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# Synthesis and electrochemical characterisation of new tantalum (V) alkythio phthalocyanines

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### ABSTRACT

The synthesis and electrochemical characterisation of octa-pentylthio (**4a**) and octa-octylthio (**4b**) – phthalocyaninato tantalum (III) hydroxide are hereby reported. These TaPc complexes absorb in the near infrared region (~800 nm in dichloromethane). They show good solubility in most common solvents especially non-viscous solvents such as dichloromethane and chloroform. NMR, mass and infrared spectroscopy and elemental analysis confirmed the structures and purity of the synthesised complexes. The cyclic voltammograms (CVs) showed reversible reduction couples and irreversible oxidation peaks. The latter exhibited adsorption behavior. The reduction processes were observed at -0.74 and -1.13 V (versus Ag|AgCl) for **4a**, and -0.67, -1.02 and -1.48 V (versus Ag|AgCl) for **4b**. Spectroelectrochemistry confirmed one metal reduction, with the rest of the redox processes being centered on the phthalocyanine ring.

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# 1. Introduction

Metallophthlocyanines (MPcs) have attracted a lot of attention for many years since their discovery in the early 1900s. Their remarkable properties that include flexibility, chemical and thermal stabilities, semiconductivity and photoconductivity [1,2] have been of great interest in research. Traditionally, phthalocyanines (Pcs) have been used as dyes and pigments. Currently, the focus of research on MPc complexes is directed to applications in material science [3-5]. These include Pcs as liquid crystals [6-8], Langmuir–Blodgetts films [9–11], electrochemical sensors [12–14] and fuel cells [15]. Phthalocyanines with sulfur substituents generally absorb in the near infrared (NIR) region [16]. Pcs absorbing in the NIR region to match the 780 and 830 nm semiconductor lasers are used for optical data storage (ODS) whilst for security applications, Pcs employed cover the 700-1000 nm region [16-18]. Thiol substituted MPcs may be used to modify gold electrode surfaces for sensor applications [19–21], where there is a spontaneous formation of SAMs due to the strong gold-sulfur interactions. Thus the synthesis of thio derivatized Pc complexes is of importance for many practical applications.

Even though MPc complexes containing transition metals have been extensively studied, very little is known about tantalum phthalocyanines due to synthetic challenges. The difficulty arises from the fact that Ta–N distances in TaPc are  $\sim$ 2.17 Å (compared to Fe–N of 1.93 Å in FePc) [22,23], while the phthalocyanine cavity has an N–N distance of 3.96 Å [22], making it difficult for Ta to fit into the Pc cavity.

This results in highly unsymmetrical MPcs that are somewhat unstable. The synthesis and X-ray crystal structure of an unsubstituted TaPc have been reported before [23], and the electrochemical behavior of unsubstituted TaPc has been reported by our group [24]. Ring substituted TaPc derivatives are unknown and are reported here for the first time.

This work reports on the syntheses of non peripherally alkylthiol substituted TaPc complexes. MPcs with electron donating substituents, in particular sulfur substituted MPcs often show interesting electrochemistry that involves the central metal, the Pc ring and the substituents on the Pc ring. This has therefore motivated the study in this work.

# 2. Experimental

# 2.1. Materials

Acetone, tantalum (V) butoxide, dimethylsulfoxide (DMSO), 1pentanethiol, 1-octanethiol, tantalum butoxide, 1,8-diazabicyclo{5.4.0}-undec-7-ene (DBU) and 1-pentanol were purchased from Sigma–Aldrich. Potassium carbonate, ammonium ferrous sulfate, deuterated chloroform (CDCl<sub>3</sub>), 2,3-dicyanohydroquinone (**1**), *p*-toluenesulfonylchloride, tetrahydrofuran (THF), toluene, chloroform and dichloromethane (DCM) were procured from Merck. Tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) was purchased from Sigma–Aldrich.



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#### 2.2. Equipment

Column chromatography was performed on silica gel 60 (0.04–0.063 mm) and preparative thin layer chromatography was performed on silica gel 60 P  $F_{254}$ . Ground state electronic absorption spectra were performed on a Varian Cary 500 UV–Vis–NIR spectro-photometer, infrared spectra (KBr pellets) on Perkin–Elmer Spectrum 2000 FT-IR Spectrometer and <sup>1</sup>H nuclear magnetic resonance signals on a Bruker EMX 400 NMR spectrometer. Elemental analysis was performed at Rhodes University using a Vario-Elementar Microcube ELIII. MALDI-TOF mass spectrometry was carried out at the University of Stellenbosch using an ABI Voyager DE-STR MALDI-TOF instrument.

#### 2.3. Electrochemical methods

Cvclic (CV) and square wave (SWV) voltammetry 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, Eco Chemie), using a conventional three-electrode system. A glassy carbon electrode (GCE, 3.0 mm diameter) was used as the working electrode. Silver-silver chloride (Ag|AgCl) and platinum wire were used as pseudo-reference and counter electrodes, respectively. Electrochemical experiments were performed in dry DCM containing TBABF<sub>4</sub> as the supporting electrolyte. Prior to scans, the working electrode was polished with alumina paste on a Buehler felt pad. This was followed by washing with de-ionised water. Spectroelectrochemical data was recorded using an optically transparent thin-layer electrochemical (OTTLE) cell which was connected to a Bioanalytical System (BAS) CV 27 voltammograph.

## 2.4. Synthesis

A procedure similar to that reported in literature [25,26] was employed for the synthesis of phthalonitriles (**2** and **3**) with slight alterations as follows.

# 2.4.1. 3,6-Bis(4'-methylphenylsulfonyloxy) phthalonitrile (**2**), Scheme 1

p-Toluenesulfonyl chloride (10.32 g, 27 mmol) was added to a mixture of 2,3-dicyanohydroquinone (1) (4.04 g, 12.5 mmol) and potassium carbonate (13.8 g, 50 mmol) in acetone (15 ml). The mixture was refluxed for 2 h. Thin layer chromatography (TLC) was performed to determine the consumption of 2,3-dicyanohydroquinone. The mixture was cooled to room temperature, poured to water (40 ml) and stirred for 1 h in water. The light brown product was filtered and oven dried to give 2. Yield: 9.51 g (79%) IR [(KBr)  $v_{max}/cm^{-1}$ ]: 3432, 3239, 3085, 2243, 2226 (CN), 1504, 1449, 1315, 1279, 1204, 1174, 1142, 1021, 1004, 979, 934, 847, 749, 694, 638, 614.

# 2.4.2. 3,6-Di(pentylthio)-4,5-dicyanobenzene (3a), Scheme 1

1-Pentanethiol (2.39 g, 22.9 mmol) was dissolved in DMSO under a nitrogen atmosphere and 3,6-bis(4'-methylphenylsulfonyloxy) phthalonitrile (**2**) (4.30 g, 9.18 mmol) was added. The mixture was stirred for 15 min and finely ground anhydrous potassium carbonate (5.07 g, 36.7 mmol) was added in portions for 2 h while stirring. The mixture was stirred under a nitrogen atmosphere for a further 12 h. Water was added and the aqueous phase extracted using chloroform ( $3 \times 50$  ml). The extracts were further treated with 5% sodium carbonate solution ( $2 \times 250$  ml). The solution was further treated with water ( $2 \times 250$  ml) and the solvent was evaporated off using a rotavapor. The product **3a** was recrystallised from ethanol. Yield: 2.19 g (71.7%). IR [(KBr) $\nu_{max}/cm^{-1}$ ]:

3084, 2951, 2930, 2864, 2378(S−C), 2225(C≡N), 1444, 1283, 1202, 1181, 1173, 1145, 877, 847, 827, 725, 547, 447.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): *δ*, ppm 7.49 (2-H, s, Ar–H), 2.99–3.02 (4-H, t, – CH<sub>2</sub>), 1.63–1.71 (4-H, m, –CH<sub>2</sub>), 1.37–1.46 (4-H, m, –CH<sub>2</sub>), 1.28– 1.36 (4-H, m, –CH<sub>2</sub>), 0.88–0.91 (6-H, t, –CH<sub>3</sub>).

# 2.4.3. 3,6-Di(octylthio)-4,5-dicyanobenzene (3b), Scheme 1

Synthesis and purification of **3b** were similar to that of compound **3a**, except 1-octanethiol was used instead of 1-pentane thiol. The amounts of reagents employed were: 1-octanethiol (2.39 g, 16.3 mmol), 3,6-bis(4'-methylphenylsulfonyloxy) phthalonitrile (**2**) (4.30 g, 9.18 mmol), ground anhydrous potassium carbonate (5.07 g, 36.7 mmol). Yield: 1.79 g, (58.1%). IR [(KBr) $\nu_{max}/$  cm<sup>-1</sup>]: 2920, 2850, 2388(S–C), 2225(C=N), 2023, 1637, 1466, 1422, 1204, 1143, 1032.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ, ppm 7.40 (2-H, s, Ar–H), 2.98–3.10 (4-H, t, – CH<sub>2</sub>), 1.62–1.75 (4-H, m, –CH<sub>2</sub>), 1.61–1.50 (4-H-broad m, –CH<sub>2</sub>), 1.40–1.52 (4-H, m, –CH<sub>2</sub>), 1.21–1.38 (18-H, m, –CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

# 2.4.4. 1,4,8,11,15,18,22,25-Octapentylthiophthalocyaninato tantalum (V) butoxide (**4a**, (OH)<sub>3</sub>TaOPTPc), Scheme 1

3,6-Dipentylthiophthalonitrile (**3a**) (0.8 g, 1.20 mmol) in 1pentanol (7.0 ml) was refluxed under a nitrogen atmosphere and tantalum (V) butoxide (0.138 g, 0.34 mmol) was added. After the addition of DBU (0.30 ml, 0.86 mmol), the reaction was continued for 6 h. The mixture was cooled and column chromatography over silica was done with CHCl<sub>3</sub> as eluent. Yield: 0.25 g (42%). UV–Vis (DCM):  $\lambda_{max}$  (nm) (log  $\varepsilon$ ) 276(6.36) 348(5.62) 722(5.44) 814 (5.81). IR [(KBr)  $\nu_{max}/cm^{-1}$ ]: 3290 (OH), 2922, 2852, 2350, 1561, 1459, 1361, 1310, 1279, 1156, 109, 932, 908(Ta–O), 750 (C–S–C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ , ppm 7.65 (8H, s, Ar–H), 3.20 (16H, broad s, S–*CH*<sub>2</sub>), 1.89 (16H, quintuplet, *CH*<sub>2</sub>), 1.61 (16H, quintuplet, *CH*<sub>2</sub>), 1.50 (16H, sextuplet, *CH*<sub>2</sub>), 1.0 (24H, t, *CH*<sub>3</sub>). *Anal.* Calc. C<sub>72</sub>H<sub>99</sub>N<sub>8</sub>S<sub>8</sub>O<sub>3</sub>Ta: C, 55.36; H, 6.38; N, 7.17. Found: C, 55.45; H, 7.21; N, 7.92%. MALDI-TOF MS *m/z*: Calcd: 1561.52 amu. Found: (M–Ta) 1330 amu.

# 2.4.5. 1,4,8,11,15,18,22,25-Octaoctylthiophthalocyaninato tantalum (V) butoxide (**4b**, (OH)<sub>3</sub>TaOOTPc), Scheme 1

Synthesis and purification of **4b** were similar to that of compound **4a**, except **3b** was employed instead of **3a**. The amounts of reagents employed were: 3,6-dioctylthiophthalonitrile (**3b**) (0.81 g, 1.20 mmol, 1-pentanol (~8 ml), tantalum (V) butoxide (0.139 g, 0.34 mmol), DBU (0.30 ml, 0.86 mmol). Yield 0.31 (48%). UV–Vis (DCM):  $\lambda_{max}$  (nm) (log  $\varepsilon$ ) 416(3.82) 662(4.00) 609(3.73) 717 (4.41), 814 (5.76). IR [(KBr)  $\nu_{max}/cm^{-1}$ ]: 3419 (OH), 2955, 2920, 2850, 2538, 2400, 1637, 1563, 1432, 1368, 1312, 1281, 1223, 1181, 1142, 1091, 1031, 910, (Ta–O), 867, 787, 751 (C–S–C), 720. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ , ppm 7.51 (8H, s, Ar–H), 3.2 (16H, broad s, S–*CH*<sub>2</sub>), 1.90 (32H, quintuplet, *CH*<sub>2</sub>), 1.79 (32H, quintuplet, *CH*<sub>2</sub>), 1.05 (56H, sextuplet, *CH*<sub>2</sub>*CH*<sub>3</sub>*C*, *Anal.* Calc. C<sub>96</sub>H<sub>147</sub>N<sub>8</sub>S<sub>8</sub>O<sub>3</sub>Ta: C, 60.72; H, 7.80; N, 5.90. Found: C, 60.92; H, 8.41; N, 6.42%. MALDI-TOF MS *m/z*: Calcd: 1898.16 amu. Found: (M–Ta) 1666.5 amu.

#### 3. Results and discussion

#### 3.1. Synthesis and characterisation

Scheme 1 gives the synthesis pathways for the TaPc complexes discussed in this work. 3,6-Bis(4'-methylphenylsulfonyloxy) phthalonitrile (**2**), was used to prepare 3,6-disubstituted phthalonitrile derivatives (**3a** and **3b**), through base-catalysed nucleophilic aromatic displacement. The reactions were carried out in DMSO at room temperature and gave yields of 71.7% for **3a** and 58.1%



Scheme 1. Synthesis of tantalum [M = (OH)<sub>3</sub>Ta<sup>V</sup> for 4a and 4b] non peripherally substituted phthalocyanine. Complexes 5a (M = OV<sup>IV</sup> [30]) 6a (M = OTi<sup>IV</sup> [29]) and 7a (M = AcMn<sup>III</sup> [29]). Ac = acetate.

for **3b**. The syntheses of TaPc complexes  $[(OH)_3TaOPTPc,$ **4a** and  $(OH)_3TaOOTPc,$ **4b**] were achieved by treatment of substituted 3,6-dicyanobenzenes **3a** and **3b** with anhydrous tantalum (V) butoxide in 1-pentanol in the presence of DBU (Scheme 1). DBU acts as a nucleophilic base which allows the reaction to proceed under mild conditions while preventing the formation of side products typical of reactions that use strong bases [27]. Tantalum is a large metal that does not fit perfectly in a phthalocyanine core center. It therefore needs high energy to insert it into the phthalocyanine ring. Thus, a solvent with a high boiling point, 1-pentanol, was used to achieve this purpose. Column and preparative thin

layer chromatography with silica gel were employed to obtain the pure products from the reaction mixtures. The synthesised complexes [(OH)<sub>3</sub>TaOPTPc, **4a** and (OH)<sub>3</sub>TaOOTPc, **4b**] show good solubility in organic solvents such as dichloromethane, chloroform and chloronaphthalene. The tantalum derivatives were characterized by UV–Vis, IR, mass and NMR spectroscopies. The analyses are consistent with the predicted structures as shown in the experimental section. After conversion into TaPc complexes, the characteristic C=N stretch at 2225 cm<sup>-1</sup> of 1,2-dicyanobenzenes **3a** and **3b** disappeared, indicative of metallophthalocyanine formation. The formation of (OH)<sub>3</sub>TaPc (containing OH instead of butoxy



Fig. 1. <sup>1</sup>H NMR spectrum of complex 4a.

groups) could be a result of the purification process. The presence OH was proved by infrared spectroscopy. C–S–C vibrations were observed at  $\sim$ 750 cm<sup>-1</sup> [28].

The substituted **TaPc** derivatives were found to be pure by <sup>1</sup>H NMR with all the substituents and ring protons observed in their respective regions, Fig. 1. This figure shows a clean <sup>1</sup>H NMR spectrum confirming the purity of the complex. The pentylthio substituted complex **4a** showed the resonances belonging to ring protons as a singlet at 7.65 ppm. Similarly, the octylthio substituted complex **4b** showed the resonances belonging to ring protons as a singlet at 7.51 ppm. Mass spectral studies confirmed the loss of Ta since as already stated Ta is a large metal and it does not fit properly into the cavity of a phthalocyanine core. Ta ion is vulnerable to displacement if exposed to harsh conditions such as during ionisation in mass spectrometry hence the observed mass. However, elemental analyses unequivocally confirmed the formation of the complexes.

The ground state electronic absorption spectra  $[(OH)_3 TaOPTPc$ , **4a** and  $(OH)_3 TaOOTPc$ , **4b**] show sharp Q bands (Fig. 2a and b), typical of unaggregated MPc complexes Beer's law was obeyed for concentrations ranging from  $1.85 \times 10^{-7}$  to  $2.28 \times 10^{-5}$  mol dm<sup>-3</sup>. The Q bands were observed at 808 and 812 nm in DCM for  $[(OH)_3 TaOPTPc$  and  $(OH)_3 TaOPTPc$ ], respectively.

The Q bands were relatively red-shifted when compared to unsubstituted TaPc [24] (Q band at 697 nm chloroform), Table 1. This is typical of MPcs with substituents on the non-peripheral position and also characteristic of MPc containing sulfur substituents. Considering the same solvent (CHCl<sub>3</sub>) and the same substituent, MnPc derivative (**7a**) [29] shows the most red shifted Q band, Table 1 (Fig. 3), followed by OVPc derivative [30]. Fig. 3 shows that the red shift is related to some extend on the ionic radii of the central metal ion, with tantalum being an exception.

The Q band is more red shifted in chlorinated solvents: CHCl<sub>3</sub>, 1-CNP and DCM. It has been reported before that there is more red



**Fig. 2.** Ground state electronic absorption spectra of TaPc complexes **4a** (a) and **4b** (b) in (i) CHCl<sub>3</sub>, (ii) chloronaphthalene, (iii) DCM, (iv) THF, (v) toluene.  $\sim$ Concentrations = 1 × 10<sup>-5</sup> M.

#### Table 1

UV-Vis spectra (Q bands only) of MPc derivatives (4a, 4b, 5, 6 and 7) derivatives in various solvents.

Complex	Solvent	Q band (nm)	Ref.
4a	Toluene THF DCM 1-CNP CHCl <sub>3</sub>	795 804 808 810 809	This work
4b	Toluene THF DCM 1-CNP CHCl <sub>3</sub>	794 800 812 815 809	This work
TaPc	CHCl <sub>3</sub>	697	25
<b>5a</b> (M = OV <sup>IV</sup> )	Toluene THF DCM CHCl <sub>3</sub>	830 834 850 841	29
<b>6a</b> (M = OTi <sup>IV</sup> )	DCM	774	28
<b>7a</b> (M = AcMn <sup>III</sup> ) <sup>a</sup>	DCM	908	28

<sup>a</sup> Ac = acetate.



**Fig. 3.** Relationship between the ionic radii of central metal ions and the red-shift of *Q* bands (*Q* band values ion chloroform).

shifting in chlorinated solvents [31]. The reported [32,33] trend based on the solvents' refractive index is not observed in Table 1.

## 3.2. Voltammetric and spectroelectrochemical characterisation

The cyclic [CV(a)] and square wave [SWV(b)] voltammetries for TaPc complexes **4a** and **4b** are shown in Figs. 4 and 5, respectively. These were performed in de-aerated DCM with TBABF<sub>4</sub> as the supporting electrolyte. The oxidation of these complexes was expected to occur at the ring and this was confirmed by spectroelectrochemistry as discussed below. For unsubstituted TaPc complex no oxidation peaks were observed [24] due to the fact that Ta<sup>V</sup> has a high oxidation state, which makes ring oxidation more difficult. The electro-rich alkylthio substituents in this work contributed to the ease of oxidation of the ring, since these substituents enhance electron density on the ring thus making it easy for oxidation to occur. Hence oxidation peaks are observed.

The cyclic and square wave voltammograms of complex **4a**, Fig. 4, show two reduction processes labelled III and IV at half-wave ( $E_{1/2}$ ) potentials of -0.74 and -1.13 V versus Ag|AgCl, respectively. The ratio of anodic to cathodic current ( $I_{pa}/I_{pc}$ ) was near unity for the two couples. The cathodic and anodic peak separations ( $\Delta E$ ) of 70 mV (similar to that of the ferrocene standard) for couples, III and IV, suggests reversibility due to fast electron transfer process. For all the reduction couples, the plots of peak currents



Fig. 4. Square wave (a), cyclic (b) voltammograms for complex 4a in DCM containing 0.1 M TBABF<sub>4</sub>. (c) Cyclic voltammgrams observed when recording from 0 V to negative or positive potentials. Scan rate = 100 mV/s.

 $(i_p)$  versus the square root of scan rate  $(v^{1/2})$  were linear suggesting that the processes were diffusion controlled. Compared to other octa pentyl-thio alpha substituted MPc complexes in Table 2, **4a** (Ta) and **6a** (Ti) are more difficult to reduce. The first reduction in all of the complexes containing the pentylthio substituent at the non-peripheral position of the Pc ring (**4a** to **7a**) occurs at the central metal. The second reduction occurs at the ring in all complexes except for OTiPc derivative (**6a**).

The oxidation of **4a** consists of irreversible processes with sharp peaks due to adsorption processes, Fig. 4. Process II has a broad pre-peak followed by a sharp peak typical of adsorption [34,35]. It is known [34] that the adsorption of a product of the electrode reaction results in the formation of a sharp peak preceded by a more regular peak, the latter being due to the diffusion of the electroactive species from solution to the electrode. On return scan, a sharp peak appeared for process II, Fig. 4b. Smaller mainly irreversible oxidation peaks are observed at larger oxidation potentials (process I). The irreversibility of oxidation processes and the adsorption behavior was also reported for OTiPc complex **6a** [30]. The SWV shows a very broad oxidation feature. Table 2 shows that in general, irreversible oxidations are observed for octapentylthiol derivatives. The irreversibility of alkyl or arylthio substituted MPc complexes in general is well documented [36,37]. There was no change in the shape oxidation processes when the potential was scanned from 0 V to negative or positive potentials, Fig. 4c.

Three reduction processes labelled III, IV and V were observed at  $E_{1/2}$  of -0.67, -1.02 and -1.48 V versus Ag|AgCl, respectively, for complex **4b**, Fig. 5. The anodic and cathodic peak separations ( $\Delta E$ ) for couples III was 60 mV, suggesting reversibility. The reduction currents for III and IV are larger than for V, suggesting the possibility of different number of electrons transferred. However, chronocoulometric analysis did not show significant differences in the number of electrons involved. The lower currents for V could be a result of the fact that this couple is at high negative potentials and hence near the limits of the electrode/electrolyte system, which may affect this peak. The effects of the limits of the system are clearer on the SWV.

Comparing the reduction potentials of **4b** with those of **4a**, shows that the former has potentials at less negative values, resulting in the shift of couple V to less negative values, hence to be located within the potential window in Fig. 5.

In order to further determine the nature of the redox processes for complex **4a** and **4b**, spectroelectrochemistry was performed in an optically transparent thin-layer electrochemical (OTTLE) cell. Fig. 6a shows the observed spectral changes for complex **4a** at potentials more negative of process III (-0.8 V versus Ag|AgCl) in DCM containing TBABF<sub>4</sub> as a supporting electrolyte. Upon reduction, the spectral changes observed include a shift of the *Q* band from 808 to 770 nm, with a slight decrease in the intensity of the *Q* band. There was also an emergence of new peaks at ~450 nm



**Fig. 5.** Square wave (i) and cyclic (ii) voltammograms for complex **4b** in DCM containing 0.1 M TBABF<sub>4</sub>. Scan rate = 100 mV/s.

and a slight change of colour of the solution in the OTTLE cell from purple to blue. Diffuse isosbestic points were observed suggesting the presence of more than one species in solution. The lack of clear isosbestic points could be a result of change of axial ligands during the reduction process. In related Ta porphyrin derivatives, axial ligand exchange reactions readily occur in slightly acid media [38]. The spectral changes observed in Fig. 6 consist of a shift in the Q band to shorter wavelengths, without the drastic decrease in intensity. These spectral changes are typical of redox processes occurring at the central metal [22], whereby the Q band shifts without a drastic decrease in intensity. The *n* value calculated for reduction of **4a** at potentials of process III processes was approximately ~1 using Eq. (1):

$$Q = nFCV \tag{1}$$

where n is the number of electrons involved; F, Faraday's constant; C, solution concentration and V, volume of the solution.

From the discussion above, process III can be associated with the reduction  $Ta^{V}Pc^{-2}$  to  $Ta^{IV}Pc^{-2}$ . Further reduction at potentials more negative of process IV (-1.2 V versus Ag|AgCl), Fig. 6b, resulted in a decrease in the intensity (without shifting in position)



**Fig. 6.** Observed UV–Vis spectral changes for complex **4a** at potentials (a) -0.8 V (process III), (b) -1.2 V (process IV) and (c) 1.1 V (process II), in DCM with 0.1 M TBABF<sub>4</sub>. Solid red line; before and dotted red line; after application of the appropriate potential. The last scan in (a) is the same as the first scan in (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the Q band and the appearance of new peaks between 500 and 650 nm together with diffuse isosbestic points near 665 and

Table 2

Electrochemical data (half-wave potential, E<sub>1/2</sub>, unless otherwise stated) for MPc derivatives (4a, 4b, 5, 6 and 7) in DCM containing TBABF<sub>4</sub>. Potentials vs. Ag|AgCl.

Redox process $(E_{1/2})$	4a	4b	<b>5a</b> (M = OV <sup>IV</sup> ) <sup>a</sup>	<b>6a</b> (M = OTiIV) <sup>b</sup>	<b>7a</b> (M = AcMn <sup>III</sup> ) <sup>b</sup>
Reduction 1	$\begin{array}{l} - \ 0.74 \\ Ta^{V}Pc^{-2}/Ta^{IV}Pc^{-2} \end{array}$	-0.67 Ta <sup>V</sup> Pc <sup>-2</sup> /Ta <sup>IV</sup> Pc <sup>-2</sup>	$-0.58 \\ V^{IV}Pc^{-2}/V^{III}Pc^{-2}$	-0.73 (Ti <sup>IV</sup> Pc <sup>-2</sup> /Ti <sup>III</sup> Pc <sup>-2</sup> )	-0.46 (Mn <sup>III</sup> Pc <sup>-2</sup> /Mn <sup>II</sup> Pc <sup>-2</sup> )
Reduction 2	-1.13 Ta <sup>IV</sup> Pc <sup>-2</sup> /Ta <sup>IV</sup> Pc <sup>-3</sup>	-1.02 Ta <sup>IV</sup> Pc <sup>-2</sup> /Ta <sup>IV</sup> Pc <sup>-3</sup>	$-0.93 \\ V^{III}Pc^{-2}/V^{III}Pc^{-3}$	-1.09 Ti <sup>III</sup> Pc <sup>-2</sup> /Ti <sup>II</sup> Pc <sup>-2</sup>	-1.24 (Mn <sup>II</sup> Pc <sup>-2</sup> /Mn <sup>II</sup> Pc <sup>-3</sup> )
Reduction 3		-1.48 Ta <sup>IV</sup> Pc <sup>-3</sup> /Ta <sup>IV</sup> Pc <sup>-4</sup>	$\begin{array}{c} -1.18 \\ V^{III}Pc^{-3}/V^{III}Pc^{-4} \end{array}$		
Oxidation processes	0.37, 0.57 ( <i>E</i> <sub>P</sub> )	0.47, 0.59, 0.99 ( <i>E</i> <sub>P</sub> )	$\begin{array}{l} 0.59 \\ V^{IV} \ Pc^{-2} / V^{IV} Pc^{-1} \\ 0.97 \\ V^{IV} \ Pc^{-1} / V^{IV} Pc^{0} \end{array}$	0.54, 0.36, 0.95	$\begin{array}{l} 0.47 \; (Mn^{IV} \\ Pc^{-2}/Mn^{III}Pc^{-2}) \\ 0.75 \\ (Mn^{IV}Pc^{-1}/Mn^{IV}\;Pc^{-2}) \end{array}$

<sup>a</sup> Data from Ref. [29].

<sup>b</sup> Data from Ref. [30], Ac = acetate.

490 nm. These changes are typical of ring reduction processed [39], i.e. Ta<sup>IV</sup>Pc<sup>-2</sup> is reduced to Ta<sup>IV</sup>Pc<sup>-3</sup>. The regeneration (to ~72%) of the initial species was achieved, confirming the reversibility of the couples. Application of the potentials more positive of process II, resulted in spectral changes shown in Fig. 6c consisting of a decrease in the Q band with no new peaks forms indicative of the degradation of the complex confirming irreversibility of the oxidation processes. However, the oxidation peaks are attributed to the Pc ring and the substituents, since no oxidation is expected on the central metal.

Similarly, spectroelectrochemical experiments were performed for the further investigation of the redox processes observed for complex **4b**. Fig. 7a shows the observed spectral changes for complex **4b**, at potentials more negative of process III (-0.7 V versus AglAgCl). The changes consisted of a shift of the O band from 814 to 765 nm, with an increase in the intensity, the emergence of new peaks at  $\sim$ 460 nm and a change of colour of the solution in the OTTLE cell from purple to blue were observed. Again isosbestic points were diffuse, due to possible axial ligation as discussed above for 4a. The observed changes are typical of redox processes occurring at the central metal [22] as discussed for 4a. Therefore, process III can be attributed to the reduction  $Ta^{V}Pc^{-2}$ to  $Ta^{IV}Pc^{-2}$ . Further reduction at potentials of process IV (-1.1 V versus Ag|AgCl), Fig. 7b, resulted in a decrease in the intensity of the Q band and the appearance of new absorptions in the 600 nm region, together with clear isosbectic points at 670 nm. These spectral changes are typical of ring reduction processed [39], i.e.  $Ta^{IV}Pc^{-2}$  is reduced to  $Ta^{IV}Pc^{-3}$ . Again, the regeneration of the initial species of  $\sim$ 69% was achieved, confirming some reversibility of the couples. Process IV is attributed to further ring reduction.



**Fig. 7.** Observed UV–Vis spectral changes for complex **4b** at potentials (a) -0.7 V (process III) and (b) -1.02 V (process IV) in DCM with 0.1 M TBABF<sub>4</sub>. Solid red line; before and dotted red line; after application of the appropriate potential. The last scan in (a) is the same as the first scan in (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Oxidation is expected to occur only on the ring for these complexes.

Based on the electrochemical observations described above the assignments for processes I–IV for complex **4a** are as follows:

$Ta^VPc^{-1} \rightarrow Ta^VPc^0 + e^-$	(Process I)
$Ta^VPc^{-2} \rightarrow Ta^VPc^{-1} + e^-$	(Process II)
$Ta^VPc^{-2} + e^- \rightarrow Ta^{IV}Pc^{-2}$	(Process III)
$Ta^{IV}Pc^{-2} + e^- \rightarrow Ta^{IV}Pc^{-3}$	(Process IV)

Similarly, processes for complex 4b are assigned as follows:

$Ta^VPc^{-2}  ightarrow Ta^VPc^{-0} + e^-$	(Process I)
	(110000331)

$$Ta^{V}Pc^{-2} \rightarrow Ta^{V}Pc^{-1} + e^{-}$$
 (Process II)

$$Ta^{V}Pc^{-2} + e^{-} \rightarrow Ta^{IV}Pc^{-2}$$
 (Process III)

$$Ta^{IV}Pc^{-2} + e^{-} \rightarrow Ta^{IV}Pc^{-3}$$
 (Process IV)

$$\Gamma a^{IV} P c^{-2} + e^{-} \rightarrow T a^{IV} P c^{-4}$$
 (Process V)

The multi-electron transfer process which was observed for the unsubstituted TaPc is not observed in this work [24] for complexes **4a** and **4b**, probably due to differences in geometry.

# 4. Conclusion

The synthesis of alkylthio substituted TaPc derivatives was successfully carried out. These complexes were relatively red shifted, absorbing at wavelengths over 800 nm in CHCl<sub>3</sub>, due to the presence of alkylthio substituents at the non-peripheral positions. The reduction couples for both complexes **4a** and **4b** were reversible, however, oxidation processes are irreversible in most cases. Spectroelectrochemistry confirmed one metal reduction, with the rest of the redox processes being centered on the phthalocyanine ring.

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