed in this work (diethylaminoethanethio) is influenced by the possibility of forming polymers and self-assembled monolayers of the complexes on suitable electrodes, thus promoting their uses as electrocatalysts and in the fabrication of electrochemical sensors. The nitrogen group in the substituent is oxidizable, hence can generate radicals necessary for initiating polymer formation [19–22].

MPc complexes containing diethylaminoethanethio on peripheral positions (either tetra- or octa-substituted) have been reported in the literature [23–27]. The central metals which have been employed in the literature include Ni(II), Zn(II) or Co(II).



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Scheme 1. Synthetic route for complexes 3a and 3b.

No manganese derivatives have been reported. It is important to note that synthesis of MPc complex containing relatively bulky substituents is dependent on the nature of the central metal [12], hence the synthesis of MnPc derivatives is important. In addition, the electrochemistry of MPc complexes containing the ligand of interest in this work has also not received much attention.

#### 2. Experimental

#### 2.1. Materials

Potassium carbonate, manganese(II) acetate (OAc), 2-(diethylaminoethanethiol) hydrochloride and 2-diethylaminoethanol were obtained from Sigma–Aldrich. Tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) (Aldrich) was used as the electrolyte for electrochemical experiments. Aluminum oxide, (WN-3 neutral for column chromatography) was purchased from Sigma–Aldrich. Dimethylformamide (DMF) and dichloromethane (DCM) were obtained from Merck, methanol (MeOH) and dimethylsulfoxide (DMSO) and were distilled before use.

#### 2.2. Electrochemical studies

All electrochemical experiments were performed using Autolab potentiostat PGSTAT 302 (Eco Chemie, Utrecht, The Netherlands) driven by the general purpose Electrochemical System data processing software (GPES, software version 4.9). Square wave voltammetric analysis was carried out at a frequency of 10 Hz, amplitude: 50 mV and step potential: 5 mV. A conventional three-electrode system was used. The working electrode was a bare glassy carbon electrode (GCE), Ag|AgCl wire and platinum wire were used as the pseudo reference and auxiliary electrodes, respectively. The potential response of the Ag|AgCl pseudo-reference electrode was less than the Ag|AgCl (3 M KCl) by 0.015 ± 0.003 V. Prior to use, the electrode surface was polished with alumina on a Buehler felt pad and rinsed with excess millipore water. All electrochemical experiments were performed in freshly distilled dry DMF containing TBABF<sub>4</sub> as supporting electrolyte.

Spectroelectrochemical data were obtained using a home-made optically transparent thin-layer electrochemical (OTTLE) cell (containing Pt grit working and auxiliary electrodes, and a Ag|AgCl pseudo-reference electrode) connected to a Bioanalytical Systems (BAS) CV 27 voltammograph. UV/Vis spectra were recorded on Cary 500 UV/Vis/NIR spectrophotometer. IR (KBr discs) was recorded on Bruker Vertex 70-Ram II spectrophotometer. Elemental analysis was performed using Vario Elementar Microcube EL111. <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR, 400 MHz) was obtained in CDCl<sub>3</sub> using Bruker EMX 400 NMR spectrometer.

#### 2.4. Synthesis

## 2.4.1. 4-(2-Diethylaminoethanethiol) phthalonitrile (**2a**) and 3-(2-diethylaminoethanethiol) phthalonitrile (**2b**)

4-Nitrophthalonitrile (compound 1a) and 3-mitrophthalonitrile (compound **1b**). Scheme 1, were synthesized according to reported procedure [28]. Compound **2a** was synthesized using the method reported for the synthesis of 1.2-bis-(diethylaminoethanethiol)-4,5-dicyanobenzene [29] with some modifications as follows: compound 1a (3.05 g, 17.63 mmol) was dissolved in anhydrous DMF (150 ml) under nitrogen and 2-diethylaminoethanethiol hydrochloride (9 g, 53.01 mmol) was added. After stirring for 10 min, finely ground anhydrous K<sub>2</sub>CO<sub>3</sub> (29.25 g, 212.04 mmol) was added in portions over 2 h with stirring. The reaction mixture was stirred at room temperature for 48 h under nitrogen. Then the solution was poured into ice (900 g). The precipitate was filtered off, washed with water, until the filtrate was neutral. The product was then dried in air. Yield: 3.42 g (75%). IR (KBr)  $v_{\text{max}}/\text{cm}^{-1}$ : 3084-3018 (Ar-C-H), 2968-2807 (Aliph-CH<sub>2</sub>), 2229 (v<sub>CN</sub>), 1582, 1542, 1471, 1384, 1289, 1225, 1198, 1142, 1072, 987, 906, 825, 732, 609, 521. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 7.66–7.54 (m, 3H, Ar–H), 3.15-3.12 (t, 2H, SCH<sub>2</sub>), 2.81-2.77 (t, 2H, NCH<sub>2</sub>), 2.62-2.57 (qnt, 4H, CH<sub>2</sub>C), 1.06–1.03 (*t*, 6H, CH<sub>3</sub>) ppm.

Compound **2b**, Scheme 1, was synthesized following the method described above for compound **2a**, using 3-nitrophthalonitrile (compound **1b**) in place of 4-nitrophthalonitrile (compound **1a**). Yield: 2.74 g (60%). IR (KBr)  $v_{max}/cm^{-1}$ : 2969–2814 (Aliph-CH<sub>2</sub>), 2229 ( $v_{CN}$ ), 1565, 1520, 1445, 1372, 1290, 1231, 1193, 1133, 1065, 1029, 987, 855, 787, 730, 547, 439. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  = 7.73–7.55 (m, 3H, Ar–H), 3.22–3.19 (*t*, 2H, SCH<sub>2</sub>), 2.82–2.79 (*t*, 2H, NCH<sub>2</sub>), 2.61–2.58 (dd, 4H, CH<sub>2</sub>C), 1.06–1.02 (*t*, 6H, CH<sub>3</sub>) ppm.

#### 2.4.2. Manganese(III) (acetate) 2(3),9(10),16(17),23(24)-tetrakis-(2diethylaminoethanethio) phthalocyanine (**3a**, Scheme 1)

Complexes 3a was synthesized following the method reported for the octa-substituted complex {manganese(III) (acetate) octakis-(2-diethylaminoethanethio) phthalocyanine, (OAcMnO-DEAETPc( $\beta$ ) [17] with some modifications. A mixture of compound **2a** (0.40 g, 1.54 mmol) and manganese(II) acetate (0.065 g, 0.38 mmol) was refluxed in 2-diethylaminoethanol (1.2 ml) for 12 h under nitrogen. Thereafter, the mixture was cooled to room temperature and treated with excess MeOH:H<sub>2</sub>O (1:1) to precipitate the crude purple product. The product was filtered and dried in air. Purification was carried out using column chromatography with neutral alumina as column material and DCM/MeOH (10:1) as eluent. Yield: 1.28 g (72%). Anal. Calc. for C<sub>56</sub>H<sub>68</sub>N<sub>12</sub>S<sub>4</sub>MnOAc.H<sub>2</sub>O: C, 57.04; H, 5.77; N, 14.26; S, 10.87). Found: C, 56.76; H, 5.72; N, 14.10; S, 11.41%. UV–Vis (DMF):  $\lambda_{max}$  (nm) (log  $\varepsilon$ ): 739 (5.1), 662 (4.5), 500 (4.4), 432 (5.5), 365 (4.7); IR (KBr)  $v_{\rm max}/$ cm<sup>-1</sup>; 2966–2802 (Aliph-CH<sub>2</sub>), 1597, 1504, 1450, 1389, 1325, 1067, 924, 878 (Mn-O), 822, 769, 741.

#### 2.4.3. Manganese(III) (acetate) 1(4),8(11),15(18).22(25)-tetrakis-(2diethylaminoethanethiol) phthalocyanine (**3b**, Scheme 1)

Complex **3b** was synthesized (Scheme 1) and purified following the same method described for complex **3a**, using compound **2b** (0.40 g, 1.54 mmol) as the starting material in place of **2a**.Yield: 1.20 g (67%). Anal. Calc. for  $C_{56}H_{68}N_{12}S_4MnOAc$ : C, 57.93%; H, 5.86; N, 14.48; S, 11.03). Found: C, 57.65; H, 5.96; N, 13.98; S, 11.33%. UV–Vis (DMF):  $\lambda_{max}$  (nm) (log  $\varepsilon$ ): 770 (5.4), 696 (4.7), 510 (4.5), 357 (5.0); IR (KBr)  $v_{max}/cm^{-1}$ ; 2967–2805 (Aliph-CH<sub>2</sub>), 1719, 1568, 1466, 1379, 1235, 1190, 1067, 915, 877 (Mn–O) 766, 738, 592.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The synthetic pathways for complexes **3a** and **3b** are shown in Scheme 1. The phthalonitriles, compounds **2a** and **2b**, were obtained via a based-catalyzed ( $K_2CO_3$ ) nucleophilic aromatic substitution reaction. Cyclotetramerization of **2a** and **2b** occurred in the presence of manganese(II) acetate to form the targeted complexes: **3a** and **3b**, respectively. Purification of **3a** and **3b** was accomplished using column chromatography on alumina. The complexes were soluble in solvents such as DMF, DCM and DMSO.

Characterizations of the complexes were carried out using IR and UV–Vis spectroscopies as well as elemental analysis. The results obtained were consistent with the predicted structures shown in Scheme 1. The formation of complexes **3a** and **3b** was confirmed by the disappearance of the sharp C $\equiv$ N vibration at 2229 cm<sup>-1</sup> of **2**a and **2b**.

Fig. 1 shows the UV–Vis spectra of complexes **3a**  $(9.48 \times 10^{-6} \text{ M})$  and **3b**  $(8.82 \times 10^{-6} \text{ M})$  in DMF. Absorption due to the Q-band of complex **3a** appeared at 739 nm. The UV–Vis spectrum of complex **3b** showed a red-shifted Q-band (770 nm) with respect to that of complex **3a**. Red-shifting of the Q-band is normal with non-peripheral substitution in MPc complexes. Increase in steric limitations, caused by non-peripheral substitution, increases the conformational stress on MPc complexes. Such conformational stress results in shift in position of Q-band [30].

It has been suggested [31,32] that equilibrium exists between MnPc species in air and in DMF as shown by Eqs. (1)-(5).

 $PcMn^{II} + O_2 \leftrightarrow PcMn^{III}(O_2) \tag{1}$ 

 $PcMn^{III}(O_2) + PcMn^{II} \leftrightarrow PcMn^{III} - O_2 - Mn^{III}Pc2$ (2)

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

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

$$4PcMn^{II} + O_2 \leftrightarrow 2PcMn^{III} - O - Mn^{III}Pc \quad (Net \ equation) \tag{5}$$

Thus in general the electronic absorption spectra in the visible region for MnPc complexes may be attributed to Mn<sup>III</sup>Pc, Mn<sup>II</sup>Pc and  $\mu$ -oxo MnPc species in air. The presence of the  $\mu$ -oxo MnPc species may be confirmed by monitoring the spectral transformations of an MnPc complex in DMF solution when not de-aerated and when de-aerated with dry N2 gas. This is discussed later in this work. Thus in Fig. 1, the weak band around 636 nm in complex 3a is associated with the formation of MnPc µ-oxo complex, which is common with MnPc complexes in DMF in the presence of oxygen [31,32]. Although, Mn(II)OAc was the metal salt employed for synthesis, the positions of O-bands in both complexes (Fig. 1) confirm the formation of  $Mn^{III}Pc^{-2}$  complexes. This is expected since the Mn<sup>III</sup>/Mn<sup>II</sup> oxidation potential is appreciably negative, making the  $Mn^{II}Pc^{-2}$  species very sensitive to air, resulting in the formation of Mn<sup>III</sup>Pc<sup>-2</sup> species during synthesis and purification [12]. Although, the solution was dearated with purified argon before spectral characterization, the possibility of the formation of MnPc  $\mu$ -oxo complex may not be completely ruled out. The tendency



Fig. 1. UV–Vis spectral of complexes 3a ( $9.48 \times 10^{-6}$  M), and 3b ( $8.82 \times 10^{-6}$  M) in DMF.

to form the MnPc  $\mu$ -oxo complex (band around 636 nm) was significantly reduced, almost absent, in complex **3b**. This may be attributed to restriction to coplanar association of the rings, via oxo-bridge, caused by the sterically crowded nature of the non-peripheral position. The prevalence of MnPc  $\mu$ -oxo species was also observed during spectral transformations involving OAcMnO-DEAETPc( $\beta$ ) containing the same substituents at the peripheral positions, but octa-substituted [17].

The peaks at 500 and 432 nm (complex **3a**) and 510 and 478 nm (complex **3b**) are associated with charge transfer in MPc complexes [14]. The complexes have well-resolved B-bands: 365 and 357 nm for **3a** and **3b**, respectively.

Fig. 2a  $(3.16 \times 10^{-6} \text{ to } 2.21 \times 10^{-5} \text{ M})$  and Fig. 2b  $(1.26 \text{ to } 8.82 \times 10^{-6} \text{ M})$  show the effect of changing concentration on the spectra of complexes **3a** and **3b**, respectively. There was no significant increase in intensity of the peak associated with the MnPc



**Fig. 2.** UV–Vis spectral of (a) complex **3a** at different concentration  $(3.16 \times 10^{-6} \text{ to } 2.21 \times 10^{-5} \text{ M})$ , and (b) complex **3b** at different concentration  $(1.26-8.82 \times 10^{-6} \text{ M})$ . Solvent: DMF. Insets: plots of absorbance versus concentration.

 $\mu$ -oxo complex in complex **3a** as concentration increased, suggesting the dominance of the Mn<sup>III</sup>Pc species. Beer's law was obeyed within the range of concentration (Fig. 2) investigated for both complexes.

#### 3.2. Voltammetric studies

Comparative study of the voltammetry properties of the complexes was carried out using cyclic and square wave voltammetries.

#### 3.2.1. Complex 3a

Figs. 3a and b, respectively, show the square wave and cyclic voltammetry profiles of  $1 \times 10^{-4}$  M of complex 3a in freshly distilled dry DMF containing 0.1 M TBABF<sub>4</sub> as supporting electrolyte. Fig. 3b shows two redox processes. Process II is a quasi-reversible metal reduction process, assigned to Mn<sup>III</sup>Pc<sup>-2</sup>/Mn<sup>II</sup>Pc<sup>-2</sup> species ( $E_{1/2} = -0.07$  V vs. Ag|AgCl), Table 1, in comparison with literature [33]. Although, process II has a cathodic to anodic current ratio of near unity, a peak separation larger than that of ferrocene standard (90 mV vs. Ag|AgCl), at the same scan rate (100 mV s<sup>-1</sup> vs. Ag|AgCl), was obtained. Process I is a quasi-reversible ring reduction, with large peak separation (171 mV vs. Ag|AgCl) and is assigned to Mn<sup>II</sup>Pc<sup>-2</sup>/Mn<sup>II</sup>Pc<sup>-3</sup> species ( $E_{1/2} = -0.78$  V vs. Ag|AgCl). No ring-based oxidation was identified in complex 3a. Table 1 shows the presence of oxidation process in OAcMnODEAETPc(β),

which is the octa-substituted derivative of **3a**); unlike complex **3a** that does not undergo any oxidation process. Expectedly, the OAcMnODEAETPc( $\beta$ ) complex is more difficult to reduce than complex **3a** (Table 1, considering first reduction). The ease of oxidation and difficulty in reduction is a result of the plurality of the sulfur containing substituents. Assignments are confirmed below for **3a** using spectroelectrochemistry.

#### 3.2.2. Complex 3b

The square wave and cyclic voltammetry profiles of  $1 \times 10^{-4}$  M of complex 3b, in freshly distilled dry DMF containing 0.1 M TBABF<sub>4</sub>, as supporting electrolyte, are shown in Fig. 4a and b, respectively. Three redox processes can be identified. Process III  $(E_p = +0.86 \text{ V vs. Ag}|\text{AgCl})$  is a weak irreversible ring-oxidation process assigned to the either the formation of  $Mn^{III}Pc^{-1}/Mn^{III}Pc^{-2}$  or  $Mn^{IV}Pc^{-2}/Mn^{III}Pc^{-2}$  species using the data in Table 1. Using redox potentials is never enough to definitely assign redox processes. The irreversibility of oxidation processes of MPc complexes containing sulfur substituents is well established [34,35]. Process II  $(E_{1/2} = -0.04 \text{ V vs. Ag}|\text{AgCl})$  is reversible with a cathodic to anodic current ratio of near unity and cathodic to anodic peak separation of 87 mV vs. Ag[AgCl. It is assigned to metal reduction,  $Mn^{III}Pc^{-2}/$  $Mn^{II}Pc^{-2}$ . Process I ( $E_{1/2} = -0.68$  V vs. Ag|AgCl), assigned to ringbased reduction  $(Mn^{II}Pc^{-2}/Mn^{II}Pc^{-3})$ , is also reversible with cathodic to anodic current ratio of near unity and peak separation of



Fig. 3. (a) Square wave and (b) cyclic voltammetry profiles of  $1 \times 10^{-4}$  M of complex 3a in freshly distilled dry DMF containing 0.1 M TBABF<sub>4</sub> supporting electrolyte. SWV parameters: Step potential: 5 mV, amplitude: 50 mV vs. Ag|AgCl, frequency: 10 Hz. Scan rate: 100 m Vs<sup>-1</sup>.

#### Table 1

Summary of peak and half wave potentials, in volt vs. Ag|AgCl, of the new complexes in comparison with that of previously reported thio derivatised MnPc complexes. Values were recorded in DMF containing TBABF<sub>4</sub> unless otherwise stated.

Complex	$Mn^{II}Pc^{-2}/Mn^{II}Pc^{-3}$	$Mn^{III}Pc^{-2}/Mn^{II}Pc^{-2}$	$Mn^{III}Pc^{-1}/Mn^{III}Pc^{-2}$	$Mn^{IV}Pc^{-2}/Mn^{III}Pc^{-2}$	$Mn^{IV}Pc^{-1}/Mn^{IV}Pc^{-2}$	Reference
3a	-0.78	-0.07				TW
3b	-0.68	-0.04	+0.86 <sup>d</sup>			TW
MnODEAETPc(β)	-0.78	-0.12	+0.78			17
MnTMPyPc <sup>a</sup>		-0.057	+1.34			6
MnOPTPc <sup>a</sup>	-1.24	-0.46		+0.47	+0.75	11
MnTBMPc <sup>a</sup>	-0.98	-0.26	+0.83			13
MnTHHTPc( $\alpha$ ) <sup>b</sup>	-1.45	-0.16		+1.03		38
MnTHHTPc(β) <sup>b</sup>	-1.34	-0.16		+1.00		38
MnPc <sup>c</sup>	-0.69	-0.14	+0.87			3

<sup>a</sup> Values recorded in DCM, using TBABF<sub>4</sub>, TW = this work.

<sup>b</sup> Values (V vs. SCE) recorded in DMSO containing tetrabutylammonium perchlorate.

<sup>c</sup> Values (V vs. SCE) recorded in DMF containing tetraethlyammonium perchlorate. Where OPTPc = octa pentathio phthalocyanine; TBMPc = tetra benzylmercapto phthalocyanine (peripheral); TMPyPc = tetra mercaptopyridine phthalocyanine; THHTPc = tetrakis (6-hydroxyhexylthio) phthalocyanine; ODEAETPc = octakis-(2-diethy-laminoethanethio) phthalocyanine.

<sup>d</sup> Assignment not confirmed by spectroelectrochemistry.



**Fig. 4.** (a) Square wave and (b) cyclic voltammetry profiles of  $1 \times 10^{-4}$  M of complex **3b** in freshly distilled dry DMF containing 0.1 M TBABF<sub>4</sub> supporting electrolyte. SWV parameters: Step potential: 5 mV, amplitude: 50 mV vs. Ag|AgCl, frequency: 10 Hz. Scan rate: 100 m Vs<sup>-1</sup>.

90 mV vs. Ag|AgCl. The presence of weak oxidation signal, which was absent in complex **3a**, coupled with a reversible metal and ring-based reduction processes, suggest better electron transfer processes in complex **3b** than in **3a**. However, complex **3a** is more

difficult to reduce than **3b**. This observation clearly defines the impact of point of substitution on the voltammetry properties of these complexes. All the processes were confirmed by spectroelectrochemistry.

#### 3.3. Spectroelectrochemical studies

#### 3.3.1. Complex 3a

Fig. 5a and b show the spectral changes observed, on the application of potential slightly more negative of process II ( $E_{1/2}$  = -0.07 V, Fig. 3), in the presence of oxygen and when de-aerated with nitrogen, respectively. The µ-oxo species was not observed in the first spectrum in Fig. 5a unlike Fig. 1. This shows that the ratios of the various MnPc species in solution are dependent on condition such as the presence of electrolyte, among others. The Q-band (743 nm) of the initial spectrum (bold solid line) was different from that shown in Fig. 1 (739 nm), due to the presence of electrolyte used for spectroelectrochemical study. Upon reduction, a drastic decrease in intensity of the Q-band and collapse of the charge transfer bands between 450 and 550 nm were observed. suggesting the formation of Mn<sup>II</sup>Pc<sup>-2</sup> species [14]. The B bands shifted to lower wavelengths. However, since spectral transformations occurred in an oxygen-rich environment, peak due to Mn<sup>II</sup>Pc<sup>-2</sup> species was not observed. There was direct conversion of the  $Mn^{II}Pc^{-2}$  species to the MnPc  $\mu$ -oxo complex, evidenced by the emergence of intense peak at 636 nm. Interestingly, isobestic points were also observed at 555 and 669 nm, suggesting the presence of two species, the starting Mn<sup>III</sup>Pc<sup>-2</sup> and the electrogenerated MnPc µ-oxo species. Fig. 5b shows spectral changes observed with N<sub>2</sub> de-aerated solution of complex **3a** in DMF. The initial spectrum (bold solid line) is the same as that discussed in Fig. 5a. Upon reduction, the position of Q-band shifted to higher energy (from 743 to 692 nm) and the charge transfer bands between 450 and 550 nm collapsed. These spectral transformations are consistent with the reduction of  $Mn^{III}Pc^{-2}$  species and the formation of  $Mn^{II}Pc^{-2}$  species [14]. Attempts to preclude the formation of the MnPc µ-oxo species were not completely successful, trace of oxygen in the OTTLE cell resulted in the formation of MnPc μ-oxo species of weak intensity (second spectrum in Fig. 5b). Interestingly, the intensity of the peak due to the u-oxo species decreased while that due to Mn<sup>II</sup>Pc<sup>-2</sup> species became dominant as reduction of  $Mn^{III}Pc^{-2}$  species continued (Fig. 5b). The presence of diffuse isobestic points supports the fact that more than two species were present (the  $Mn^{11}Pc^{-2}$ ,  $Mn^{11}Pc^{-2}$  and  $MnPc \mu$ -oxo species). The complete absence of the  $Mn^{II}Pc^{-2}$  species during spectral transformations in Fig. 5a, as result of its direct conversion to the  $\mu$ -oxo complex, unlike that in Fig. 5b, clearly shows the effect of



**Fig. 5.** UV–Vis spectral changes observed for complex **3a** during controlled potential electrolysis at the potential more negative of process **II** (-0.10 V vs. Ag[AgCl) (a) in the presence of oxygen and (b) in N<sub>2</sub> de-aerated solution. Bold solid line (spectrum before electrolysis) and bold dashed line (spectrum after electrolysis). Electrolyte = DMF containing 0.1 M TBABF<sub>4</sub>.

the presence of oxygen on the electronic absorption spectra of MnPc complexes in the visible region, as discussed previously. The prevalence of MnPc  $\mu$ -oxo species was also observed for the OAcMnODEAETPc( $\beta$ ) complex, which is the octa-substituted derivative of complex **3a**, but was not too evident for complex **3b** below.

The number of electrons involved cannot be accurately determined as a result of the contribution of the  $\mu$ -oxo complex. Further reduction of the Mn<sup>II</sup>Pc<sup>-2</sup> using spectroelectrochemistry was not successful due to complications arising from the formation of the MnPc  $\mu$ -oxo species in Fig. 5. But in Table 1 we have assigned process I to ring-based process in comparison with complex **3b** below.

#### 3.3.2. Complex 3b

The spectral transformations shown in Fig. 6a were obtained on the application of potential more negative of process **II** (Fig. 4). The Q-band (778 nm) of the initial spectrum (bold solid line) is different from that shown in Fig. 1 (770 nm). The difference is usually associated with presence of electrolyte used for spectroelectrochemical studies. There was a blue-shift in Q-band (778 to 713 nm) upon reduction and a slight decrease in intensity of the charge transfer band around 511 nm. The B band decreased in intensity. The color of the complex also changed from red to green. There was no clear formation of the MnPc  $\mu$ -oxo species in Fig. 6a on reduction as was the case for complex **3a**. This implies restriction to coplanar association of the rings, via  $\mu$ -oxo-bridge, in complex **3b**, thus preventing the growth of the MnPc  $\mu$ -oxo complex. This is expected because of the sterically hindered nature of the non-peripheral position. This shows that the extent of the occurrence of the  $\mu$ -oxo complex in MnPc complexes depends largely on the position of substituent.

A shift in the position of Q-band with the same intensity is characteristic of metal-based electro reduction process. Specifically, blue-shift in Q-band (778–713 nm in this regard) is consistent with the reduction of  $Mn^{II}Pc^{-2}$  to  $Mn^{II}Pc^{-2}$  [14]. These spectral transformations (Fig. 6a) confirm the assignment of process **II** in Fig. 4 to  $Mn^{II}Pc^{-2}/Mn^{II}Pc^{-2}$  species. The number of electron transfer was calculated to be approximately 1 using Eq. (6)

$$Q = nFVC, \tag{6}$$

where, *n*, *F*, *V* and *C* are the number of electrons transferred, Faraday's constant, volume and concentration of the electroactive species, respectively. The species in Fig. 6a was further reduced on the application of potential more negative of process I (Fig. 4), Fig. 6b. There was a decrease in the intensity of the new peak and



**Fig. 6.** UV–Vis spectral changes observed for complex **3b** during controlled potential electrolysis at (**a**) -0.10 V (process **II**), (**b**) -0.75 V (process **I**) vs. Ag|AgCl. Bold solid line (spectrum before electrolysis) and bold dashed line (spectrum after electrolysis). Electrolyte = DMF containing 0.1 M TBABF<sub>4</sub>. The final spectrum in (**a**) is the starting spectrum in (**b**).

increase in the absorption intensity between 400 and 600 nm (531 nm), which are consistent with ring-based redox process in MPc complexes [36–38]. These spectral transformations are a confirmation that process I ( $E_{1/2} = -0.68$  V vs. Ag|AgCl, Fig. 4) is due to the formation of Mn<sup>II</sup>Pc<sup>-2</sup>/Mn<sup>II</sup>Pc<sup>-3</sup> species. The number of electrons transferred was estimated to be approximately 1 using Eq. (6).

The origin of process **III** (+0.86 V, Fig. 4b) was investigated on the application of potential slightly more positive of +0.86 V. There was gradual degradation of the complex (figure not shown) as reported previously for other thio-derivatised MPc complexes [39]. Therefore, we can not categorically assign process **III** to either ring oxidation ( $Mn^{III}Pc^{-1}/Mn^{III}Pc^{-2}$ ) or metal ( $Mn^{IV}Pc^{-2}/Mn^{III}Pc^{-2}$ ) oxidation.

#### 4. Conclusions

The syntheses and effect of point of substitution on the spectral, voltammetric and spectroelectrochemical properties of new manganese phthalocyanine complexes, peripherally (complex 3a) and non-peripherally (complex 3b) substituted with diethylaminoethanethio group are reported. The differences in spectral properties were explained in terms of position of substituent and existence of the MnPc µ-oxo complex. The difference in the position of substituent resulted in differences in voltammetry properties in terms of the number of observed processes, half wave potentials and cathodic to anodic peak separations. Based on these criteria, complex 3b was considered to have better voltammetry properties in terms of reversibility of the redox processes. Spectroelectrochemical studies were employed to confirm cyclic and square wave voltammogram assignments. Reduction of Mn<sup>III</sup>Pc<sup>-2</sup> to Mn<sup>II</sup>Pc<sup>-2</sup> species was complicated by the emergence of the MnPc  $\mu$ -oxo species for **3a** but not for **3b**. The presence of the MnPc  $\mu$ -oxo species was significantly affected by point of substitution on the complex and the concentration of oxygen in the solution of the complex being investigated.

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