






Electroanalytical characterization of chloroquinoline substituted redox-active phthalocyanines

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Abstract

In the first part of this study, the synthesis and characterization of organosoluble 5-chloroquinolin-8-yloxy substituted iron(II) (2) and oxo-titanium (IV) phthalocyanines (3) are reported for the first time. These compounds have been characterized by elemental analysis, Fourier transform infrared, electronic spectroscopy, and mass spectra. Electrochemical behaviors of metal-free and cobalt phthalocyanines and further new types of iron and oxo-titanium phthalocyanines were investigated using electroanalytical methods, such as cyclic (CV) and square wave voltammetry (SWV). According to the electrochemical results, phthalocyanines by and large showed one-electron metal- and/or ligand-based reversible or quasi-reversible reduction and oxidation processes.

All in all, this study's results inevitably create a useful way to use them in possible future studies, which will particularly attempt to use the compound investigated in potential areas of use.

Keywords: Iron, titanium, electrochemistry, redox-active, chloroquinoline

1. Introduction

Phthalocyanines (Pcs) are planar heteroatomic molecular systems constituted by four isoindole units linked with nitrogen atoms. Of several well-known properties; the most significant ones are thermal stability, chemical resistance, optical properties, and liquid or crystal properties. More than seventy different elements have so far been used in phthalocyanine rings as central atoms to date. Phthalocyanines have been of great interest to researchers and hence the subject of extensive research in the past few decades. Some of the critical subjects studied so far are lithium batteries, optical data storage, solar energy conversion, catalysis, etc. [1–10]. In addition to the potential of their use in pure material science, phthalocyanines are known to be rather fascinating and thought-provoking compounds in terms of their electroanalytical properties [11–13]. Many studies in the literature examine the electroanalytical and spectroelectroanalytical properties of phthalocyanines [14–16].

A neutral formula can summarize the electroanalytical behavior of phthalocyanines, which is presented as a dianion, Pc^{2-} that can be reduced or

oxidized sequentially. The electrochemical activity of the metal-free Pcs is attributed to the boundary orbitals of the molecular structure, where the oxidation is the removal of the electron (s) from the HOMO (a_{1u}). On the other hand, the reduction is the addition of electrons (s) to LUMO (e_g). While two electrons are being removed from the HOMO yielding Pc^{-1} and Pc^{-2} , four electrons are added to the doubly degenerate e_g orbitals of the LUMO yielding Pc^{-3} , Pc^{-4} , Pc^{-5} and Pc^{-6} . Besides, metallated Pcs containing electroactive central metals exhibit electroactivity, commonly associated with the central metals located at the core of the ring [17]. While the common examples of electroactive metals include iron, cobalt, manganese, and titanium, electrochemically inactive metals include nickel, zinc, and magnesium. A plurality of species can thus be formed by subsequent oxidation or reducing the phthalocyanine ring and/or the central metal ion. Each oxidation or reduction product is of a different spectrum to be used for characterization. In addition to the nature and oxidation state of the central metal and the substituents' nature in

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the Pc ring, the nature of any axial ligand and solvents play a crucial role in the characterization [17].

In some of our previous papers, we reported the synthesis and electroanalytical characterization of a large number of tetra-substituted metal-free and metallophthalocyanines [18–20]. In literature, it can be seen that the aromatic methyl-substituted quinoline ring increases the conjugation effect thereby improving GCE's performance (Glassy carbon electrode) to detect nitrites [21]. In this regard, the synthesis and characterization of the 5-chloroquinolin-8-yloxy group substituted novel phthalocyanines (FePc (2), oxo-TiPc (3)) were performed in this study. In addition to synthesis, electrochemistry of 5-chloroquinolin-8-yloxy group substituted novel phthalocyanines (FePc (2), oxo-TiPc (3)) and H₂Pc (4), CoPc (5) previously synthesized by our working group [22] were determined and characterized by electroanalytical methods such as example cyclic (CV) and square wave voltammetry (SWV). In the examination of the electrochemical properties of phthalocyanines, redox-active (Mn, Fe, Co, and Ti) centers and redox-inactive (Ni, Cu, and Zn) centers can be preferred. The first oxidation and first reduction processes occur at the metallic center of the MPc. For redox-inactive derivatives, redox processes arise only on the Pc ring. The reason why Co, Fe and Ti central metals are chosen in this study is that they yield the redox-active center in metallophthalocyanine complexes.

2. Experimental

2.1. Materials and Methods

All reagents and solvents were dried and purified as described in Perrin and Armarego [23]. 5-chloroquinolin-8-ol (1) was obtained from commercial supplier. 4-nitro phthalonitrile [24], 4-(5-chloroquinolin-8-yloxy)phthalonitrile (1) [22], unmetallated phthalocyanine (4) [3] and 2,9(10), 16(17), 23(24)-tetrakis-[(5-chloroquinolin-8-yloxy)phthalocyanato] cobalt (II) (5) [3] were prepared according to the reported procedures.

All electrochemical measurements were carried out with Gamry Interface 1000 potentiostat/galvanostat utilizing a three-electrode configuration at 25°C. The working electrode was a Pt disc with a surface area of 0.071 cm². A Pt wire was served as the counter electrode and saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure dichloromethane (DCM) was employed as the supporting electrolyte at a concentration of 0.10 mol dm⁻³.

2.2. Synthesis

2.2.1. 2, 9(10), 16(17), 23(24) -Tetrakis-[5-chloroquinolin-8-yloxy] phthalocyaninato iron (II) (2)

After 4-(5-chloroquinolin-8-yloxy)phthalonitrile (3) (0.20 g, 0.65 mmol) was dissolved in 1 mL dry n-pentanol in a sealed tube, anhydrous Fe(CH₃COO)₂ (57 mg, 0.33 mmol) and three drops of 1,8-diazabicyclo[5.4.0]undec-7-ene were added to the reaction medium. The mixture was stirred under a nitrogen atmosphere at 160 °C for 18 hours. Next, the reaction mixture was cooled to room temperature, n-hexane (20 mL) was added, and the crude product was filtered off. Purification of this new compound was carried out by silica gel column chromatography using chloroform-methanol (83:17) solvent system as an eluent.

Yield: 127 mg (61 %), M.p.: > 300 °C (decomposition). FT-IR $\nu_{\max}/\text{cm}^{-1}$: 3058 (Ar-H), 1606, 1459, 1383, 1226, 1121, 1077, 929, 816, 783, 746. MALDI-TOF, m/z : Calc.: 1278,74 for C₆₈H₃₂N₁₂Cl₄O₄Fe, Found: 1278,40 [M]⁺. UV/vis (Chloroform, 1x10⁻⁵ M): λ , nm (log ϵ): 363 (5.00), 594 (4.49), 690 (5.04). Anal. Calc. for C₆₈H₃₂N₁₂Cl₄O₄Fe: C, 63.87; H, 2.52; N, 13.14 %, Found: C, 61.93; H, 2.58; N, 13.09 %.

2.2.2. 2, 9(10), 16(17), 23(24) -Tetrakis-[5-chloroquinolin-8-yloxy] phthalocyaninato oxotitanium (IV) (3)

The synthesis method of compound 2 was used to synthesize compound 3 except that titanium (IV) butoxide salt was used instead of Fe (CH₃COO)₂ salt. The amounts of the reagents were; 4-(5-chloroquinolin-8-yloxy)phthalonitrile (1) (0.20 g, 0.65 mmol), anhydrous Ti(OBu)₄ (0,23 mL, 0.65 mmol). The obtained product was purified by washing with different solvents.

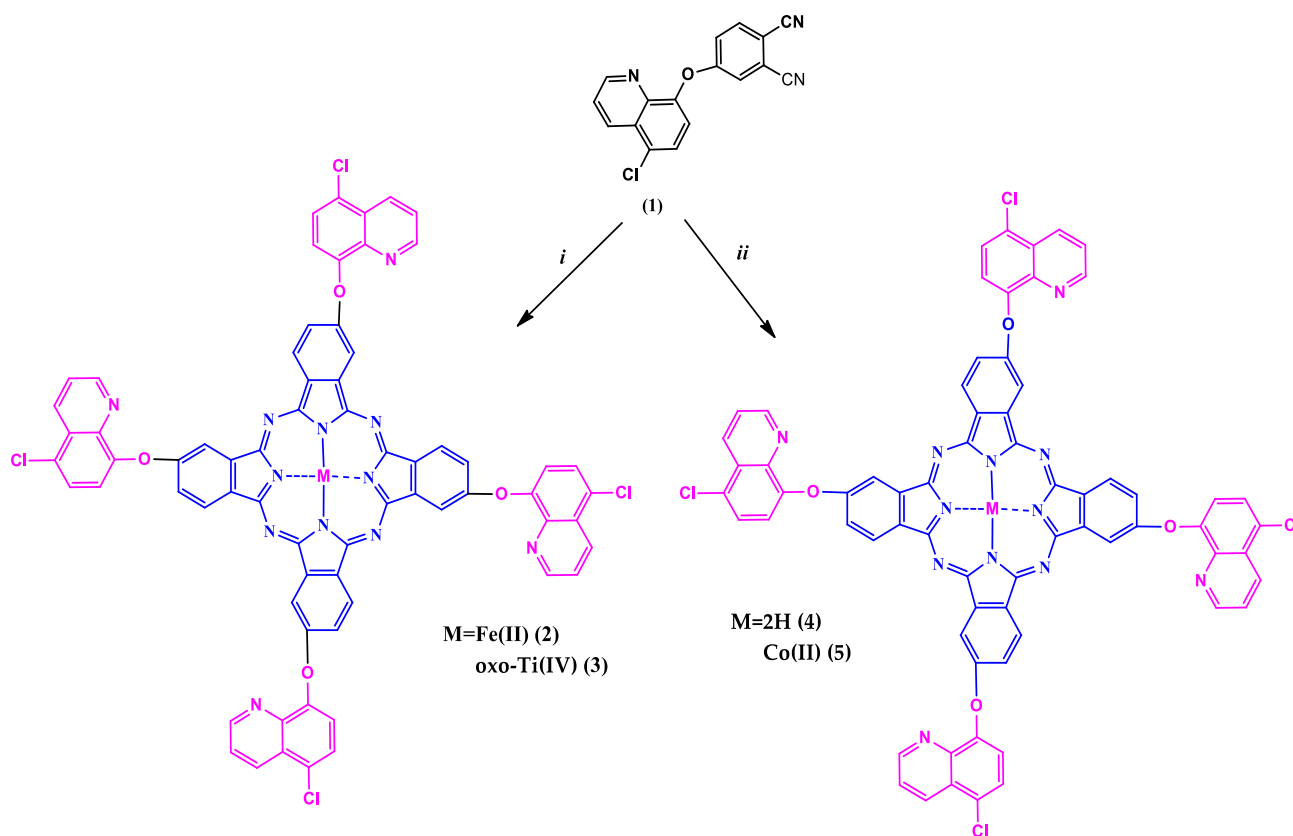
Yield: 87 mg (41 %), M.p.: >300 °C (decomposition). FT-IR $\nu_{\max}/\text{cm}^{-1}$: 3058 (Ar-H), 1715, 1586, 1460, 1296, 1228, 1036, 931, 822, 784, 747. MALDI-TOF, m/z : Calc.: 1286,77 for C₆₈H₃₂N₁₂Cl₄O₅Ti, Found: 1286,20 [M]⁺. UV/vis (Chloroform, 1x10⁻⁵ M): λ , nm (log ϵ): 342 (4.97), 398 (4.57), 630 (4.63), 664 (4.76), 700 (5.27). Anal. Calc. for C₆₀H₃₆N₂₀O₄Zn: C, 63.47; H, 2.51; N, 13.06 %, Found: C, 63.54; H, 2.46; N, 13.10 %.

3. Results and Discussion

3.1. Synthesis and characterization

The phthalonitrile 1, metal-free phthalocyanine 4 and Co(II) phthalocyanine compounds 5 were obtained according to the procedure expressed in a previously published article [22]. The complete method used in all synthesized compounds is set out in Scheme 1 in detail.

The structure of new compounds was illuminated using FT-IR, UV-Vis, MALDI-TOF mass spectroscopic techniques and elemental analyses.



Scheme 1. Synthesis of novel phthalocyanines (2-3), reaction conditions: *i*: *n*-pentanol, 1,8-diazabicyclo[5.4.0]undec-7-ene and related metal salts (Fe(ac)₂, titanium (IV) butoxide) at 160 °C. *ii*: [22]

Synthesis of novel iron (II) and titanium (IV) phthalocyanine compounds (2 and 3) were achieved by the treatment of phthalonitrile 1 in the presence of related anhydrous metal salts (Fe(CH₃COO)₂ and Ti(OBu)₄). The yields of the reactions carried out in dried *n*-pentanol at 160 °C were determined as 61% and 41%, respectively. Iron (II) phthalocyanine was purified using column chromatography, while titanium (IV) phthalocyanine was washed with different solvents to remove impurities.

In the FT-IR spectra of phthalocyanines 2 and 3, the loss of peak belonging to the C≡N vibration observed at 2233 cm⁻¹ of 4-(5-chloroquinolin-8-yloxy)phthalonitrile

(3) is a shred of strong evidence that the compounds 2 and 3 were formed by cyclotetramerization of the dinitrile compound. Besides, upon the cyclotetramerization, there were no further significant changes available in the IR spectra of these compounds. Mass spectra of phthalocyanine compounds 2 and 3 reasonably supported the expected structures when observing molecular ion peaks at 1278,40 as [M]⁺ for 2 and 1286,20 as [M]⁺ for 3 (Fig. 1 and Fig. 2), respectively.

3.2. UV-Vis absorption spectra

The UV-vis spectroscopy for characterization of the phthalocyanine compounds is a mean, which is known to be one of the best available approaches.

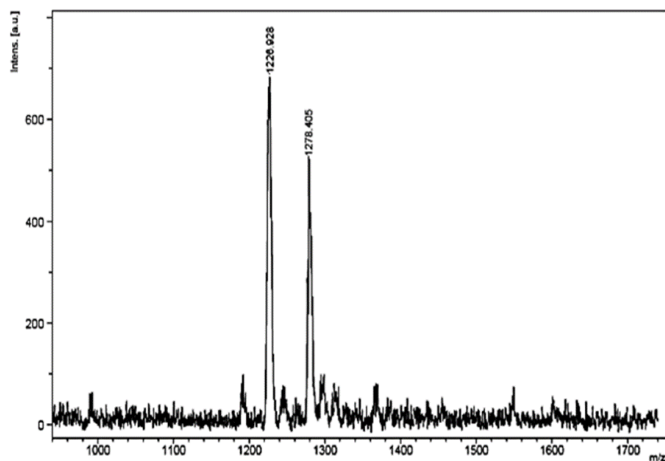


Figure 1. Mass spectrum of compound 2

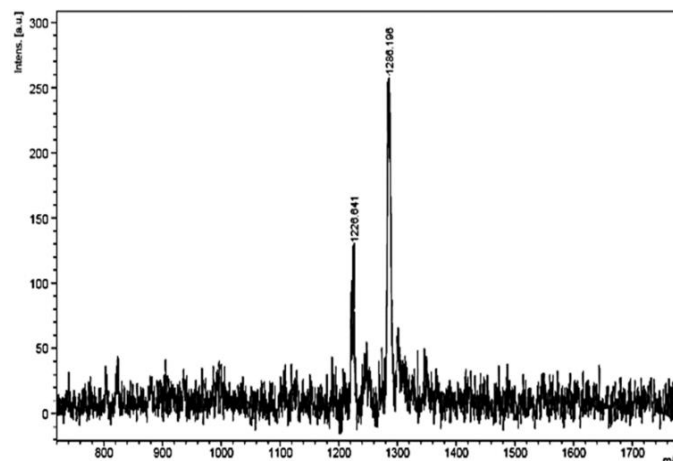


Figure 2. Mass spectrum of compound 3

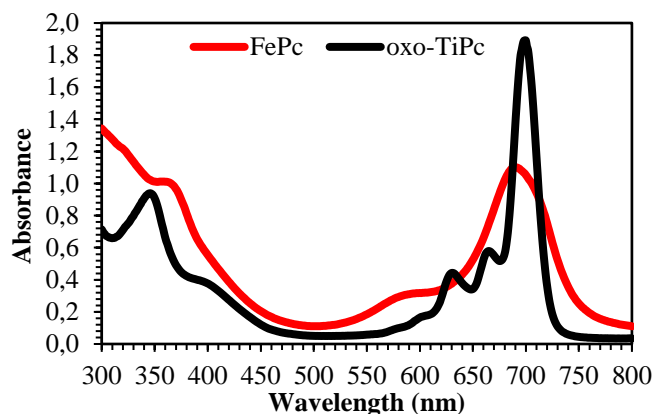


Figure 3. Absorption spectra of novel synthesized compounds in chloroform at 1.10^{-5}M

In the UV-vis spectrum of metallophthalocyanines, two characteristic peaks called **Q** and **B** bands emerging from $\pi \rightarrow \pi^*$ electronic transitions are observed [17]. In our case, the Q band appeared at about 600–750 nm, while the B band arised at about 300–450 nm.

Oxotitanium phthalocyanine compounds displayed remarkable absorption property and photosensitivity in the near-infrared region was characterized by the sharp absorption Q band with two small peaks as shoulders [25,26].

In the UV-Vis spectrum of the newly synthesized oxotitanium phthalocyanine **3**, the intense Q-band was recorded at 700 nm. Two shoulders appeared at 664, 630 nm, and the B-band at 342 nm as expected. FePc **2**, another novel phthalocyanine, yielded Q band at 690 nm with shoulders at 594 and B band at 363 nm in the UV region set out in Fig. 3 and Table 1.

It is well-known fact that the absorption of the Q-band of the phthalocyanine compounds in the UV-vis spectrum is more or less influenced by several factors: namely, due to the existence of metal ion in the central ring, ligand-bound in the axial position, the binding position of the substituent and aggregation in solvents [17]. The Q band of oxotitanium phthalocyanine **3** exhibited red-shifted approximately 10 nm compared to that of the iron phthalocyanine, because **3** consists of oxygen atom as an axial ligand [27].

3.3. Electrochemical Studies

The definitions of the redox couples and electrochemical data, including the half-wave peak potentials ($E_{1/2}$), peak-to-peak potential separations (ΔE_p), and the difference between the first oxidation and reduction potentials ($\Delta E_{1/2}$) are listed in Table 2.

Table 1. Absorption spectral data for the substituted **2** and **3** in chloroform in 20 °C

Compound	λ_{max} , nm (log ϵ)	
	B band	Q band
2	363 (5.00)	594 (4.49), 690 (5.04)
3	342 (4.97), 398 (4.57)	630 (4.63), 664 (4.76), 700 (5.27)

Table 2. Voltammetric data of the phthalocyanines. All voltammetric data were given versus SCE

Phthalocyanines	Label	$^a E_{1/2}$	$^b \Delta E_p$ (mV)	$^c \Delta E_{1/2}$
2	R ₁	-0.61	153	1.47
	R ₂	-0.98	144	
	R ₃	-1.25	234	
	O ₁	0.86	86	
	O ₂	1.26	151	
3	R ₁	-0.55	130	1.56
	R ₂	-0.72	141	
	R ₃	-0.89	125	
	R ₄	-1.04	148	
	O ₁	1.01	245	
4	R ₁	-0.70	158	1.87
	R ₂	-1.19	149	
	O ₁	0.68	162	
	O ₂	1.17	220	
5	R ₁	-0.21	96	0.89
	R ₂	-0.51	138	
	R ₃	-1.44	89	
	O ₁	0.68	130	

Fig. 4 shows the cyclic and square-wave voltammograms of **4** in DCM. **4** gives ring-based, quasi-reversible, two one-electron reductions (R₁ = -0.70 V, R₂ = -1.19 V) and two oxidation (O₁ = 0.68 V, O₂ = 1.17 V) processes.

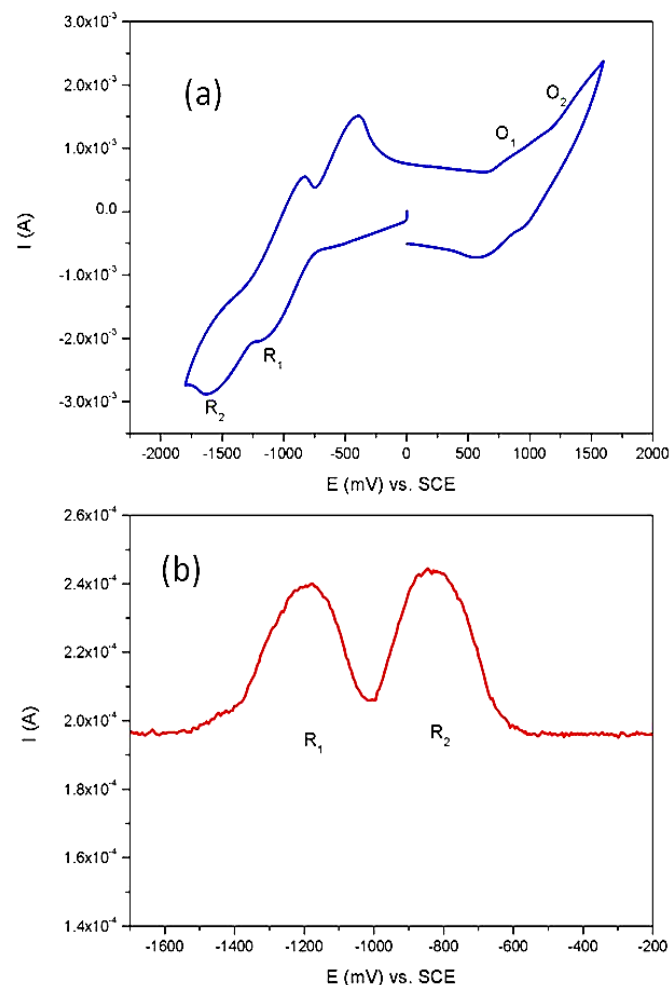


Figure 4. (a) Cyclic voltammogram of **4** on Pt in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ electrolyte. (b) Square wave voltammogram of **4** on Pt in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ electrolyte, step size = 5 mV; pulse size = 100 mV; Frequency = 25Hz

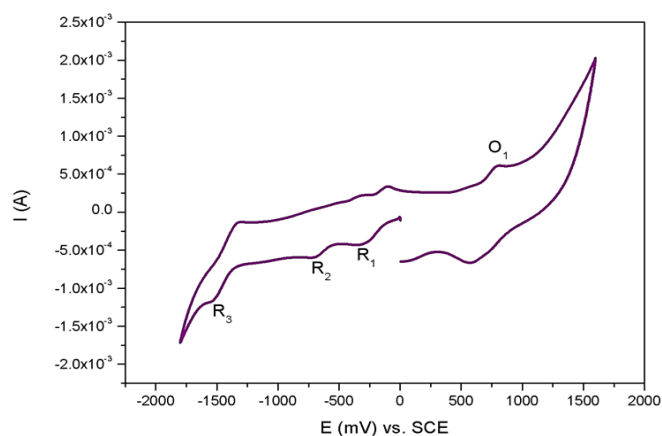


Figure 5. (a) Cyclic voltammogram of **5** on Pt in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ electrolyte

The general redox character of the **4** was found to be consistent with the known **4** behavior available in the literature [28]. As is shown in Table 2, the involvement of Co(II), Fe(II), and Ti(IV) in the center instead of 2H increased the redox richness of the phthalocyanines with an extra electron transfer process. Fig. 5 shows the CV response of **5**. Compound **5** signifying three reduction process labeled as R_1 ($E_{1/2} = -0.21$ V, reversible), R_2 ($E_{1/2} = -0.51$ V, quasi-reversible), R_3 ($E_{1/2} = -1.44$ V, reversible) and one quasi-reversible oxidation reaction process labeled as O_1 ($E_{1/2} = 0.68$ V), respectively. R_1 is a metal-based reduction process, R_2 and R_3 are ring based reduction processes. Fig. 6 shows CV and SWV responses of **2** in DCM/TBAP electrolyte. Compound **2** gave three quasi-reversible reduction processes and two oxidation processes. On the one hand, the process R_1 of the **2** was in a metal-based character. On the other hand, second and third reduction reactions (R_2 and R_3) were determined as probable ring-based processes. Fig. 7 shows CV and SWV responses of **3** in DCM/TBAP electrolyte on a Pt working electrode. **3** gave four reductions, R_1 at -0.55 V ($\Delta E_p = 130$ mV), R_2 at -0.72 V ($\Delta E_p = 141$ mV), R_3 at -0.89 V ($\Delta E_p = 125$ mV), R_4 at -1.04 V ($\Delta E_p = 148$ mV) and one oxidation reaction O_1 at 1.01 V ($\Delta E_p = 245$ mV) within the potential window of DCM/TBAP electrolyte system. R_1 , R_2 , R_3 , R_4 reduction processes are attributed to metal-ring-based electron transfer processes [29]. According to the ΔE_p values of reduction and oxidation, **3** gave four quasi-reversible (R_1 , R_2 , R_3 , R_4) reduction and one irreversible oxidation (O_1) reactions. HOMO–LUMO gaps of **4** ($\Delta E_{1/2} = 1.87$), **5** ($\Delta E_{1/2} = 0.89$), **2** ($\Delta E_{1/2} = 1.47$), **3** ($\Delta E_{1/2} = 1.56$) were found to be rather consistent with those of the phthalocyanines early reported in the literature [30–32].

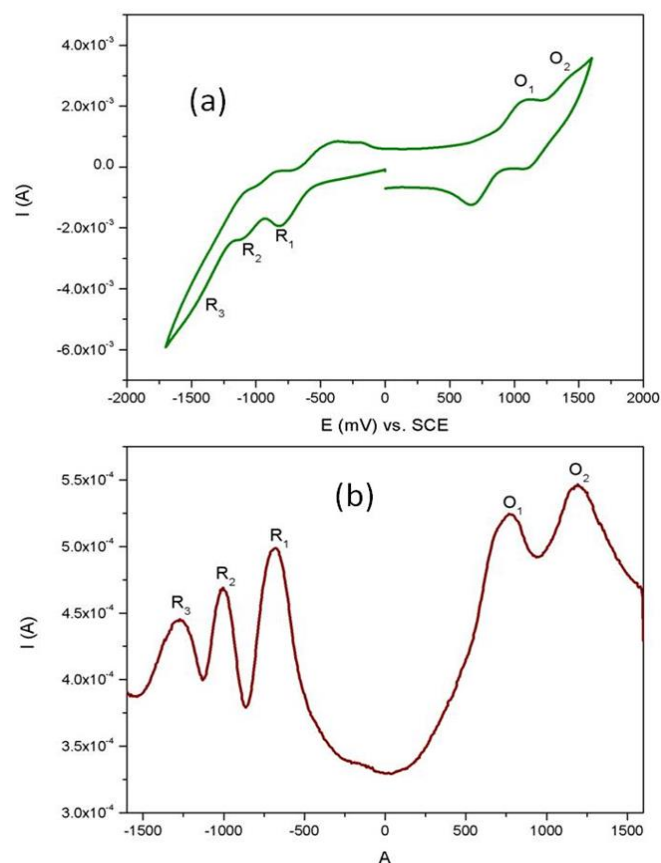


Figure 6. (a) Cyclic voltammogram of **2** on Pt in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ electrolyte. (b) Square wave voltammogram of **2** on Pt in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ electrolyte, step size = 5 mV; pulse size = 100 mV; Frequency = 25Hz

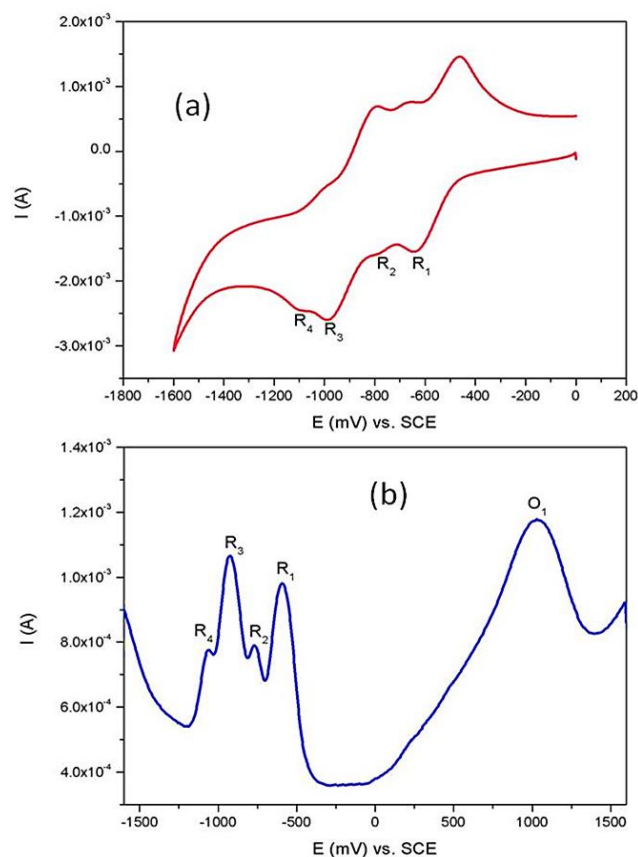


Figure 7. (a) Cyclic voltammogram of **3** on Pt in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ electrolyte. (b) Square wave voltammogram of **3** on Pt in $\text{CH}_2\text{Cl}_2/\text{TBAP}$ electrolyte, step size = 5 mV; pulse size = 100 mV; Frequency = 25Hz

4. Conclusion

In this study, the synthesis of novel peripherally chloroquinoline substituted **2**, and **3** compounds were determined and characterized using different spectroscopic techniques (e.g. FT-IR, elemental analysis, mass spectroscopy, UV/Vis spectral data) for the first time. Voltammetric analysis of 5-chloroquinolin-8-yloxy group substituted phthalocyanines were studied in solution with voltammetric measurements. While metal-free phthalocyanine **4** gave Pc ring based redox processes, metallophthalocyanines (Fe²⁺, Co²⁺, Ti⁴⁺) gave metal-based electron transfer reactions in addition to the Pc based redox reactions, which enriched the possible usage of the complex in various electrochemical technologies such as electrocatalytic and electrochromic applications.

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