



New water soluble and amphiphilic titanium(IV) phthalocyanines and investigation of electropolymerization properties



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ABSTRACT

Peripherally tetra-substituted oxo-titanium(IV) phthalocyanines bearing (2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy) and (2-{2-[3-(diethylamino)phenoxy]ethoxy}ethoxy) groups and their cationic derivatives have been synthesized. Electrochemical properties of the complexes **5** and **6** were determined with cyclic voltammetry and square wave voltammetry techniques. Electrochemical studies reveal that metallophthalocyanines containing redox active metal center such as Ti(IV) extends the redox richness of the phthalocyanine ring. Although titanium phthalocyanines complexes give common reduction processes, titanium phthalocyanines electropolymerized on the working electrode during anodic and whole potential scans. Electropolymerization mechanism changes with changing the potential window of the electrolyte system.

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1. Introduction

Phthalocyanines and their metal complexes have attracted significant interest because of their interesting chemical and physical properties [1]. In addition, metallophthalocyanines are well-known usage as dyes and pigments, they have found applications in diverse fields such as gas sensing [2], catalysts [3], non-linear optics [4], molecular electronics [5], optical data storage [6], photodynamic therapy agents [7], solar cells [8]. Owing to intermolecular interactions unsubstituted phthalocyanines are insoluble in common organic solvents and water so, application of phthalocyanines is limited. Insolubility of phthalocyanines in common organic solvents and water can be overcome by introducing alkyl, alkoxy, phenoxy, macrocyclic, amino substituents onto the peripheral positions of phthalocyanine [9–17]. Moreover, polyethylene oxide derivatives are amphiphilic functional compound which can increase the solubility of phthalocyanines [18–21].

Phthalocyanines and their metal complexes are used in such electrochemical technologies, such as electrosensing [22,23], electrocatalytic [24,25] electrochromic [26] applications because of their excellent redox behavior. Changing with metal center and types electrochemical properties of phthalocyanines also alters. Especially titanium phthalocyanines have attracted significant

interest owing to usage in applications such as photocatalysts, photoconductivity, electrophotography [27]. There is a increasing attention about the oxo-titanium(IV) phthalocyanines, because of their different oxidation states [28–30]. Consequently in this paper we aimed to synthesis, characterization and investigation of the electrochemical properties and possible application fields of the synthesized peripherally tetra-substituted titanium(IV) phthalocyanines.

2. Experimental

The used materials, equipments and the electrochemical measurements were supplied as [Supplementary information](#).

2.1. Synthesis

2.1.1. 4-(2-{2-[3-(Dimethylamino)phenoxy]ethoxy}ethoxy) phthalonitrile (**3**)

2-{2-[3-(Dimethylamino)phenoxy]ethoxy}ethanol **1** (1.5 g, 6.66×10^{-3} mol), 4-nitrophthalonitrile (1.15 g, 6.66×10^{-3} mol) and K_2CO_3 (2.75 g, 19.98×10^{-3} mol) in dry DMF (0.015 L) were stirred at 60 °C for 4 days under a nitrogen atmosphere. Then, reaction mixture was poured into water. The aqueous phase was extracted with chloroform (3×0.07 L). The combined extracts were dried over anhydrous $MgSO_4$ and then filtered. Solvent was evaporated and the crude product was purified by column chromatography with basic alumina as column material and $CHCl_3$ as eluent.

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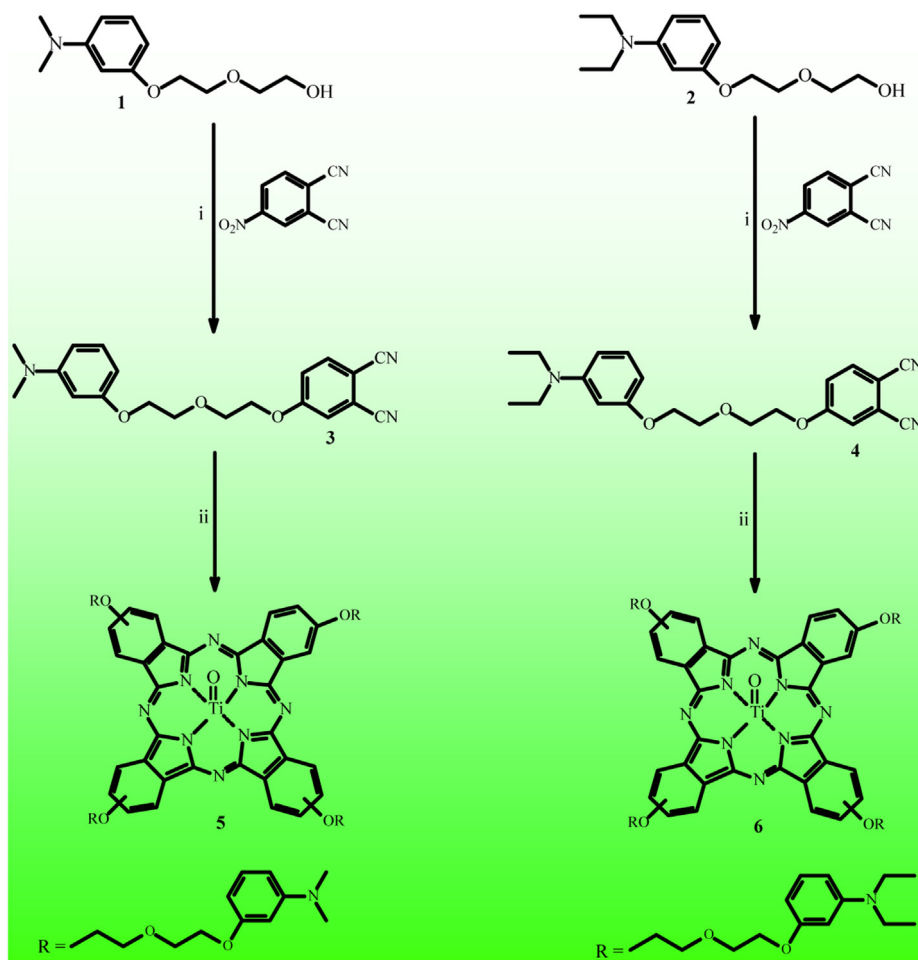


Fig. 1. The synthesis of non-ionic titanium(IV) phthalocyanines. (i) K_2CO_3 , N_2 , DMF, (ii) *n*-pentanol, DBU, 160°C , titanium(IV)butoxide.

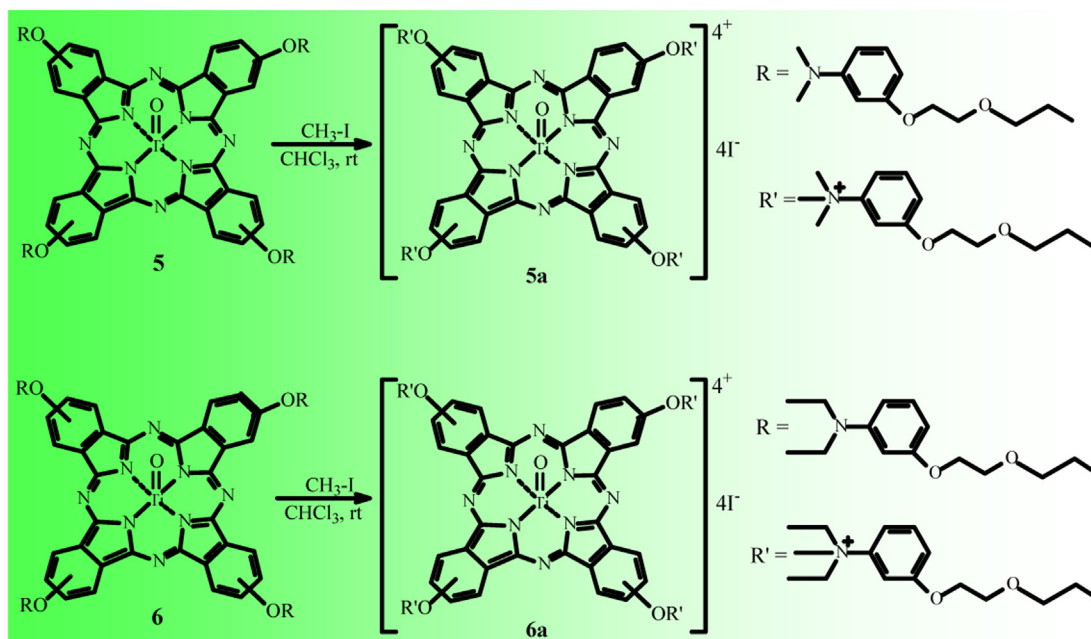


Fig. 2. The synthesis of cationic titanium(IV) phthalocyanines.

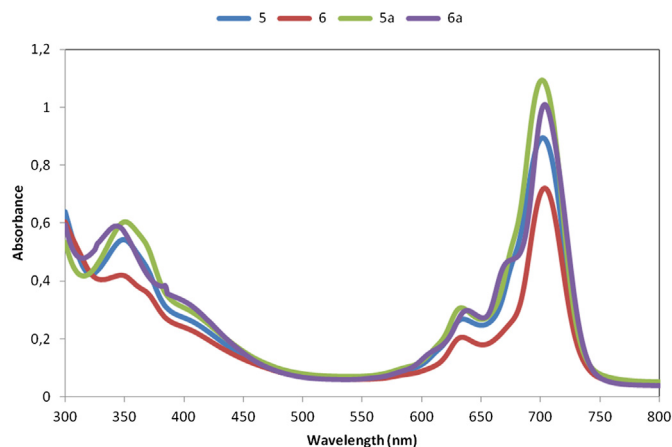


Fig. 3. UV–Vis spectra of **5**, **6**, **5a** and **6a** in DMF.

Yield: 1.75 g (75%). IR (KBr Tablet), ν/cm^{-1} : 3082 (Ar–H), 2925–2877 (Alif. C–H), 2230 (C≡N), 1672, 1602, 1599, 1573, 1503, 1449, 1355, 1321, 1294, 1254, 1170, 1132, 1098, 1066, 999, 967, 877, 829, 755, 687, 524. ^1H NMR (CDCl_3), (δ :ppm): 7.67 (d, 1H, Ar–H), 7.25–7.11 (m, 3H, Ar–H), 6.37 (d, 1H, Ar–H), 6.23 (s, 2H, Ar–H), 4.21–4.12

Table 1

Voltammetric data of the complexes. All voltammetric data were given versus SCE.

Complex	Polymerization waves		Reductions		
TiOPc 5	$E_{1/2}^a$	—	1.13 ^f (0.63) ^g	–0.57 ^d	–0.92 ^e
	ΔE_p (mV) ^b	—	—	120	140
	$I_{p,a}/I_{p,c}^c$	—	—	0.94	0.93
TiOPc 6	$E_{1/2}^a$	—	1.12 ^f (0.65) ^g	–0.53 ^d	–0.89 ^e
	ΔE_p (mV) ^b	—	—	130	150
	$I_{p,a}/I_{p,c}^c$	—	—	0.95	0.97

^a $E_{1/2}$ values ($(E_{pa} + E_{pc})/2$) were given versus SCE at 0.100 Vs^{-1} scan rate.

^b $\Delta E_p = E_{pa} - E_{pc}$.

^c $I_{p,a}/I_{p,c}$ for reduction, $I_{p,c}/I_{p,a}$ for oxidation processes.

^d This process is assigned to $\text{Ti}^{\text{IV}}\text{OPc}/\text{Ti}^{\text{III}}\text{OPc}$.

^e This process is assigned to $\text{Ti}^{\text{III}}\text{OPc}/\text{Ti}^{\text{II}}\text{OPc}$.

^f E_{pa} of first CV cycle.

^g E_{pc} of first CV cycle.

(m, 4H, $-\text{CH}_2-\text{O}$), 3.94–3.90 (m, 4H, $-\text{CH}_2-\text{O}$), 2.90 (s, 6H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3), (δ :ppm): 162.2, 159.9, 152.2, 135.4, 129.9, 120.2, 119.7, 117.4, 116.0, 115.6, 107.4, 106.2, 101.9, 99.9, 70.4, 69.5, 68.9, 67.4, 40.8. MS (ESI), (m/z): 352 $[\text{M} + \text{H}]^+$.

2.1.2. 4-(2-{3-(Diethylamino)phenoxy}ethoxy)ethoxy phthalonitrile (**4**)

Synthesized similarly to **3** from **2**. Yield: 1 g (45%). IR (KBr Tablet), ν/cm^{-1} : 3082 (Ar–H), 2971–2868 (Alif. C–H), 2231 (C≡N),

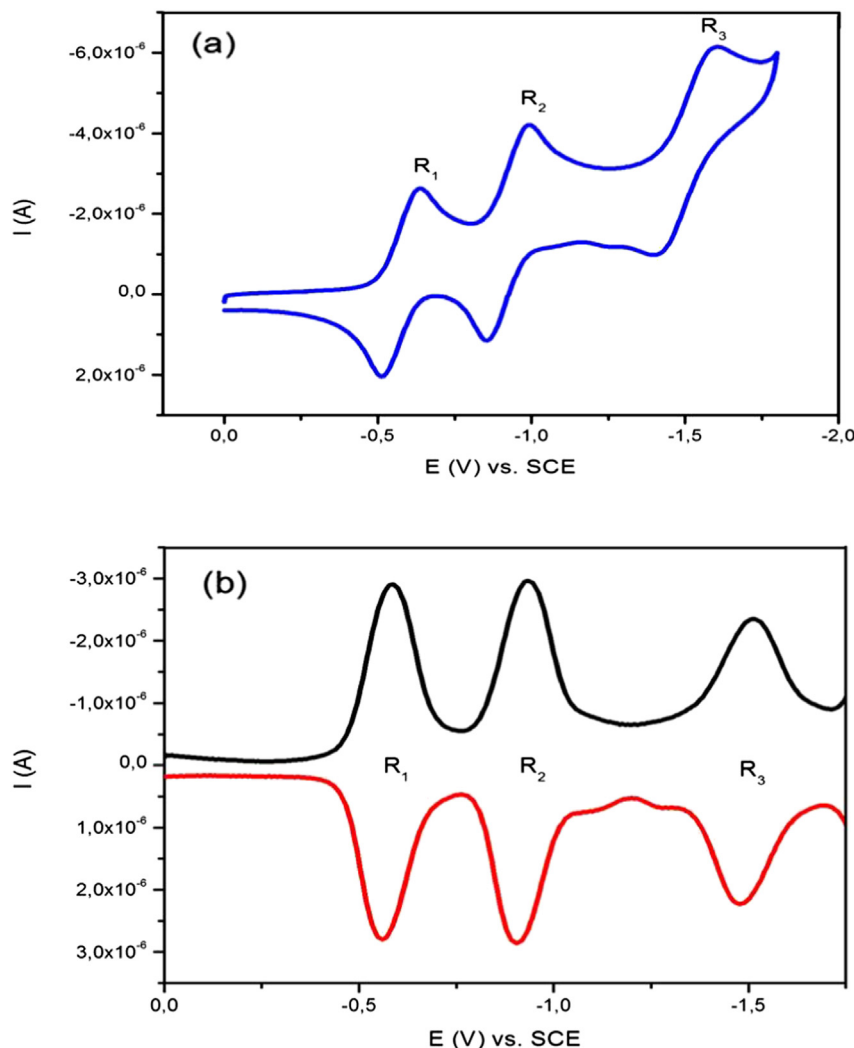


Fig. 4. (a) CVs of TiOPc **5**. (b) SWVs of TiOPc **5**.

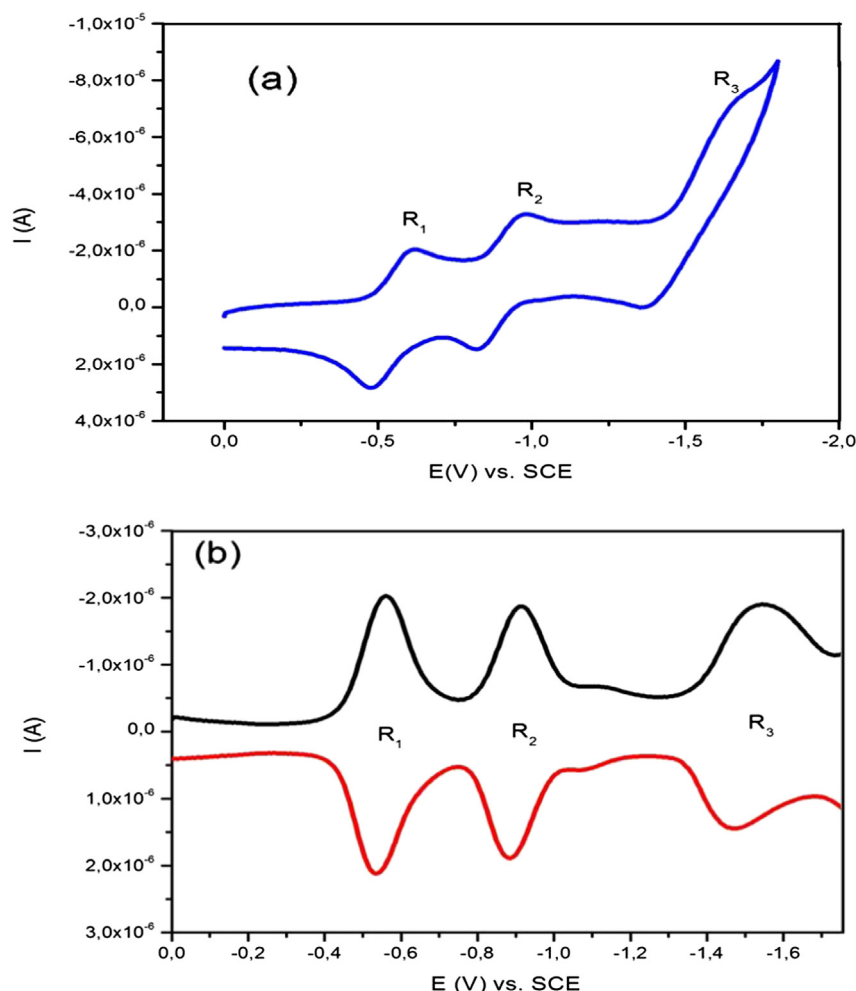


Fig. 5. (a) CVs of TiOPc 6. (b) SWV of TiOPc 6.

1599, 1563, 1500, 1396, 1357, 1311, 1283, 1250, 1216, 1200, 1136, 1097, 1024, 988, 968, 833, 755, 687. ^1H NMR (CDCl_3), (δ :ppm): 7.69 (m, 1H, Ar–H), 7.26–7.19 (m, 2H, Ar–H), 7.10 (t, 1H, Ar–H), 6.59 (d, 1H, Ar–H), 6.34–6.16 (m, 2H, Ar–H), 4.24 (m, 2H, $-\text{CH}_2-\text{O}$), 4.14 (m, 2H, $-\text{CH}_2-\text{O}$), 3.98–3.91 (m, 4H, $-\text{CH}_2-\text{O}$), 3.33 (m, 4H, $-\text{CH}_2-\text{N}$), 1.17 (m, 6H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3), (δ :ppm): 162.6, 160.2, 150.1, 135.5, 131.2, 130.1, 121.6, 120.2, 119.7, 117.6, 115.9, 109.6, 106.6, 103.5, 99.1, 70.4, 69.5, 68.9, 67.3, 44.6, 12.9. MS (ESI), (m/z): 380 $[\text{M} + \text{H}]^+$.

2.1.3. 2(3),9(10),16(17),23(24)-Tetrakis-(2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy)-phthalocyaninato oxotitanium(IV) (5)

A mixture of 4-(2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy)phthalonitrile **3** (0.25 g, 0.71×10^{-3} mol), $\text{Ti}(\text{O}i\text{Bu})_4$ (0.25×10^{-3} L, 0.71×10^{-3} mol), 5 drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in *n*-pentanol (0.0025 L) was refluxed with stirring for 12 h under N_2 . After cooling to room temperature, 0.03 L ethanol was added to precipitate the product. The precipitate was filtered and dried in vacuo. Lastly, purification was achieved using column chromatography with basic alumina as column material and CHCl_3 as eluent. Yield: 0.158 g (61%). IR(KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3077 (Ar–H), 2924–2869 (Aliph. C–H), 1604, 1573, 1486, 1447, 1394, 1338, 1283, 1232, 1118, 1058, 998, 958, 822, 747, 685. ^1H NMR (CDCl_3), (δ :ppm): 7.78 (m, 4H, Ar–H), 7.24–7.18 (m, 12H, Ar–H), 6.44–6.32 (m, 12H, Ar–H), 4.37–4.17 (m, 32H, $-\text{CH}_2-\text{O}$), 2.95 (s, 24H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3), (δ :ppm): 159.0, 152.7, 150.2, 139.8, 135.3, 131.5, 127.9, 125.3, 121.4, 112.6, 108.5, 107.9, 106.5, 100.6, 69.7,

68.7, 40.6. UV–vis (DMF): λ_{max} , nm (log ϵ): 349 (4.73), 635 (4.42), 702 (4.95). MALDI-TOF-MS m/z : 1470 $[\text{M} + \text{H}]^+$.

2.1.4. 2(3),9(10),16(17),23(24)-Tetrakis-(2-{2-[3-(diethylamino)phenoxy]ethoxy}ethoxy)-phthalocyaninato oxotitanium(IV) (6)

Synthesized similarly to **5** from **4**. Yield: 0.097 g (38%). IR(KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3079 (Ar–H), 2968–2870 (Aliph. C–H), 1609, 1570, 1499, 1450, 1395, 1374, 1278, 1218, 1113, 1074, 1023, 964, 826, 749, 686. ^1H NMR (CDCl_3), (δ :ppm): 7.76 (m, 4H, Ar–H), 7.35–7.20 (m, 12H, Ar–H), 6.43–6.35 (m, 12H, Ar–H), 4.38 (m, 8H, $-\text{CH}_2-\text{O}$), 4.18 (m, 8H, $-\text{CH}_2-\text{O}$), 3.96 (m, 16H, $-\text{CH}_2-\text{O}$), 3.37 (m, 16H, $-\text{CH}_2-\text{N}$), 1.17 (m, 24H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3), (δ :ppm): 160.2, 155.7, 153.1, 149.3, 149.2, 141.9, 133.5, 129.9, 129.9, 123.8, 110.1, 105.4, 100.8, 99.2, 70.4, 70.2, 67.1, 66.4, 44.4, 12.7. UV–vis (DMF): λ_{max} , nm (log ϵ): 347 (4.62), 634 (4.31), 704 (4.85). MALDI-TOF-MS m/z : 1582 $[\text{M}]^+$.

2.1.5. 2(3),9(10),16(17),23(24)-Tetrakis-(2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy)-phthalocyaninato oxotitanium(IV)iodide (5a)

Titanium(IV) phthalocyanine **5** (0.045 g, 0.03×10^{-3} mol) was resolved in 0.003 L of CHCl_3 and 0.004 L iodomethane was added to this solution. This reaction mixture was stirred at room temperature for 5 days. The precipitate was filtered off, washed with chloroform, acetone and diethyl ether. Then, water-soluble ionic titanium(IV) phthalocyanine was dried in vacuo. Yield: 0.043 g

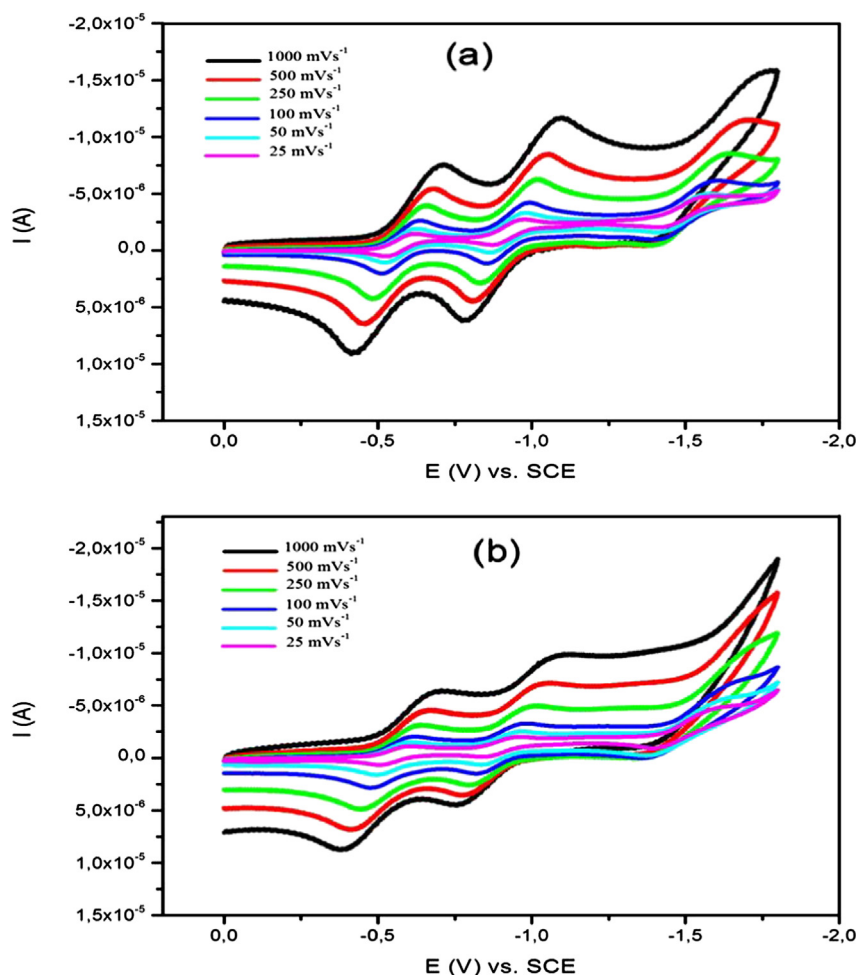


Fig. 6. (a) CV of complex **5** at various scan rates (ranging from 25 to 1000 mV s^{-1}) on a Pt working electrode in DCM/TBAP. (b) CV of complex **6** at various scan rates (ranging from 25 to 1000 mV s^{-1}) on a Pt working electrode in DCM/TBAP.

(70%). IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3014 (Ar–H), 2925–2872 (Aliph. C–H), 1605, 1487, 1398, 1336, 1231, 1116, 1054, 958, 828, 745, 684. UV–vis (DMF): λ_{max} , nm ($\log \epsilon$): 350 (4.78), 633 (4.48), 701 (5.03). MALDI-TOF-MS m/z : 384 $[\text{M} - 4\text{I} + 2]^{+4}$.

2.1.6. 2(3),9(10),16(17),23(24)-Tetrakis-(2-{2-[3-(diethylamino)phenoxy]ethoxy}ethoxy)-phthalocyaninato oxotitanium(IV)iodide (**6a**)

Synthesized similarly to **5a** from **6**. Yield: 0.014 g (30%). IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3014 (Ar–H), 2924–2867 (Aliph. C–H), 1603, 1484, 1450, 1396, 1333, 1237, 1116, 1069, 956, 870, 826, 747, 689. UV–vis (DMF): λ_{max} , nm ($\log \epsilon$): 344 (4.77), 638 (4.47), 671 (4.66), 704 (5.01). MALDI-TOF-MS m/z : 411 $[\text{M} - 4\text{I} + 1]^{+4}$.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of the non-ionic and cationic titanium phthalocyanines are shown in Figs. 1 and 2. The first step is the synthesis of 4-(2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy)phthalonitrile **3** and 4-(2-{2-[3-(diethylamino)phenoxy]ethoxy}ethoxy)phthalonitrile **4**. Second step is the cyclotetramerization of the phthalonitrile derivatives **3** and **4** in a high-boiling solvent (*n*-pentanol) in the presence of a few drops DBU as a strong base and titanium(IV)butoxide at reflux temperature under a nitrogen atmosphere afforded the titanium phthalocyanines **3** and **4**. Finally, cationic titanium phthalocyanines **5a** and **6a** were obtained by the

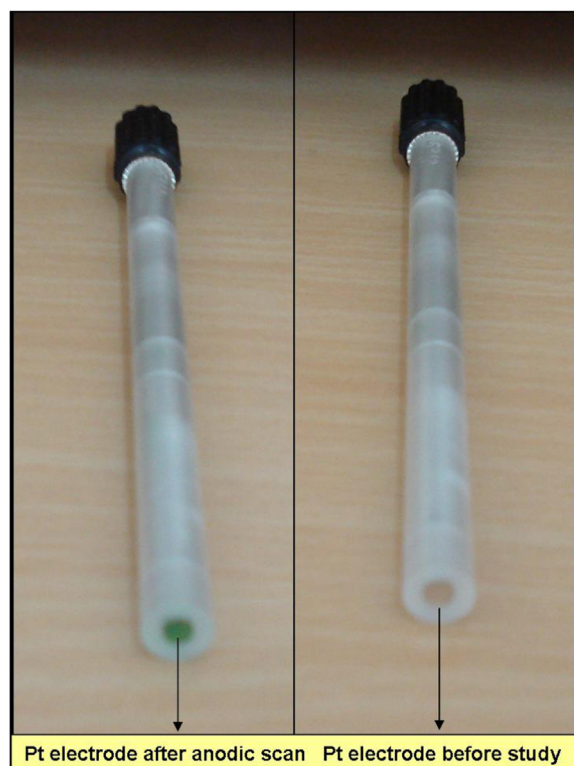


Fig. 7. Electropolymerized working electrode.

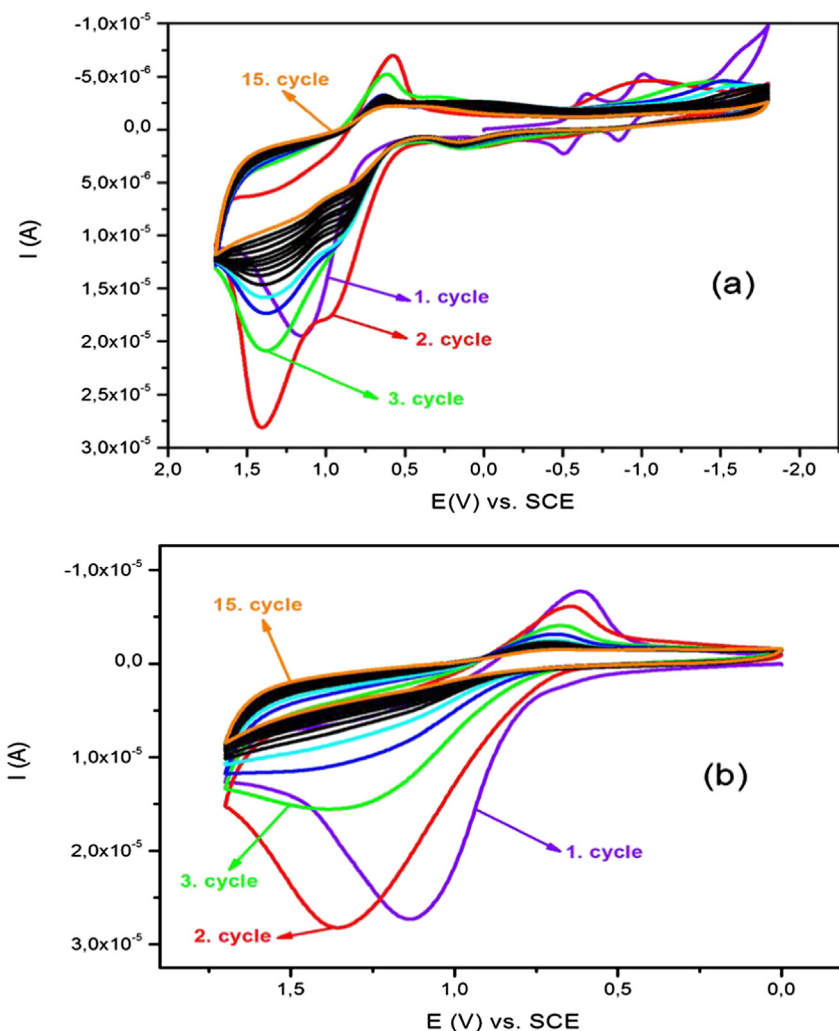


Fig. 8. (a) Repetitive CVs of **TiOPc 5** recorded with in the whole potential windows of DCM/TBAP electrolyte system at 0.100 Vs⁻¹ scan rate on a Pt working electrode. (b) Repetitive CVs of **TiOPc 5** recorded at anodic potential windows of DCM/TBAP electrolyte system at 0.100 Vs⁻¹ scan rate on a Pt working electrode.

reaction of complexes **5** and **6** with excess iodomethane in CHCl₃ at room temperature.

In the IR spectrum of **3** and **4**, stretching vibrations of C≡N groups appeared as a single intense peak at 2230 and 2231 cm⁻¹ as expected, respectively. In ¹H NMR spectrum of **3** and **4**, the disappearance of the OH peaks of **1** and **2**, besides presence of additional aromatic protons indicated that nucleophilic aromatic nitro displacement was achieved. In ¹³C NMR spectrum of **3** and **4** were observed the new peaks at (116.0, 115.6 ppm) for **3**, (117.6, 115.9 ppm) for **4** belonging to nitrile carbons. The molecular ion peaks of **3** and **4** were found at *m/z* 352 [M + H]⁺, 380 [M + H]⁺, respectively.

After conversion of the phthalonitrile derivatives **3** and **4** into the titanium phthalocyanines, the sharp peaks for the C≡N vibrations completely disappeared in the IR spectra. No major changes in the IR spectra for **3a** and **4a** were observed after quaternization.

The ¹H NMR spectrum of complexes **5** and **6** were very similar and the integral ratio of the aromatic protons to aliphatic protons were similar to corresponding phthalonitrile derivatives **3** and **4**. The ¹³C NMR spectrum of complexes **5** and **6** were in good agreement with the structures. For example, the ¹³C NMR spectrum of **5** and **6** showed typical chemical shifts for aliphatic protons between

69.7 and 40.6 ppm for **5**, 70.4–12.7 ppm for **6** aromatic protons between 159.0 and 100.6 ppm for **5**, 160.2–99.2 ppm for **6**. Finally, the structure of non-ionic and cationic titanium phthalocyanines was confirmed using mass spectral data. The molecular ion peaks of **5**, **6**, **5a** and **6a** were observed at 1470 [M + H]⁺, 1582 [M]⁺, 384 [M – 4I + 2]⁺ and 411 [M – 4I + 1]⁺, respectively.

The UV/Vis spectra of **5**, **6**, **5a**, **6a** in DMF at room temperature is shown in Fig. 3. In UV–Vis spectra of the titanium phthalocyanines Q-bands were observed at around 702 nm for **5**, 704 nm for **6**, 701 nm for **5a** and 704 nm for **6a** with the shoulders at around 635 nm for **5**, 634 nm for **6**, 633 nm for **5a** and (671, 638) nm for **6a** and the B bands were observed between 350 and 344 nm.

3.2. Electrochemical studies

Voltammetric studies of the complexes were investigated by using cyclic voltammetry (CV) and square wave voltammetry (SWV) in DCM/TBAP electrolyte system on a Pt working electrode to find application of the complexes in areas of electrochemical technologies. The results of voltammetric analyses are given in Table 1. Redox active metal center such as titanium increases the redox richness of the complex with extra electron transfer processes of the metal centers.

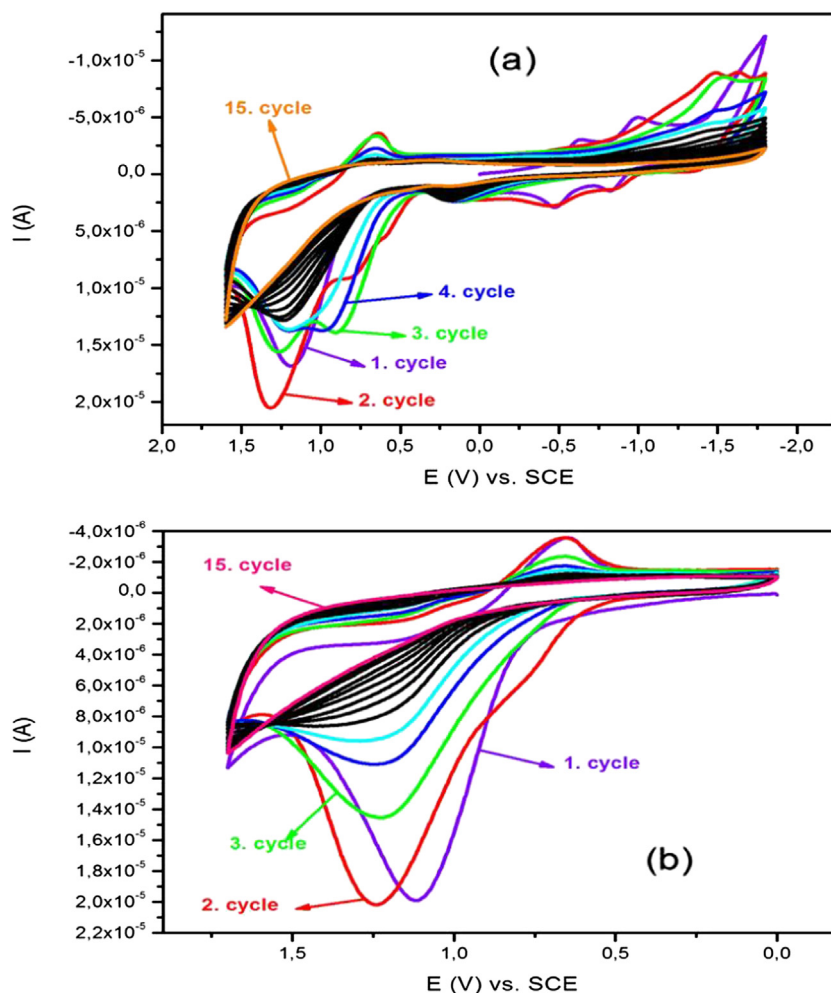


Fig. 9. (a) Repetitive CVs of **TiOPc 6** recorded with in the whole potential windows of DCM/TBAP electrolyte system at 0.100 Vs^{-1} scan rate on a Pt working electrode. (b) Repetitive CVs of **TiOPc 6** recorded at anodic potential windows of DCM/TBAP electrolyte system at 0.100 Vs^{-1} scan rate on a Pt working electrode.

Figs. 4 and 5 illustrate the CV and SWVs of **TiOPc 5** and **6**, respectively during the cathodic potential scans. As shown in these figures, three reduction processes labeled as R_1 at -0.57 V , R_2 at -0.92 V and R_3 at -1.50 V for complex **5**, R_1 at -0.53 V , R_2 at -0.89 V , R_3 at -1.51 V for complex **6** are observed. As shown in Figs. 4a and 5a **TiOPc 5** give quasi-reversible reduction (R_1 and R_2), irreversible reduction (R_3), in the same way, **TiOPc 6** give quasi-reversible reduction (R_1 and R_2), irreversible reduction (R_3) during the cathodic scans. In addition, the electrochemical reversibility of the processes can be efficiently evaluated from the symmetry of the redox couple recorded with SWVs (Figs. 4b and 5b). As shown in Fig. 6a for complex **5**, Fig. 6b for complex **6**, the peak currents increased linearly with the square root of the scan rates for scan rates ranging from 25 to 1000 mV s^{-1} , indicating purely diffusion-controlled behavior [31–33].

TiOPc complexes **5** and **6** are oxidative electropolymerized on the working electrode (Fig. 7). On the other hand, applied potential ranges affects the polymerization mechanism. For the usage of the **TiOPc** complexes in different areas electropolymerization processes are very important. Fig. 8a shows the repetitive CV scans with in the whole potential windows of DCM/TBAP. In Fig. 8a, an anodic wave was recorded at 1.14 V and its reverse couple is recorded at 0.61 V during the first CV cycle. During the second CV cycle, the anodic wave increases with a potential shift at 1.41 V . After this point, it decreases in current intensity until the 15. cycle. These voltammetric data are evidence electropolymerization of the complex **5** on

the working electrode. When only anodic potentials are scanned for complex **5** the similar electropolymerization behavior was seen (Fig. 8b).

On the other hand, electropolymerization behavior of **TiOPc 6** is seen in Fig. 9. When anodic potentials are scanned after the cathodic potentials continually, **TiOPc 6** is electropolymerized on the working electrode (Fig. 9a). During the first CV cycle, an anodic wave was recorded at 1.19 V and its reverse couple is recorded at 0.65 V . Electropolymerized wave increases up to 2. CV cycle with a potential shift. During the third CV cycle a new wave is observed at 0.90 V with decreasing in current intensity. After 2 CV cycles waves starts to decrease to 15. cycle with potential shift, exhibiting electropolymerization of the **TiOPc 6** on the working electrode. When only positive potentials are scanned instead of the whole potentials for complex **6**, polymerization mechanism showed very little changes as shown in Fig. 9b. In spite of each of two titanium(IV) complexes are soluble in dichloromethane, after the electropolymerization on the working electrode they are insoluble in DCM.

4. Conclusion

In this study, amphiphilic non-ionic and cationic titanium(IV) phthalocyanines have been successfully synthesized and these new complexes have been characterized by IR, ^1H and ^{13}C NMR, mass and UV–Vis spectroscopy techniques. Cyclic and square wave

voltammetry were used in order to investigation of electrochemical properties of TiOPc complexes. Electrochemical studies reveal that TiOPc complexes are electropolymerized on the working electrode during the anodic and cathodic–anodic scans. The character of the polymerization processes is affected by potential window of the technique and the cycle number of CV. For preparation of composite electrode, electropolymerization is a desired property.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorgchem.2013.12.004>.

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