#### Dyes and Pigments 89 (2011) 49-55



Contents lists available at ScienceDirect

### Dyes and Pigments



journal homepage: www.elsevier.com/locate/dyepig

# Synthesis, electrochemical, in-situ spectroelectrochemical and in-situ electrocolorimetric characterization of non-peripheral tetrasubstituted metal-free and metallophthalocyanines

Zekeriya Bıyıklıoğlu<sup>a</sup>, Volkan Çakır<sup>b</sup>, Atıf Koca<sup>c</sup>, Halit Kantekin<sup>b,\*</sup>

<sup>a</sup> Macka Vocational School, Karadeniz Technical University, 61750, Macka, Trabzon, Turkey
<sup>b</sup> Department of Chemistry, Faculty of Arts & Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey

<sup>c</sup> Department of Chemical Engineering, Faculty of Engineering, Marmara University, Göztepe 34722, İstanbul, Turkey

#### ARTICLE INFO

Article history: Received 20 June 2010 Received in revised form 5 September 2010 Accepted 8 September 2010 Available online 17 September 2010

Keywords: 6-Hydroxyquinoline Phthalocyanine Synthesis Non-peripheral Cyclic voltammetry Differantial pulse voltammetry

#### 1. Introduction

Metallophthalocyanines (MPcs) have a attracted a lot of attention for many years since their discovery in the early 1900s. Their remarkable properties that include flexibility, chemical and thermal stabilities, semiconductivity and photoconductivity [1] have been of great interest in research. Phthalocyanines, which are of enormous technological importance for the manufacture of green and blue pigments [2] and are of considerable interest owing to their fascinating electronic and optical properties [3], don't occur in nature [4]. In many fields, phthalocyanines have been remarkably used because of their magnificently versatile properties to illustrate photodynamic reagents for cancer therapy [5,6], and other medical applications [7], for optical read-write discs [8], in chemical sensors, in photocopying machines [9,10], Langmuir-Blodgett films [11], solar cells, electrochromism, high energy batteries [12], fibrous assemblies [13], coloring for plastics and metal surfaces and dyestuffs for clothing [8].

#### ABSTRACT

The synthesis of new metal-free, nickel, zinc, cobalt and copper phthalocyanines with four 6-oxyquinoline groups on the non-peripheral position were prepared by cyclotetramerization of a novel 3-(quinolin-6-yloxy)phthalonitrile. All new compounds were characterized by the ways of IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS spectral data, all of which were compatible with the proposed structures. Electrochemical properties of metal-free, Ni(II) and Zn(II) phthalocyanines were investigated by using cyclic voltammetry and differential pulse voltammetry techniques. The metal-free phthalocyanines give very similar voltammetric responses with slightly potential shift due to the different metal center.

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The range of solubility in phthalocyanines becomes very important for these applications, since many phthalocyanines are poorly soluble in organic solvents and water. The solubility of phthalocyanins can be enhanced by adding different kinds of substituents such as bulky or long chain alkyl, alkylthio or alkoxy groups at the periphery axial positions of the phthalocyanine ring [14–17]. The most extensively investigated soluble substituted phthalocyanines are the tetra- and octasubstituted derivatives and tetrasubstituted ones exhibit usually a higher solubility [18,19].

Microwaves have been previously used for the synthesis of phthalocyanines and include a wider range of references on the topic [20–27]. In this paper, we describe the synthesis and characterization of metal-free and metallophthalocyanines (MPc; M=Zn (II), Ni(II) and Co(II)) substituted with 3-(quinolin-6-yloxy) groups by microwave irradiation.

The phthalocyanine ring often can be reduced to the mono-, di-, tri-, and tetraanionic states or oxidized to the mono- and dicationic states. In addition, Pc's with redox-active metal ions or substituents typically show additional metal-based or substituent based redox couples [28]. In this study we perform electrochemical characterization of newly synthesized Pc complexes bearing  $2H^+$  ( $H_2Pc$ , **4**), Ni<sup>2+</sup> (NiPc, **5**), and Zn<sup>2+</sup> (ZnPc, **6**) Pc ring centers. Voltammetric responses of the complexes were analyzed to support the proposed

<sup>\*</sup> Corresponding author. Tel.: +90 462 377 25 89; fax: +90 462 325 31 96. *E-mail address:* halit@ktu.edu.tr (H. Kantekin).

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structures by comparing with each other and with the similar MPc in the literature [28–33]. In-situ spectroelectrochemical and electrocolorimetric measurements were performed to assign the redox processes and to determine the spectral and color states of the electro-generated anionic and cationic form of the complexes.

#### 2. Experimental

#### 2.1. Materials

3-Nitrophthalonitrile (**2**) [34] was prepared according to the literature. 6-Hydroxyquinoline was purchased from Aldrich. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [35].

#### 2.2. Equipment

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR Spectrophotometer, using KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in CDCl<sub>3</sub>, and chemical shifts were reported ( $\delta$ ) relative to Me<sub>4</sub>Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ ULTIMA LC-MS/MS spectrometer. Melting points were measured on an electrothermal apparatus and are uncorrected. The elemental analyses were performed on a Costech ECS 4010 instrument. The cvclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm<sup>2</sup>. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade TBAP in extra pure DCM was employed as the supporting electrolyte at a concentration of 0.10 mol dm<sup>-3</sup>. UV–Vis absorption spectra and chromaticity diagrams were measured by an OceanOptics OE65000 diode array spectrophotometer. In-situ electrocolorimetric measurements, under potentiostatic control, were obtained using an OceanOptics QE65000 diode array spectrophotometer at color measurement mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell. The standard illuminant A with 2 degree observer at constant temperature in a light booth designed to exclude external light was used. Prior to each set of measurements, background color coordinates (x, y, and z values)were taken at open-circuit, using the electrolyte solution without the complexes under study. During the measurements, readings were taken as a function of time under kinetic control, however only the color coordinates at the beginning and final of each redox processes were reported.

#### 2.3. Synthesis

#### 2.3.1. Synthesis of 3-(quinolin-6-yloxy)phthalonitrile (3)

6-Hydroxyquinoline **1** (2 g,  $13.8 \times 10^{-3}$  mol) was dissolved in dry DMF (0.02 L) under N<sub>2</sub> atmosphere and 3-nitrophthalonitrile **2** (2.4 g,  $13.8 \times 10^{-3}$  mol) was added to the solution. After stirring 10 min, finely ground anhydrous K<sub>2</sub>CO<sub>3</sub> (5 g,  $36 \times 10^{-3}$  mol) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under N<sub>2</sub> at 50 °C for 2 days. Then the solution was poured into ice-water (0.2 L). The precipitate formed was filtered off, washed first with water until the filtrate was neutral and then diethyl ether and dried in vacuo over P<sub>2</sub>O<sub>5</sub>. The crude product was crystallized from ethanol. Yield: 1.56 g (42%), mp: 196–198 °C. IR (KBr tablet)  $\nu_{max}/cm^{-1}$ : 3164, 3070, 3019 (Ar–H),

2923, 2862, 2229 (C=N), 1621, 1598, 1581, 1501, 1455, 1375, 1327, 1279, 1149, 1113, 996, 888, 835, 805, 731, 697, 614. <sup>1</sup>H NMR. (CDCl<sub>3</sub>), ( $\delta$ :ppm): 8.96 (br s, 1H, Ar–H), 8.23–8.11 (m, 2H, Ar–H), 7.65–7.51 (m, 5H, Ar–H), 7.17 (d, 1H, Ar–H). <sup>13</sup>C NMR. (CDCl<sub>3</sub>), ( $\delta$ :ppm): 160.59, 151.95, 150.86, 146.35, 135.94, 134.94, 132.74, 129.23, 127.87, 123.42, 122.42, 121.34, 117.63, 116.96, 115.30, 112.86, 106.75. MS (ES<sup>+</sup>), (*m*/*z*): 271 [M]<sup>+</sup>. Anal. Calcd for C<sub>17</sub>H<sub>9</sub>N<sub>3</sub>O: C, 75.34; H, 3.34; N, 15.50. Found: C, 75.23; H, 3.37; N, 15.48.

#### 2.3.2. Synthesis of metal-free phthalocyanine (4)

A mixture of 3-(quinolin-6-yloxy)phthalonitrile **3** (0.25 g,  $0.92 \times 10^{-3}$  mol) and  $0.9 \times 10^{-3}$  mol of 1.8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.0005 L) in 0.0025 L of dry n-pentanol was heated and stirred at 160 °C for 12 h under N<sub>2</sub>. After cooling to room temperature the green suspension was precipitated with diethyl ether and then dried in vacuo. Finally, pure metal-free phthalocyanine was obtained by column chromatography which is placed aluminium oxide using CHCl<sub>3</sub> as solvent. Yield: 0.1 g (40%), mp > 300 °C. IR (KBr tablet)  $\nu_{max}/cm^{-1}$ : 3291 (N–H), 3032 (Ar–H), 2929, 2851, 1622, 1591, 1499, 1487, 1463, 1375, 1322, 1257, 1219, 1148, 1136, 1106, 1027, 968, 941, 866, 834. <sup>1</sup>H NMR. (CDCl<sub>3</sub>), (δ:ppm): 8.68-8.56 (m, 4H, Ar-H), 7.97-7.72 (m, 4H, Ar-H), 7.58-7.47 (m, 4H, Ar-H), 7.26-6.95 (m, 16H, Ar-H), 6.89-6.80 (m, 4H, Ar-H), 6.60-6.51 (m, 4H, Ar-H), -3, 22 (s, 2H, N-H). <sup>13</sup>C NMR. (CDCl<sub>3</sub>), (δ:ppm): 156.85, 153.73, 153.50, 148.83, 148.40, 144.30, 137.95, 134.65, 130.70, 129.81, 128.68, 124.82, 123.45, 122.14, 118.65, 117.36, 110.20. UV–vis (chloroform):  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 331 (4.94), 625 (4.59), 659 (4.73), 689 (5.18), 721 (5.24). MS (ES<sup>+</sup>), (m/z): 1108  $[M + Na - 2H]^+$ .

## 2.3.3. General procedures for metallophthalocyanine derivatives (5–8)

A mixture of 3-(quinolin-6-yloxy)phthalonitrile **1** (0.25 g, 0.92  $\times$  10<sup>-3</sup> mol), anhydrous metal salts [NiCl<sub>2</sub> (0.059 g), Zn (CH<sub>3</sub>COO)<sub>2</sub> (0.084 g), CoCl<sub>2</sub> (0.059 g), CuCl<sub>2</sub> (0.062 g)] and 2-(dimethylamino)ethanol (0.0025 L) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product which was filtered off and dried in vacuo over P<sub>2</sub>O<sub>5</sub>. Finally, pure metallophthalocyanines were obtained by column chromatography which is placed aluminium oxide using CHCl<sub>3</sub>:CH<sub>3</sub>OH (10:0.5) as solvent system.

#### 2.3.4. Nickel(II) phthalocyanine (5)

Yield: 0.126 g (48%). IR (KBr tablet)  $\nu_{max}/cm^{-1}$ : 3054, 3027 (Ar–H), 2956, 2926, 1621, 1593, 1530, 1499, 1479, 1463, 1375, 1331, 1257, 1217, 1166, 1135, 1113, 1090, 1011, 987, 956, 913, 834, 797, 747. <sup>1</sup>H NMR. (CDCl<sub>3</sub>), ( $\delta$ :ppm): 8.70–8.50 (m, 8H, Ar–H), 7.76 (m, 4H, Ar–H), 7.57–7.44 (m, 4H, Ar–H), 7.19–6.88 (m, 12H, Ar–H), 6.89–6.80 (m, 4H, Ar–H), 6.51–6.35 (m, 4H, Ar–H). <sup>13</sup>C NMR. (CDCl<sub>3</sub>), ( $\delta$ :ppm): 157.21, 154.25, 153.68, 149.47, 148.60, 144.58, 138.73, 137.97, 134.87, 131.50, 128.83, 128.41, 124.43, 122.90, 121.42, 116.26, 110.31. UV–vis (chloroform):  $\lambda_{max}$ , nm (log ε): 299 (4.68), 331 (4.64), 625 (4.50), 693 (5.24). MS (ES<sup>+</sup>), (*m*/*z*): 1143 [M]<sup>+</sup>. Anal. Calcd for C<sub>68</sub>H<sub>36</sub>N<sub>12</sub>O<sub>4</sub>Ni: C, 71.40; H, 3.17; N, 14.69. Found: C, 71.46; H, 3.22; N, 14.72.

#### 2.3.5. *Zinc*(II) *phthalocyanine* (6)

Yield: 0.135 g (51%). IR (KBr tablet)  $\nu_{max}/cm^{-1}$ : 3076, 3021 (Ar–H), 2924, 2854, 1729, 1662, 1621, 1604, 1586, 1503, 1482, 1463, 1377, 1330, 1245, 1114, 1079, 976, 878, 833, 748. <sup>1</sup>H NMR. (CDCl<sub>3</sub>), ( $\delta$ :ppm): 8.91 (br s, 4H, Ar–H), 8.25 (br s, 4H, Ar–H), 7.92 (s, 4H, Ar–H), 7.71 (m, 8H, Ar–H), 7.53 (m, 4H, Ar–H), 6.90–6.79 (m, 12H, Ar–H). <sup>13</sup>C NMR. (CDCl<sub>3</sub>), ( $\delta$ :ppm): 170.39, 167.77, 157.19, 155.17, 150.19, 135.71, 135.06, 133.12, 132.34, 130.88, 129.13, 128.75, 123.59,

122.78, 121.32, 114.64, 114.04. UV–vis (chloroform):  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 329 (4.72), 631 (4.53), 699 (5.30). MS (ES<sup>+</sup>), (*m*/*z*): 1150 [M]<sup>+</sup>. Anal. Calcd for C<sub>68</sub>H<sub>36</sub>N<sub>12</sub>O<sub>4</sub>Zn: C, 70.90; H, 3.15; N, 14.60. Found: C, 70.95; H, 3.21; N, 14.59.

#### 2.3.6. Cobalt(II) phthalocyanine (7)

Yield: 0.155 g (59%). IR (KBr tablet)  $\nu_{max}/cm^{-1}$ : 3054, 2924 (Ar–H), 2851, 1728, 1594, 1500, 1475, 1459, 1374, 1324, 1247, 1215, 1114, 987, 834, 750. UV–vis (chloroform):  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 321 (5.22), 623 (4.64), 689 (5.26). MS (ES<sup>+</sup>), (*m*/*z*): 1144 [M]<sup>+</sup>. Anal. Calcd for C<sub>68</sub>H<sub>36</sub>N<sub>12</sub>O<sub>4</sub>Co: C, 71.39; H, 3.17; N, 14.69. Found: C, 71.39; H, 3.19; N, 14.69.

#### 2.3.7. Copper(II) phthalocyanine (8)

Yield: 0.161 g (61%). IR (KBr tablet)  $\nu_{max}/cm^{-1}$ : 3043 (Ar–H), 2923, 2862, 1764, 1725, 1706, 1618, 1593, 1500, 1473, 1459, 1380, 1316, 1242, 1152, 1119, 1050, 976, 875, 828, 801, 749. UV–vis (DMF):  $\lambda_{max}$ , nm (log  $\varepsilon$ ): 315 (5.23), 629 (4.39), 695 (4.83). MS (ES<sup>+</sup>), (*m/z*): 1147 [M – H]<sup>+</sup>. Anal. Calcd for C<sub>68</sub>H<sub>36</sub>N<sub>12</sub>O<sub>4</sub>Cu: C, 71.10; H, 3.15; N, 15.46. Found: C, 71.40; H, 3.10; N, 14.65.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

Starting from 6-hydroxyquinoline **1** and 3-nitrophthalonitrile **2**, the general synthetic route for the synthesis of new metal-free and metallophthalocyanines are given in Figs. 1 and 2. The synthesis of non-peripheral substituted phthalonitrile derivative 3 is based on the reaction of 6-hydroxyquinoline with 3-nitrophthalonitrile (in dry DMF and in the presence of dry  $K_2CO_3$  as base, at 50 °C in 48 h). Cyclotetramerization of the phthalonitrile derivative **3** to the metal-free phthalocyanine **4** was accomplished in *n*-pentanol in the presence of a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at 160 °C in sealed tube. The metal-lophthalocyanines **5**–**8** were obtained by the anhydrous metal salts



Fig. 1. The synthesis of the metal-free phthalocyanine.



Fig. 2. The synthesis of the metallophthalocyanines.

[NiCl<sub>2</sub>, Zn(CH<sub>3</sub>COO)<sub>2</sub>, CoCl<sub>2</sub> and CuCl<sub>2</sub>] in 2-(dimethylamino) ethanol by microwave irradiation. The structures of the target compounds were confirmed using IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS spectral data. All the results were consistent with the predicted structures as shown in the Experimental section.

The IR spectra of the phthalonitrile compound **3** clearly indicate the presence of C=N group by the intense stretching bands at 2229 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectra of phthalonitrile compound **3** were recorded in CDCl<sub>3</sub>. In the <sup>1</sup>H NMR spectrum of compound **3**, OH group of 6-hydroxyquinoline disappeared as expected. In the <sup>1</sup>H NMR spectrum of **3** the aromatic protons appear at 8.96 (br s), 8.23–8.11 (m), 7.65–7.51 (m), 7.17 (d) ppm. In the <sup>13</sup>C NMR spectrum of compound **3** indicated the presence of nitrile carbon atom at  $\delta$  = 116.96, 115.30 ppm. In the mass spectra of phthalonitrile compound **3**, the molecular ion peak was observed at *m*/*z* 271 [M]<sup>+</sup>.

Cyclotetramerization of the dinitriles **3** to the phthalocyanine **4–8** was confirmed by the disappearance of the sharp  $C \equiv N$ vibration at 2229 cm<sup>-1</sup>. IR bands characteristic of the metal-free phthalocyanine ring is an N–H stretching at 3291 cm<sup>-1</sup>. The IR spectra of metal-free **4** and metallophthalocyanines **5–8** are very similar, except these v (NH) vibrations of the inner phthalocyanine core in the metal-free molecule. These protons are also very well characterized by the <sup>1</sup>H NMR spectrum which shows a peak at  $\delta$ : -3.22 ppm, as a result of the 18  $\pi$ -electron system of the phthalocyanine ring. The <sup>1</sup>H NMR spectra of **4** indicated characteristic aromatic protons at 8.68-8.56 (m, 4H, Ar-H), 7.97-7.72 (m, 4H, Ar-H), 7.58-7.47 (m, 4H, Ar-H), 7.26-6.95 (m, 16H, Ar-H), 6.89–6.80 (m, 4H, Ar–H), 6.60–6.51 (m, 4H, Ar–H) ppm. The <sup>13</sup>C NMR spectra of **4** indicated characteristic aromatic carbon atoms between at 156.85–110.20 ppm. The mass spectrum of 4 displayed the  $[M + Na - 2H]^+$  parent ion peak at m/z = 1108, which confirms the same structure.

In the IR spectra of the metallophthalocyanines (**5–8**) cyclotetramerization of **3** was confirmed by the disappearance of the sharp C $\equiv$ N stretching vibration at 2229 cm<sup>-1</sup>. The IR spectra of NiPc, ZnPc, CoPc and CuPc are also very similar to that of the precursor H<sub>2</sub>Pc. The <sup>1</sup>H NMR spectra of these compound were almost identical to those of H<sub>2</sub>Pc **4**. <sup>1</sup>H NMR spectra of compounds **5**, **6** were the broad signals encountered in the case of compound **5**, **6** as a result of the aggregation of phthlocyanine cores at the considerable high concentration used for the NMR measurements [36]. <sup>1</sup>H NMR measurements of the cobalt(II) and copper(II) phthalocyanine **7**, **8** were precluded due to its paramagnetic nature. In the mass spectrum of compounds **5**, **6**, **7** and **8** the presence of molecular ion peaks at m/z = 1143 [M]<sup>+</sup>, 1150 [M]<sup>+</sup>, 1144 [M]<sup>+</sup> and 1147 [M – H]<sup>+</sup> respectively, confirmed the proposed structures.

The metal-free and metallophthalocyanines display typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–350 nm (B band) and the other one in the visible region at 600–700 nm (Q band) [37]. The best indications for phthalocyanine systems are given by their UV–Vis spectra in solution (Fig. 3). UV–Vis spectra of metal-free derivative **4** (in CHCl<sub>3</sub>) split Q bands appeared at 721, 689, 659, 625 nm, while the B band remained at 331 nm. UV–Vis spectra of metallo phthalocyanines **5–8** (in CHCl<sub>3</sub>) exhibited an intense single Q band absorption of  $\pi \rightarrow \pi^*$  transitions around 699–689 nm and B bands in the UV region around 329–299 nm [38,39].

#### 3.2. Electrochemical measurements

Fig. 4a and b illustrates CVs and SWVs of 4 (H<sub>2</sub>Pc) in DCM/TBAP electrolyte on a Pt working electrode. Complex 4 exhibits two reversible Pc ring-based one-electron reduction couples with respect to  $\Delta E_p$  values, which are easily assigned to  $[H_2Pc^{-2}]/[H_2Pc^{-3}]^-$  at  $-0.67 \text{ V} (\Delta E_p = 58 \text{ mV} \text{ and } I_{p,a}/I_{p,c} = 0.40 \text{ at} 0.100 \text{ mV s}^{-1} \text{ scan rate})$  and  $[H_2Pc^{-3}]^-/[H_2Pc^{-4}]^{2-}$  at  $-1.07 \text{ V} (\Delta E_p = 62 \text{ mV} \text{ and } I_{p,a}/I_{p,c} = 0.95 \text{ at} 0.100 \text{ mV s}^{-1} \text{ scan rate})$  and one quasi-reversible Pc ring-based one-electron oxidation couple assigned to  $[H_2Pc^{-2}]/[H_2Pc^{-1}]^+$  at 1.05 V ( $\Delta E_p = 165$  mV and  $I_{p,c}/I_{p,a} = 0.90$  at 0.100 mV s<sup>-1</sup> scan rate). Although  $\Delta E_p$  values of the first reduction couple is in reversible range, the values of  $I_{pa}/I_{pc}$  are less than unity at all scan rates suggesting existence of a fast irreversible chemical reaction succeeding the second reduction reaction [40]. The following chemical reaction is dominant when the solution is concentrated. As shown in Fig. 4a inset, as the potential is switched just after the first reduction reaction, the values of  $I_{pa}$  $I_{pc}$  is almost unity however, when the switching potentials go to negative potentials, a third irreversible reduction reaction is recorded at -1.23 V, which may due to the reduction of the chemical reaction's product. When the switching potential passes the second reduction reaction, the reverse couples of the first and second reduction reactions, and consequently  $I_{pa}/I_{pc}$  values get smaller. These data support the proposed chemical reaction.

Replacement of the 2H<sup>+</sup> with Ni<sup>2+</sup> (NiPc), and Zn<sup>2+</sup> (ZnPc) significantly affect the redox behavior of the complexes. The complexes **5** and **6** give very similar voltammetric responses with slightly potential shift due to the different metal center, thus the CV and SWV responses of the complex **5** are given in Fig. 5a and b as a representative of these complexes. In the cathodic scan, the complex **5** exhibits two quasi-reversible one-electron reduction couples, which are easily assigned to  $[Ni^{II}Pc^{-2}]/[Ni^{II}Pc^{-3}]^{-}$  at  $-0.67 \text{ V} (\Delta E_p = 58 \text{ mV and } I_{p,a}/I_{p,c} = 0.90 \text{ at } 0.100 \text{ mV s}^{-1} \text{ scan rate})$  and  $[Ni^{II}Pc^{-3}]^{-}/[Ni^{II}Pc^{-4}]^{2-}$  at  $-1.07 \text{ V} (\Delta E_p = 62 \text{ mV and } I_{p,a}/I_{p,a})$ 



Fig. 3. UV-vis spectra of compounds  $4\left(-\right),5\left(-\right)$  and  $6\left(-\right)$  in chloroform.



**Fig. 4.** a) CVs of **4** (1.0  $10^{-4}$  mol dm<sup>-3</sup>) at various scan rates on a Pt working electrode in DCM/TBAP (inset CV of **4** (5.0  $10^{-4}$  mol dm<sup>-3</sup>) recorded with different switching potential at 0.100 V s<sup>-1</sup>scan rate). b) SWV of **4** recorded with SWV parameters: step size = 5 mV; pulse size = 100 mV; Frequency = 25 Hz.

 $I_{p,c} = 0.75$  at 0.100 mV s<sup>-1</sup> scan rate). When compared with the redox potentials of the compound **4**, these couples shift to negative potentials ca. 0.15 V due to the effective nuclear charge differences of the central ions. However oxidation behavior of **5** and **6** are completely different than the compound **4**. Both complexes polymerize on the working electrode electrochemically during the anodic potential scans. As shown in Fig. 5a, the complex **5** gives ill-defined oxidation waves and peak current of these processes



**Fig. 5.** a) SWVs and CVs of **5** ( $5.0 \ 10^{-4} \ mol \ dm^{-3}$ ) at various scan rates in cathodic side and repetitive CVs in the anodic side at 0.100 V s<sup>-1</sup> scan rate on a Pt working electrode in DMSO/TBAP. b) Repetitive CVs of **5** ( $5.0 \ 10^{-4} \ mol \ dm^{-3}$ ) recorded in the whole potential window of the DMSO/TBAP electrolyte system at 0.100 Vs<sup>-1</sup> scan rate on a Pt working electrode.

increases continuously during the repetitive cycles. Switching potential affects the polymerization mechanism significantly. When whole potential window of the electrolyte system is scanned instead of the positive potentials, the peak currents of the oxidation processes do not increase, but a new wave is recorded at -0.37 V, which increases with negative shifting with repetitive CV cycles (Fig. 5b). These voltammetric data indicate the polymerization of the complexes with different mechanism as a function of the switching potentials.

#### 3.3. Spectroelectrochemical studies

Spectroelectrochemical studies were employed to confirm the assignments in the CVs of the complexes. The complexes **4–6** have all redox inactive centers. Therefore, in-situ UV–Vis spectral changes of them indicate the Pc ring-based redox characters.

To represent the in-situ spectroelectrochemical response of the metal-free phthalocyanines, spectral chances of **4** during the controlled potential application at the redox potentials are given in Fig. 6. For the metal-free phthalocyanines, the symmetry is  $D_{2h}$  and therefore there are two sharp bands (split Q band) at 683 and 702 nm [28,33,41,42]. Due to the presence of aggregation and/or may due to performing of the measurements with high concentration, splitting of the Q band is shadowy. When the working electrode is polarized at -0.80 V versus SCE,  $[H_2Pc^{2-}]$  is one-electron reduced to form the  $[H_2Pc^{3-}]^{1-}$  anion. During the reduction of  $[H_2Pc^{2-}]$  at constant potential application, the split Q band decreases in intensity while a new band is recorded at 547 nm (Fig. 6a). During this process, a well-defined isosbestic point is

observed at 617 nm, which demonstrates that the reduction proceeds cleanly in deoxygenated DCM to give a single, reduced species. Rollmann and Iwamoto [11] and Koca et al. [30,42] also reported similar spectroscopic chances for one-electron reduction of H<sub>2</sub>Pc complexes. It was mentioned that there might be a symmetry change from D<sub>2h</sub> to D<sub>4h</sub> because of the substitution of central hydrogens by cations of supporting electrolyte. It was shown that the pair of excited states which usually give rise to the O band doubling in the  $[H_2Pc^{3-}]^{1-}$  species, is still present but the states are too close together to be resolved. During the potential application at -1.20 V versus SCE,  $[H_2Pc^{3-}]^{1-}$  is one-electron reduced to form the  $[H_2Pc^{4-}]^{2-}$  dianion (Fig. 6b). Spectroscopic changes show that while the band at 547 nm increases in intensity with shifting to 552 nm, the Q bands decrease. At the same time a new band is recorded at 582 nm. Clear isosbestic points are recorded at 620 and 809 nm in the spectra. During the oxidation of H<sub>2</sub>Pc at 1.20 V applied potential, intensity of the Q bands decrease in intensity while the region between 450-550 nm and the NIR region increase (Fig. 6c). The isosbestic points at 410, 575 and 750 nm vibrates continuously during the oxidation process which indicates decomposition of the complex during the oxidation process.

The color change of the solution of the complexes during the redox processes were recorded using in-situ colorimetric measurements. Fig. 6d gives the chromaticity diagram of the complex **4** recorded simultaneously during the spectroelectrochemical measurements. Without any potential application, the solution of **4** is green (x = 0.269 and y = 0.387). As the potential is stepped from 0 to -0.80 V, color of neutral **4** starts to change and



**Fig. 6.** *In-situ* UV–Vis spectral changes of **4.** a)  $E_{app} = -0.80 \text{ V}$ . b)  $E_{app} = -1.20 \text{ V}$ . c)  $E_{app} = 1.20 \text{ V}$ . d) Chromaticity diagram (each symbol represents the color of electro-generated species;  $\Box$ :  $H_2Pc^{-2}$ ,  $\bigcirc$ :  $H_2Pc^{-3}$ ,  $\triangle$ :  $H_2Pc^{-4}$ ,  $\stackrel{\sim}{\sim}$ :  $H_2Pc^{-1}$ .



**Fig. 7.** *In-situ* UV–Vis spectral changes of **5.** a)  $E_{app} = -0.80$  V. b)  $E_{app} = -1.40$  V. c)  $E_{app} = 1.20$  V. d) Chromaticity diagram (each symbol represents the color of electro-generated species;  $\Box$ : Ni<sup>II</sup>Pc<sup>-3</sup>,  $\bigcirc$ : Ni<sup>II</sup>Pc<sup>-4</sup>,  $\stackrel{\sim}{\hookrightarrow}$ : Ni<sup>II</sup>Pc<sup>-1</sup>.

blue color (x = 0.282 and y = 0.263) of monoanionic form of **4** was obtained at the end of the first reduction. Similarly color of the dianionic species was recorded as deep blue (x = 0.261 and y = 0.203) and monocationic species has yellowish green color (x = 0.345 and y = 0.367). Measurement of the xyz coordinates allows quantification of each color of redox species that is very important to decide their possible electrochromic application.

Fig. 7 shows the in-situ UV–Vis spectral changes of 5 under the controlled potential application. During the potential application at -0.80 V, the Q band shifts from 680 nm to 673 nm with decreasing and new bands in the LMCT region at 590 and 935 nm are observed (Fig. 7a). Although the band in the LMCT region and decreasing of the Q band are characteristics of the ring-based redox processes [29,43–46], differently shifting of the Q band is not a common spectral change for the MPc having redox inactive metal center. This unusual change may due to the conformational changes of the complex during reduction process. A band observed at 648 nm may also due to this conformational change. While the process gives clear isosbestic point at 760 nm in the spectra, isosbestic point at 662 nm tremble which indicate the formation more than one product during the process, which support the conformational change. Then at the -1.40 V potential application, while the bands at 648 and 673 nm decrease in intensity, new bands are recorded at 465 and 817 nm. At the same time the band at 935 nm increases in intensity. These spectroscopic changes are easily assigned to the reduction of the monomeric species,  $[Ni^{II}Pc^{-3}]^{-1}$  to  $[Ni^{II}Pc^{-4}]^{-2}$ dianionic species (Fig. 7b) [29,43-46]. Spectroscopic changes given in Fig. 7c are not characteristics of the oxidation of  $[M^{II}Pc^{-2}]$ . Since while the Q band decreases in intensity with a new band in the LMCT region during the Pc ring-based oxidation processes of MPc complexes having redox inactive metal center (like the complex **5**), all bands of the complex **5** increase in intensity which cause to the broadening of the Q band especially. These spectroscopic changes support the polymerization of the complex on the electrode during the anodic CV scans. It is well known that MPcs coated on an electrode have the Q band which is broader than those in solution [47,48]. The color change of the solution of the complex during the redox processes were recorded using in-situ colorimetric measurements. Fig. 7d gives the chromaticity diagrams of the complex **5** recorded simultaneously during the spectroelectrochemical measurements. Without any potential application, the solution of **5** is greenish blue (x = 0.247 and y = 0.342). As the potential is stepped from 0 to -1.50 V color of neutral **5** gets deep blue (x = 0.202 and y = 0.226) and then blue (x = 0.238 and y = 0.254) for the anionic forms of **5** respectively.

#### 4. Conclusion

In this study, the syntheses, spectral and electrochemical properties of soluble non-peripheral 6-oxyquinoline substituted metalfree, nickel, zinc, cobalt and copper phthalocyanines (**4**, **5**, **6**, **7** and **8**) are discussed. The target symmetrical phthalocyanines were separated by column chromatography which is placed aluminium oxide and characterized by a combination of IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, elemental analysis and MS spectral data. This study content electrochemical and spectroelectrochemical characterization of H<sub>2</sub>Pc (**4**), Ni(II)Pc (**5**), Zn(II)Pc (**6**). Complex **4** exhibits two reversible Pc ringbased one-electron reduction couples with respect to  $\Delta E_p$  values, which are easily assigned to  $[H_2Pc^{-2}]/[H_2Pc^{-3}]^-$  and  $[H_2Pc^{-3}]^-/[H_2Pc^{-4}]^{2-}$  and one quasi-reversible Pc ring-based one-electron oxidation couple assigned to  $[H_2Pc^{-2}]/[H_2Pc^{-1}]^+$ . The complexes **5** and **6** give very similar voltammetric responses with slightly potential shift due to the different metal center. The complex **5** exhibit two quasi-reversible one-electron reduction couples, which are easily assigned to  $[Ni^{II}Pc^{-2}]/[Ni^{II}Pc^{-3}]^-$  and  $[Ni^{II}Pc^{-3}]^-/[Ni^{II}Pc^{-4}]^{2-}$ . When compared with the redox potentials of the compound **4**, these couples shift to negative potentials ca. 0.15 V due to the effective nuclear charge differences of the central ions. However oxidation behavior of **5** and **6** are completely different than the compound **4**.

#### Acknowledgement

This study was supported by the Research Fund of Karadeniz Technical University.

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