



## Research Article

## Synthesis and electrochemical properties of new tetra-2-(4-benzyloxyphenyl) ethanol substituted metal free and metallophthalocyanines

Rıza Bayrak<sup>1\*</sup>, Ümit Demirbaş<sup>2</sup>, Zekeriya Bıyıklıoğlu<sup>2</sup>, Hakkı Türker Akçay<sup>3</sup>, Halit Kantekin<sup>2</sup>

<sup>1</sup>Vocational School of Health Services, Sinop University, 57000 Sinop, Turkey

<sup>2</sup>Faculty of Science, Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey

<sup>3</sup>Faculty of Arts and Science, Department of Chemistry, Recep Tayyip Erdoğan University, 53100 Rize, Turkey

**ABSTRACT**

**Keywords:**  
Synthesis,  
phthalonitrile,  
phthalocyanine,  
electrochemistry

The novel dinitrile compound (3) and peripherally tetra 2-(4-benzyloxyphenyl)ethanol substituted metal-free (4), zinc(II) (5), cobalt(II) (6) and copper(II) (7) phthalocyanines were synthesized and characterized for the first time in this study. Electrochemical characterization of metal-free and metallophthalocyanines were determined by using cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. Metal-free and metallophthalocyanines having redox inactive centers ( $Zn^{+2}$ ,  $Cu^{+2}$ ) showed similar Pc based electron transfer processes. On the other hand,  $Co^{II}$  metal ion behaves as redox active cations in the core of the Co- phthalocyanine. Therefore, Co- phthalocyanine gives one metal based reduction reaction  $[Co^{II}Pc-2] / [CoIPc-2]^{-1}$ .

TR

### Yeni tetra-2-(4-benziloksifenil)etanol süstitüe metalsiz ve metalloftalosiyaninlerin sentezi ve elektrokimyasal özellikleri

**Ö Z E T**

**Anahtar Kelimeler:**  
Sentez,  
ftalonitril,  
ftalosiyanin,  
elektrokimya

Yeni dinitril bileşiği (3) ve periferik tetra 2-(4-benziloksifenil)etanol substitute metalsiz (4), çinko(II) (5), kobalt(II) (6) ve bakır(II) (7) ftalosiyaninlerin sentezi ve karakterizasyonu bu çalışmada ilk defa gerçekleştirilmiştir. Metalsiz ve metalloftalosiyaninlerin elektrokimyasal özellikleri siklik voltametri (CV) ve kare dalga voltametri (SVW) teknikleri kullanılarak incelenmiştir. Metalsiz ve redoks inaktif merkezlere sahip olan metalloftalosiyaninler ( $Zn^{+2}$ ,  $Cu^{+2}$ ) benzer ftalosiyanin temelli elektron transfer prosesi göstermişlerdir. Diğer yandan Co- ftalosiyanin komplekslerinin merkezindeki  $Co^{II}$  metal iyonu redoks aktif katyon olarak davranmaktadır. Dolayısıyla, Co- ftalosiyanin metal temelli indirgenme reaksiyonu  $[Co^{II}Pc-2] / [CoIPc-2]^{-1}$  göstermiştir.

**1. Introduction**

Phthalocyanines (Pcs), porphyrin derivative macrocyclic compounds containing highly delocalized electronic constitution have high thermal determination and optical features and they are useful in areas like as chemical detectors [1-3], electrochromic imaging systems [4], non-linear optics [5], solar cells [6], photo-voltaic optics, molecular electronics [7], semiconductors [8], liquid crystals [9], optical storage devices [10], laser dyes [11], catalyst [12] and photo dynamic therapeutic agents (PDT) [13].

The main drawback of the unsubstituted Pc is its insolubility and aggregation because aggregation and insolubility of Pcs limits their usage in many technological applications. So scientists have been focused on synthesizing of non-aggregated and soluble Pcs. The bulky substituents can change the solubility, aggregation properties, electrochemical and electronic absorption behaviors [14].

The electrochemistry of Pcs, especially MPcs containing redoxactive metal centers, have attracts great attention due to their rich metal- and ligand-based redox properties [15]. The electrochemical properties of MPcs with redox active metal

centers are immensely affected by different ingredients such as the nature of the supporting electrode and solvents, the existence of oxygen, nature and position of the substituents [16].

Although there are many investigations about the synthesis of Pcs containing different benzyloxyphenyl groups and investigation of their different properties [17-18], the electrochemical behaviors of a benzyloxyphenyl substituted metal free Pc and MPcs ( $Zn(II)$ ,  $Co(II)$  and  $Cu(II)$ ) were performed for the first time in this study.

**2. Materials and Methods**

All reactions were carried out using schlenk system and under dry and oxygen free nitrogen atmosphere. DMF (dimethylformamide) was dried and purified as described by Perrin and Armarego [19]. 2-(4-Benzyloxyphenyl)ethanol (**1**), and 4-nitrophthalonitrile (**2**) were bought from Sigma-Aldrich. <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra were measured by a Varian XL-200 NMR spectrometer and chemical shifts were recorded ( $\delta$ ) relative to  $Me_4Si$  o(tetramethylsilane) as standard. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR technique. The MS spectra were recorded on a Thermo Quantum Access Mass spectrometer with H-ESI probe. UV-Vis spectral measurements were performed by Perkin Elmer Lambda 25 spectrometer, using 1 cm path length cuvettes at room temperature. Melting points were measured by an electrothermal apparatus.

**2.1. Electrochemical measurements**

Electrochemical investigations were performed with Gamry Interface

\*Corresponding author: bayrakriza@gmail.com  
+90 (368) 287 62 54

Citation: Bayrak, R., Demirbaş, Ü., Bıyıklıoğlu, Z., Akçay, H. T., Synthesis and electrochemical properties of new tetra-2-(4-benzyloxyphenyl)ethanol substituted metal free and metallophthalocyanines (Yeni tetra-2-(4-benziloksifenil)etanol süstitüe metalsiz ve metalloftalosiyaninlerin sentezi ve elektrokimyasal özellikleri), *Karadeniz Chem. Sci. Tech.* 2018, 03, XX-XX.

DOI:  
ISSN:

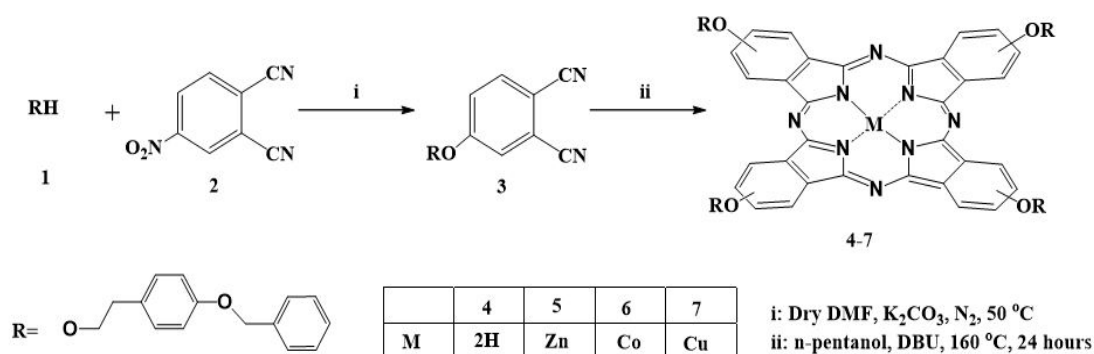


Fig. 1. Synthetic route of novel phthalocyanine compounds

1000 potentiostat/galvanostat operating three-electrode configuration at 25°C. Pt disc with a surface area of 0.071 cm<sup>2</sup> has been used as working electrode and a Pt wire was utilized 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<sup>-3</sup>.

## 2.2. Synthesis

### 2.2.1. 4-(4-(benzyloxy)phenethoxy)phthalonitrile (3)

2-(4-Benzyloxyphenyl)ethanol (1) (2.00 g, 8.76 mmol) and 4-nitrophthalonitrile (2) (1.52 g, 8.76 mmol) was dissolved in dry DMF (20 mL). Anhydrous K<sub>2</sub>CO<sub>3</sub> (3.63 g 26.28 mmol) was added portion wise within 2 h. to reaction mixture. The mixture was stirred at 50 °C for 3 days under inert N<sub>2</sub> atmosphere. Then the mixture was poured into 200 mL ice-water, stirred for 1 h. at room temperature and was filtered off. The solid product was crystallized from acetone. Yield 2.11 g (68 %), mp 105-107 °C. IR (KBr tablet)  $\nu_{\max}$  / cm<sup>-1</sup>: 3077, 3040, 2937, 2872, 2226 (C≡N), 1594, 1497, 1323, 1257, 1233, 1091, 1010, 827, 732. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>), (δ: ppm): 8.03-8.01 (d, 1H/ArH), 7.77 (s, 1H/ArH), 7.45-7.22 (m, 8H/ArH), 6.96-6.94 (d, 2H/ArH), 5.08 (s, 2H/OCH<sub>2</sub>), 4.33-4.30 (t, 2H/OCH<sub>2</sub>), 3.01-2.97 (t, 2H/CH<sub>2</sub>). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>), (δ: ppm): 162.29, 157.50, 137.67, 136.21, 130.47, 130.25, 130.20, 130.16, 128.88, 128.23, 122.10, 128.06, 120.80, 120.57, 116.76, 116.70, 116.18 (C≡N), 115.19 (C≡N), 114.99, 106.34, 70.14 (OCH<sub>2</sub>), 69.60 (OCH<sub>2</sub>), 34.01 (CH<sub>2</sub>). MS (ESI), (m/z): Calculated: 354.14; Found: 355.56 [M+H]<sup>+</sup>.

### 2.2.2. General Procedure for Synthesis of phthalocyanines (4-7)

The mixture of compound (3) (0,2 g, 0,56 mmol), equivalent amounts of related anhydrous metal salts (for compound 5 Zn(CH<sub>3</sub>COO)<sub>2</sub>, 6 CoCl<sub>2</sub>·7 CuCl<sub>2</sub>) or no metal salts for metal-free compound 4, dry n-pentanol and 1,8-Diazabicyclo [4.5.0] undec-7-ene (DBU) (5 drops) was heated to 160 °C and stirred for 24 h. Then, the raw products were precipitated by hexane. After washing with hot acetone and ethanol, the products were purified by silica gel column chromatography.

#### 2.2.2.1. Synthesis of metal-free (II) phthalocyanine (4)

Solvent system; chloroform:methanol (100:2). Yield: 102 mg (49%), mp>300 °C. IR (KBr tablet)  $\nu_{\max}$  / cm<sup>-1</sup>: 3288 (-NH), 3061, 3031, 2920, 1608, 1509, 1455, 1380, 1223, 1175, 1009, 820, 743. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>), (δ: ppm): 7.45-7.24 (m, 40H/ArH), 6.96-6.94 (m, 8H/ArH), 5.08 (s, 8H/OCH<sub>2</sub>), 4.36-4.30 (t, 8H/OCH<sub>2</sub>), 3.02-2.99 (t, 8H/CH<sub>2</sub>). UV-vis (DMF)  $\lambda_{\max}$ /nm: [(10<sup>-5</sup> ε, dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 705 (5.10), 672 (5.09), 646 (4.79), 616 (4.64), 345 (5.00). MS (ESI), (m/z): Calculated: 1419.57, Found: 1421.25 [M+H]<sup>+</sup>.

#### 2.2.2.2. Synthesis of zinc (II) phthalocyanine (5)

Solvent system; chloroform:methanol (100:1.5) as eluent. Yield: 117 mg (56%), mp>300 °C. IR (KBr tablet)  $\nu_{\max}$  / cm<sup>-1</sup>: 3062, 3032, 2919, 1720, 1606, 1510, 1488, 1337, 1229, 1045, 822, 731. <sup>1</sup>H-NMR

(DMSO-*d*<sub>6</sub>), (δ: ppm): 7.57-7.24 (m, 40H/ArH), 7.11-7.04 (m, 4H/ArH), 6.96-6.94 (m, 4H/ArH), 5.10 (s, 8H/OCH<sub>2</sub>), 4.34-4.30 (t, 8H/OCH<sub>2</sub>), 3.02-2.98 (t, 8H/CH<sub>2</sub>). UV-vis (DMF)  $\lambda_{\max}$ /nm: [(10<sup>-5</sup> ε, dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 682 (5.17), 615 (4.45), 358 (4.84). MS (ESI), (m/z): Calculated: 1481.48, Found: 1482.96 [M+H]<sup>+</sup>.

#### 2.2.2.3. Synthesis of cobalt (II) phthalocyanine (6)

Solvent system; chloroform:methanol (100:1) as eluent. Yield: 79 mg (38%), mp>300 °C. IR (KBr tablet)  $\nu_{\max}$  / cm<sup>-1</sup>: 3061, 3032, 2989, 2918, 1608, 1509, 1411, 1230, 1092, 1015, 820, 731. UV-vis (DMF)  $\lambda_{\max}$ /nm: [(10<sup>-5</sup> ε, dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 670 (5.12), 611 (4.60), 334 (4.93). MS (ESI), (m/z): Calculated: 1476.48, Found: 1477.71 [M+H]<sup>+</sup>.

#### 2.2.2.4. Synthesis of copper (II) phthalocyanine (7)

Solvent system; chloroform:methanol (100:2.5) as eluent. Yield: 88 mg (42%), mp>300 °C. IR (KBr tablet)  $\nu_{\max}$  / cm<sup>-1</sup>: 3061, 3032, 2918, 1723, 1607, 1509, 1487, 1343, 1230, 1051, 820, 731. UV-vis (DMF)  $\lambda_{\max}$ /nm: [(10<sup>-5</sup> ε, dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 683 (5.12), 618 (4.56), 347 (4.83). MS (ESI), (m/z): Calculated: 1480.48, Found: 1543.65 [M+Na+K+H]<sup>+</sup>.

## 3. Results and Discussion

### 3.1. Synthesis and characterization

The synthetic procedure of newly prepared structures was showed in Fig. 1. The substituted phthalonitrile compound 4-(4-(benzyloxy)phenethoxy)phthalonitrile (3) was obtained from the reaction of 4-nitrophthalonitrile with compound 1 in the presence of K<sub>2</sub>CO<sub>3</sub> [20]. The new vibration appeared at 2226 cm<sup>-1</sup> was the clear indication of the presence of the nitrile group for compound 3 in the IR spectral data. The absence of the OH proton signal of compound 1 in <sup>1</sup>H-NMR spectrum and the presence of new peaks of nitrile carbons at 116.18 ppm and 115.19 ppm in the <sup>13</sup>C-NMR spectrum are the proof of substitution. Furthermore, [M+H]<sup>+</sup> peak at 355.56 in the mass spectra of compound (3) was showed that the compound was successfully synthesized (fig. 2).

The novel Pcs were characterized by IR, <sup>1</sup>H-NMR, mass spectrometry and UV/Vis. The disappearance of -C≡N vibration of compound 3 in the IR spectra of all novel phthalocyanines, support the proposed structures. Due to the presence of paramagnetic cobalt and copper ions the <sup>1</sup>H-NMR spectra of compounds 6 and 7 could not be determined [21]. The <sup>1</sup>H-NMR spectra of phthalocyanines 4, and 5 were taken in DMSO at room temperature. The spectra of the compounds were very similar. For substituted (4), the typical shielding of inner core protons could not be observed due to the probable strong aggregation between Pc molecules at NMR measurement concentration [22]. The mass spectra of the compounds 4-7 were good correlation with proposed structure (fig. 3). The absorption spectra of Pcs (4-7) were measured in DMF and Q bands were observed at 705 and 672, 683, 670 and 682 nm (Fig. 2) and the shoulders were observed at: 646 and 616, 615, 611, 618, respectively [23]. Furthermore, B bands were observed at: 345, 358, 334 and 347 nm for 4-7, respectively (Fig. 4).

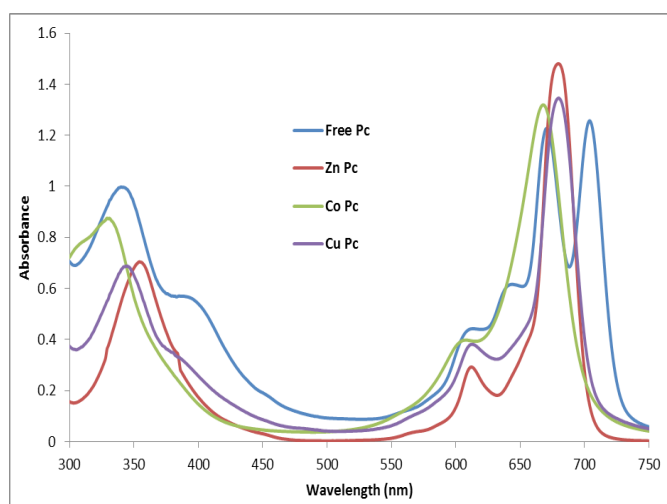


Fig. 2. UV-Vis absorption spectra of compounds 4-7 in DMF at  $1 \times 10^{-5}$  mol dm $^{-3}$

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

Compounds	Redox processes	$^a E_{1/2}$	$^b \Delta E_p$ (mV)	$^c \Delta E_{1/2}$
<b>H<sub>2</sub>Pc</b>	$R_1 \rightarrow [H_2Pc^{2+}] / [H_2Pc^{3+}]^{-1}$	-0.79	133	
	$R_2 \rightarrow [H_2Pc^{3+}]^{-1} / [H_2Pc^{4+}]^{-2}$	-1.12	142	
	$O_1 \rightarrow [H_2Pc^{2+}] / [H_2Pc^{1+}]^{-1}$	0.34	185	
	$O_2 \rightarrow [H_2Pc^{1+}]^{-1} / [H_2Pc^{0}]^{-2}$	0.99	191	1.13
<b>ZnPc</b>	$R_1 \rightarrow [Zn^{II}Pc^{2+}] / [Zn^{III}Pc^{3+}]^{-1}$	-1.15	174	
	$R_2 \rightarrow [Zn^{III}Pc^{3+}]^{-1} / [Zn^{IV}Pc^{4+}]^{-2}$	-1.52	102	
	$O_1 \rightarrow [Zn^{II}Pc^{2+}] / [Zn^{III}Pc^{3+}]^{-1}$	0.61	162	
	$O_2 \rightarrow [Zn^{III}Pc^{3+}]^{-1} / [Zn^{IV}Pc^{4+}]^{-2}$	1.39	142	1.76
<b>CoPc</b>	$R_1 \rightarrow [Co^{II}Pc^{2+}] / [Co^{III}Pc^{3+}]^{-1}$	-0.40	186	
	$O_1 \rightarrow [Co^{II}Pc^{2+}] / [Co^{III}Pc^{3+}]^{-1}$	0.72	190	1.12
<b>CuPc</b>	$R_1 \rightarrow [Cu^{II}Pc^{2+}] / [Cu^{III}Pc^{3+}]^{-1}$	-0.94	162	
	$R_2 \rightarrow [Cu^{III}Pc^{3+}]^{-1} / [Cu^{IV}Pc^{4+}]^{-2}$	-1.24	175	
	$O_1 \rightarrow [Cu^{II}Pc^{2+}] / [Cu^{III}Pc^{3+}]^{-1}$	0.86	230	
	$O_2 \rightarrow [Cu^{III}Pc^{3+}]^{-1} / [Cu^{IV}Pc^{4+}]^{-2}$	1.44	114	1.80

<sup>a</sup>:  $E_{1/2}$  values ( $(E_{pa} + E_{pc})/2$ ) were given versus SCE at 0.100 Vs $^{-1}$  scan rate. <sup>b</sup>:  $\Delta E_p = E_{pa} - E_{pc}$ . <sup>c</sup>:  $\Delta E_{1/2} = E_{1/2}$  (first oxidation) -  $E_{1/2}$  (first reduction).

### 3.2. Electrochemical Measurements

Electrochemical measurements of Pcs were realized with CV and SWV measurements in dichloromethane (DCM) / tetrabutylammoniumperchlorate (TBAP) electrolyte system on a Pt working electrode. Basic electrochemical parameters, the assignments of the redox couples and estimated electrochemical parameters including the half-wave potentials ( $E_{1/2}$ ), peak to peak potential separations ( $\Delta E_p$ ) and difference between the first oxidation and reduction processes ( $\Delta E_{1/2}$ ), are derived from the analyses of the complexes and these data are given in Table 1.

Fig. 3 shows CV and SWV responses of H<sub>2</sub>Pc (**4**) in DCM/TBAP. During the cathodic potential scans, H<sub>2</sub>Pc (**4**) goes two electrochemically and chemically reversible reduction reactions, R<sub>1</sub> at -0.79 V ( $\Delta E_p = 133$  mV) and R<sub>2</sub> at -1.12 V ( $\Delta E_p = 142$  mV) during the anodic potential scans. Moreover, two quasi-reversible oxidation reactions O<sub>1</sub> and O<sub>2</sub> are observed at 0.34 V ( $\Delta E_p = 185$  mV), 0.99 V ( $\Delta E_p = 191$  mV). All redox processes are in harmony with the ring based electron transfer reactions of metal free phthalocyanines in the literature [24, 25]. Therefore  $E_{1/2}$ ,  $\Delta E_p$ ,  $\Delta E_{1/2}$  data of H<sub>2</sub>Pc (**4**) support proposed structure of the complex.

MPcs having redox inactive ion centers (ZnPc and CuPc) shows similar CV and SWV responses with those of H<sub>2</sub>Pc (**4**) as shown in Fig. 4 and 5, respectively. ZnPc gives two reductions, R<sub>1</sub> (quasi-

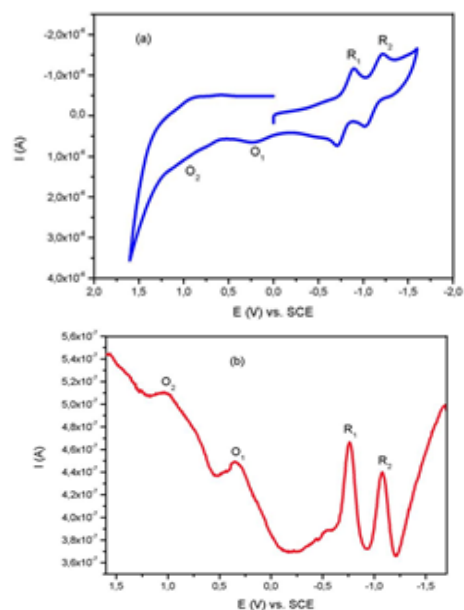


Fig. 3. (a) CV of H<sub>2</sub>Pc (b) SWV of H<sub>2</sub>Pc.

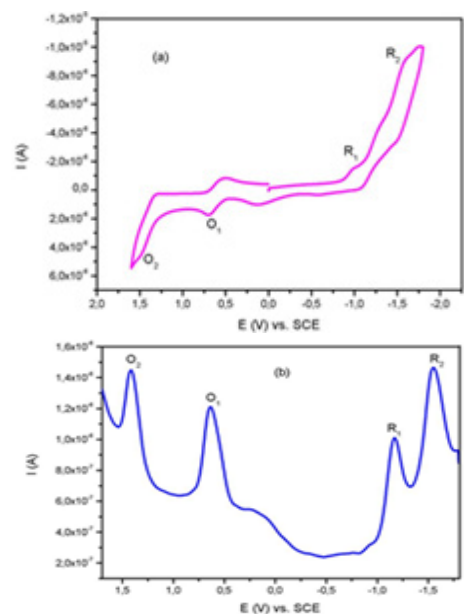


Fig. 4. (a) CV of ZnPc (b) SWV of ZnPc

reversible) at -1.15 V ( $\Delta E_p = 174$  mV), R<sub>2</sub> (reversible) at -1.52 V ( $\Delta E_p = 102$  mV) and two oxidation reactions O<sub>1</sub> (quasi-reversible) at 0.61 V ( $\Delta E_p = 162$  mV), O<sub>2</sub> (reversible) at 1.39 V ( $\Delta E_p = 142$  mV). Also, CuPc gives two (quasi-reversible) reductions, R<sub>1</sub> at -0.94 V ( $\Delta E_p = 162$  mV), R<sub>2</sub> at -1.24 V ( $\Delta E_p = 175$  mV) and two oxidation reactions O<sub>1</sub> (irreversible) at 0.86 V ( $\Delta E_p = 230$  mV), O<sub>2</sub> (quasi-reversible) at 1.44 V ( $\Delta E_p = 114$  mV) within the potential window of DCM/TBAP electrolyte system. Incorporation of a metal ion into the core of Pc ring shift the reduction peaks towards the more negative potentials. This potential shifts extent  $\Delta E_{1/2}$  values of the complexes. Redox processes of metallophthalocyanines studied here are in harmony with reported metallophthalocyanines having redox inactive ion centers [26, 27].

Pc-Co complexes mainly give metal based reduction process at around 0 V because of the electron giving to the empty Co(II) d orbitals located between the HOMO and LUMO orbitals of Pc ring in noncoordinating solvents like DCM. Figure 6 represents CV and SWV responses of CoPc in DCM/TBAP electrolyte on a Pt working electrode. CoPc gives one (quasi-reversible) reduction, R<sub>1</sub> at -0.40 V ( $\Delta E_p = 186$  mV) and one (quasi-reversible) oxidation reaction O<sub>1</sub> at 0.72 V ( $\Delta E_p = 190$  mV) within the potential window of DCM/TBAP electrolyte system. Electrochemical behavior of CoPc is in agreement

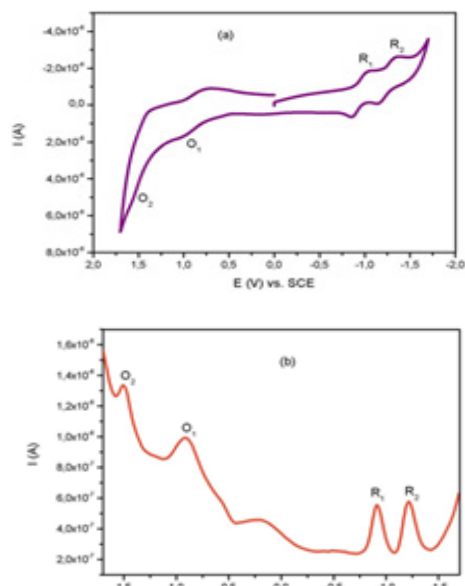


Fig. 5. (a) CV of CuPc (b) SWV of CuPc

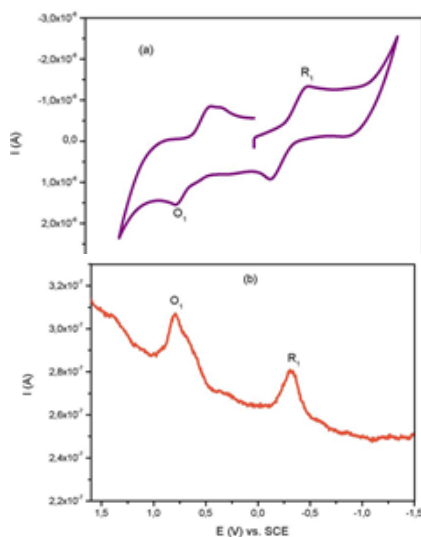


Fig. 6. (a) CV of CoPc (b) SWV of CoPc

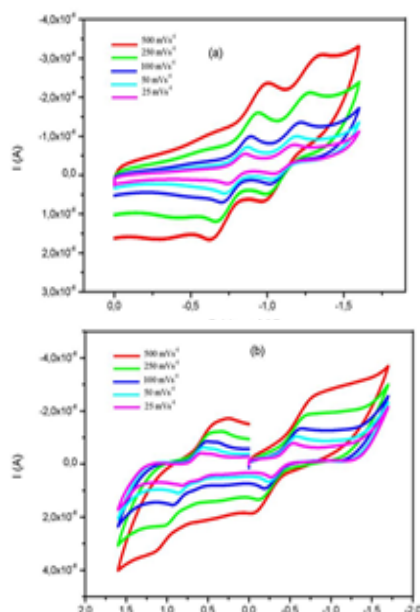


Fig. 7. (a) CV of  $H_2Pc$  at various scan rates (ranging from 25 to 500  $mV \cdot s^{-1}$ ) on a Pt working electrode in DCM/TBAP. (b) CV of CoPc at various scan rates (ranging from 25 to 500  $mV \cdot s^{-1}$ ) on a Pt working electrode in DCM/TBAP.

with the similar CoPc complexes reported in the literature [28, 29], which support the proposed structure of the complex synthesized here. Also, HOMO-LUMO gap of CoPc ( $\Delta E_{1/2} = 1.12$  V) is in compliance with the CoPc reported in the literature [30]. Also, the peak currents increased linearly with the square root of the scan rates for scan rates ranging from 25 to 500  $mV \cdot s^{-1}$  (for example Figure 7a for  $H_2Pc$ , Figure 7b for CoPc), respectively.

#### 4. Conclusions

We synthesized of new 2-(4-benzyloxyphenyl)ethanol substituted phthalonitrile and its metal-free, zinc(II), cobalt(II) and copper(II) phthalocyanines for the first time in this work and characterized these novel compounds FT-IR,  $^1H$ -NMR,  $^{13}C$ -NMR and mass spectra. Electrochemistry of  $H_2Pc$ , ZnPc, CuPc and CoPc are studied in solution with voltammetric measurements. Electrochemical measurement results of the compounds promote the proposed structure of the  $H_2Pc$  and MPcs. While  $H_2Pc$ , ZnPc and CuPc gives Pc ring based redox processes, in addition to the Pc based redox reactions, CoPc presents only metal based electron transfer reactions and fortify the potential utilization of the complex in different electrochemical technologies.

#### Acknowledgement

This research has been supported by Sinop University Scientific Research Projects Coordination Unit. Project Number: SHMYO-1901-16-26, 2016.

#### References

- Leznoff, C.C., A.B.P. Lever, A.B.P., Phthalocyanines Properties and Applications, vol. 1, New York: VCH Publisher, 1989.
- Parra, V., Bouvet, M., Brunet, J., Rodríguez-Méndez, M.L. and Saja, J.A., On the effect of ammonia and wet atmospheres on the conducting properties of different lutetium bisphthalocyanine thin films, Thin Solid Films, 2008, 516, 9012-9019.
- Bouvet, M., Phthalocyanine-based field-effect transistors as gas sensors, Anal. Bioanal. Chem. 2006, 384, 366-373.
- Leznoff, C.C. and Lever, A.B.P., Phthalocyanines Properties and Applications, vol. 3, New York: VCH Publisher, 1993.
- De La Torre, G., Vazquez, P., Agullo-Lopez, F. and Torres, T., Phthalocyanines and related compounds: organic targets for nonlinear optical applications, J. Mater. Chem. 1998, 8, 1671-1683.
- Yang, F. and Forrest, S.R., Photocurrent generation in nanostructured organic solar cells, ACS Nano, 2008, 2, 1022-1032.
- Forrest, S.R., Ultrathin organic films grown by organic molecular beam deposition and related techniques, Chem. Rev. 1997, 97, 1793-1896.
- Bilgin, A. Ertem, B. and Gök, Y., Synthesis and characterization of new metal-free and metallophthalocyanines containin spherical or cylindrical macrotricyclic moieties, Polyhedron, 2005, 24, 1117-1124.
- Leznoff, C.C. and Lever, A.B.P., Phthalocyanines Properties and Applications, vol. 2, New York, VCH Publisher, 1993.
- Emmelius, M. Pawlowski, G. and Vollmann, H.W., Materials for optical data storage, Angew. Chem. Int. Edit., 1989, 28, 1445-1471.
- Leznoff, C.C. and Lever, A.B.P., Phthalocyanines, Properties and Applications, vol. 4, New York, VCH Publisher, 1996.
- Yılmaz, F., Özer, M., Kani, İ. and Bekaroğlu, Ö., Catalytic activity of a thermoregulated, phase-seperable Pd(II)-perfluoroalkylphthalocyanine complex in an organic/fluorous biphasic system: Hydrogenation of olefins, Catal. Lett., 2009, 1, 642-647.
- Rosenthal, I., Phthalocyanines as photodynamic sensitizers, Photochem. Photobiol., 1991, 53, 589-870.
- Demirbaş, Ü., Kobak, R.Z.U., Akçay, H.T., Ünlüer, D., Koca, A., Çelik, F. and Kantekin, H., Synthesis, characterization, electrochemical and spectroelectrochemical properties of novel peripherally tetra-1,2,4-triazole substituted phthalocyanines, Synthetic Metals, 2016, 215, 68-76, 2016.
- Koç, I., Özer, M., Özkaya, A.R. and Bekaroğlu, Ö., Electrocatalytic activity, methanol tolerance and stability of perfluoroalkyl-substituted mononuclear, and ball-type dinuclear cobalt phthalocyanines for oxygen reduction in acidic medium, Dalton Trans., 2009, 32, 6368-6376.

16. Bilgiçli, A.T., Yaraşır, M.N., Kandaz, M. and Özkaya, A.R., H-type aggregation of functional metal ion sensing phthalocyanines: Synthesis, characterization and electrochemistry, *Polyhedron*, 2010, 29, 2498–2510.
17. Tau, P. and Nyokong, T., Electrochemical characterisation of tetra- and octa-substituted oxo(phthalocyaninato)titanium(IV) complexes, *Electrochimica Acta*, 2007, 52, 3641-3650.
18. Seven, Ö., Dindar, B. and Gültekin, B., Microwave-assisted synthesis of some metal-free phthalocyanine derivatives and a comparison with conventional methods of their synthesis, *Turkish Journal of Chemistry*, 2009, 33, 123-134.
19. Perin, D.D. and Armarego, W.L.F., *Purification of laboratory chemicals*, Oxford, Pergamon, 1989.
20. Bayrak, R., Akçay, H.T., Durmuş, M. and Değirmenciöğlü, İ., Synthesis, photophysical and photochemical properties of highly soluble phthalocyanines substituted with four 3,5-dimethylpyrazole-1-methoxy groups, *J. Organomet. Chem.*, 2011, 696, 3807-3815.
21. Bayrak, R., Akçay, H.T., Pişkin, M., Durmuş, M. and Değirmenciöğlü, İ., Azine-bridged binuclear metallophthalocyanines functioning photophysical and photochemical-responsive, *Dyes Pigments*. 2012, 95, 330-337.
22. Değirmenciöğlü, İ., Bayrak, R., Er, M. and Serbest, K., New olefinicentred binuclear clamshell type phthalocyanines: Design, synthesis, structural characterisation, the stability and the change in the electron cloud at olefine-based symmetrical diphthalonitrile fragment by the combined application of UV-Vis electronic structure and theoretical methods, *Polyhedron*, 2011, 30, 1628-1636.
23. Bayrak, R., Karaoğlu, K., Ünver, Y., Sancak, K., Dumludağ, F. and Değirmenciöğlü, İ., Synthesis, characterization, spectral and electrical properties of peripherally tetra-triazole-substituted phthalocyanines and its metal complexes, *J. Organomet. Chem.*, 2012, 712, 57-66.
24. Alemdar, A., Özkaya, A.R. and Bulut, M., Synthesis, spectroscopy, electrochemistry and in situ spectroelectrochemistry of partly halogenated coumarin phthalonitrile and corresponding metal-free, cobalt and zinc phthalocyanines, *Polyhedron*, 2009, 28, 3788-3796.
25. Aktaş, A., Acar, İ., Bıyıklıoğlu, Z., Saka, E.T. and Kantekin, H., Synthesis, electrochemistry of metal-free, copper, titanium phthalocyanines and investigation of catalytic activity of cobalt, iron phthalocyanines on benzyl alcohol oxidation bearing 4-{2-[3-trifluoromethyl]phenoxy}ethoxy groups, *Synthetic Metals*, 2014, 198, 212-220.
26. Bıyıklıoğlu, Z., Çakır, V., Çakır, D. and Kantekin, H., Crown ether-substituted water soluble phthalocyanines and their aggregation, electrochemical studies, *J. Organomet. Chem.*, 2014, 749, 18-25.
27. Özgül, G., Taştemel, A., Özkaya, A.R. and Bulut, M., Synthesis, characterization and comparative electrochemistry of beta and alpha tetra-[4-oxy-3-methoxybenzoic acid]-substituted Zn(II), Co(II) and Cu(II) phthalocyanines, *Polyhedron*, 2015, 85, 181-189.
28. Sevim, M., Yaraşır, M.N., Koca, A. and Kandaz, M., Novel scorpion type phthalocyanine chemosensors for detection of selective-metal ion by inducing H- and J-aggregations in solution; synthesis, characterization and electrochemistry, *Dyes Pigments*, 2014, 111, 190-201.
29. Odabaş, Z., Orman, E.B., Durmuş, M., Dumludağ, F. and Bulut, M., Novel alpha-7-oxy-4-(4-methoxyphenyl)-8-methylcoumarin substituted metal-free, Co(II) and Zn(II) phthalocyanines: Photochemistry, photophysics, conductance and electrochemistry, *Dyes Pigments*, 2012, 95, 540-552.
30. Günsel, A., Kandaz, M., Koca, A. and Salih, B., Peripheral and non-peripheral-designed multifunctional phthalocyanines; synthesis, electrochemistry, spectroelectrochemistry and metal ion binding studies, *Polyhedron*, 2011, 30, 1446-1455.

Note: This is an Open Access article distributed under the terms of the Creative Commons Attribution regulations with the licence type "Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND 4.0)", which, for non-commercial purposes, lets others distribute and copy the article, and include in a collective work (such as an anthology), as long as they credit the author(s) and provided they do not alter or modify the article.