Electrochemical characterisation of tetra- and octa-substituted oxo(phthalocyaninato)titanium(IV) complexes

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Abstract

The synthesis and electrochemical characterisation of the following oxotitanium tetra-substituted phthalocyanines are reported: 1,(4)-(tetrabenzyloxyphthalocyaninato)titanium(IV) oxide (5a); 1,(4)-{tetrakis[4-(benzyloxy)phenoxy]phthalocyaninato}titanium(IV) oxide (5b); 2,(3)-(tetrabenzyloxyphthalocyaninato)titanium(IV) oxide (6a) and 2,(3)-{tetrakis[4-(benzyloxy)phenoxy]phthalocyaninato}titanium(IV) oxide (6b). The electrochemical characterisation of complexes octa-substituted with 4-(benzyloxy)phenoxy (9b), phenoxy (9c) and *tert*-butylphenoxy (9d) groups is also reported. The cyclic voltammograms of the complexes exhibit reversible couples I–III and couple IV is quasi-reversible for complexes 5a, 5b, 6a and 6b. The first two reductions are metal-based processes, confirmed by spectroelectrochemistry to be due to $Ti^{IV}Pc^{2-}/Ti^{III}Pc^{2-}$ and $Ti^{III}Pc^{2-}/Ti^{II}Pc^{2-}$ redox processes and the last two reductions are ring-based processes due to $Ti^{II}Pc^{2-}/Ti^{II}Pc^{3-}$ and $Ti^{II}Pc^{3-}/Ti^{II}Pc^{4-}$. Chronocoulometry confirmed a one-electron transfer at each reduction step. The electrochemistry of the above complexes is also compared to the previously reported 5c, 5d, 6c and 6d.

1. Introduction

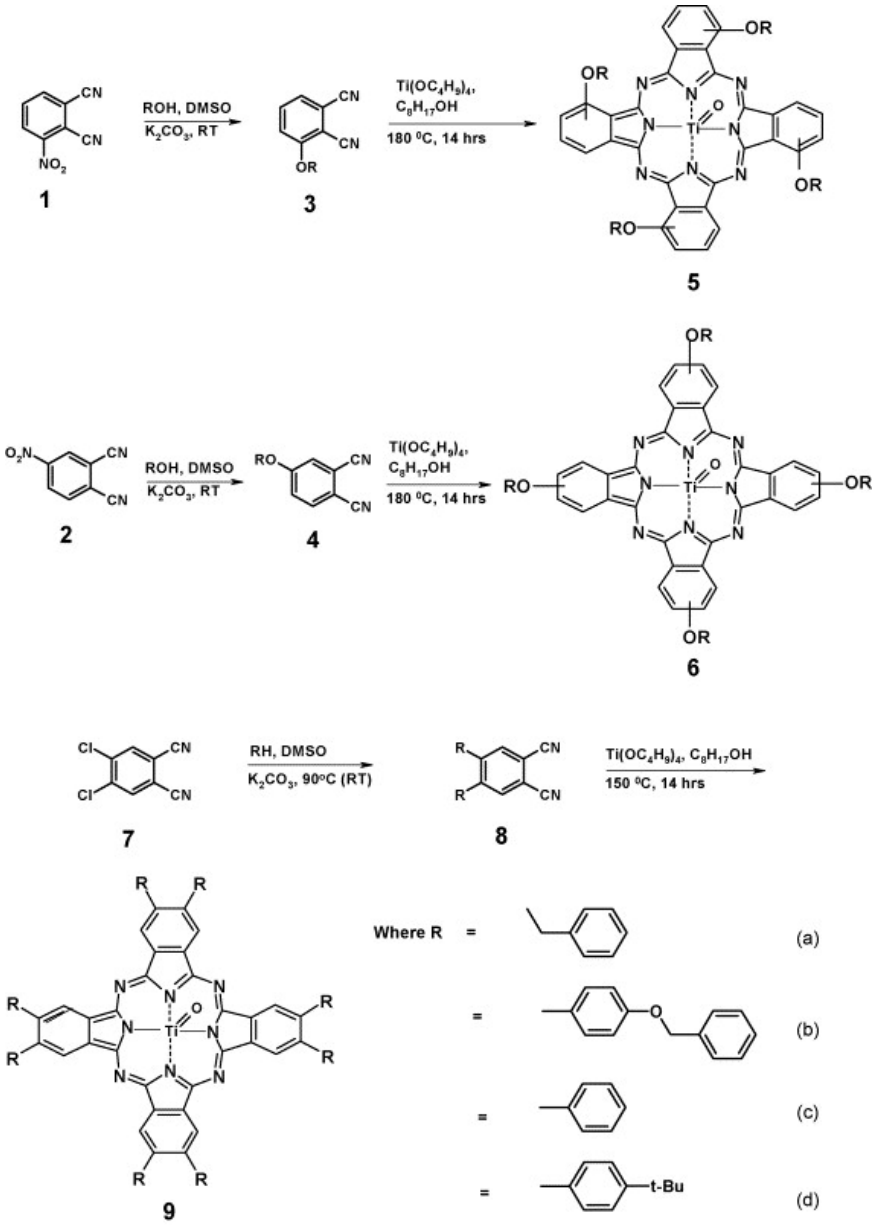
Over the past 7 decades metallophthalocyanines (MPcs) have been extensively studied [1], [2] and [3]. Phthalocyanines have attracted a great deal of attention due to their intense colour and diverse redox chemistry associated with both the 18π electron system of the phthalocyanine (Pc) ring and the central metal atom. The high chemical inertness and thermal stability of MPcs have led to the exploration of their technological utility as industrial dyes, catalysts [4], in gas diffusion electrodes [5], as biosensors [6], as photosensitizers for photodynamic therapy of cancer [7], [8] and [9] and in non-linear optics [10] and [11].

The chemistry and especially the electrochemistry of titanium phthalocyanines (TiPcs) is growing [12], [13], [14], [15], [16], [17], [18], [19], [20], [21] and [22], though their properties are relatively unexplored compared to other first row transition MPcs. There is, thus, a considerable interest in the full development of the chemistry and applications of these complexes. Unsubstituted oxotitanium phthalocyanine (OTiPc), a well-known near-IR-active photoconductive dye, was first synthesised by Taube [23]. Owing to the poor solubility of OTiPc in common organic solvents, its spectroscopic data is extremely limited. Properties of these macrocycles can be tailored through substitution on the periphery and at the same time, their solubility is enhanced such that many applications are facilitated. Solubility is more enhanced for tetra-substituted Pc derivatives than the corresponding octa-substituted derivatives due to their lower degree of order in the solid state [24], as well as the formation of constitutional isomers and the high dipole moment that results from the unsymmetrical arrangement of the substituents at the periphery [24] and [25].

Substituents at the sites α to the point of fusion to the heterocyclic ring cause the Q-band to be further shifted into the red [26], [27] and [28]. Substitution at this more sterically crowded non-peripheral position also reduces aggregation tendencies more than substitution at the peripheral position [29], [30], [31], [32] and [33]. Introduction of different kinds of substituents onto the periphery and changing the central metal can alter spectroscopic and electrochemical properties. In fact, the choice of substituents and metal strongly influence the electrochemical properties of these macrocycles. For example, multi-electron redox processes are common in biological systems and are needed for reduction of species such as carbon dioxide and oxygen. Hence, the study of the electrochemistry of MPc complexes, which show potential as catalysts for multi-electron processes such as TiPc [13] is essential. One-step two electron processes are rare but have been reported in some MPc complexes [2]. We have reported on TiPc complexes with overlapped reduction processes, hence showing a cyclic voltammetry with currents representative of two electrons [13]. Overlapping or one-step multi-electron transfers are very rare in

phthalocyanine electrochemistry. This prompted us to extent the study to more TiPc complexes containing a wider range of substituents, including octa-substituents in an effort to try to understand the electrochemical behaviour of these molecules.

This work compares the electrochemical properties of the tetra-substituted TiPcs containing benzyloxy, 4-(benzyloxy)phenoxy, phenoxy and *tert*-butylphenoxy groups at the non-peripheral (complexes 5a–5d) and peripheral (complexes 6a–6d) positions. The complexes are: 1,(4)-(tetrabenzyloxyphthalocyaninato)titanium(IV) oxide (5a); 1,(4)-{tetrakis[4-(benzyloxy)phenoxy]phthalocyaninato}titanium(IV) oxide (5b); 1,(4)-(tetraphenoxyphthalocyaninato)titanium(IV) oxide (5c); 1,(4)-(tetra-*tert*-butylphenoxyphthalocyaninato)titanium(IV) oxide (5d); 2,(3)-(tetrabenzyloxyphthalocyaninato)titanium(IV) oxide (6a); 2,(3)-{tetrakis[4-(benzyloxy)phenoxy]phthalocyaninato}titanium(IV) oxide (6b); 2,(3)-(tetraphenoxyphthalocyaninato)titanium(IV) oxide (6c); 2,(3)-(tetra-*tert*-butylphenoxyphthalocyaninato)titanium(IV) oxide (6d); Scheme 1. The synthesis and electrochemistry of complexes 5c, 5d, 6c and 6d were reported before [13]. We also report on the electrochemistry of the peripherally octa-substituted complexes: octakis[(4-benzyloxy)phenoxy]phthalocyaninato titanium(IV) oxide (9b); octaphenoxyphthalocyaninato titanium(IV) oxide (9c) and octakis(4-*tert*-butylphenoxy)phthalocyaninato titanium(IV) oxide (9d).



Scheme 1. Synthesis of tetra- and octa-substituted oxo(phthalocyaninato)titanium(IV) derivatives.

2. Experimental

2.1. Materials

Acetone, ethanol, dimethylsulphoxide (DMSO), dimethylformamide (DMF), 1-octanol, methanol, hexane, chloroform ($CHCl_3$), tetrahydrofuran (THF), were purchased from either SAARCHEM or Aldrich and were dried and distilled before use. Deuterated DMSO (d_6-DMSO) and $CDCl_3$, benzyl alcohol, 4-(benzyloxy)phenol, urea and titanium butoxide were purchased from Aldrich. Chromatography was performed on silica gel 60 (0.04–0.063 mm). 3-Nitrophthalonitrile (1), 4-nitrophthalonitrile (2) and 4,5-dichlorophthalonitrile (7) were synthesised as in literature [18], [34] and [35]. All other reagents were of analytical grade and were used as received from the suppliers.

2.2. Equipment

UV–vis spectra were recorded on a Cary 500 UV-Vis/NIR spectrophotometer. IR spectra (KBr pellets) were recorded on a Perkin-Elmer spectrum 2000 FTIR spectrometer. ^{1}H NMR spectra were recorded using a Bruker EMX 400 MHz NMR spectrometer. MALDI TOF spectra were recorded with Perseptive Biosystems Voyager DE-PRO Biospectrometry Workstation and Processing Delayed Extraction Technology at the University of Cape Town. Elemental Analyses were also performed at the University of Cape Town.

Electrochemical data were obtained under purified nitrogen gas with BioAnalytical Systems (BAS) model 100B/W Electrochemical Workstation. Cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) data were collected using a conventional three-electrode set-up with glassy carbon electrode (GCE, 3 mm diameter) as a working electrode, platinum wire as counter electrode and Ag|AgCl wire as pseudo-reference electrode. Electrochemical experiments were performed in dry DMF containing tetrabutylammonium tetrafluoroborate ($TBABF_4$) as a supporting electrolyte. Prior to scans, the working electrode was polished with alumina paste on a Buehler felt pad, followed by washing with deionised water and rinsing with methanol and DMF. Spectroelectrochemical data were recorded using a home-made optically transparent thin-layer electrochemical (OTTLE) cell with a design similar to that previously reported [36]. The OTTLE cell was connected to a BAS CV 27 voltammograph.

2.3. Synthesis

The synthesis of complexes 5c, 5d, 6c and 6d was reported before [13].

2.3.1. 3-Benzyloxyphthalonitrile (3a)

In a stream of nitrogen, benzyl alcohol (4.54 g, 42.0 mmol) and 3-nitrophthalonitrile (6.00 g, 35.0 mmol) were dissolved in dry DMSO (30 ml). To this suspension was added anhydrous K_2CO_3 (9.70 g, 70.0 mmol) and the mixture stirred at room temperature. Further K_2CO_3 (2.43 g, 18.0 mmol) was added after 4 h and again after 24 h of stirring. After 48 h total reaction time, the mixture was poured into water (100 ml), thus forming a precipitate that was thoroughly washed with water and recrystallised from methanol to yield a brownish yellow title compound. Yield: 7.38 g (90%). IR [(KBr) ν_{max}/cm^{-1}]: 2226 (CN), 1250 (C–O–C). ^{1}H NMR (DMSO-d_6): δ, ppm 7.82 (1H, t, Ar–H), 7.71 (1H, d, Ar–H), 7.62 (1H, d, Ar–H), 7.49 (2H, d, Ar′–H), 7.41 (2H, t, Ar′–H), 7.33 (1H, t, Ar′–H), 5.36 (2H, s, CH_2).

2.3.2. 3-[4-(Benzyloxy)phenoxy]phthalonitrile (3b)

Synthesis and purification of 3b was as described for compound 3a, using 4-(benzyloxy)phenol (8.41 g, 42.0 mmol), 3-nitrophthalonitrile (6.00 g, 35.0 mmol) and DMSO (30 ml). Yield: 10.28 g (90%). IR [(KBr) ν_{max}/cm^{-1}]: 2240 (CN), 1260 (C–O–C). ^{1}H NMR (DMSO-d_6): δ, ppm 7.53 (1H, s, Ar–H), 7.47–7.32 (6H, m, Ar–H, Ar′–H), 7.05 (5H, m, Ar″–H), 5.10 (2H, s, CH_2).

2.3.3. 4-Benzyloxyphthalonitrile (4a)

Synthesis and purification of 4a was as described for compound 3a, using benzyl alcohol (4.54 g, 42.0 mmol), 4-nitrophthalonitrile (6.00 g, 35.0 mmol) and DMSO (30 ml). Yield: 6.97 g (85%). IR [(KBr) ν_{max}/cm^{-1}]: 2224 (CN), 1252 (C–O–C). ^1H NMR (DMSO-d_6): δ, ppm 8.01 (2H, d, Ar–H), 7.60–7.32 (6H, m, Ar–H, Ar′–H), 5.30 (2H, s, CH_2).

2.3.4. 4-[4-(Benzyloxy)phenoxy]phthalonitrile (4b)

Synthesis and purification of 4b was as described for compound 3a, using 4-(benzyloxy)phenol (8.41 g, 42.0 mmol), 4-nitrophthalonitrile (6.00 g, 35.0 mmol) and DMSO (30 ml). Yield: 9.36 g (82%). IR [(KBr) ν_{max}/cm^{-1}]: 2235 (CN), 1253 (C–O–C). ^1H NMR (DMSO): δ, ppm 7.52 (1H, d, Ar–H), 7.49–7.32 (5H, m, Ar″–H), 7.21 (2H, m, Ar–H), 7.00 (4H, q, Ar′–H), 5.10 (2H, s, CH_2).

2.3.5. 4,5-Bis[4-(benzyloxy)phenoxy]phthalonitrile (8b)

A mixture of 4,5-dichlorophthalonitrile (6.00 g, 30.5 mmol), 4-(benzyloxy)phenol (18.32 g, 91.4 mmol) and dry DMSO (46 ml) was stirred at 90 °C, while anhydrous K_2CO_3 (8 × 8.43 g, 8 × 61.0 mmol) was added every 5 min until eight portions have been added. The reaction mixture was stirred at 90 °C for an additional 45 min and allowed to cool. Thereafter, the mixture was added to ice water (100 ml) and the aqueous phase extracted with $CHCl_3$ (3× 50 ml). The combined extracts were first washed with Na_2CO_3 (5%), then with water and dried over $MgSO_4$. The solvent was evaporated and the product recrystallised from ethanol and dried at room temperature. Yield: 11.20 g (70%). IR [(KBr) ν_{max}/cm^{-1}]: 2229 (s) (C≡N), 1244 (C–O–C). ^1H NMR (DMSO-d_6): δ, ppm 8.50 (2H, s, Ar–H), 7.45 (8H, br d, Ar′–H), 7.10 (10H, d, Ar′–H), 5.21 (4H, s, CH_2).

2.3.6. 4,5-Diphenoxyphthalonitrile (8c)

Synthesis and purification of 8c was as described for compound 8b, using phenol (8.60 g, 91.4 mmol), 4,5-dichlorophthalonitrile (6.00 g, 30.5 mmol) and K_2CO_3 (8 × 8.43 g, 8 × 61.0 mmol) in dry DMSO (61 ml). Yield: 7.81 g (82%). IR [(KBr) ν_{max}/cm^{-1}]: 2227 (s) (C≡N), 1245 (C–O–C). ^1H NMR (DMSO-d_6): δ, ppm 7.68 (2H, s, Ar–H), 7.42 (4H, d, Ar′–H), 7.30 (4H, d, Ar′–H), 7.22 (2H, s, Ar′–H).

2.3.7. 4,5-Bis(4-*tert*-butylphenoxy)phthalonitrile (8d)

Synthesis and purification of 8d was as described for compound 8b, using 4-*tert*-butylphenol (10.36 g, 69 mmol), 4,5-dichlorophthalonitrile (4.50 g, 23 mmol) and K_2CO_3 (8 × 6.36 g, 8 × 43 mmol), DMSO (46 ml). Yield: 7.03 g (72%). IR [(KBr) ν_{max}/cm^{-1}]: 2900 (Bu^t), 2233 (s) (C≡N), 1242 (C–O–C). ^1H NMR (DMSO-d_6): δ, ppm 7.70 (2H, s, Ar–H), 7.20 (4H, d, Ar′–H), 6.76 (4H, d, Ar′–H), 1.32 (18H, s, Bu^t).

2.3.8. 1,(4)-(Tetrabenzyloxyphthalocyaninato)titanium(IV) oxide (5a, Scheme 1)

In 1-octanol (32 ml), compound 3a (4.00 g, 17.0 mmol), titanium butoxide (1.45 g, 4.25 mmol) and urea (1.02 g, 17.0 mmol) were stirred under a blanket of nitrogen at 150 °C for 14 h. The reaction mixture was allowed to cool, thereafter, methanol (80 ml) was added and the mixture was refluxed for 2 h. After cooling, the mixture was filtered, and the resulting solid sequentially washed with methanol and water and then dried. The crude product was purified by column chromatography, using THF as the eluting solvent. After evaporation of solvent, the product was further purified by washing with acetone and then with ethanol in a Soxhlet apparatus to afford the title compound as a dark-green solid. Yield: 1.19 g (28%). UV–vis ($CHCl_3$): λ_{max} (nm) (log ε) 350 (4.78), 648 (4.67), 728 (5.38). IR [(KBr) ν_{max}/cm^{-1}]: 1248 (C–O–C), 970 (Ti=O). ^1H NMR ($CDCl_3$): δ, ppm 8.90–8.1 (4H, m, Pc–H), 8.0–6.9 (28H, m, Pc–H, phenyl-H), 5.2 (8H, m, CH_2). $C_{60}H_{40}N_8O_5Ti$: Calc. C 72.00, H 4.03, N 11.20. Found: C 71.67, H 3.97, N 11.01. MALDI-TOF-MS *m*/*z*: Calc. 1000.9; Found (M^+) 1001.1.

2.3.9. 1,(4)-{Tetrakis[4-(benzyloxy)phenoxy]phthalocyaninato}titanium(IV) oxide (5b)

Synthesis and purification was as outlined for 5a except 3b instead of 3a was employed. The amounts of the reagents employed were: 3b (2.50 g, 7.70 mmol), titanium butoxide (0.66 g, 1.93 mmol) and urea (0.46 g, 7.70 mmol) in 1-octanol (15 ml). Yield: 0.79 g (30%). UV–vis ($CHCl_3$): λ_{max} (nm) (log ε) 346 (4.87), 656 (4.74), 730 (5.41). IR [(KBr) ν_{max}/cm^{-1}]: 1257 (C–O–C), 972 (Ti═O). ^1H NMR ($CDCl_3$): δ, ppm 8.85–8.40 (3H, m, Pc–H), 8.00–7.60 (3H, m, Pc–H), 7.59–6.92 (42H, m, Pc–H, phenyl-H), 5.11 (8H, m, CH_2). $C_{84}H_{56}N_8O_9Ti$: Calc. C 73.68, H 4.12, N 8.18. Found: C 73.76, H 4.16, N 8.14. MALDI-TOF-MS *m*/*z*: Calc. 1369.3. Found (M^+) 1368.3.

2.3.10. 2,(3)-(Tetrabenzyloxyphthalocyaninato)titanium(IV) oxide (6a)

Synthesis and purification was as outlined for 5a except 4a instead of 3a was employed. The amounts of the reagents employed were: 4a (4.00 g, 17.0 mmol), titanium butoxide (1.45 g, 4.25 mmol) and urea (1.02 g, 17.0 mmol) in 1-octanol (32 ml). Yield: 1.36 g (32%). UV–vis ($CHCl_3$): λ_{max} (nm) (log ε) 294 (4.71), 347 (4.88), 633 (4.61), 703 (5.21). IR [(KBr) ν_{max}/cm^{-1}]: 1241 (C–O–C), 965 (Ti═O). ^1H NMR ($CDCl_3$): δ, ppm 8.81–6.82 (32H, m, Pc–H, phenyl-H), 5.10 (8H, m, CH_2). $C_{60}H_{40}N_8O_5Ti$: Calc. C 72.00, H 4.03, N 11.20. Found: C 71.33, H 3.93, N 11.45. MALDI-TOF-MS *m*/*z*: Calc. 1000.9. Found (M^+) 1001.6.

2.3.11. 2,(3)-{Tetrakis[4-(benzyloxy)phenoxy]phthalocyaninato}titanium(IV) oxide (6b)

Synthesis and purification was as outlined for 5a except 4b instead of 3a was employed. The amounts of the reagents employed were: 4b (2.50 g, 7.70 mmol), titanium butoxide (0.66 g, 1.93 mmol) and urea (0.46 g, 7.70 mmol) in 1-octanol (15 ml). Yield: 0.92 g (35%). UV–vis ($CHCl_3$): λ_{max} (nm) (log ε) 293 (4.73), 347 (4.86), 635 (4.57), 705 (5.24). IR [(KBr) ν_{max}/cm^{-1}]: 1252 (C–O–C), 966 (Ti═O). ^1H NMR ($CDCl_3$): δ, ppm 8.88–8.18 (7H, m, Pc–H), 7.82–7.18 (41H, m, Pc–H, phenyl-H), 5.19 (8H, m, CH_2). $C_{84}H_{56}N_8O_9Ti$: Calc. C 73.68, H 4.12, N 8.18. Found: C 73.81, H 4.03, N 8.13. MALDI-TOF-MS *m*/*z*: Calc. 1369.3. Found (M^+) 1368.4.

2.3.12. 2,3,9,10,16,17,23,24-{Octakis[(4-benzyloxy)phenoxy]phthalocyaninato}titanium(IV) oxide (9b)

Synthesis and purification was as outlined for 5a except 8b instead of 3a was employed. The amounts of the reagents employed were: 8b (5.00 g, 11.4 mmol), titanium butoxide (0.97 g, 2.85 mmol) and urea (0.68 g, 11.4 mmol) in 1-octanol (21 ml). Yield: 2.34 g (38%). UV–vis ($CHCl_3$): λ_{max} (nm) (log ε) 299 (4.93), 349 (5.09), 636 (4.87), 705 (5.44). IR [(KBr) ν_{max}/cm^{-1}]: 1299 (C–O–C), 963 (Ti═O). ^1H NMR ($CDCl_3$): δ, ppm 8.80 (8H, s, Pc–H), 7.80–7.00 (72H, m, phenyl-H, 'phenyl-H), 5.20 (16H, s, CH_2). $C_{136}H_{96}N_8O_{17}Ti$: Calc. C 75.55, H 4.48, N 5.18. Found: C 74.90, H 4.22, N 5.02. MALDI-TOF-MS *m*/*z*: Calc. 2162.1. Found (M^+) 2161.9.

2.3.13. 2,3,9,10,16,17,23,24-Octaphenoxyphthalocyaninato titanium(IV) oxide (9c)

Synthesis and purification was as outlined for 5a except 8c instead of 3a was employed. The amounts of the reagents employed were: 8c (4.00 g, 12.8 mmol), titanium butoxide (1.45 g, 4.25 mmol) and urea (1.02 g, 17.0 mmol) in 1-octanol (32 ml). Yield: 1.95 g (35%). UV–vis ($CHCl_3$): λ_{max} (nm) (log ε) 296 (4.61), 350 (4.75), 632 (4.32), 703 (5.19). IR [(KBr) ν_{max}/cm^{-1}]: 1268 (C–O–C), 965 (Ti═O). ^1H NMR ($CDCl_3$): δ, ppm 8.70 (8H, s, Pc–H) 7.45–7.10 (40H, m, phenyl-H). Calc. $C_{80}H_{48}N_8O_9Ti$: C 73.17, H 3.68, N 8.53. Found: C 72.97, H 3.57, N 8.49. MALDI-TOF-MS *m*/*z*: Calc. 1313.2. Found (M^+) 1314.00.

2.3.14. 2,3,9,10,16,17,23,24-[Octakis(4-*t*-butylphenoxyphthalocyaninato)]titanium(IV) oxide (9d)

Synthesis and purification was as outlined for 5a except 8d instead of 3a was employed. The amounts of the reagents employed were: 8d (8.00 g, 19.0 mmol), titanium butoxide (1.62 g, 4.75 mmol) and urea (1.14 g, 19.0 mmol) in 1-octanol (35 ml). Yield: 2.09 g (20%). UV–vis ($CHCl_3$): λ_{max} (nm) (log ε) 298

(4.73), 348 (4.80), 634 (4.53), 706 (5.34). IR [(KBr) ν_{max}/cm^{-1}]: 2916 (C–H), 1269 (C–O–C), 962 (Ti=O). ^{1}H NMR ($CDCl_3$): δ, ppm 8.90 (8H, s, Pc–H), 7.43 (16H, d, phenyl-H), 7.22 (16H, d, phenyl-H), 1.40 (72H, s, Bu^t). $C_{112}H_{112}N_8O_9Ti$: Calc. C 76.34, H 6.41, N 6.36. Found: C 75.51, H 6.26, N 6.25. MALDI-TOF-MS *m*/*z*: Calc. 1762.0. Found (M^+) 1763.3.

3. Results and discussion

3.1. Synthesis and characterisation

The syntheses of the phthalocyanines tetra-substituted at the non-peripheral (5a and 5b) and peripheral (6a and 6b) with benzyloxy and 4-(benzyloxy)phenoxy groups are depicted in Scheme 1. The base-catalysed nucleophilic aromatic nitro displacement of 3-nitrophthalonitrile and 4-nitrophthalonitrile yielded the corresponding substituted phthalonitriles. Similarly; treatment of 4-(benzyloxy)phenol, phenol, and 4-*tert*-butylphenol, with 4,5-dichlorophthalonitrile (7), respectively, gave the dinitriles 8b, 8c and 8d under alkaline conditions. Using stoichiometric amounts, the substituted phthalonitriles were converted to the corresponding phthalocyanines. The tetra-substituted compounds were soluble in most organic solvents such as chloroform ($CHCl_3$), DCM, THF, toluene, DMSO and DMF. The octa-substituted complexes 9 were soluble in solvents such as CNP, DCM, $CHCl_3$ and THF and sparingly soluble in DMSO and DMF. After purification by Soxhlet extraction of impurities, relatively low yields (20–40%) of the phthalocyanines were obtained.

The new compounds were characterized by UV–vis, IR, NMR, MALDI-TOF and elemental analysis and are consistent with the predicted structures (see Section 2). Conversion into the corresponding phthalocyanine derivatives resulted in the disappearance of the C≡N stretch at ~2220 cm^{-1} of phthalonitriles 3, 4 and 8, which is indicative of MPc formation with typical Ti=O stretches at ~965 cm^{-1}. The complexes were found to be pure by ^{1}H NMR with substituent and Pc ring protons observed between 6.80 and 8.90 ppm, methylene protons at ~5.15 ppm and 9d *tert*-butyl protons integrating for 72 were observed at 1.40 ppm. The ^{1}H NMR spectra of complexes 5a and 6a were almost identical and similarly for complexes 5b and 6b. The observed peaks were broad and more so for the benzyloxy-substituted complexes thus making it difficult to differentiate between distinct protons. It has been reported [37], [38] and [39] that aggregation – due to the high concentrations used for the NMR measurements – and the presence of positional isomers results in weak and broad peaks. Integration of the peaks however correctly corresponded to the expected total number of protons for each complex, hence confirming the purity of the complexes, i.e. 40 protons for complexes 5a and 6a, and 56 protons for complexes 5b and 6b. The purity of the complexes was further confirmed by the more sensitive MALDI-TOF and elemental analysis experiments (see Section 2).

The electronic absorption spectra of all the complexes in $CHCl_3$ are typical of monomeric phthalocyanines with intense single (narrow) Q-bands due to π–π* transitions observed at 728 nm (5a), 730 nm (5b), 703 nm (6a) and 705 nm (6b), Fig. 1(a) and (b). The Q-band maxima of all the complexes are summarised in Table 1. The spectra of complexes 5, 6 and 9 exhibit typical B-bands, which are broad due to the superimposition of the B_1- and B_2-bands [40]. The peripherally substituted complexes 6 and 9 however exhibit a sharper B-band, Fig. 1 (for 6), accompanied by a broad band between 400 and 450 nm, that is typical of substituted TiPcs [12], [13] and [41]. The latter is also observed for non-peripherally substituted complexes 5, but it is weaker. This band may be due to charge transfer from the electron-rich ring to the electron-poor metal. A rarely occurring N-band arising from deeper π levels to LUMO transitions [1], [42] and [43] is observed at ~300 nm, Fig. 1. The Q-bands of the non-peripherally substituted complexes 5a–5d are red-shifted by ~25 nm (Table 1, for both chloroform and DMF) when compared to the corresponding peripherally substituted complexes 6a–6d. The shift to longer wavelengths is typical of MPc with electron donating groups bound at the non-peripheral position of the Pc ring [27], [32] and [44]. This difference can be explained in terms of the orbital energies of the complexes. At the non-peripheral positions, the HOMO has a larger amplitude compared to that at the peripheral positions [45] and [46]. Thus, substitution at the non-peripheral positions causes an effective shift of the energy of the orbital, such that a diminished HOMO-LUMO gap is obtained, hence a significant red spectral shift is observed.

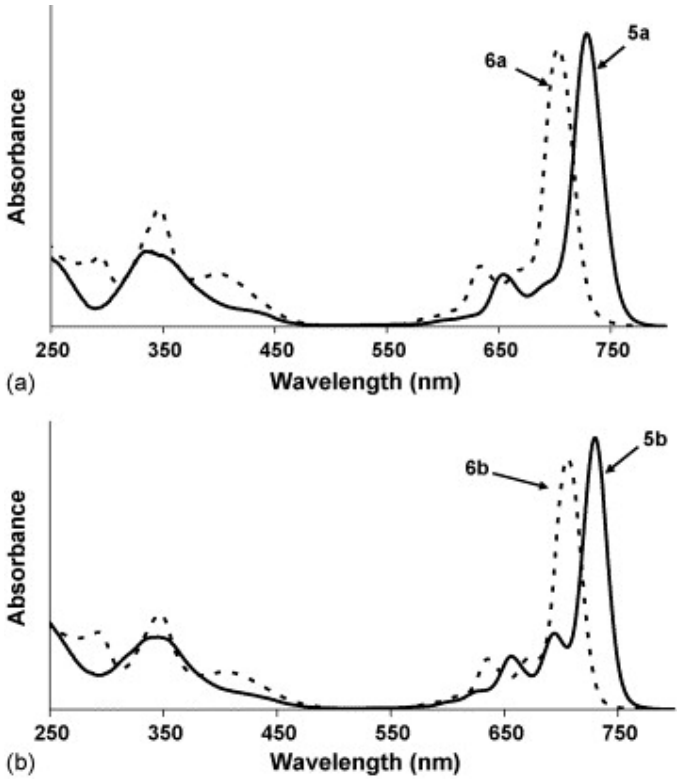


Fig. 1. UV–vis spectra of (a) 5a and 6a and (b) 5b and 6b in $CHCl_3$. Concentration = ca. 1×10^{-5} mol dm^{-3}.

Table 1.

UV–vis data (λ_Q, nm) for the TiPc complexes in DMF containing 0.1 M $TBABF_4$ unless otherwise stated

Complex	$Ti^{IV}Pc$[a] (log ε)	$Ti^{IV}Pc$	$Ti^{III}Pc$	$Ti^{II}Pc$
5a	728 (5.38)	724	717	711
5b	730 (5.41)	727	721	715
5c	728 (5.41)	720	708	703
5d	730 (5.29)	727	715	710
6a	703 (5.21)	701	694	687
6b	705 (5.24)	702	696	689
6c	702 (5.21)	700	690	684
6d	704 (5.40)	701	690	683
9b	705 (5.44)	701	695	690
9c	703 (5.19)	697	692	687
9d	706 (5.34)	698	693	687

Only Q-band positions shown.
[a] in $CHCl_3$.

3.2. Voltammetric and spectroelectrochemical characterisation

Detailed electrochemical characterisation of substituted OTiPcs is still under-developed. The cyclic voltammogram (CV) and square wave voltammogram (OSWV) of complexes 5a, 5b, 6a, 6b and 9b–9d were performed in deaerated DMF containing $TBABF_4$ as electrolyte, Fig. 2 and Fig. 3. For complexes 5a, 5b, 6a, and 6b, only one set of the CV and OSWV are shown since complexes displayed similar electrochemical behaviour. Similarly for complexes 9, the CV and OSWV of 9d are shown as representative of the rest of the complexes. The half-wave potentials ($E_{1/2}$) of the couples are listed in Table 2. The CV and OSWV of complexes 5a, 5b, 6a and 6b exhibit four reduction processes labelled I–IV. Complexes 9 exhibit three couples labelled I–III. The anodic to cathodic peak separation (ΔE) of couples I–III at 0.1 V s^{-1} ranged from 60 to 70 mV for complexes 5, 6 and 9, thus suggesting that couples I–III are reversible. The ΔE of process IV was ~60 mV for complexes 5a, 5b, 6a, and 6b; however, the current for the forward (cathodic) peak was much more enhanced than the current of the return (anodic) peak, thus suggesting quasi-reversible behaviour. The cathodic to anodic peak current ratio (I_{pc}/I_{pa}) were near unity for couples I–III. Linear plots of I_p as a function of the square root of the scan rate ($\upsilon^{1/2}$) were obtained, thus suggesting diffusion control. The nature of the couples as well as the number of electrons transferred was confirmed by spectroelectrochemistry below. The $E_{1/2}$ values of the complexes (Table 2) show that the benzyloxy appended complexes (5a and 6a) are marginally more difficult to reduce than the respective 4-(benzyloxy)phenoxy appended complexes (5b and 6b). Table 2 also shows that the benzyloxy and 4-(benzyloxy)phenoxy appended complexes (5a, 5b, 6a and 6b) are much easier to reduce (1st and 2nd reduction) than the phenoxy and *tert*-butylphenoxy-substituted complexes (5c, 5d, 6c and 6d). The *tert*-butylphenoxy-substituted complexes (5d and 6d) contain strong electron donating ligands making reduction more difficult. Complexes 9 are even easier to reduce (1st and 2nd reduction) than the rest of the complexes. However, the 3rd reduction does not follow the same trend for all the complexes. Of the octa-substituted complexes, 9d is expected to be more difficult to reduce than 9b and 9c due to the electron donating nature of the *tert*-butylphenoxy substituents, as was the case for the corresponding tetra-substituted complexes (5d and 6d compared to 5a–c and 6a–c, respectively). However, the three (9c–d) complexes have about the same 1st reduction potentials. It is not clear at the moment why the *tert*-butylphenoxy substituents did not shift the reduction potential to more negative values for the octa-substituted derivatives. First reductions for 5a, 5b, 6a, 6b and 9 are shifted to more positive potentials compared to the rest of the complexes, implying that the first oxidations are also shifted to more positive values, hence outside the usable range of the solvent-electrolyte-electrode system employed in this work. For complexes 5c, 5d, 6c and 6d, we reported [13] an overlap of voltammograms whereby 2 one-electron reductions resulted in one couple, Table 2. For the rest of the complexes it will be further proved below that they are one-electron process without overlapping of currents.

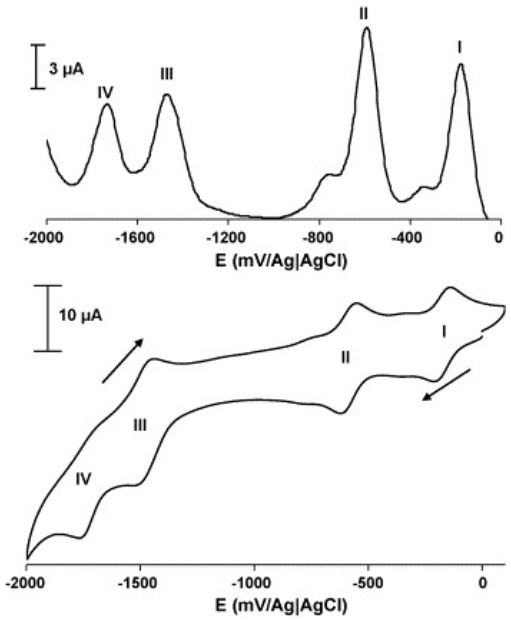


Fig. 2. Cyclic and square wave (top) voltammograms of 6a in DMF containing 0.1 M $TBABF_4$. Scan rate 0.1 V s^{-1}.

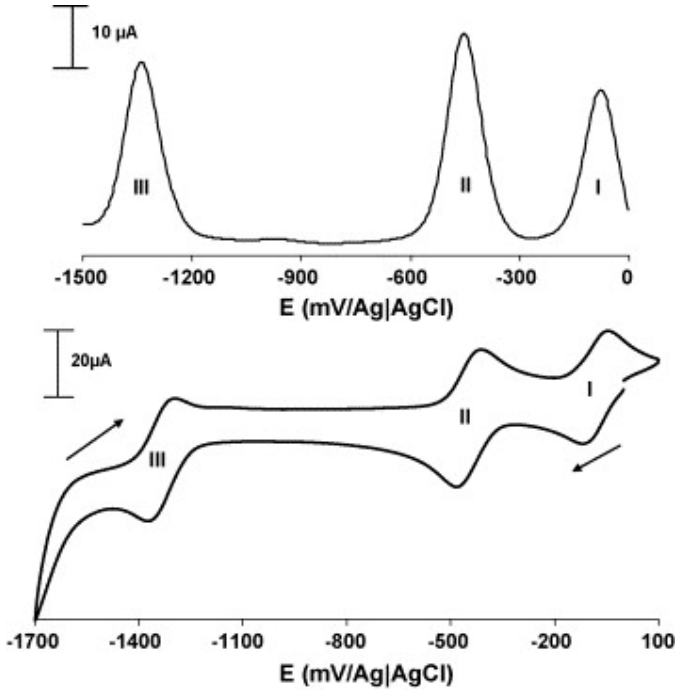


Fig. 3. Cyclic and square wave (top) voltammograms of 9d in DMF containing 0.1 M $TBABF_4$. Scan rate 0.1 V s^{-1}.

Table 2.

List of redox potentials for complexes 5a–5d, 6a–6d and 9b–9d in DMF containing $TBABF_4$ as electrolyte

Complex	Redox process [$E_{1/2}$ (V)]				Oxidations	Reference
	I ($Ti^{IV}Pc^{2-}/Ti^{III}Pc^{2-}$)	II ($Ti^{III}Pc^{2-}/Ti^{II}Pc^{2-}$)	III ($Ti^{II}Pc^{2-}/Ti^{II}Pc^{3-}$)	IV ($Ti^{II}Pc^{3-}/Ti^{II}Pc^{4-}$)		
5a	−0.18	−0.58	−1.51	−1.76	–	TW
5b	−0.14	−0.55	−1.42	−1.71	–	TW
5c	−0.37[a]	−0.78[b]	−1.04[c]	–	0.81, 0.99, 1.19	[13]
5d	−0.40[a]	−0.77[b]	−1.08[c]	–	0.81, 1.00, 1.20	[13]
6a	−0.17	−0.59	−1.48	−1.74	–	TW
6b	−0.14	−0.52	−1.40	−1.70	–	TW
6c	−0.32[a]	−0.74[b]	−1.05[c]	–	0.88, 0.99, 1.19	[13]
6d	−0.37[a]	−0.78[b]	−1.01[c]	–	0.82, 1.01, 1.40	[13]
9b	−0.09	−0.41	−1.26	–	–	TW
9c	−0.10	−0.47	−1.32	–	–	TW
9d	−0.08	−0.42	−1.33	–	–	TW

TW, this work.
[a] Two-electron reduction assigned to $Ti^{IV}Pc^{2-}/Ti^{II}Pc^{2-}$.
[b] Two-electron reduction assigned to $Ti^{II}Pc^{2-}/Ti^{I}Pc^{3-}$.
[c] One-electron reduction assigned to $Ti^{I}Pc^{3-}/Ti^{I}Pc^{4-}$.

Oxidation of TiPc is expected to occur only at the ring, while reduction is expected to occur at both the central metal as well as the ring. Within the potential window of 0–1.50 V, no oxidation peaks were observed for complexes 5a, 5b, 6a, 6b and 9. Oxidation was observed for complexes 5c, 5d, 6c and 6d [13], but is not observed for the rest of the complexes. Aromatic ring substituents function as electron donors hence are expected to enhance oxidation. Complexes 5d and 6d containing *tert*-butylphenoxy substituents should oxidise easily, hence the reported oxidation peaks [13]. Complexes 5c and 6c containing phenoxy substituents were also reported to show oxidation peaks [13], due to the electron donating behaviour of the phenoxy group. The arguments above should also apply to 9c and 9d, however no oxidation peaks were observed for these complexes. This might imply differences in the electrochemical behaviour of octa- versus tetra-substituted derivatives. The octa-substituted derivatives are easier to reduce compared to the rest of the complexes implying that the redox processes are shifted to more positive values.

For a more accurate measurement of the redox equivalency of couples I–IV for complexes 5a, 5b, 6a and 6b, chronocoulometry was employed. For the complexes, plots of Q versus $t^{1/2}$ (not shown) yielded linear responses with slopes in a 1:1:1:1 ratio, for potential steps encompassing processes I–IV. Similarly for complexes 9, processes I–III, a 1:1:1 ratio for the slopes was obtained. The observation suggests that a one-electron transfer process is involved in each redox step. Our earlier work [13] on complexes 5c, 5d, 6c and 6d, showed that for these complexes the ratio was 2:2:1 for the CV couples of the 1st, 2nd and 3rd reductions respectively. Spectroelectrochemistry of these complexes confirmed a step-wise reduction, hence showing that the two electrons are not transferred in one step.

To obtain further information on the nature of the redox processes observed in Fig. 2 and Fig. 3, spectroelectrochemistry performed in DMF containing $TBABF_4$ as electrolyte was employed. Complexes 5a, 5b, 6a and 6b showed similar spectroelectrochemical behaviour (except for differences in peak positions shown in Table 1), hence complex 6a is employed as an example. Complex 9d is used as a representative of the octa-substituted derivatives. Reduction at potentials of couple I, resulted in the spectral changes shown in Fig. 4(a) for 6a and (b) for 9d, which consisted of a shift of the Q band from 701 to 694 nm for complex 6a and from 698 to 693 nm for complex 9d. The observed spectral changes are typical of a metal-based reduction in MPcs [1]. A one-electron transfer ($\approx$1) was confirmed by coulometry ($Q = n$FVC), therefore suggesting a metal reduction from $Ti^{IV}Pc$ to $Ti^{III}Pc$ species. Further reduction at potentials of couple II resulted in the spectral changes observed in Fig. 5(a) for 6a and (b) for 9d. At the potentials of couple II, the Q-band shifted from 694 to 687 nm for 6a, thus suggesting another metal-based reduction. Coulometry confirmed a one-electron transfer thus suggesting that $Ti^{III}Pc$ was reduced $Ti^{II}Pc$. For 9b, a shift from 693 to 687 occurred. Thus, both processes shown in Fig. 4 and Fig. 5 involve reduction at the central metal as judged by the shift in Q-band positions without significant loss in intensity [1]. The spectral changes occurred with clear isosbestic points showing that only two species are involved in each transformation. Reduction at the central metal is expected to result in the loss of the oxygen atom, resulting in irreversibility, however the CV showed reversibility and the original spectra in Fig. 4, could be regenerated (>75%) by applying 0 V following reduction. Spectral changes observed during the reduction of complexes 5a, 5b, 6a and 6b to give $Ti^{III}Pc$ followed by $Ti^{II}Pc$ is in agreement with the reported reduction of 5c, 5d, 6c and 6d in that distinct spectral changes were observed for each species ($Ti^{III}Pc$ and $Ti^{II}Pc$), Table 1, even though the CV of the latter complexes showed only one couple for both processes. Thus an overlap of one-electron reductions were observed for 5c, 5d, 6c and 6d, but was separated for 5a, 5b, 6a and 6b and complexes 9. Pc ring substitutions are expected to modify the redox potentials of the central metal. It seems for the tetra-substituted phenoxy and tetra-substituted *tert*-butylphenoxy TiPc complexes; the first reduction is shifted to more negative potential values to an extent that it overlaps with the second reduction. However, for the octa-substituted derivatives containing the same ring substituents, the overlap of reduction potentials is not evident. Isomers could also play a role on the reduction potentials of the complexes. Tetra-substituted complexes have isomers while the octa-substituted derivatives do not. From Table 1, it seems that the easily reduced complexes (5a, 5b, 6a, 6b, 9b, 9c and 9d) are the ones that do not exhibit overlap of redox processes, as opposed to 5c, 5d, 6c and 6d.

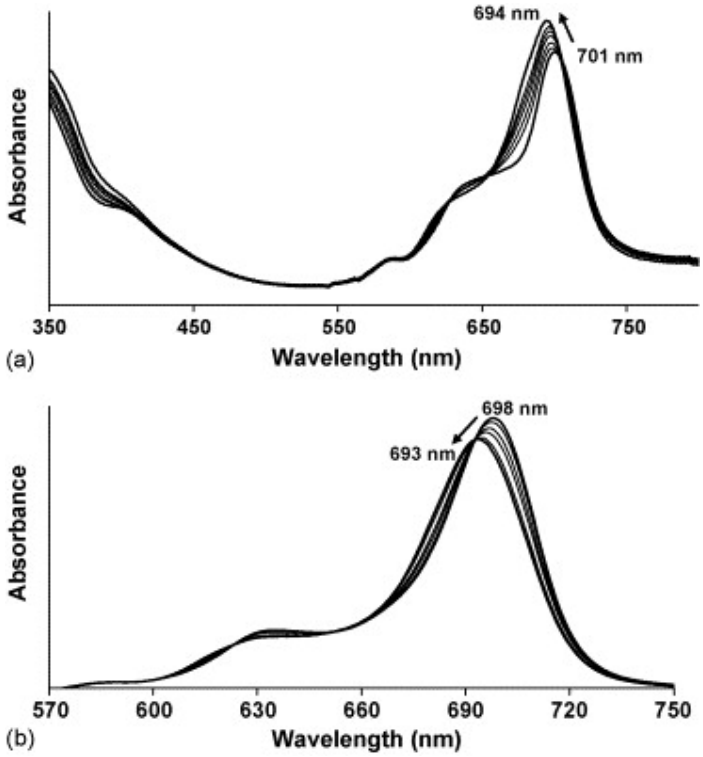


Fig. 4. UV–vis spectral changes observed during controlled potential (OTTLE cell) reduction of (a) 6a at an applied potential of couple I (−0.14 V) and (b) 9d at an applied potential of couple I (−0.08 V) in DMF containing 0.1 M $TBABF_4$.

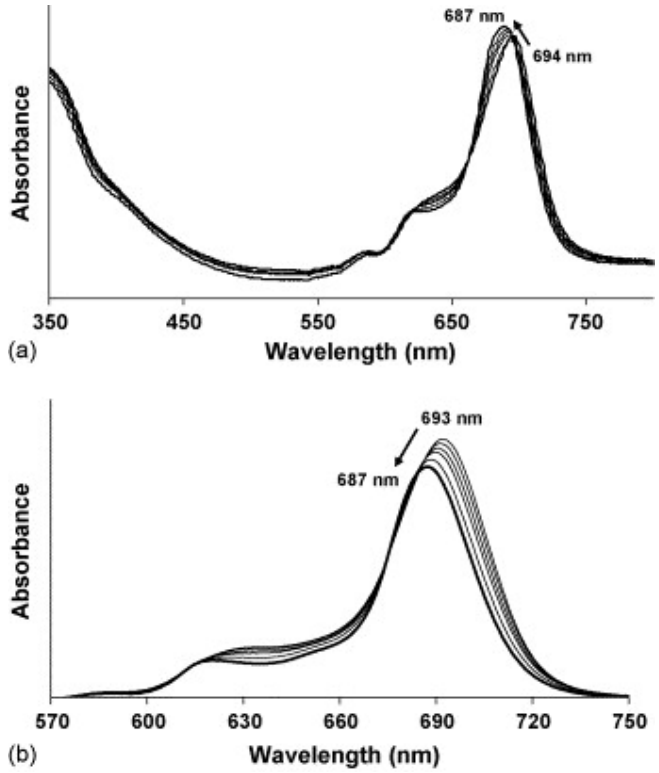


Fig. 5. UV–vis spectral changes observed during controlled potential (OTTLE cell) reduction of (a) 6a at an applied potential of couple II (−0.6 V) and (b) 9d at an applied potential of couple II (−0.4 V) in DMF containing 0.1 M $TBABF_4$. The first scans in (a) and (b) are the same as the last scans in Fig. 4(a) and (b), respectively.

An even further reduction at potentials of couple III resulted in spectral changes observed in Fig. 6(a) and (b), which consisted of a decrease in the Q-band maxima accompanied by an increase in intensity in the 500–600 nm region. The spectral changes observed are typical of ring-based processes in MPc, therefore, suggesting formation of $Ti^{II}Pc^{3-}$ [47]. Further reduction at potentials of couple IV for complex 6a resulted in the spectral changes observed in Fig. 7. The Q-band maxima further decreased while there was an emergence of a broad peak at ~ 500 nm. This is typical [47] of a reduction of Pc^{3-} to Pc^{4-}, thus suggesting that $Ti^{II}Pc^{3-}$ is further reduced to $Ti^{II}Pc^{4-}$ for 6a. Coulometry also confirmed a one-electron transfer for couples III and IV. Up to four Pc ring reductions are possible however limitations due to electrolyte, solvent and electrode can impose difficulty in observing at times, the last two ring reductions. It is interesting to note that for complexes 5c, 5d, 6c and 6d, reduction to the $T^{I}Pc^{4-}$ species was reported [13], but in the case of 5a, 5b, 6a and 6b and 9, reduction to the $T^{II}Pc^{4-}$ is observed without going through the $Ti^{I}Pc$ species.

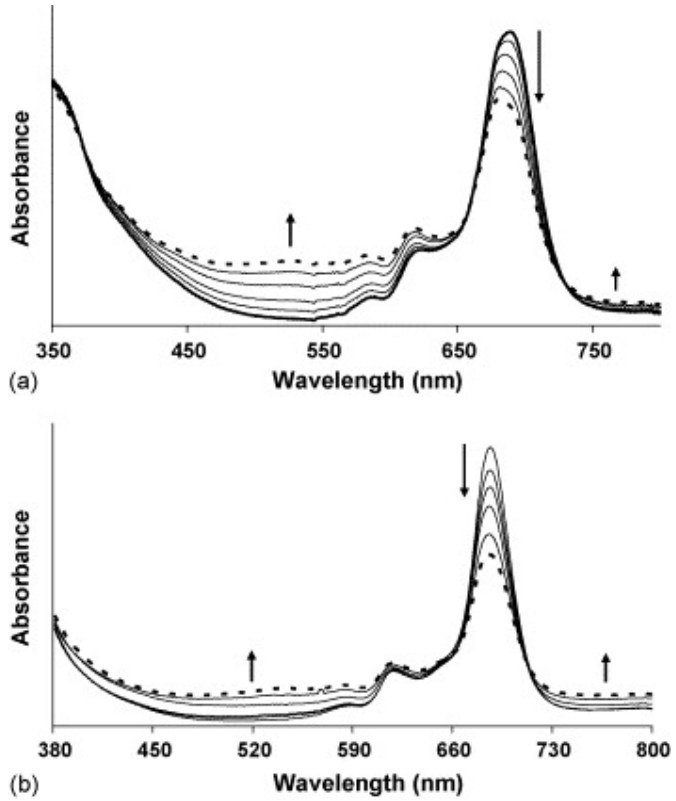


Fig. 6. UV–vis spectral changes observed during controlled potential (OTTLE cell) reduction of (a) 6a at an applied potential of couple III (−1.4 V) and (b) 9d at an applied potential of couple III (−1.3 V) in DMF containing 0.1 M $TBABF_4$. The first scans in (a) and (b) are the same as the last scans in Fig. 5(a) and (b), respectively.

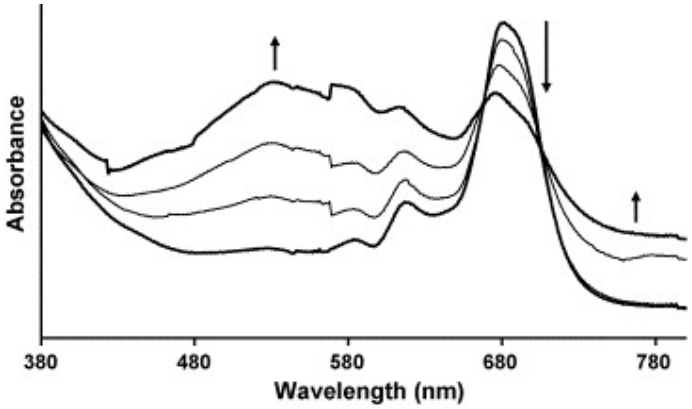


Fig. 7. UV–vis spectral changes observed during controlled potential (OTTLE cell) reduction of 6a at an applied potential of couple IV (−1.71 V) in DMF containing 0.1 M $TBABF_4$. The first scan in Fig. 7 is the same as the last scan in Fig. 6(a).

Based on the discussed electrochemical techniques, i.e. CV, SWV, chronocoulometry and spectroelectrochemistry; the following mechanism for the reduction [Eqs. (1), (2), (3) and (4)] of the newly synthesised tetra-substituted (5a, 5b, 6a, 6b) and octa-substituted (9) TiPc complexes is proposed:

$$Ti^{IV}Pc + e^{1-} \rightarrow Ti^{III}Pc \quad (1)$$

$$Ti^{III}Pc + e^{1-} \rightarrow Ti^{II}Pc \quad (2)$$

$$Ti^{II}Pc + e^{1-} \rightarrow Ti^{II}Pc^{3-} \quad (3)$$

$$Ti^{II}Pc^{3-} + e^{1-} \rightarrow Ti^{II}Pc^{4-} \quad (4)$$

for complexes 5a, 5b, 6a and 6b.

In conclusion, the synthesis and electrochemistry of peripherally and non-peripherally substituted TiPc complexes is reported. The electrochemistry of the complexes (5a, 5b, 6a, 6b) was compared to that of 5c, 5d, 6c and 6d as well as 9b–9d. Cyclic voltammetry shows that the first three reductions are reversible for complexes 5a, 5b, 6a, 6b as well as 9b–9d and a quasi-reversible fourth process for complexes 5a, 5b, 6a, 6b is observed. Coulometry confirmed a one-electron transfer process in each couple. Spectroelectrochemistry confirmed that the first two reductions occur at the central metal giving the $Ti^{III}Pc^{2-}$ and $Ti^{II}Pc^{2-}$ species. The last two reductions both occur at the ring thus giving the $Ti^{II}Pc^{3-}$ and $Ti^{II}Pc^{4-}$ species. Work is underway to further understand factors, which affect the electrochemistry of TiPc complexes.

Acknowledgements

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