

Synthesis and electrochemistry of phthalocyanines bearing [(3,4-dimethoxybenzyl)oxy] groups

İpek ÖMEROĞLU, Zekeriya BIYIKLIOĞLU*

Department of Chemistry, Faculty of Science, Karadeniz Technical University, Trabzon, Turkey

Received: 27.08.2014

Accepted/Published Online: 05.12.2014

Printed: 30.04.2015

Abstract: In this study peripherally tetra-substituted metal-free, metallophthalocyanines bearing (3,4-dimethoxybenzyl)oxy groups have been synthesized and characterized. Electrochemical properties of novel phthalocyanines **4**, **5**, **6**, and **7** were determined by cyclic and square wave voltammetry in order to define their possible applications in different electrochemical technologies. Co^{II} and Ti^{IV} metal ions behave as redox active cations in the core of the CoPc and TiOPc complexes, respectively. Voltammetric studies revealed that phthalocyanines have reversible/irreversible redox processes, which are the main requirement for the technological usage of these compounds.

Key words: Phthalocyanine, oxotitanium, cobalt, electrochemistry, voltammetry

1. Introduction

Phthalocyanines are important compounds having thermal and chemical stability. Therefore, this class of compounds exhibits technological applications in different areas such as chemical sensors,^{1–3} solar cells,^{4–6} gas sensors,^{7–9} liquid crystals,^{10,11} optical data storage,^{12,13} photodynamic therapy,^{14–18} nonlinear optics,¹⁹ and electrochemical applications such as electrocatalytic,^{20,21} electroensing,^{22,23} and electrochromic materials.²⁴ Although phthalocyanines display wide technological applications, because of the low solubility of phthalocyanines, their application is limited. To enhance the solubility, alkyl, alkoxy, phenoxy, methoxy, and macrocyclic groups can be attached to the peripheral positions of phthalocyanines.^{25–29}

Metallophthalocyanines are studied owing to their interesting electrochemical properties.^{30,31} Their electrochemical properties are easily arranged by changing the metal center, number, and position of substituents. Metallophthalocyanines have proven to be functional species for electrocatalysts, sensors, and electrochromic devices because of their rich redox behavior owing to central metals having different oxidation states.^{32,33} Because of different oxidation states of CoPc and TiOPc, there is a growing interest about the CoPc and TiOPc complexes.^{34–36} Despite this, studies of the electrochemical properties of CoPc and TiOPc are still rare in the literature.^{37–39} Thus, in this paper, we aimed to synthesize a new class of phthalocyanines bearing [(3,4-dimethoxybenzyl)oxy] groups on peripheral positions of phthalocyanine. For these reasons, we have synthesized and investigated electrochemical properties of these peripherally tetra-substituted metal-free cobalt(II), copper(II), and titanium(IV) phthalocyanines.

*Correspondence: zekeriya@ktu.edu.tr

2. Results and discussion

2.1. Syntheses and characterization

The synthesis of the new compounds is summarized in Figure 1. In the IR spectrum of phthalonitrile derivative **3**, the characteristic $C\equiv N$ stretching vibrations were observed at 2229 cm^{-1} . After the reaction of cyclotrimerization, this sharp peak disappeared in the spectra of **4**, **5**, **6**, and **7**. On the other hand, the IR spectra of metal-free **4** and metallophthalocyanines **5**, **6**, and **7** were very similar, except for the ν (NH) and (Ti=O) vibrations at 3289 and 958 cm^{-1} , respectively.

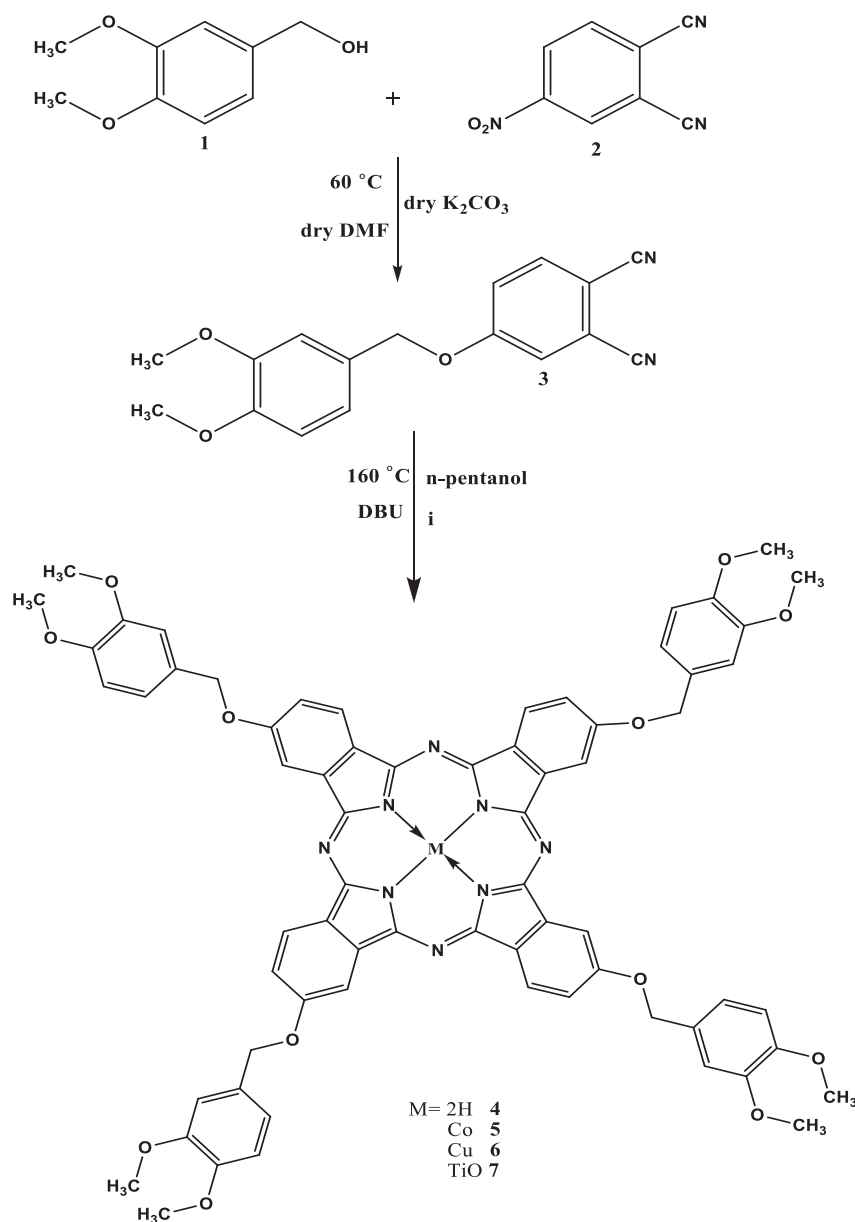


Figure 1. The synthesis of the phthalonitrile metal-free and metallophthalocyanines. (i) $CoCl_2$, $CuCl_2$, $Ti(OCH_2CH_2CH_2CH_3)_4$, n-pentanol, DBU, $160\text{ }^\circ\text{C}$.

The ^1H NMR spectra of compounds **3**, **4**, and **7** were taken in CDCl_3 at room temperature. In the ^1H NMR spectrum of **3**, the aromatic protons appeared at between 7.72 and 6.87 ppm as a multiplet, and aliphatic protons appeared at 5.08 and 3.90 ppm as singlets. The NH proton of metal-free phthalocyanine was also identified in the ^1H NMR spectra with a broad peak at -6.92 ppm, presenting the typical shielding of inner core protons.⁴⁰ The ^1H NMR spectra of **4** and **7** were almost the same. ^1H NMR measurements were precluded owing to the paramagnetic nature of cobalt and copper phthalocyanines **5** and **6**.^{41,42} The ^{13}C NMR spectra of compounds **3**, **4**, and **7** were in good correlation with the structure of these compounds.

In the mass spectrum of phthalonitrile derivative **3**, the presence of molecular ion peaks at $m/z = 317$ $[\text{M} + \text{Na}]^+$ confirmed the proposed structures. The molecular ion peaks of phthalocyanines **4**, **5**, **6**, and **7** were observed at $m/z = 1180$ $[\text{M} + \text{H}]^+$, 1237 $[\text{M} + \text{H}]^+$, 1241 $[\text{M} + \text{H}]^+$, and 1241 $[\text{M}]^+$, by using the MALDI-TOF technique, respectively.

Metal-free **4** and metallophthalocyanines **5–7** became highly soluble in various organic solvents, including dichloromethane, chloroform, tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide, owing to the incorporation of four 3,4-dimethoxybenzyloxy groups into the phthalocyanine rings.

The electronic spectra of phthalocyanines show two strong absorption regions, one in the UV region at about 300–350 nm (B band) and the other in the visible region at 600–700 nm (Q band). The UV-Vis spectra of $\text{H}_2\text{-Pc}$ (**4**), Co-Pc (**5**), Cu-Pc (**6**), and TiO-Pc (**7**) in DMF are given in Figure 2. The Q bands of metal-free phthalocyanine **4** were observed at 705–671 nm and 643 nm with a shoulder at 615 nm in DMF. On the other hand, the Q bands of metallophthalocyanines **5–7** were observed expectedly at 669, 681, and 706 nm, respectively. The B band absorptions of phthalocyanines **4–7** describing the transition of deeper π levels to LUMO were observed at 340, 335, 344, and 343 nm, respectively.

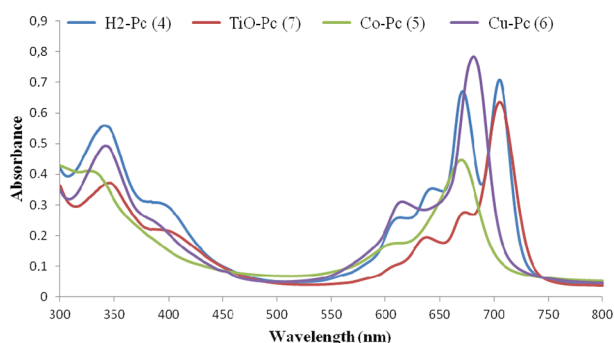


Figure 2. UV-Vis spectra of $\text{H}_2\text{-Pc}$ (**4**), Co-Pc (**5**), Cu-Pc (**6**), and TiO-Pc (**7**) in DMF (concentration = 1×10^{-5} mol dm^{-3}).

2.2. Aggregation studies

The aggregation tendency of phthalocyanines is owing to the interactions between their 18 π -electron systems, which often cause weak solubility in many solvents. In this study, the aggregation behavior of the $\text{H}_2\text{-Pc}$ (**4**), Co-Pc (**5**), Cu-Pc (**6**), and TiO-Pc (**7**) were investigated in different solvents (CHCl_3 , CH_2Cl_2 , DMF, DMSO, THF) (Figure 3). The absorption intensities of the Q bands were markedly altered by the solvent. For example, in Figure 3 for metal-free phthalocyanine **4** and titanium phthalocyanine **7**, Q bands are very sharply intense in CHCl_3 , CH_2Cl_2 , DMF, and THF. Therefore, metal-free phthalocyanine **4** and titanium phthalocyanine **7** did not show any aggregation in CHCl_3 , CH_2Cl_2 , DMF, or THF because of very sharp

Q band intensities. On the contrary, for cobalt and copper phthalocyanines **5** and **6**, Q bands were very sharply intense in DMF and THF, whereas Q bands remarkably decreased in CHCl_3 and CH_2Cl_2 . Therefore, cobalt and copper phthalocyanines **5** and **6** did not show any aggregation in DMF and THF, but they showed aggregation in CHCl_3 and CH_2Cl_2 . We also examined the $\text{H}_2\text{-Pc}$ (**4**), Co-Pc (**5**), Cu-Pc (**6**), and TiO-Pc (**7**) spectra monitored at different concentrations ranging from 2.0×10^{-6} to 12×10^{-6} mol dm^{-3} as given in DMSO. As shown in Figure 4, the intensity of absorption bands increased with increasing concentration and no new bands were observed, signifying no aggregation behavior at these concentrations for all phthalocyanines.

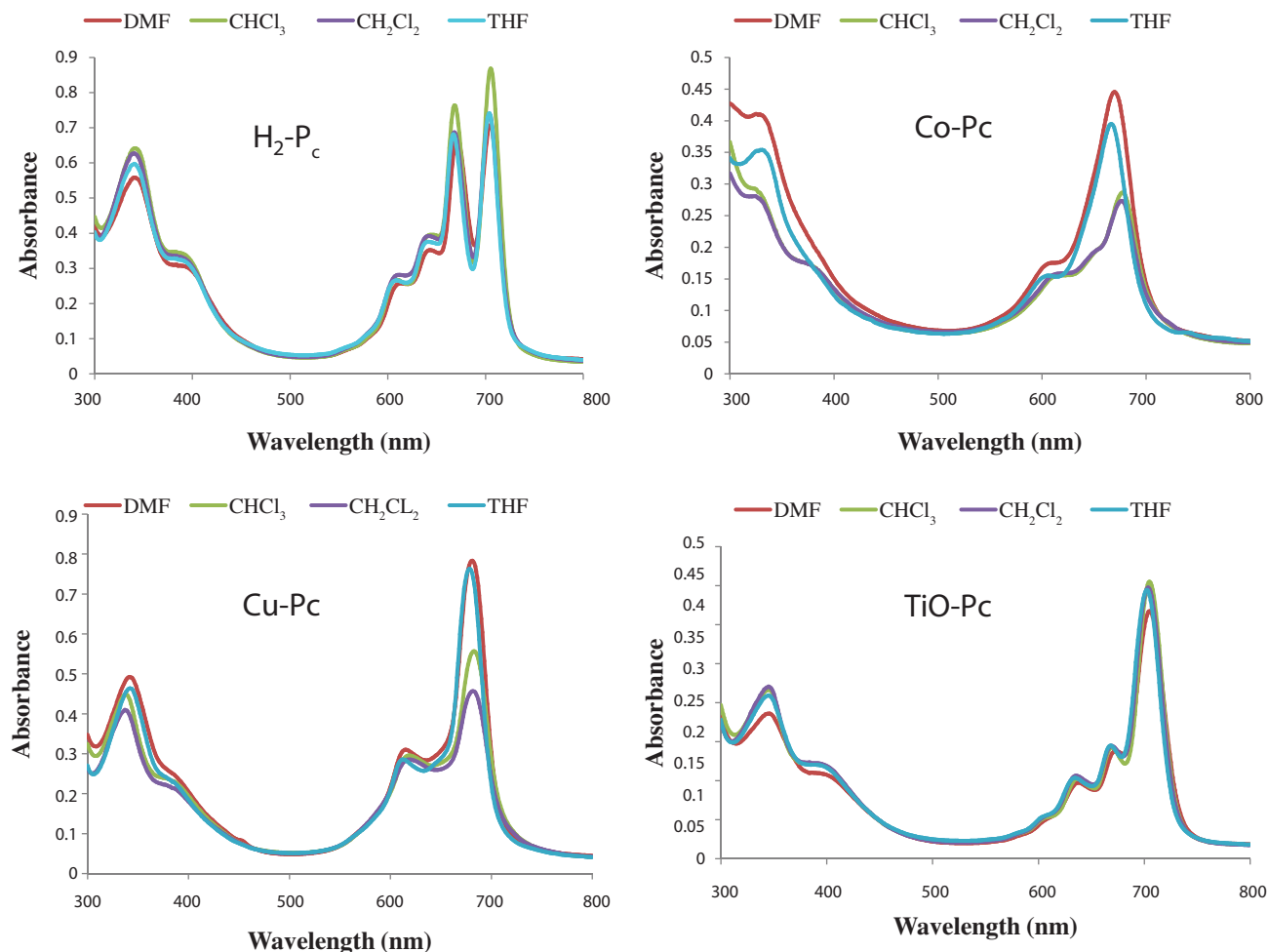


Figure 3. UV-Vis spectrum of $\text{H}_2\text{-Pc}$, Co-Pc, Cu-Pc, and TiO-Pc (**4-7**) in different solvents (concentration = 1×10^{-5} mol dm^{-3}).

2.3. Electrochemical studies

The cyclic voltammetry (CV) and square wave voltammetry (SWV) of phthalocyanines **4-7** were recorded in a dichloromethane DCM/TBAP electrolyte system on a Pt working electrode. The results of voltammetric analyses are given in the Table. Metallophthalocyanines such as MnPc, CoPc, FePc, and TiOPc, having a metal that possesses energy levels lying between the HOMO and the LUMO of the Pc ligand, in general exhibit redox processes centered on the metal. Conversely, redox processes of the Ni and Zn phthalocyanines take place on the Pc ring.⁴³⁻⁴⁶

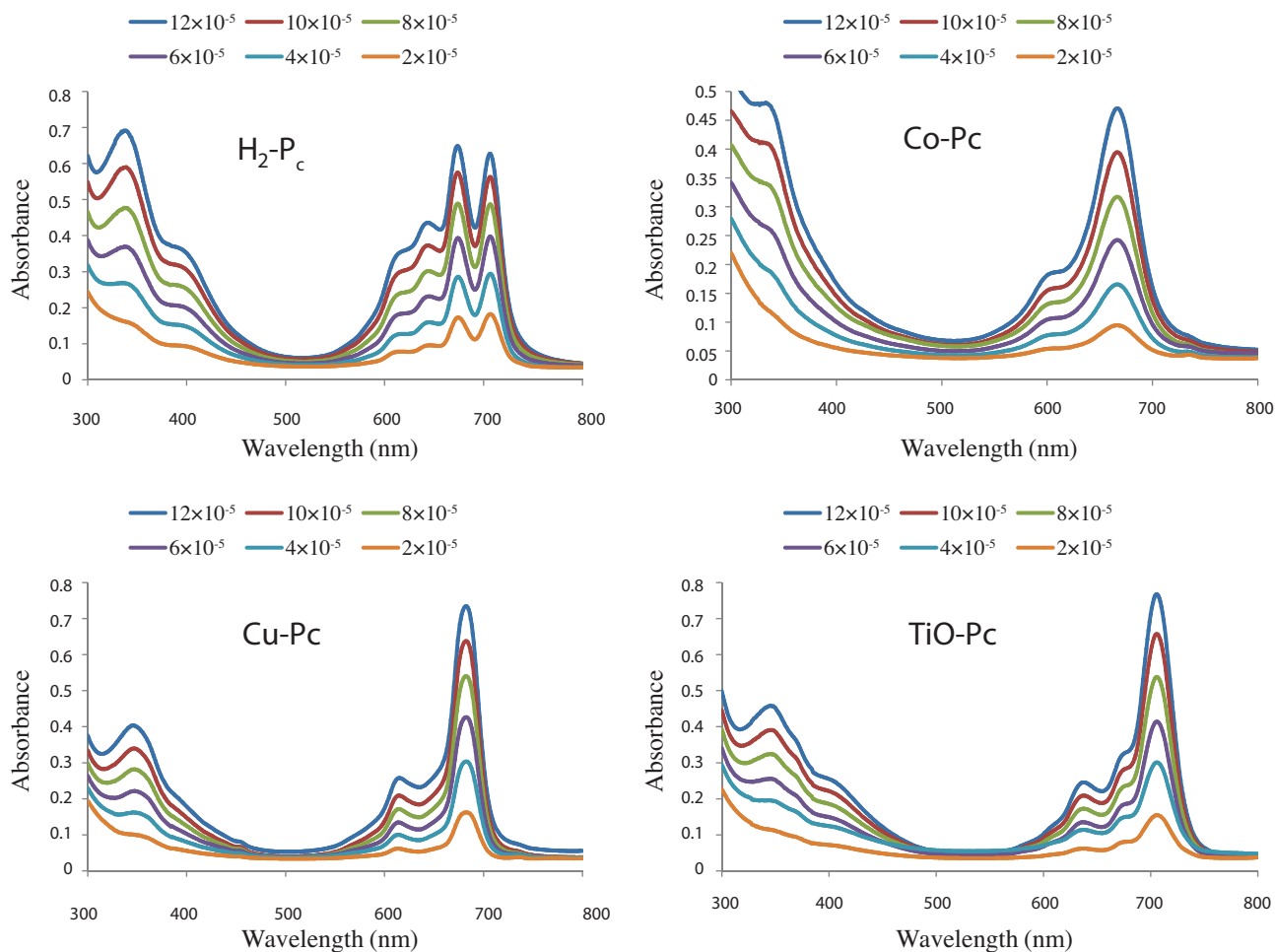


Figure 4. UV-Vis spectra of H₂-Pc, Co-Pc, Cu-Pc, and TiO-Pc (4–7) in DMSO at different concentrations (12×10^{-6} , 10×10^{-6} , 8×10^{-6} , 6×10^{-6} , 4×10^{-6} , 2×10^{-6} mol dm⁻³).

Figures 5a and 5b show CV and SWV responses of metal-free phthalocyanine **4**. It shows two reversible reduction reactions labeled as R₁ ($E_{1/2} = -0.76$ V; $\Delta E_p = 100$ mV; $\Delta E_{1/2} = 1.74$ V) and R₂ ($E_{1/2} = -1.06$ V; $\Delta E_p = 90$ mV) and one oxidation couple labeled as O₁ ($E_{1/2} = 0.98$ V; $\Delta E_p = 210$ mV). While reduction processes are both electrochemically and chemically reversible, the oxidation process is irreversible with respect to the ΔE_p value. The square wave voltammogram of the H₂Pc supports reduction-reversible characters of the processes, because these couples show symmetric cathodic peaks with the same peak currents (Figure 5b). The HOMO-LUMO gap of the metal-free phthalocyanine ($\Delta E_{1/2} = 1.74$ V) is in compliance with the H₂Pc reported in the literature.^{47,48} In the case of copper phthalocyanine (Figures 6a and 6b), three redox processes labeled as R₁, R₂, and O₁ are observed. For the copper phthalocyanine, all the observed couples are ring-based since the central metal is known to be electrochemically inactive. Copper phthalocyanine complex **6** showed similar electrochemical behavior to that of the metal-free phthalocyanine. It displayed two reversible reduction reactions labeled as R₁ ($E_{1/2} = -0.92$ V; $\Delta E_p = 120$ mV; $\Delta E_{1/2} = 1.81$ V) and R₂ ($E_{1/2} = -1.18$ V; $\Delta E_p = 90$ mV) and one oxidation couple labeled as O₁ ($E_{1/2} = 0.89$ V; $\Delta E_p = 230$ mV). In addition, $\Delta E_{1/2}$ values

of the metal-free and copper phthalocyanine were in harmony with the metal-free and metallophthalocyanines having redox inactive metal centers. The only difference was the shifting of the redox processes toward the negative potentials with respect to similar compounds.^{49,50}

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

Pc	Redox processes	^a $E_{1/2}$	^b ΔE_p (mV)	^c $\Delta E_{1/2}$
H ₂ Pc	R ₁	-0.76	100	1.74
	R ₂	-1.06	90	
	O ₁	0.98	210	
Co-Pc	R ₁	-0.37 ^d	120	1.00
	R ₂	-1.43 ^e	100	
	O ₁	0.63	130	
Cu-Pc	R ₁	-0.92	120	1.81
	R ₂	-1.18	90	
	O ₁	0.89	230	
TiOPc	R ₁	-0.58 ^f	120	1.53
	R ₂	-0.78 ^g	120	
	R ₃	-0.93	120	
	R ₄	-1.09	100	
	O ₁	0.95	160	

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

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

^c: $\Delta E_{1/2} = E_{1/2}$ (first oxidation) $-E_{1/2}$ (first reduction).

^d: This process is assigned to Co^{II}Pc/Co^IPc.

^e: This process is assigned to Pc²⁻/Pc³⁻.

^f: This process is assigned to Ti^{IV}OPc/Ti^{III}OPc.

^g: This process is assigned to Ti^{III}OPc/Ti^{II}OPc.

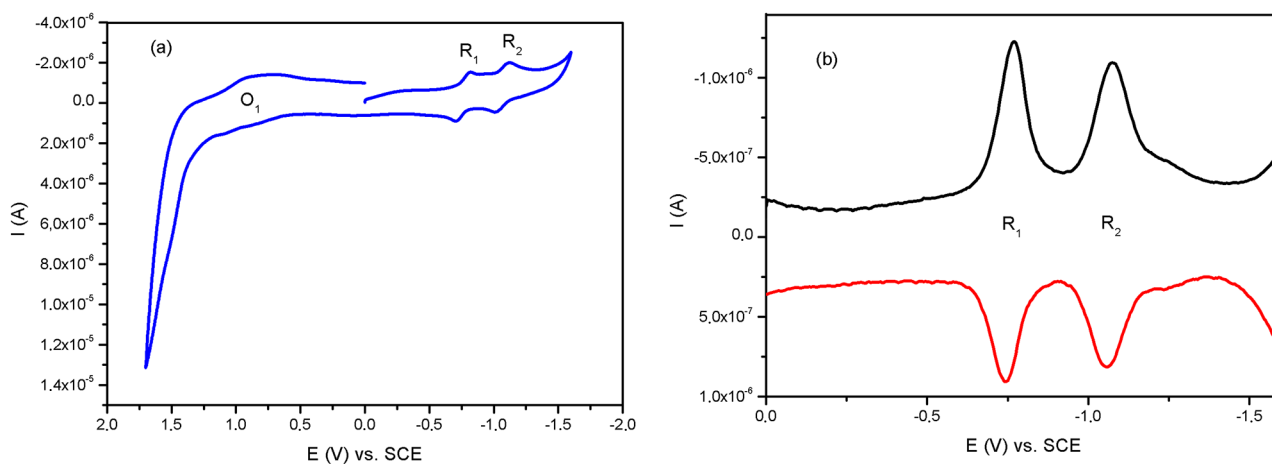


Figure 5. (a) CV of metal-free phthalocyanine **4**. (b) SWV of metal-free phthalocyanine **4**.

On the other hand, cobalt and titanium phthalocyanine complexes **5** and **7** have redox active metal centers, and thus they generally give metal-based redox processes.⁵¹ While cobalt and titanium phthalocyanines give metal- and Pc-based reduction processes, metal-free and copper phthalocyanines display only Pc-based electron transfer reactions. Figure 7 shows the cyclic voltammogram of the prepared cobalt phthalocyanine in

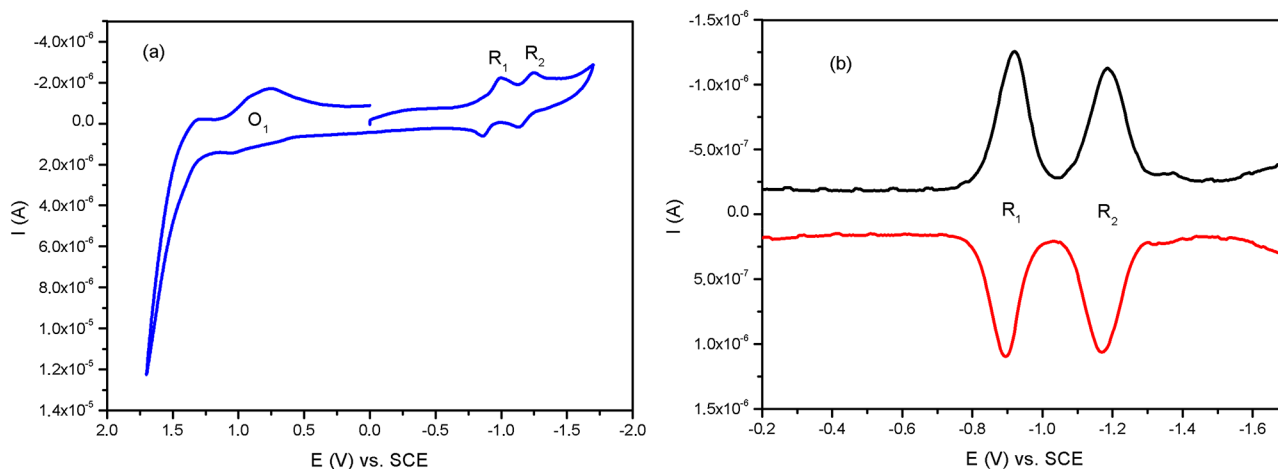


Figure 6. (a) CV of copper phthalocyanine **6**. (b) SWV of copper phthalocyanine **6**.

a dichloromethane DCM/TBAP electrolyte system on a Pt working electrode. As shown in Figure 7, cobalt phthalocyanine shows two reversible reduction reactions labeled as R_1 ($E_{1/2} = -0.37$ V; $\Delta E_p = 120$ mV; $\Delta E_{1/2} = 1.00$ V) and R_2 ($E_{1/2} = -1.43$ V; $\Delta E_p = 100$ mV) and one oxidation couple labeled as O_1 ($E_{1/2} = 0.63$ V; $\Delta E_p = 130$ mV). The two reduction couples labeled R_1 and R_2 that are observed at -0.37 V and -1.43 V respectively may be assigned to $[\text{Co}^{II}\text{Pc}^{2-}]/[\text{Co}^I\text{Pc}^{2-}]^-$ and $[\text{Co}^I\text{Pc}^{2-}]^-/[\text{Co}^I\text{Pc}^{3-}]^{2-}$ in comparison with literature data.⁵² Figures 8a and 8b display the CV and SWV responses of peripherally tetra-substituted TiOPc **7** in a DCM/TBAP electrolyte system. Titanium phthalocyanine complexes generally give four sequential reduction processes, and while a metal-metal-ring-ring-based reduction sequence was proposed in some papers, a metal-ring-metal-ring-based reduction sequence was also commonly suggested.^{53,54} In this paper, titanium phthalocyanine complex **7** shows four sequential well-resolved electrochemically reversible (Figure 9a) and diffusion-controlled reductions (R_1 at -0.58 V, R_2 at -0.78 V, R_3 at -0.93 V, R_4 at -1.09 V) and one irreversible oxidation process (O_1 at 0.95 V). $\Delta E_{1/2}$ values of titanium phthalocyanine are in harmony with

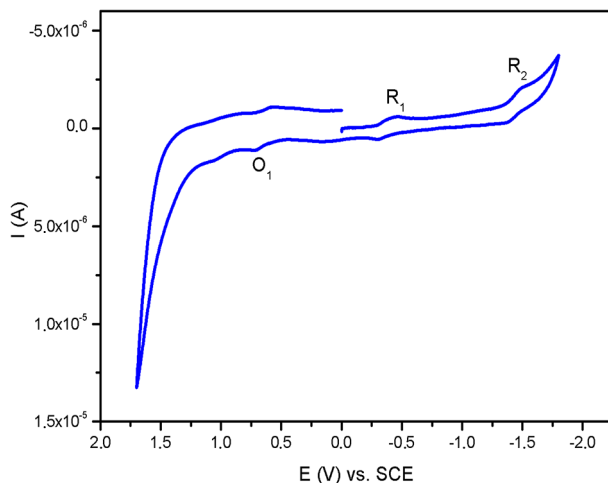


Figure 7. CV of cobalt phthalocyanine **5**.

titanium phthalocyanines having redox active metal centers.⁵³ In addition, for complex **7**, the electrochemical reversibility of the processes can be efficiently evaluated from the symmetry of the redox couple recorded with SWV (Figure 9b). Finally, the peak currents for phthalocyanines **4**, **5**, **6**, and **7** increased linearly with the square root of the scan rates for scan rates ranging from 50 to 1000 mV s⁻¹ (Figure 10a for **4**, Figure 10b for **5**, Figure 10c for **6**, and Figure 10d for **7**).

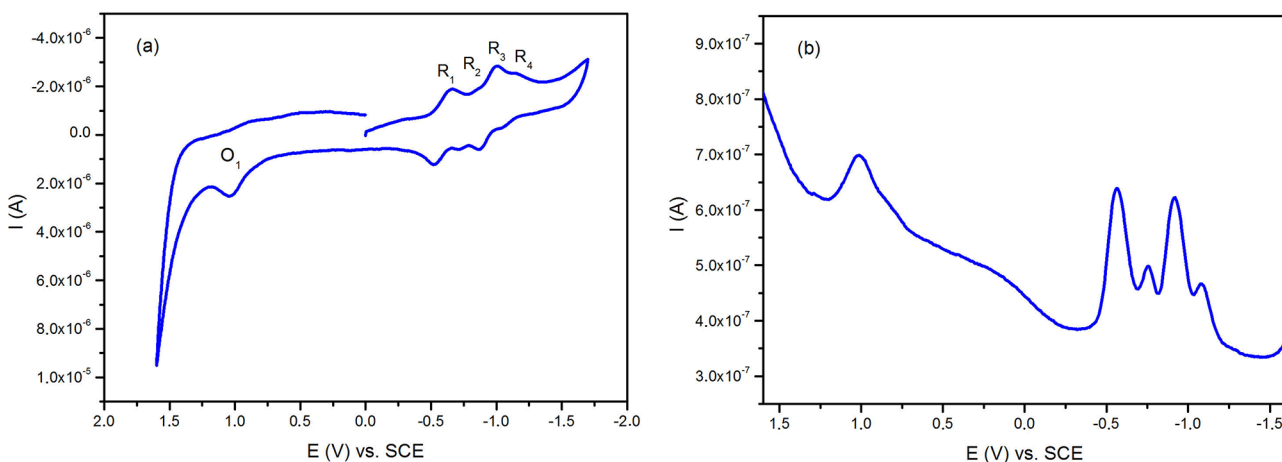


Figure 8. (a) CV of titanium phthalocyanine **7** at -2 to $+2$ V. (b) SWV of titanium phthalocyanine **7** at -1.6 to 1.6 V.

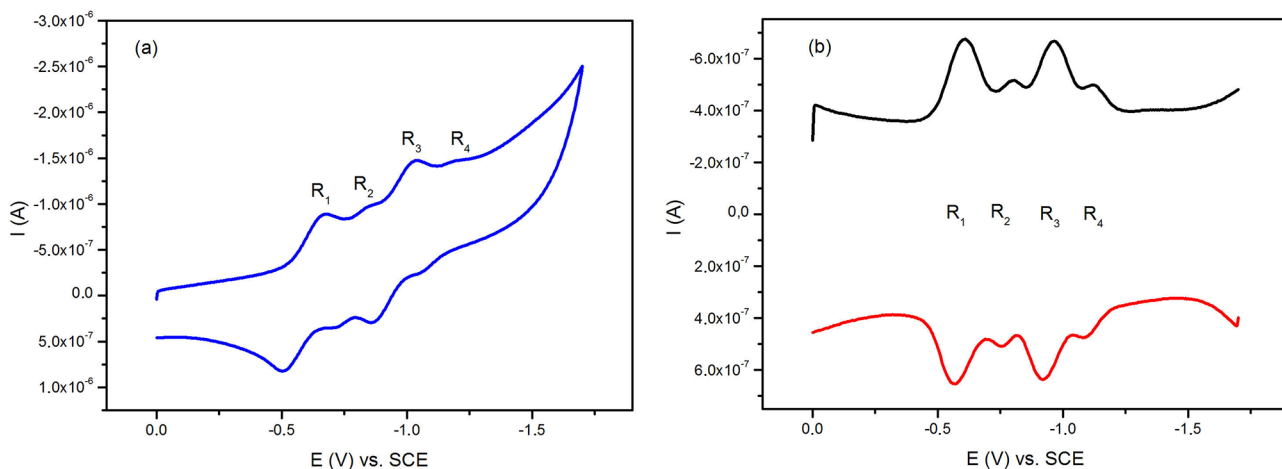


Figure 9. (a) CV of titanium phthalocyanine **7** at 0 to -1.6 V. (b) SWV of titanium phthalocyanine **7** at 0 to -1.6 V.

3. Experimental

3.1. Equipment

The IR spectra were taken on a PerkinElmer 1600 FT-IR Spectrophotometer (400 – 4000 cm⁻¹) with the samples prepared as KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer in CDCl₃ and chemical shifts were reported (δ) relative to Me₄Si as an internal standard. Optical spectra in the UV-vis region were recorded with a PerkinElmer Lambda 25 spectrophotometer. The MS spectra were measured with a Thermo Quantum Access Mass spectrometer with H-ESI probe. MALDI-MS images of complexes were

obtained in dihydroxybenzoic acid as a MALDI matrix using a nitrogen laser accumulating 50 laser shots using a Bruker Microflex LT MALDI-TOF mass spectrometer. The CV and SWV measurements were carried out with a Gamry Interface 1000 potentiostat/galvanostat controlled by an external Pc and utilizing a three-electrode configuration at 25 °C.

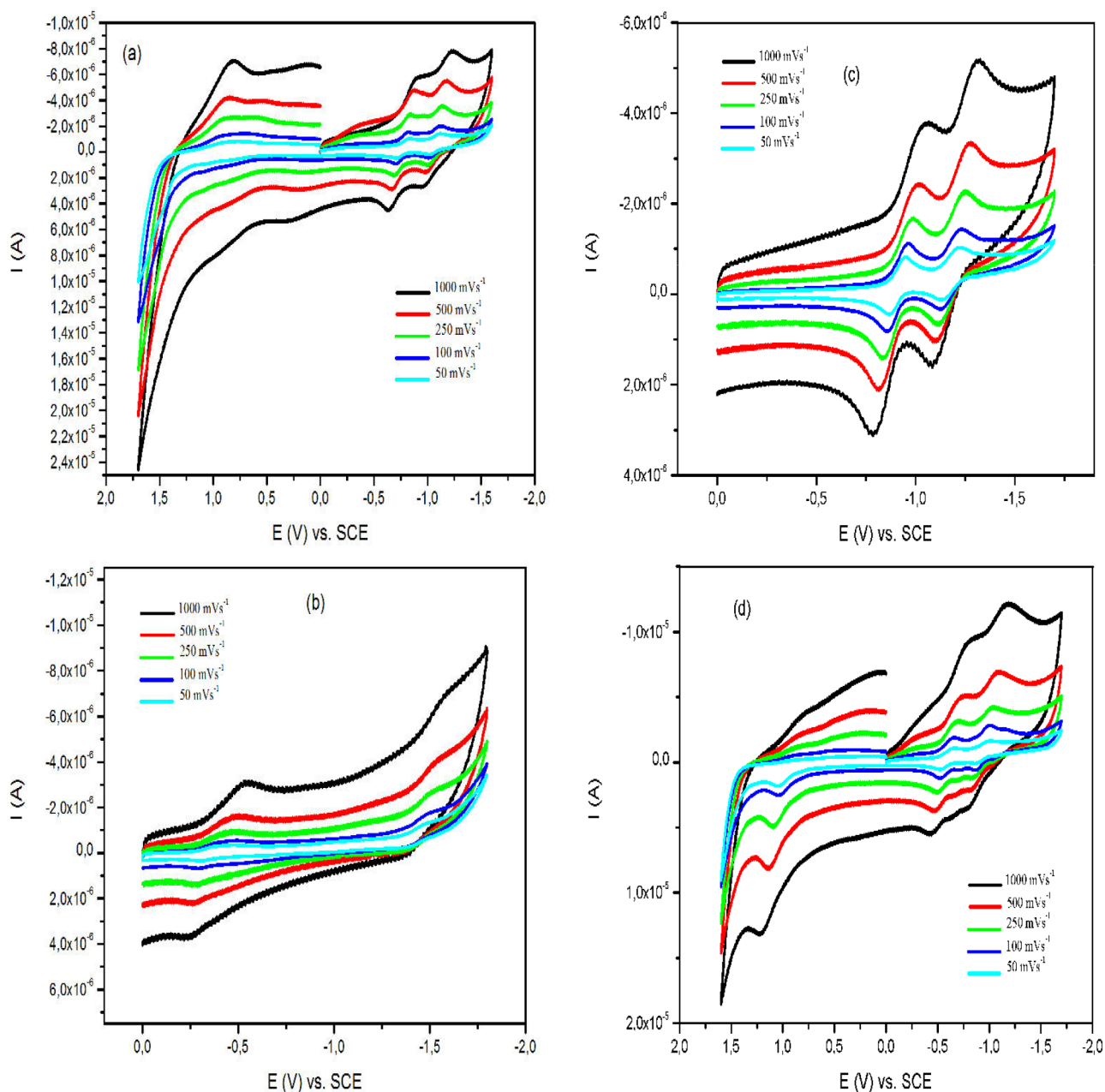


Figure 10. (a) CV of metal-free phthalocyanine **4**, (b) CV of cobalt phthalocyanine **5** at various scan rates (ranging from 50 to 1000 mV s^{-1}) on a Pt working electrode in DCM/TBAP. (c) CV of copper phthalocyanine **6**, (d) CV of titanium phthalocyanine **7** at various scan rates (ranging from 50 to 1000 mV s^{-1}) on a Pt working electrode in DCM/TBAP.

3.2. Synthesis

3.2.1. 4-[(3,4-Dimethoxybenzyl)oxy]phthalonitrile (3)

About 1 g (5.95 mmol) of **1**, 1.02 g (5.95 mmol) of **2**, and 2.46 g (17.85 mmol) of anhydrous K_2CO_3 in dry DMF (10 mL) were stirred at 60 °C for 4 days under a nitrogen atmosphere. The solution was then poured into ice water (150 g). The precipitate was filtered, washed with water, and dried in vacuo. The raw product was crystallized from the ethanol. Yield: 1 g (57%), mp: 132–133 °C. IR (KBr tablet) ν_{max}/cm^{-1} : 3094 (Ar-H), 2958–2837 (Aliph. C-H), 2229 (C≡N), 1597, 1559, 1515, 1489, 1467, 1384, 1298, 1285, 1243, 1163, 1140, 1026, 987, 896, 858, 812, 761. 1H NMR. ($CDCl_3$), (δ :ppm): 7.72 (d, 1H, J = 6.2 Hz, Ar-H), 7.34 (d, 1H, J = 8.6 Hz, Ar-H), 7.26 (m, 1H, Ar-H), 6.94–6.87 (m, 3H, Ar-H), 5.08 (s, 2H, -CH₂-O), 3.90 (s, 6H, -OCH₃). ^{13}C NMR. ($CDCl_3$), (δ :ppm): 149.80, 149.61, 135.43, 126.99, 120.89, 120.83, 120.14, 119.97, 117.69, 115.84, 115.45, 111.40, 111.07, 107.73, 71.43, 56.19. MS (ESI), (m/z): 317 [M + Na]⁺.

3.2.2. Metal-free phthalocyanine (4)

A mixture of compound **3** (0.2 g, 0.68 mmol) and two drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 2.5 mL of dry n-pentanol was stirred at 160 °C for 12 h under N₂. The green crude product was then precipitated with ethanol and dried in vacuo. Finally, the crude product was purified by column chromatography using aluminum oxide as the stationary phase and $CHCl_3:CH_3OH$ (100:3) as the eluent. Yield: 0.06 g (30%). IR (KBr tablet) ν_{max}/cm^{-1} : 3289 (N-H), 3070 (Ar-H), 2932–2834 (Aliph. C-H), 1607, 1514, 1480, 1459, 1419, 1323, 1260, 1228, 1157, 1136, 1095, 1007, 925, 848, 810, 744, 711. 1H NMR. ($CDCl_3$), (δ :ppm): 6.92–6.72 (m, 24H, Ar-H), 4.27 (s, 8H, -CH₂-O), 3.82–3.71 (s, 24H, -CH₃O), –6.92 (bs, 2H, NH). ^{13}C NMR. ($CDCl_3$), (δ :ppm): 159.43, 148.96, 148.92, 128.81, 122.00, 120.80, 120.69, 120.59, 120.53, 120.44, 111.36, 111.30, 111.03, 110.79, 69.65, 55.78. UV-Vis (DMF): λ_{max} , nm (log ϵ): 705 (4.85), 671 (4.82), 643 (4.54), 615 (4.41), 340 (4.74). MALDI-TOF-MS m/z: 1180 [M + H]⁺.

3.2.3. Cobalt(II) phthalocyanine (5)

The synthetic method for compound **4** was used to obtain compound **5** using a mixture of compound **3** (0.2 g, 0.68 mmol), anhydrous $CoCl_2$ (0.043 g, 0.34 mmol), dry n-pentanol (2.5 mL), and DBU (2 drops). Yield: 0.09 g (43%). IR (KBr tablet) ν_{max}/cm^{-1} : 3060 (Ar-H), 2929–2834 (Aliph. C-H), 1607, 1513, 1460, 1416, 1375, 1343, 1261, 1226, 1157, 1120, 1094, 1023, 851, 812, 749. UV-Vis (DMF): λ_{max} , nm (log ϵ): 669 (4.64), 605 (4.23), 335 (4.60). MALDI-TOF-MS m/z: 1237 [M + H]⁺.

3.2.4. Copper(II) phthalocyanine (6)

The synthetic method of compound **4** was used to obtain compound **6** using a mixture of compound **3** (0.2 g, 0.68 mmol), anhydrous $CuCl_2$ (0.044 g, 0.33 mmol), dry n-pentanol (2.5 mL), and DBU (2 drops). Yield: 0.094 g (45%). IR (KBr tablet) ν_{max}/cm^{-1} : 3072 (Ar-H), 2928–2834 (Aliph. C-H), 1606, 1592, 1510, 1459, 1407, 1375, 1261, 1224, 1157, 1118, 1055, 1024, 944, 848, 808, 744, 682. UV-Vis (DMF): λ_{max} , nm (log ϵ): 681 (4.89), 614 (4.49), 344 (4.69). MALDI-TOF-MS m/z: 1241 [M + H]⁺.

3.2.5. Oxo-titanium (IV) phthalocyanine (7)

The synthetic method of compound **4** was used to obtain compound **7** using a mixture of compound **3** (0.2 g, 0.68 mmol), $\text{Ti}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$ (0.112 g, 0.34 mmol), dry n-pentanol (2.5 mL), and DBU (2 drops). Yield: 0.063 g (30%). IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3066 (Ar-H), 2932–2833 (Aliph. C-H), 1605, 1514, 1483, 1451, 1418, 1375, 1336, 1262, 1224, 1157, 1119, 1070, 1022, 958 (Ti=O), 851,747. ^1H NMR. (CDCl_3), (δ :ppm): 7.21–6.97 (m, 24H, Ar-H), 5.04 (s, 8H, $-\text{CH}_2\text{-O}$), 3.98–3.91 (s, 24H, $-\text{OCH}_3$). ^{13}C NMR. (CDCl_3), (δ :ppm): 161.45, 149.26, 149.13, 138.64, 130.91, 128.81, 128.75, 128.67, 124.46, 120.92, 111.52, 111.26, 111.14, 111.03, 70.79, 56.00. UV-Vis (DMF): λ_{max} , nm ($\log \epsilon$): 706 (4.80), 673 (4.44), 639 (4.28), 343 (4.56). MALDI-TOF-MS m/z: 1241 $[\text{M}]^+$.

4. Conclusion

We have synthesized new metal-free and metallophthalocyanine complexes carrying four (3,4-dimethoxybenzyl)oxy groups. Electrochemical measurements supported the proposed structures of the complexes. Presence of Co^{II} and Ti^{IV} O metal centers in the core of the Pc ring enhanced the redox richness of the complexes due to the metal-based redox processes of the CoPc and TiOPc complexes. On the other hand, while metal-free and copper phthalocyanines give ligand-based redox processes, the cobalt and oxotitanium phthalocyanine complexes give both metal and ligand-based redox processes. Rich redox behaviors of the complexes are the desired properties for electrochemical applications, especially electrocatalytic, electrochromic, and electroensing applications.

Acknowledgment

This study was supported by the Research Fund of Karadeniz Technical University (Project No. 9670), Trabzon, Turkey.

References

- Valli, L. *Adv. Col. Inter. Sci.* **2005**, *116*, 13–44.
- Sousa, A. L.; Santos, W. J. R.; Luz, R. C. S.; Damos, F. S.; Kubota, L. T.; Tanaka, A. A.; Tanaka, S. M. *Talanta* **2008**, *75*, 333–338.
- Bohrer, F. I.; Colesniuc, C. N.; Park, J.; Schuller, I. K.; Kummel, A. C.; Trogler, W. C. *J. Am. Chem. Soc.* **2008**, *130*, 3712–3713.
- Vasseur, K.; Rand, B. P.; Cheyns, D.; Temst, K.; Froyen, L.; Heremans, P. *J. Phy. Chem. Lett.* **2012**, *3*, 2395–2400.
- Xu, H.; Wada, T.; Ohkita, H.; Bente, H.; Ito, S. *Electrochim. Acta* **2013**, *100*, 214–219.
- Lane, P. A.; Rostalski, J.; Giebler, C.; Martin, S. J.; Bradley, D. D. C.; Meissner, D. *Sol. Ener. Mat. Sol. Cell.* **2000**, *63*, 3–13.
- Van Faassen, E.; Kerp, H. *Sensors Actuat. B Chem.* **2003**, *88*, 329–333.
- Harbeck, M.; Taşaltın, C.; Gürol, I.; Musluoğlu, E.; Ahsen, V.; Öztürk, Z. Z. *Sensors Actuat. B Chem.* **2010**, *150*, 616–624.
- Sizun, T.; Bouvet, M.; Chen, Y.; Suisse, J. M.; Barochi, G.; Rossignol, J. *Sensors Actuat. B Chem.* **2011**, *159*, 163–170.
- Basova, T.; Hassan, A.; Durmuş, M.; Gürek, A. G.; Ahsen, V. *Synth. Met.* **2011**, *161*, 1996–2000.
- Lee, W.; Yuk, S. B.; Choi, J.; Jung, D. H.; Choi, S. H.; Park, J.; Kim, J. P. *Dyes Pigments* **2012**, *92*, 942–948.
- Eu, S.; Katoh, T.; Umeyama, T.; Matano, Y.; Imahori, H. *Dalton T.* **2008**, *40*, 5476–5483.

13. Majumdar, H. S.; Bandyopadhyay, A.; Pal, A. J. *Org. Electr.* **2003**, *4*, 39–44.
14. Ishii, K. *Coord. Chem. Rev.* **2012**, *256*, 1556–1568.
15. Camerin, M.; Magaraggia, M.; Soncin, M.; Jori, G.; Moreno, M.; Chambrier, I.; Cook, M. J.; Russell, D. A. *Eur. J. Cancer*, **2010**, *46*, 1910–1918.
16. Tuncel, S.; Dumoulin, F.; Gailer, J.; Sooriyaarachchi, M.; Atilla, D.; Durmuş, M.; Bouchu, D.; Savoie, H.; Boyle, R. W.; Ahsen, V. *Dalton T.* **2011**, *40*, 4067–4079.
17. Stylli, S. S.; Hill, J. S.; Sawyer, W. H.; Kaye, A. H. *J. Clin. Neurosci.* **1995**, *2*, 146–151.
18. Kolarova, H.; Nevrelouva, P.; Bajgar, R.; Jirova, D.; Kejllova, K.; Strnad, M. *Toxicol. In Vitro* **2007**, *21*, 249–253.
19. Ayhan, M. M.; Singh, A.; Hirel, C.; Gürek, A. G.; Ahsen, V.; Jeanneau, E.; Ledoux-Rak, I.; Zyss, J.; Andraud, C.; Bretonniere, Y. *J. Am. Chem. Soc.* **2012**, *134*, 3655–3658.
20. Tau, P.; Nyokong, T. *Electrochim. Acta* **2007**, *52*, 4547–4553.
21. Osmanbas, A. O.; Koca, A.; Ozcesmeci, I.; Okur, A. I.; Gul, A. *Electrochim. Acta* **2008**, *53*, 4969–4980.
22. Ceken, B.; Kandaz, M.; Koca, A. *Synth. Met.* **2012**, *162*, 1524–1530.
23. Liu, L.; Guo, L. P.; Bo, X. J.; Bai, J.; Cui, X. J. *Anal. Chim. Acta* **2010**, *673*, 88–94.
24. Demir, F.; Biyiklioglu, Z.; Koca, A. *J. Electrochem. Soc.* **2014**, *161*, G1–G6.
25. Kalkan, A.; Aytekin, A.; Bayır, Z. A. *Trans. Met. Chem.* **2006**, *31*, 720–723.
26. Biyikhoğlu, Z.; Yıldız, S. Z.; Kantekin, H. *J. Organomet. Chem.* **2010**, *695*, 1729–1733.
27. Biyiklioglu, Z. *Synth. Met.* **2011**, *161*, 508–515.
28. Kantekin, H.; Biyiklioglu, Z.; Celenk, E. *Inorg. Chem. Commun.* **2008**, *11*, 633–635.
29. Acar, İ.; Biyikhoğlu, Z.; Durmuş, M.; Kantekin, H. *J. Organomet. Chem.* **2012**, *708*, 65–74.
30. Kobayashi, N.; Fukuda, T. *B. Chem. Soc. Jpn.* **2009**, *82*, 631–663.
31. Sakamoto, K.; Ohno, E. *Prog. Org. Coat.* **1997**, *31*, 139–145.
32. Bernstein, P. A.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 603–608.
33. Nyokong, T. *Polyhedron* **1993**, *12*, 375–381.
34. Mbambisa, G.; Tau, P.; Antunes, E.; Nyokong, T. *Polyhedron* **2007**, *26*, 5355–5364.
35. Arslanoğlu, Y.; Sevim, A. M.; Hamuryudan, E.; Gül, A. *Dyes Pigments* **2006**, *68*, 129–132.
36. Barthel, M.; Dini, D.; Vagin, S.; Hanack, M. *Eur. J. Org. Chem.* **2002**, *22*, 3756–3762.
37. Koca, A.; Ozkaya, A. R.; Arslanoglu, Y.; Hamuryudan, E. *Electrochim. Acta* **2007**, *52*, 3216–3221.
38. Tau, P.; Nyokong, T. *Dalton T.* **2006**, *37*, 4482–4490.
39. Law, W. F.; Lui, K. M.; Ng, D. K. P. *J. Mater. Chem.* **1997**, *7*, 2063–2067.
40. Biyikhoğlu, Z.; Çakır, V.; Koca, A.; Kantekin, H. *Dyes Pigments*, **2011**, *89*, 49–55.
41. Yabaş, E.; Süllü, M.; Saydam, S.; Dumludağ, F.; Salih, B.; Bekaroğlu, Ö. *Inorg. Chim. Acta* **2011**, *365*, 340–348.
42. Biyiklioglu, Z.; Koca, A.; Kantekin, H. *Polyhedron* **2009**, *28*, 2171–2178.
43. Şener, M. K.; Koca, A.; Gül, A.; Koçak, M. B. *Polyhedron* **2007**, *26*, 1070–1076.
44. Kulaç, D.; Bulut, M.; Altındal, A.; Özkaya, A. R.; Salih, B.; Bekaroğlu, Ö. *Polyhedron* **2007**, *26*, 5432–5440.
45. Özer, M.; Altındal, A.; Özkaya, A. R.; Bulut, M.; Bekaroğlu, Ö. *Polyhedron* **2006**, *25*, 3593–3602.
46. Koca, A.; Dinger, H. A.; Çerlek, H.; Gül, A.; Koçak, M. B. *Electrochim. Acta* **2006**, *52*, 1199–1205.
47. Uğur, A. L.; Erdoğan, A.; Koca, A.; Avciata, U. *Polyhedron* **2010**, *29*, 3310–3317.
48. Djellab, H.; Dalard, F. *J. Electroanal. Chem.* **1987**, *221*, 105–113.
49. Nas, A.; Kantekin, H.; Koca, A. *J. Organomet. Chem.* **2014**, *757*, 62–71.
50. Arıcı, M.; Arıcan, D.; Uğur, A. L.; Erdoğan, A.; Koca, A. *Electrochim. Acta* **2013**, *87*, 554–566.
51. Sevim, A. M.; Yenilmez H. Y.; Aydemir, M.; Koca, A.; Bayır, Z. A. *Electrochim. Acta* **2014**, *137*, 602–615.
52. Obirai, J.; Rodrigues, N. P.; Bedioui, F.; Nyokong, T. *J. Porphy. Phthalocyan.* **2003**, *7*, 508–520.
53. Demir, F.; Erdoğan, A.; Koca, A. *J. Electroanal. Chem.* **2013**, *703*, 117–125.
54. Aktaş, A.; Acar, İ.; Koca, A.; Biyikhoğlu, Z.; Kantekin, H. *Dyes Pigments*, **2013**, *99*, 613–619.