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Electropolymerizable Peripherally Tetra-{2-[3-(Diethylamino)phenoxy]ethoxy} Substituted As Well As Axially (4-Phenylpiperazin-1-yl)propanoxy-Disubstituted Silicon Phthalocyanines and Their Electrochemistry

Zekeriya Biyiklioglu[a*], **Hakan Alp**[a]

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A novel type of peripherally tetra-susbstituted as well as axially disubstituted silicon(IV) phthalocyanines containing electropolymerizable ligands were designed and synthesized for the first time. Axial bis-hydroxy silicon phthalocyanine **2** was prepared from the 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}phthalocyanine **1** in dichloromethane by using 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) and trichlorosilane. Peripherally tetra and axially di-substituted silicon phthalocyanine **4** was synthesized from the 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine dihydroxide **2** with 1-(3-chloropropyl)-4-phenylpiperazine **3** in toluene in the presence of NaH at 120 °C. These complexes were fully characterized by various spectroscopic techniques such as ^{1}H-NMR, ^{13}C-NMR, IR, UV-Vis, MALDI-TOF spectra and elemental analysis as well. Electropolymerization properties of silicon(IV) phthalocyanine complexes were investigated by cyclic and square wave voltammetry. Electrochemical studies reveal that silicon(IV) phthalocyanine complexes were electropolymerized on the working electrode during the anodic potential scan. This study is the first example of electropolymerization of both peripherally tetra and axially di-substituted silicon phthalocyanines on the same molecule.

1. Introduction

Phthalocyanines are macrocyclic compounds with 18π-electrons in the inner core. Although phthalocyanines are used as dyes and pigments in ancient years, currently their usage includes liquid crystals,[1,2] non-linear optical materials,[3] semiconductors,[4,5] gas sensors,[6-8] electrocatalysis,[9,10] solar cell,[11-13] optical data storage,[14,15] catalysts[16-18] and photodynamic therapy.[19-22] The major drawback with phthalocyanines are aggregation of phthalocyanines and their poor solubility in common organic solvents which limits their application. To overcome solubility problem of phthalocyanines, bulky substituents can be introduced onto the phthalocyanine ring.[23-28] On the other hand, to overcome aggregation problem of phthalocyanines, many axially disubstituted silicon phthalocyanine complexes have been synthesized.[29-32]

Axial substitution is an attractive feature for phthalocyanines because of following reasons: (i) having different substituents macrocycle prevents aggregation and increases the solubility of phthalocyanines, (ii) the ligands can be highly functionalized, (iii) silicon phthalocyanines are resistant under chemical treatments.[33] Although there are many examples of no peripherally but axially substituted silicon phthalocyanines, only a few studies about peripherally or non-peripherally as well as axially substituted on the same molecule are known in the literature.[34-36] To the best of our knowledge, there is no report about the investigation of the electropolymerization properties of peripherally as well as axially substituted silicon phthalocyanines on the same molecule in the literature. Only one study published our research group was devoted to the electropolymerization properties of only axially disubstituted silicon phthalocyanines.[37] For these reasons, the aim of the present study is to synthesize new type of silicon phthalocyanines containing peripherally-{2-[3-(diethylamino)phenoxy]ethoxy} as well as axially di-(3-(4-phenylpiperazin-1-yl)propanoxy) groups and investigate of their electropolymerization properties. Owing to electropolymerization properties, these complexes might be a good candidate in different electrochemical technologies such as, electrocatalytic, electrochromic and electrosensing applications.

2. Experimental Section

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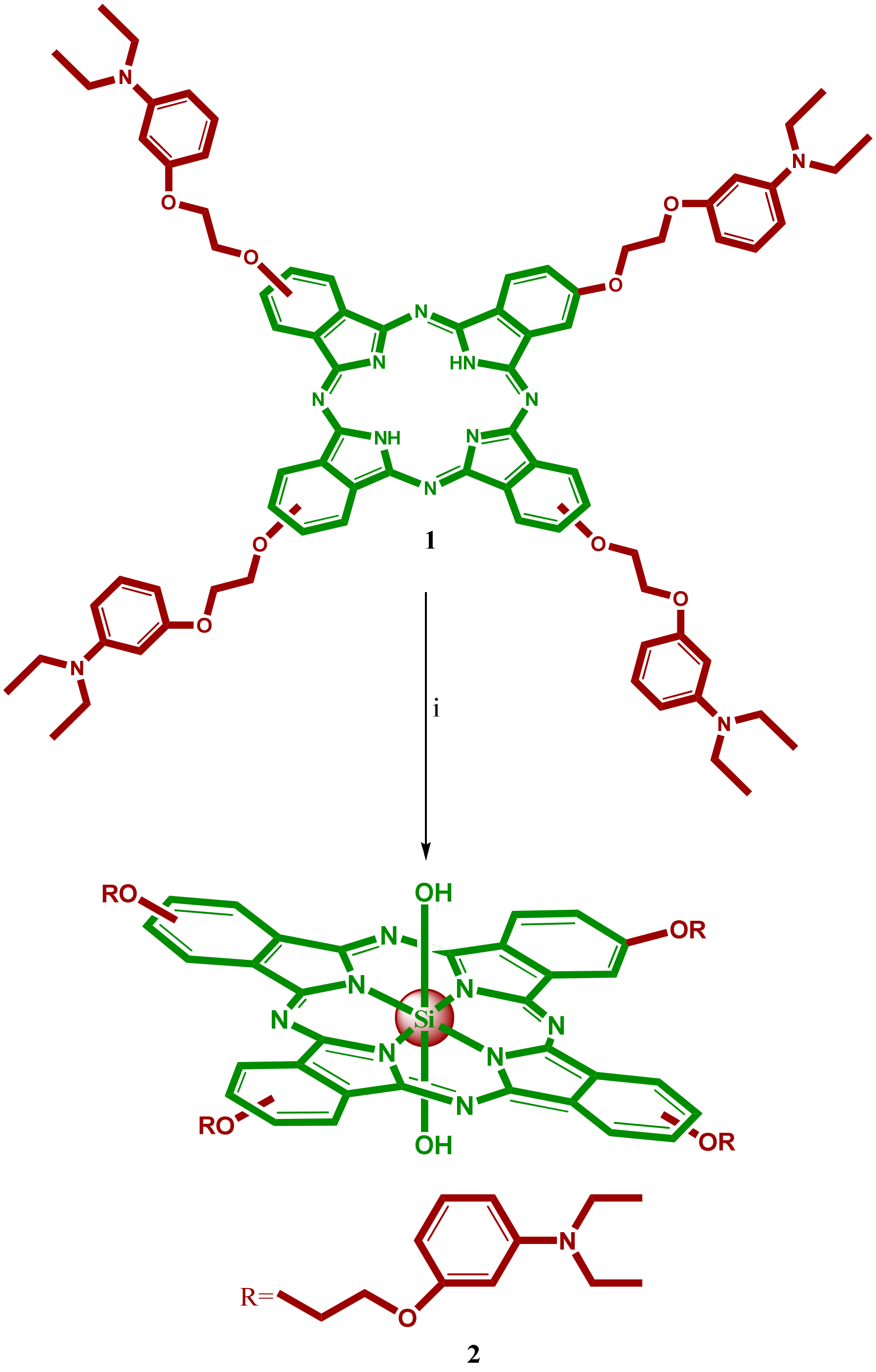
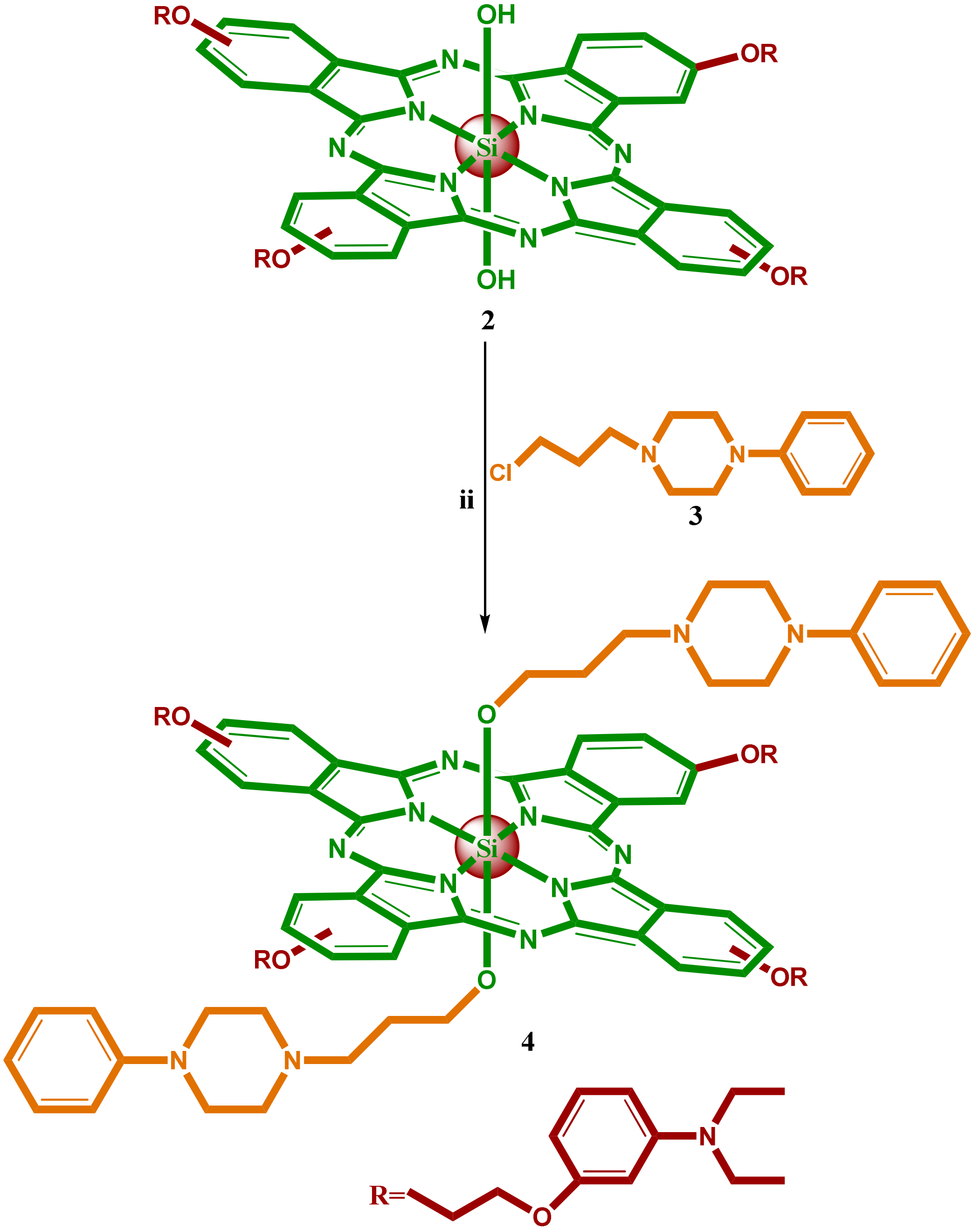


Scheme 1. The synthesis of silicon phthalocyanine **2.** (i) $HSiCl_3$, DBU, DCM,



Scheme 2. The synthesis of axially disubstituted silicon phthalocyanine **4**. (ii) Toluene, NaH, 120 °C.

2.1. Materials and methods

The used materials, equipments and the electrochemical measurements were supplied as supplementary information.

2.2. Synthesis

2.2.1. *Synthesis of SiPc (2)*

A portion of 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}phthalocyanine (300 mg, 0.22 mmol) was dissolved in dry dichloromethane (150 mL) and dry 1.8-diazabicyclo[5.4.0]undec-7-ene (16.4 mL). The solution was degassed with nitrogen for 10 min, followed by addition of trichlorosilane (4.4 mmol, 0.5 mL) and allowed to stir at room temperature for 18 h under nitrogen. Then, H_2O (50 mL) was added and the mixture was allowed to stir at room temperature for an 3 h. The organic phase was dried over $MgSO_4$, filtered and rotary evaporated. After evaporating the solvent in vacuo, the residue was purified by column chromatography over a aluminum oxide using a mixture of $CHCl_3$:MeOH (100:2) as solvent system. Yield: 128 mg (41%), m.p. > 250 ºC. IR (KBr) ν_{max}/cm^{-1}: 3399 (O-H), 3071 (Ar-H), 2965-2870 (Aliph. C-H), 1606, 1571, 1498, 1449, 1411, 1351, 1245, 1210, 1130, 1064, 1019, 801, 754, 685. ^{1}H-NMR. (400 MHz, $CDCl_3$), (δ:ppm): 7.54-7.49 (m, 8H, Ar-H), 7.15 (m, 4H, Ar-H), 6.39-6.30 (m, 16H, Ar-H), 4.40 (m, 16H, CH_2-O), 3.34 (m, 16H, CH_2-N), 1.16 (m, 24H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$), (δ:ppm): 165.11, 154.02, 149.30, 145.57, 138.98, 132.18, 130.44, 127.94, 125.95, 116.15, 113.18, 100.45, 99.24, 96.12, 65.04, 61.58, 44.38, 12.62. UV-Vis (chloroform): λ_{max}, nm (log ε): 684 (5.00), 616 (4.47), 353 (4.92), 339 (4.93). MALDI-TOF-MS m/z calc. 1403.69; found: 1404.55 $[M+H]^+$. Elemental Analysis : (Found: C 68.68, H 6.02, N 12.25%, $C_{80}H_{86}N_{12}O_{10}Si$ (1403.69) requires C 68.45, H 6.18, N 11.97%).

2.2.2. *Synthesis of SiPc (4)*

The $SiPc(OH)_2$ **2** (100 mg, 0.07 mmol) was dissolved in dry toluene (15 mL) under inert nitrogen atmosphere. Then 1-(3-chloropropyl)-4-phenylpiperazine **3** (33.3 mg, 0.14 mmol) and dry NaH (3.3 mg, 0.14 mmol) were added. The reaction mixture was heated and stirred under reflux at 120 °C for 24 h. After evaporating the solvent in vacuo, the residue was purified by column chromatography over a aluminum oxide using a mixture of $CHCl_3$:MeOH (100:4) as solvent system. Yield: 70 mg (55%), m.p. > 250 ºC. IR (KBr) ν_{max}/cm^{-1}: 3060 (Ar-H), 2928-2818 (Aliph. C-H), 1599, 1572, 1497, 1448, 1352, 1276, 1212, 1132, 1068, 1023, 924, 806, 755, 689. ^{1}H-NMR. (400 MHz, $CDCl_3$), (δ:ppm): 7.64 (d, 2H, *J*= 8, Ar-H), 7.30-7.14 (m, 22H, Ar-H), 6.96-6.93 (m, 6H, Ar-H), 6.89-6.87 (m, 4H, Ar-H), 6.45-6.43 (m, 4H, Ar-H), 4.65-4.63 (m, 8H, CH_2-O), 4.40-4.36 (m, 8H, CH_2-O), 3.40-3.34 (m, 24H, Ar-CH_2-N), 2.72-2.70 (m, 8H, CH_2-N), 1.20 (m, 24H, CH_3), -0.28 (m, 4H, CH_2-N), -1.31 (m, 4H, -CH_2-), -2.01 (m, 4H, Si-O-CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$), (δ:ppm): 160.10, 157.12, 156.66, 151.35, 149.38, 130.05, 129.13, 129.09, 128.96, 119.94, 119.64, 116.18, 116.01, 114.09, 105.67, 100.69, 99.40, 99.21, 69.18, 64.69, 58.92, 55.57, 53.29, 49.14, 44.44, 27.18, 12.67. UV-Vis (chloroform): λ_{max}, nm (log ε): 683 (5.03), 615 (4.44), 355 (5.82). MALDI-TOF-MS m/z calc. 1808.29; found: 1808.03 $[M]^+$. Elemental Analysis : (Found: C 70.67, H 6.54, N 12.70%, $C_{106}H_{122}N_{16}O_{10}Si$ (1808.29) requires C 70.41, H 6.80, N 12.39%).

3. RESULTS AND DISCUSSION

3.1. Characterization

The synthesis of 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine dihydroxide **2** and bis(3-(4-phenylpiperazin-1-yl)propanoxy), 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine **4** are shown in Scheme 1 and 2. Silicon insertion into the free-base 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}phthalocyanine[43] involved using trichlorosilane in a mixture of dichloromethane and 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) at room temperature to yield the dihydoxy silicon phthalocyanine **2**. Then, silicon(IV) phthalocyanine complex **4** was synthesized by heating silicon phthalocyanine dihydroxide **2** with 1-(3-chloropropyl)-4-phenylpiperazine[44] **3** in the presence of NaH in toluene at 120 ºC for 24 h. The structures of novel compounds were characterized by a combination of ^{1}H NMR, ^{13}C NMR, IR, UV-vis, mass spectroscopic data and elemental analysis as well.

In the IR spectra, the formation of silicon phthalocyanine dihydroxyide **2** were clearly confirmed by disappearance of the N-H band (3292 cm^{-1}) belonging to compound **1** and the appearance of the OH band at 3399 cm^{-1}. In the ^{1}H-NMR spectra the formation of silicon phthalocyanine dihydroxyide **2** were clearly confirmed by disappearance of the N-H group (-5.38 ppm) belonging to compound **1**. Also, ^{13}C-NMR spectra was also in good agreement with the structure of silicon phthalocyanine dihydroxyide **2**. Finally, the presence of a molecular ion peak at m/z= 1404.55 $[M+H]^+$ confirmed the proposed structure of silicon phthalocyanine dihydroxyide **2**.

The formation of bis(3-(4-phenylpiperazin-1-yl)propanoxy), 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine **4** was clearly confirmed by disappearance of the OH band at 3399 cm^{-1}. Examining the ^{1}H-NMR spectra of bis(3-(4-phenylpiperazin-1-yl)propanoxy), 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine **4** in $CDCl_3$ exhibited the expected chemical shifts. Also, H protons of Si-O-CH_2 at -2.01 ppm, H protons of -CH_2- at -1.31 ppm and H protons of -CH_2-N at -0.28 ppm have shifted negative area due to magnetic anisotropy of silicon phthalocyanine ring.[38-40] ^{13}C-NMR spectra were also in good agreement with the structure of bis(3-(4-phenylpiperazin-1-yl)propanoxy), 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine **4.** Final evidence of silicon phthalocyanine **4** was given by MALDI-MS where molecular ion peaks at m/z: 1808.03 $[M]^+$ is in accordance with the expected values.

In absorption spectroscopy generally, phthalocyanines have two strong absorption regions which one is around 300–500 nm called as "B" or "Soret" band and the other one is around 600–750 nm called as "Q" band.[41,42] The absorption spectra of silicon phthalocyanines **2** and **4** in chloroform at 1×10^{-5} mol.dm^{-3} concentration are shown in Fig. 1. The electronic spectra of the studied silicon phthalocyanines **2** and **4** showed characteristic absorptions in the Q band region at 684 and 683 nm, respectively, approving the monomeric structure. Also, B bands of the silicon phthalocyanines **2** and **4** were observed at around (353, 339 nm) for **2** and 355 nm for **4** in $CHCl_3$.

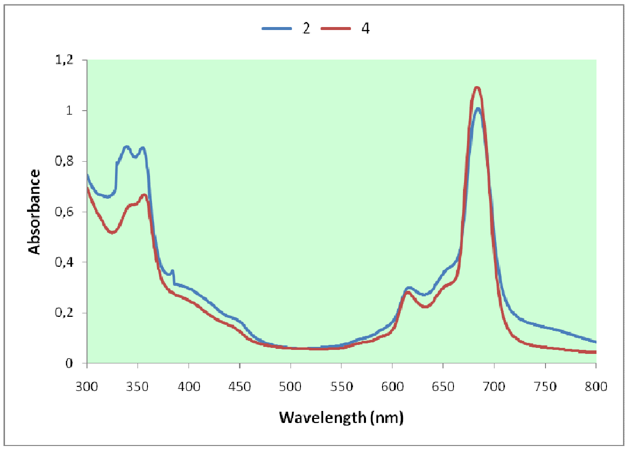


Fig. 1. UV-Vis spectrum of **2** and **4** in $CHCl_3$.

3.2. Electrochemical studies

Voltammetric studies of SiPcs **2** and **4** were carried out in dichloromethane (DCM)/tetrabutylammoniumperchlorate (TBAP) electrolyte system on a Pt working electrode with CV and SWV techniques. Basic redox parameters were derived from the voltammetric analyses and they are listed in Table 1.

2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine dihydroxide **2** and bis(3-(4-phenylpiperazin-1-yl)propanoxy), 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine **4** showed similar voltammetric responses in DCM/TBAP electrolyte system. CV and SWVs of silicon(IV)phthalocyanine dihydroxide **2** are represented in Fig. 2a and 2b. Silicon(IV)phthalocyanine dihydroxide **2** gave three reductions, $\mathbf{R_1}$ at -0.67 V (ΔE_p = 121 mV), $\mathbf{R_2}$ at -1.06 V(ΔE_p = 114 mV) and $\mathbf{R_3}$ at -1.30 V(ΔE_p = 107 mV) within the potential window of DCM/TBAP electrolyte system. Three reduction reactions (R_1 R_2 and R_3) are reversible with respect to ΔE_p values. SWV of the silicon(IV)phthalocyanine dihydroxide **2** illustrate these analyses results more clearly as shown in Fig 2b.

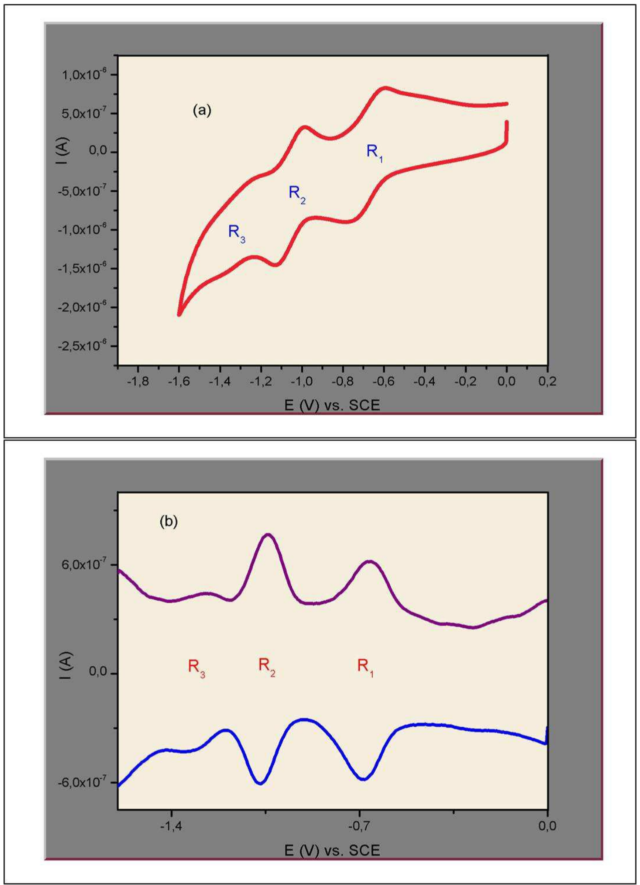


Fig. 2 (a) CVs of SiPc **2** at 0.100 V.s^{-1} in TBAP/DCM. (b) SWV of SiPc **2** at 0.100 V.s^{-1} in TBAP/DCM**.**

Fig. 3a and 3b show the CV and SWV responses of bis(3-(4-phenylpiperazin-1-yl)propanoxy), 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine **4** in DCM/TBAP electrolyte system. The cyclic voltammogram of silicon(IV)phthalocyanine **4** gave two reduction processes (Fig. 3a). It displays two reversible reduction reactions labeled as $\mathbf{R_1}$ ($E_{1/2}$ = -0.73 V; ΔE_p = 142 mV), $\mathbf{R_2}$ ($E_{1/2}$ = -1.16 V; ΔE_p = 149 mV). On the other hand, SVWs of the silicon(IV)phthalocyanine **4** clearly support these reversible characters of the processes, since these couples show symmetric cathodic peaks with the same peak currents (Fig. 3b). All reduction processes in silicon(IV) phthalocyanines **2** and **4** occur at the phthalocyanine ring, because the central Si(IV) metal is redox inactive, therefore the couples observed for SiPcs **2** and **4** due to ring-based reductions and oxidations. The difference between the silicon phthalocyanines **2** and **4** is the shifting of the redox processes of silicon phthalocyanine **4** toward the negative potentials with respect to silicon(IV)phthalocyanine dihydroxide **2.**

Table 1. Voltammetric data of the SiPcs. All voltammetric data were given versus SCE.

Complexes		Polymerization Waves	Reductions		
SiPc 2	$^aE_{1/2}$	1.01^c $(0.65)^d$	-0.67	-1.06	-1.30
	$^b\Delta E_p$ (mV)	-	121	114	107
SiPc 4	$^aE_{1/2}$	$1.30^c(0.56)^d$	-0.73	-1.16	-
	$^b\Delta E_p$ (mV)	-	142	149	-

$^{\mathbf{a}}$**:** $E_{1/2}$ values ((E_{pa}+E_{pc})/2) were given versus SCE at 0.100 Vs^{-1} scan rate. $^{\mathbf{b}}$**:** ΔE_p= E_{pa}-E_{pc}. ^{c}: E_{pa} of first CV cycle; ^{d}: E_{pc} of first CV cycle.

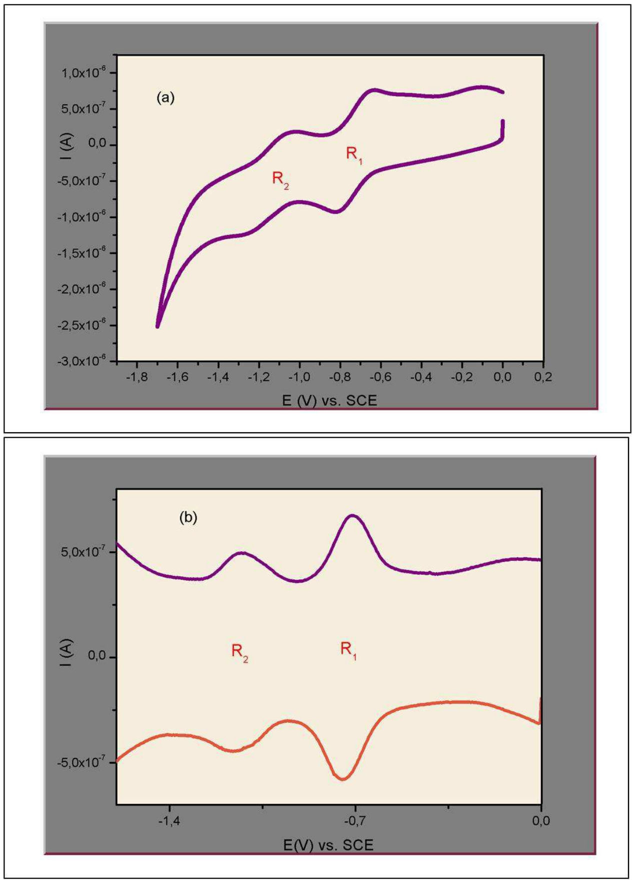


Fig. 3 (a) CVs of SiPc **4** at 0.100 V.s^{-1} in TBAP/DCM. (b) SWV of SiPc **4** at 0.100 V.s^{-1} in TBAP/DCM**.**

Also, the peak currents increased linearly with the square root of the scan rates for scan rates ranging from 25 to 500 mV.s^{-1} for these silicon(IV) phthalocyanines **2** and **4** (Fig. 4a for SiPc **2** and Fig. 4b for SiPc **4**).

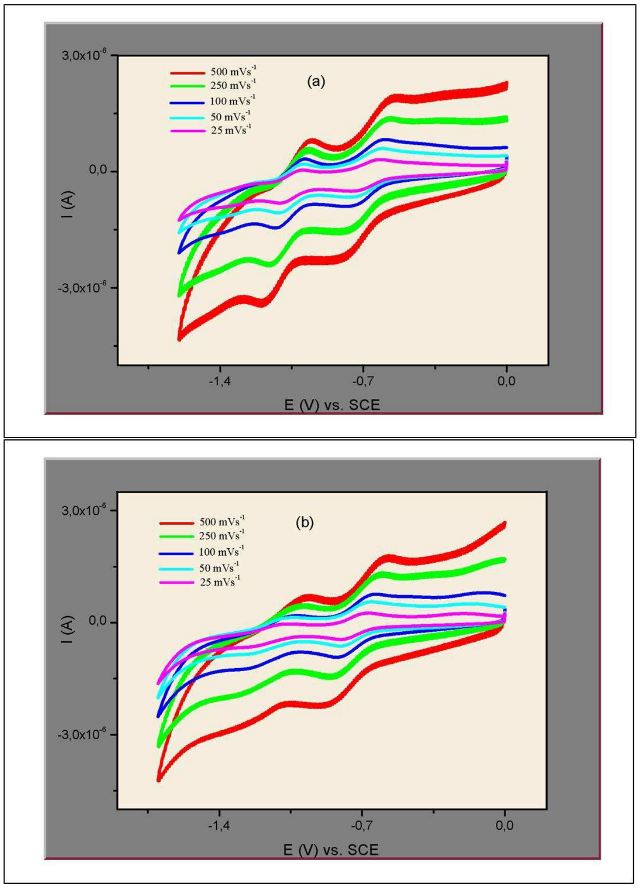


Fig. 4 (a) CV of silicon phthalocyanine **2** at various scan rates (ranging from 25 to 500 mV.s^{-1}) on a Pt working electrode in DCM/TBAP. (b) CV of silicon phthalocyanine **4** at various scan rates (ranging from 25 to 500 mV.s^{-1}) on a Pt working electrode in DCM/TBAP.

2(3),9(10),16(17),23(24)-Tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine dihydroxide **2** and bis(3-(4-phenylpiperazin-1-yl)propanoxy), 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine **4** showed different redox responses during the oxidation reaction. While the silicon(IV) phthalocyanines **2** and **4** gave common reduction reactions during the cathodic potential scans, they were oxidatively electropolymerized on the working electrode in DCM. Figure 5 shows repetitive CVs of 2(3),9(10),16(17),23(24)-tetrakis-{2-[3-(diethylamino)phenoxy]ethoxy}silicon(IV)phthalocyanine dihydroxide **2** recorded at 0.100Vs^{-1} scan rate within positive potential window of DCM/TBAP. While the first anodic CV cycle, a big wave is observed at 1.01 V which triggers polymerization of the complex. As shown in Fig. 5, during the first anodic scans, it gives an anodic wave at 1.01 V and its reverse cathodic wave at 0.65 V. During the repetitive potential scans, a new huge anodic wave is recorded at 1.32 V, which increases with positive potential shift up to 6. CV cycles. After 6. CV cycles this wave starts to decrease to 20. cycle with potential shift, indicating electropolymerization of the silicon(IV)phthalocyanine dihydroxide **2** on the working electrode. The film on the electrode surface was seen easily with naked eyes.

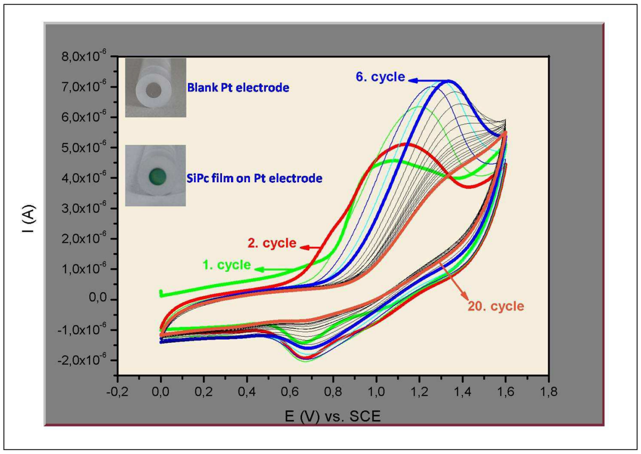


Fig. 5 Repetitive CVs of silicon(IV) phthalocyanine **2** recorded at anodic potential windows of DCM/TBAP electrolyte system at 0.100 Vs^{-1} scan rate on a Pt working electrode.

Figure 6 shows repetitive CVs of silicon(IV) phthalocyanine **4** recorded at 0.100Vs^{-1} scan rate within positive potential window of DCM/TBAP. During the first anodic CV cycle, anodic redox couple was recorded at 1.30 V and its cathodic couple was recorded at 0.56 V. During the second, third and fourth CV cycles, the anodic wave decreases with a potential shift at 1.42 V with increasing current intensity. After this point, it decreases in current intensity until the 20. cycle. These voltammetric behavior of the silicon(IV) phthalocyanine **4** illustrate coating of the complex on the working electrode with an electropolymerization process. The film on the electrode surface was seen easily with naked eyes. Although silicon(IV) phthalocyanines **2** and **4** show highly solubility in DCM, electropolymerized silicon(IV) phthalocyanines **2** and **4** is insoluble in DCM. In previous papers, authors reported electropolymerization of peripherally tetra-substituted metallophthalocyanines bearing various amino moieties,[45,46] ethylenedioxythiophene,[47] hydroquinoline groups.[48] But this study is the first example of electropolymerization of both peripherally tetra and axially di-substituted silicon phthalocyanines on the same molecule.

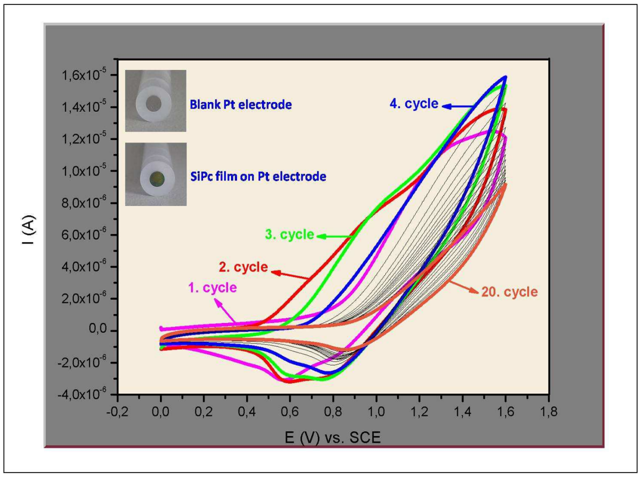


Fig. 6 Repetitive CVs of silicon(IV) phthalocyanine **4** recorded at anodic potential windows of DCM/TBAP electrolyte system at 0.100 Vs^{-1} scan rate on a Pt working electrode.

4. Conclusion

In conclusion, in this study synthesis, spectral characterization, and electrochemical properties of novel peripherally tetra-{2-[3-(diethylamino)phenoxy]ethoxy} substituted silicon phthalocyanine dihydroxide and peripherally tetra-{2-[3-(diethylamino)phenoxy]ethoxy}, axially di-(3-(4-phenylpiperazin-1-yl)propanoxy) substituted silicon phthalocyanine were presented for the first time. These complexes were fully characterized by various spectroscopic techniques such as ^{1}H-NMR, ^{13}C-NMR, IR, UV-Vis, MALDI-TOF spectra and elemental analysis as well. Electrochemical measurements indicate that peripheral substitution of the complex with 2-[3-(diethylamino)phenoxy]ethoxy} groups and axial substitution of the complex with (3-(4-phenylpiperazin-1-yl)propanoxy) groups supply electropolymerization of the complexes on the working electrode. As a result, this study is the first example of electropolymerization of both peripherally tetra and axially di-substituted silicon phthalocyanines on the same molecule. Electropolymerization behaviors of the silicon phthalocyanines are the desired properties of the electrochemical applications, especially, electrocatalytic, electrochromic and electrosensing applications.

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Notes and references

[a] *Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey, ; Tel: +90 462 377 36 64; E-mail: zekeriya_61@yahoo.com*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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