

Synthesis, electrochemistry, spectroelectrochemistry and electropolymerization of metal-free and metallophthalocyanines



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ABSTRACT

Metal-free **4** and metallophthalocyanine complexes **5–7** (MPcs, M = Ni, Co, Cu) substituted with the electropolymerizable (2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy) group have been synthesized and their structure have been identified by IR, ¹H and ¹³C NMR, mass and UV–Vis spectroscopy techniques. The electrochemical characterization of the phthalocyanines sustained the submitted structures of the complexes, since the half wave peak potentials of the redox processes are in harmony with the common electrochemical behavior of MPcs. CoPc gives a metal based reduction process in addition to the ligand based electron transfer processes, which enrich the possible usage of the complex in various electrochemical technologies. All the complexes were coated on the working electrode with an oxidative electropolymerization process during the anodic potential scans.

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1. Introduction

Phthalocyanine (Pc) and its derivatives have received increasing attention due to their unique physical, chemical, biological and spectral properties [1]. They have been used for a wide range of applications in various areas, such as liquid crystals, electronic devices, gas and chemical sensors, electrochromic and electroluminescent displays, non-linear optics, photovoltaics, semiconductors, catalysis and photodynamic therapy (PDT) [2–11]. As a new class of phthalocyanine, electropolymerizable phthalocyanines have been studied in recent years.

In our previous papers, we studied the electrochemical characterization and electrochemical application of various MPcs bearing different metal centers and substituent environments [12–16]. Our studies indicated that incorporating redox active and/or functional substituents to the Pcs extend the redox richness and application possibilities of MPcs. Thus, in the last few years, we have narrowed our research to MPcs bearing a redox active metal center and substituents, such as quinoline [17], thiophene [18,19] and amino groups. Nowadays, we are interested in the electrochemistry of MPcs carrying amino containing substituents because of the electropolymerization of MPcs with the assistance of the amino groups. In this paper, we have investigated the electrochemistry and electropolymerization of MPcs bearing dimethylamino substituents to

extend our previous research and to find possible application fields for these complexes.

2. Experimental

2.1. Materials

2-[2-[3-(Dimethylamino)phenoxy]ethoxy]ethanol (**1**) [20], 4-nitrophthalonitrile (**2**) [21], 4-(2-[2-[3-(dimethylamino)phenoxy]ethoxy]ethoxy)phthalonitrile (**3**) [22] and cobalt(II) phthalocyanine (**6**) [23] were prepared according to the literature procedures. 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 [24].

2.2. Equipment

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer, using KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer in CDCl₃, and chemical shifts were reported (δ) relative to Me₄Si as an internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. MALDI-MS of complexes were obtained in dihydroxybenzoic acid as the MALDI matrix, using a nitrogen laser accumulating 50 laser shots, with a Bruker Microflex LT MALDI-TOF mass spectrometer. Optical spectra in the UV–Vis region were recorded with a Perkin Elmer

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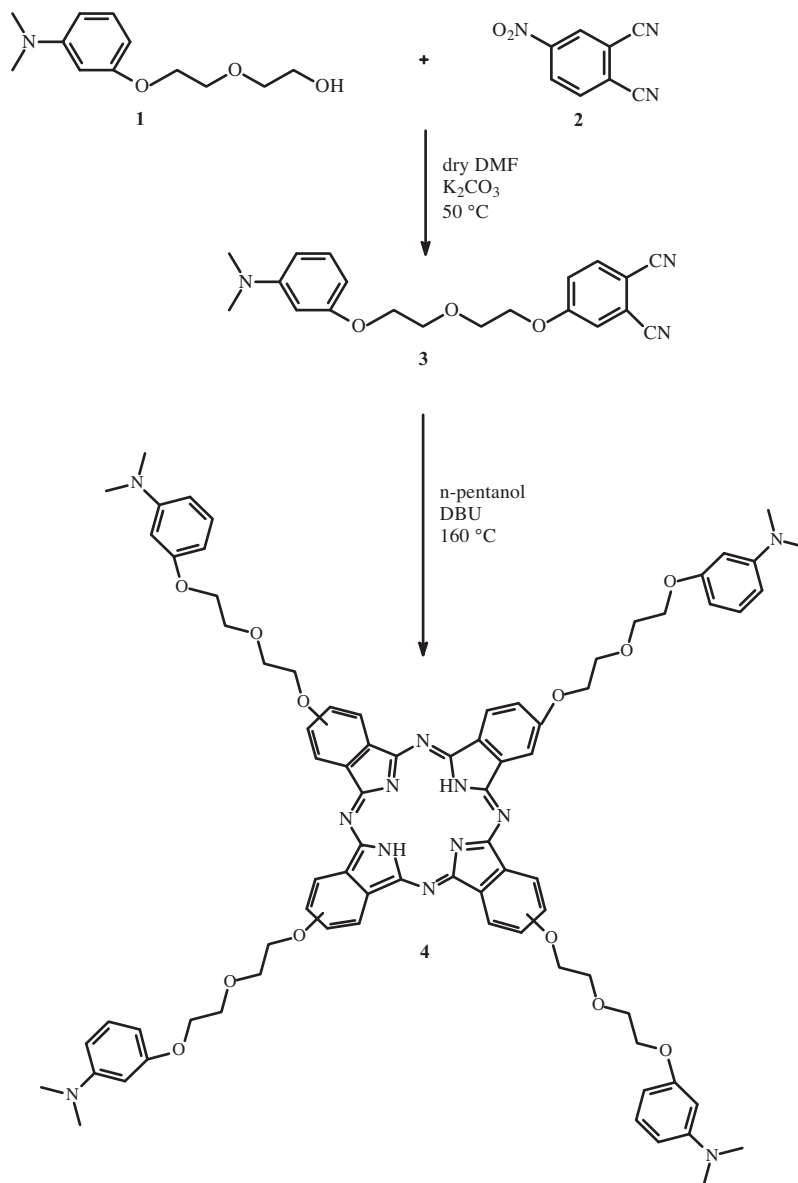


Fig. 1. The synthetic route for the metal-free phthalocyanine.

Lambda 25 spectrophotometer. Melting points were measured on an electrothermal apparatus and are uncorrected.

2.3. Electrochemical and spectroelectrochemical measurements

All the electrochemical measurements were carried out with Gamry Reference 600 potentiostat/galvanostat controlled by the following procedure. The working electrode was a Pt disc with a surface area of 0.071 cm². A Pt wire served as the counter electrode. A saturated calomel electrode (SCE) was employed as the reference electrode. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in dichloromethane (DCM) was employed as the supporting electrolyte. An OceanOptics QE65000 diode array spectrophotometer was used for UV–Vis absorption spectra and chromaticity diagram measurements. *In situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz thin-layer spectroelectrochemical cell, consisting of a Pt tulle working electrode, a Pt wire counter electrode and a SCE reference electrode.

2.4. Synthesis

2.4.1. 2(3),9(10),16(17),23(24)-Tetrakis-(2-{2-[3-(dimethylamino)phenoxy]ethoxy}ethoxy) phthalocyanine (**4**)

A solution of compound **3** (0.3 g, 0.00085 mol) in dry *n*-pentanol (3×10^{-3} L) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (4 drops) were heated and stirred in a glass sealed tube at 160 °C for 24 h under a N₂ atmosphere. After cooling to room temperature, a green product was precipitated by adding ethanol. The green solid product was filtered and then washed with hot ethanol, diethyl ether and dried in a vacuum. Finally, the pure metal-free phthalocyanine **4** was obtained by column chromatography, using aluminium oxide with CHCl₃ as the solvent system. Yield: 0.15 g (50%). IR (KBr tablet, $\nu_{\max}/\text{cm}^{-1}$): 3292 (N–H), 3074 (Ar–H), 2921–2800 (Aliph. C–H), 1606, 1572, 1499, 1482, 1447, 1346, 1322, 1283, 1233, 1116, 1095, 1058, 998, 951, 820, 746, 685. ¹H NMR (CDCl₃, δ/ppm): 8.15–7.96 (m, 4H, Ar–H), 7.26–7.09 (m, 12H, Ar–H), 6.45–6.38 (m, 12H, Ar–H), 4.31–4.11 (m, 32H, CH₂–O), 2.93 (s, 24H, CH₃–N). ¹³C NMR (CDCl₃, δ/ppm): 160.23,

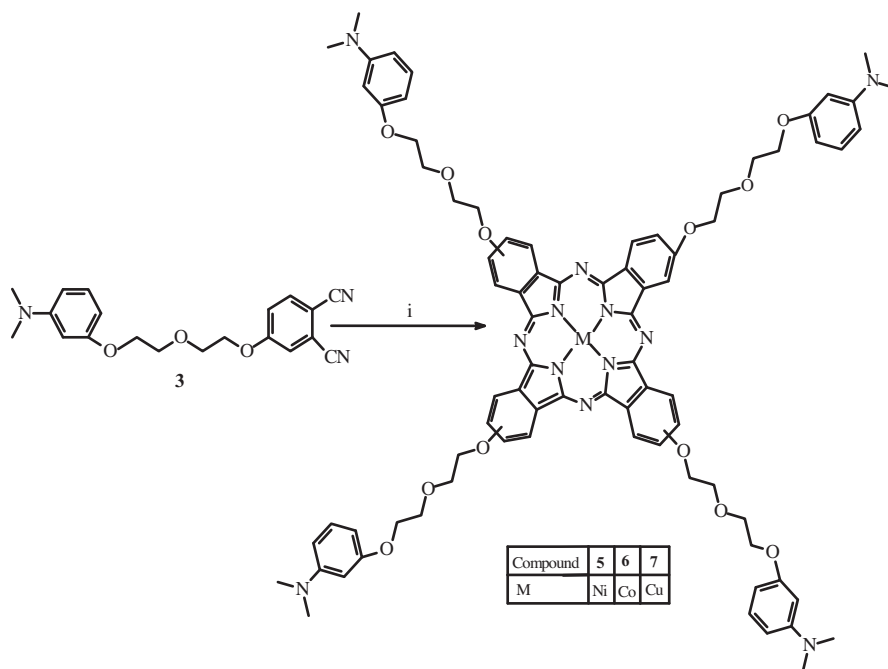


Fig. 2. The synthetic route for the nickel, cobalt and copper phthalocyanines. Reagents and conditions: (i) *n*-pentanol, DBU, 160 °C, NiCl₂, CoCl₂, CuCl₂.

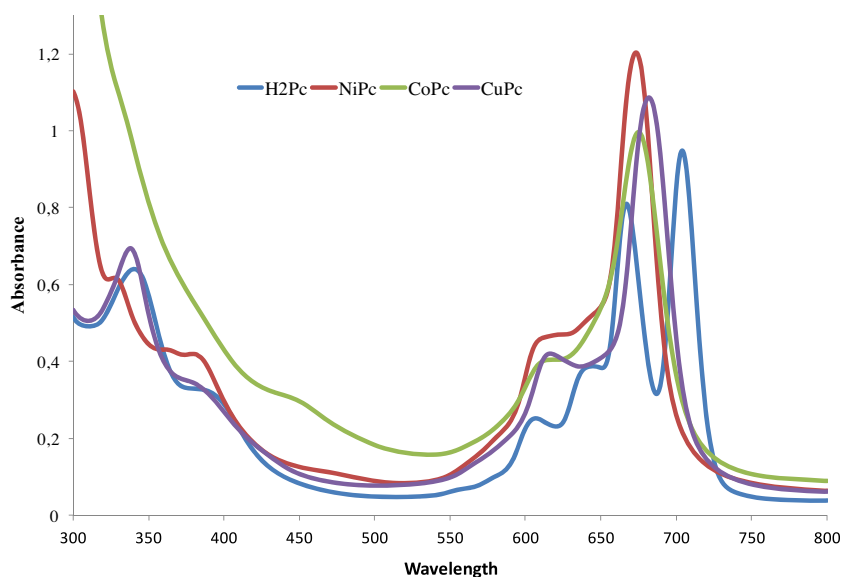


Fig. 3. UV-Vis spectra of 4–7 in chloroform.

159.95, 152.25, 130.05, 129.91, 106.27, 106.20, 106.17, 102.42, 102.38, 102.14, 100.21, 100.09, 100.06, 70.50, 67.64, 40.95. UV-Vis (chloroform, $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$): 704 (4.97), 667 (4.90), 645 (4.57), 607 (4.39), 378 (4.50), 340 (4.79). MALDI-TOF-MS m/z : 1407 [M]⁺.

2.4.2. 2(3),9(10),16(17),23(24)-Tetrakis-(2-(2-[3-(dimethylamino)phenoxy]ethoxy)ethoxy)phthalocyaninato nickel(II) (5)

A mixture of 4-(2-(2-[3-(dimethylamino)phenoxy]ethoxy)ethoxy)phthalonitrile (**3**) (0.25 g 0.00071 mol), anhydrous NiCl₂ (0.045 g, 0.00035 mol), dry *n*-pentanol (3×10^{-3} L) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 drops) were heated in a sealed tube with efficient stirring at 160 °C for about 24 h under

a N₂ atmosphere. After the reaction mixture was cooled, the product was precipitated by adding ethanol. The crude solid product was filtered and then washed with hot ethanol, diethyl ether and dried in a vacuum. Finally, the pure nickel(II) phthalocyanine **5** was obtained by column chromatography, using aluminium oxide with CHCl₃:CH₃OH (100:2) as the solvent system. Yield: 0.18 g (70%). IR (KBr tablet, $\nu_{\text{max}}/\text{cm}^{-1}$): 3072 (Ar-H), 2919–2798 (Aliph. C-H), 1719, 1607, 1572, 1499, 1447, 1416, 1348, 1275, 1233, 1118, 1091, 1062, 997, 1021, 988, 962, 818, 749, 685. ¹H NMR. (CDCl₃, δ /ppm): 7.69–7.53 (m, 4H, Ar-H), 7.26–7.19 (m, 12H, Ar-H), 6.40–6.39 (m, 12H, Ar-H), 4.25–4.04 (m, 32H, CH₂-O), 2.91 (s, 24H, CH₃-N). ¹³C NMR. (CDCl₃, δ /ppm): 152.29, 152.21, 130.06, 130.03, 123.39, 109.98, 106.22, 106.20, 106.14,

Table 1
Voltammetric data of the complexes. All voltammetric data were given vs. SCE.

Complex		Electropolymerization	M^{II}/M^I	Ring reductions	
CoPc	^a $E_{1/2}$	0.97 ^d (0.60) ^e	-0.37 (-0.72)	-1.47	-
	^b ΔE_p (mV)	-	120	112	-
	^c $I_{p,a}/I_{p,c}$	-	0.93	0.89	-
H₂Pc	^a $E_{1/2}$	0.97 ^d (0.57) ^e	-	-0.70	-1.02
	^b ΔE_p (mV)	-	-	160	175
	^c $I_{p,a}/I_{p,c}$	-	-	0.94	0.93
CuPc	^a $E_{1/2}$	0.90 ^d (0.61) ^e	-	-0.85	-1.15
	^b ΔE_p (mV)	-	-	150	120
	^c $I_{p,a}/I_{p,c}$	-	-	0.96	0.91
NiPc	^a $E_{1/2}$	0.88 ^d (0.64) ^e	-	-0.87	-1.19
	^b ΔE_p (mV)	-	-	80	70
	^c $I_{p,a}/I_{p,c}$	-	-	0.96	0.91

^a $E_{1/2}$ values ($(E_{pa} + E_{pc})/2$) were given vs. SCE at 0.100 V s⁻¹ scan rate.

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

^c $I_{p,a}/I_{p,c}$ for reduction, $I_{p,c}/I_{p,a}$ for oxidation processes.

^d Anodic peak of the electropolymerization reaction recorded during first CV cycle.

^e Cathodic peak of the electropolymerization reaction recorded during first CV cycle.

102.36, 102.33, 100.21, 100.20, 100.18, 70.44, 67.57, 40.83. UV-Vis (chloroform λ_{max}/nm ($\log \epsilon$): 673 (5.07), 624 (4.66), 379 (4.61), 327 (4.78). MALDI-TOF-MS m/z : 1465 [M+H]⁺.

2.4.3. 2(3),9(10),16(17),23(24)-Tetrakis-(2-[2-[3-(dimethylamino)phenoxy]ethoxy]ethoxy) phthalocyaninato cobalt(II) (6)

A similar preparation method to that of complex 5 was used to obtain cobalt(II) phthalocyanine 6, using a mixture of compound 3 (0.25 g 0.00071 mol), anhydrous CoCl₂ (0.046 g, 0.00035 mol), dry *n*-pentanol (3×10^{-3} L) and 1,8-diazabicyclo[5.4.0]undec-7-ene

(DBU) (3 drops). The pure cobalt(II) phthalocyanine 6 was obtained by column chromatography, using aluminium oxide with CHCl₃:CH₃OH (100:2) as the solvent system. Yield: 0.094 g (36%). IR (KBr tablet, ν_{max}/cm^{-1}): 3088 (Ar-H), 2919–2802 (Aliph. C-H), 1714, 1607, 1572, 1481, 1447, 1410, 1382, 1349, 1280, 1233, 1122, 1093, 1063, 998, 961, 819, 751, 686. UV-Vis (chloroform, λ_{max}/nm ($\log \epsilon$): 675 (4.99), 618 (4.60), 448 (4.46), 387 (4.69). MS (ESI) m/z : 1464 [M]⁺.

2.4.4. 2(3),9(10),16(17),23(24)-Tetrakis-(2-[2-[3-(dimethylamino)phenoxy]ethoxy]ethoxy) phthalocyaninato copper(II) (7)

A similar preparation method to that of complex 5 was used to obtain the copper(II) phthalocyanine 7, using a mixture of compound 3 (0.25 g 0.00071 mol), anhydrous CuCl₂ (0.047 g, 0.00035 mol), dry *n*-pentanol (3×10^{-3} L) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 drops). The pure copper(II) phthalocyanine 7 was obtained by column chromatography, using aluminium oxide with CHCl₃:CH₃OH (100:2) as the solvent system. Yield: 0.080 g (30%). IR (KBr tablet, ν_{max}/cm^{-1}): 3074 (Ar-H), 2921–2800 (Aliph. C-H), 1719, 1606, 1501, 1447, 1403, 1343, 1280, 1234, 1118, 1094, 1061, 998, 959, 819, 745, 685. UV-Vis (chloroform, λ_{max}/nm ($\log \epsilon$): 682 (5.03), 616 (4.61), 379 (4.53), 338 (4.83). MALDI-TOF-MS m/z : 1470 [M+H]⁺.

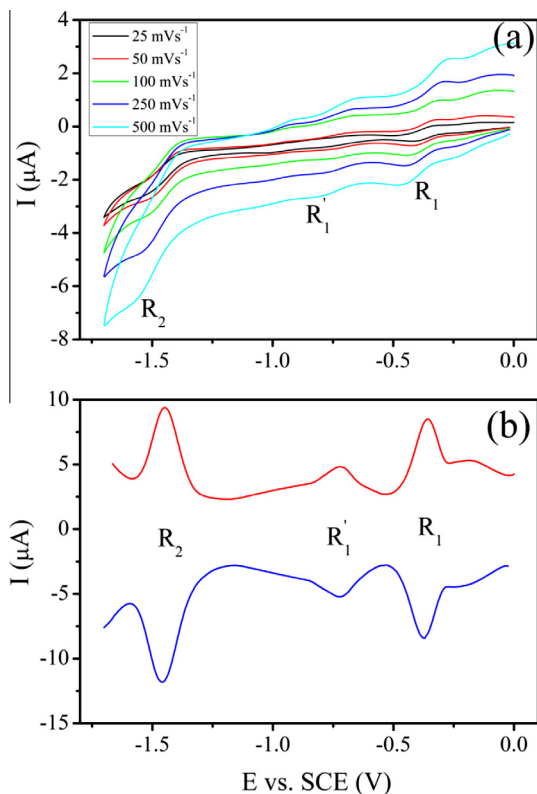


Fig. 4. (a) CV and SWV of CoPc recorded at various scan rates on a Pt working electrode in DCM/TBAP (b) SWV of CoPc.

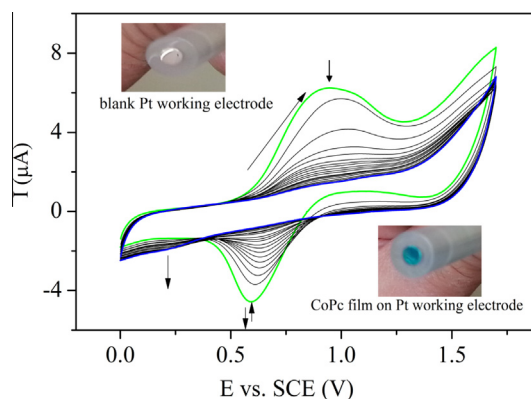


Fig. 5. Repetitive CVs of CoPc recorded between 0.0 and 1.70 V in the DCM/TBAP electrolyte system at 0.100 V s⁻¹ scan rate on a Pt working electrode.

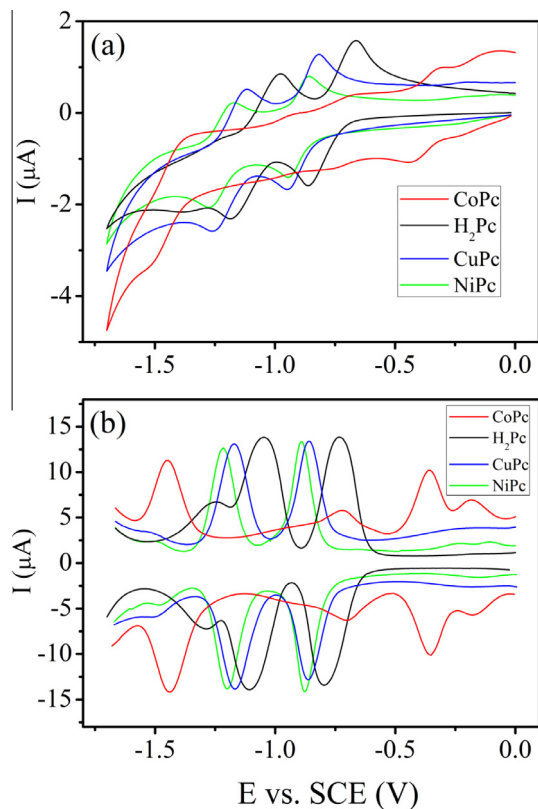


Fig. 6. (a) CVs of H₂Pc, CuPc, NiPc and CoPc recorded at cathodic potentials at 0.100 V s⁻¹ scan rate on a Pt working electrode in DCM/TBAP and (b) SWV of the complexes recorded with SWV parameters: step size = 5 mV; pulse size = 100 mV; Frequency = 25 Hz.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of substituted metal-free and metallophthalocyanines starts generally with the preparation of the corresponding phthalonitrile precursors. The syntheses of the target metal-free **4** and metallophthalocyanines **5–7** undertaken in this work are shown in Figs. 1 and 2.

According to the IR spectrum of compound **4**, the signals for the CN groups at 2233 cm⁻¹ for compound **3** disappeared and new peaks appeared at 3292 and 1606 cm⁻¹, that are dedicated to the N–H group in the phthalocyanine core of **4**. In the ¹H NMR spectrum of **4**, the typical shielding of the inner core protons could not be observed due to the probable strong aggregation of the molecules [25]. The ¹H NMR spectrum of compound **4** exhibited the aromatic protons, integrating to a total of 7 protons, at 8.15–7.96, 7.26–7.09 and 6.45–6.38 ppm. Also the CH₂-O and CH₂-N protons of metal-free **4** were observed between 4.31 and 2.93 ppm, which integrated to 14 protons. The ¹H NMR spectrum of compound **4** is in agreement with the proposed structure. The ¹³C NMR data of **4** confirm the results of the ¹H NMR spectrum. The UV–Vis spectrum of the phthalocyanine core is dominated by two intense bands, the Q band, at around 600–710 nm, and the B band in the near UV region, at about 300–400 nm, both correlated with π–π* transitions. In the electronic spectrum of **4** in chloroform, intense Q absorption bands were observed at 667 and 704 nm, respectively. B absorption bands of the metal-free phthalocyanine **4** were observed at 340 and 378 nm, respectively. The MALDI-TOF mass spectrum of compound **4** was measured as

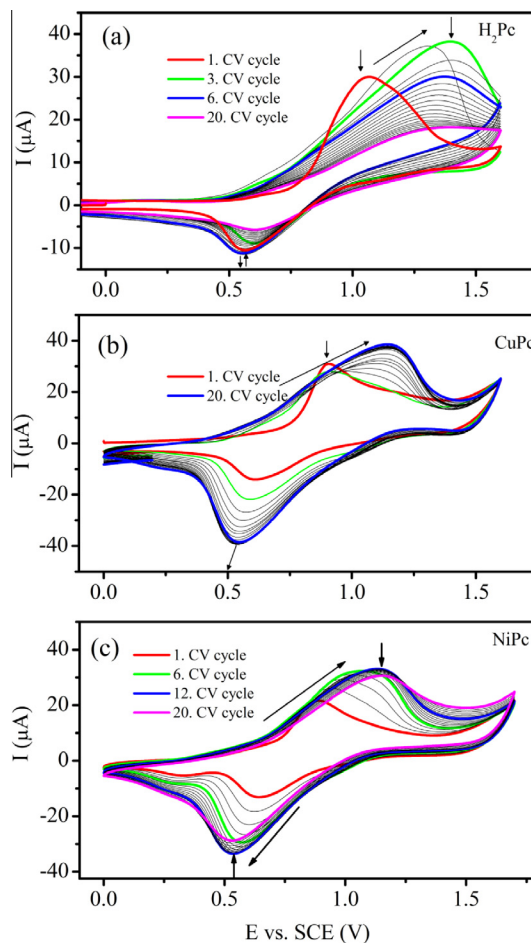


Fig. 7. Repetitive CVs of (a) H₂Pc, (b) CuPc, and (c) NiPc recorded between 0.0 and 1.70 V in the DCM/TBAP electrolyte system at 0.100 V s⁻¹ scan rate on a Pt working electrode.

$m/z = 1407 [M]^+$ and this result is in good accord with the suggested structure.

In the IR spectra of the metallophthalocyanines **5–7**, the cyclotetramerization of **3** was confirmed by the disappearance of the sharp CN stretching vibration at 2233 cm⁻¹. The IR spectra of NiPc, CoPc and CuPc are also very similar to that of the precursor H₂Pc, except for the disappearance of the N–H vibration of the phthalocyanine core. The ¹H NMR spectrum of **5** exhibited signals at $\delta = 7.69$ – 7.53 (m, 4H, Ar–H), 7.26– 7.19 (m, 12H, Ar–H), 6.40– 6.39 (m, 12H, Ar–H), 4.25– 4.04 (m, 32H, CH₂-O) and 2.91 (s, 24H, CH₂-N), belonging to aromatic and aliphatic protons. The ¹³C NMR spectrum of **5** indicated carbon atoms at $\delta = 152.29$, 152.21, 130.06, 130.03, 123.39, 109.98, 106.22, 106.20, 106.14, 102.36, 102.33, 100.21, 100.20, 100.18, 70.44, 67.57 and 40.83. ¹H NMR measurements of the cobalt(II) and copper(II) phthalocyanines **6** and **7** were precluded due to their paramagnetic nature [26]. The UV–Vis absorption spectra of the metal-free and metallophthalocyanines **4–7** in chloroform at room temperature are shown in Fig. 3. The electronic spectra of metallophthalocyanines **5–7** in chloroform show an intense Q absorption at $\lambda_{\max} = 673$, 675 and 682 nm, with a weaker absorption at 624, 618 and 616 nm, respectively. The single Q bands in metallo derivatives **5**, **6** and **7** are characteristic. B band absorptions of compounds **5**, **6** and **7** were observed at $\lambda_{\max} = (387, 448)$, (327, 379) and (338, 379) nm as expected, respectively. In the mass spectra of compounds **5**, **6** and **7**, the presence of molecular ion peaks at $m/z = 1465 [M+H]^+$,

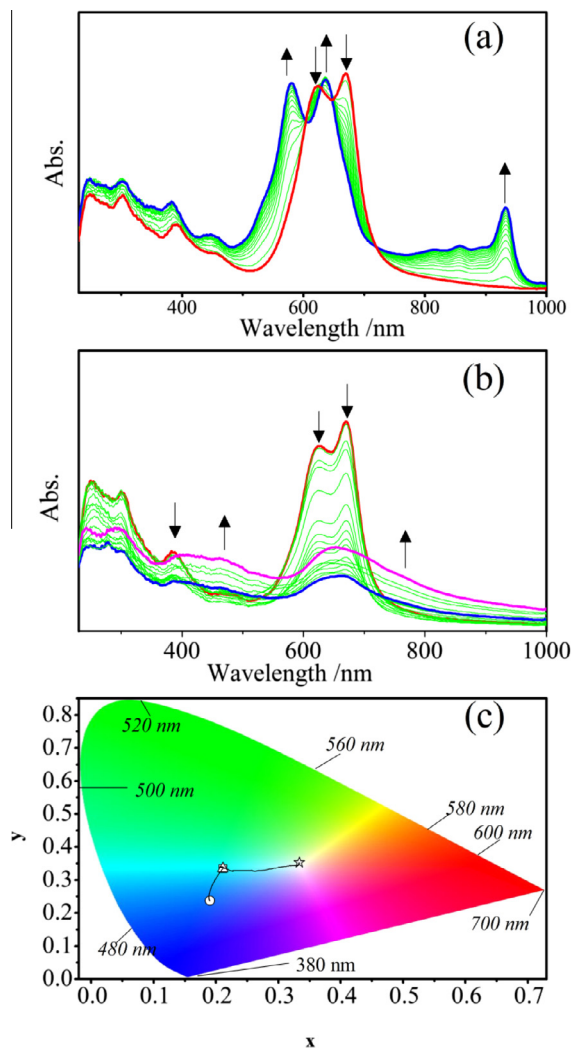


Fig. 8. *In situ* UV-Vis spectral changes of NiPc in DCM/TBAP. (a) $E_{app} = -1.00$ V. (b) $E_{app} = 1.30$ V. (c) Chromaticity diagram (each symbol represents the color of the electro-generated species; \square : $[\text{Ni}^{\text{II}}\text{Pc}^{-2}]$, \circ : $[\text{Ni}^{\text{II}}\text{Pc}^{-3}]^{-1}$, \star : polymer. (Color online.)

1464 $[\text{M}]^+$ and 1470 $[\text{M}+\text{H}]^+$, respectively, confirmed the proposed structures.

3.2. Voltammetric measurements

The electrochemical features of MPcs were examined to derive basic electrochemical parameters for the complexes, which are need to decide their usage in different electrochemical technologies. For this purpose, the electrochemical properties of the complexes were determined in solution with CV and SWV techniques and then the voltammetric responses of the complexes were analyzed. The derived electrochemical parameters of the complexes, presented in Table 1, are in agreements with similar complexes in the literature [27–30]. As shown in Table 1, while CoPc gives a metal based redox process in addition to the Pc based redox reactions, H_2Pc , CuPc and NiPc show common Pc based reduction reactions. All the complexes studied electropolymerized during the anodic potential scans.

Fig. 4 represents the CV responses of CoPc recorded on the cathodic potential side of the TBAP/DCM electrolyte system on a Pt working electrode. CoPc gives a metal based reduction couple R_1 at -0.37 V, a wave R'_1 assigned to aggregated CoPc species at -0.72 V and a Pc based reduction couple R_2 at -0.9147 V during the cathodic potential scans. These redox processes were recorded

at different scan rates and they were analyzed with respect to the half-wave peak potentials ($E_{1/2}$), anodic to cathodic peak potential separation (ΔE_p), peak width ($\Delta E_p - E_{p/2}$) and the anodic to cathodic peak current ratio (I_{pa}/I_{pc}). The analyses of the redox processes indicate the presence of a chemical reaction succeeding the R_1 process. This chemical reaction is most probably an aggregation–disaggregation equilibria. Observation of R'_1 supports the presence of aggregated CoPc species. Voltammetric analyses performed with different concentrations at different scan rates support the aggregation assignment of the R'_1 wave. Large ΔE_p values of the reduction reactions (higher than 100 mV at even very slow scan rates) indicate that both of the reduction processes R_1 and R_2 have electrochemically quasi-reversible character.

While CoPc illustrates common metal and Pc ring based reduction reactions during the cathodic potential scans, it gives extraordinary redox responses during the anodic potential scans. Fig. 5 represents repetitive CVs of CoPc recorded during anodic CV cycles. CoPc gives a huge anodic wave at 0.97 V and its reverse cathodic couple at 0.60 V during the first anodic CV scan. This CV behavior indicates the oxidation of the amino groups on the substituents of the complex. Oxidation of amino groups triggers an oxidative electropolymerization process and the complex was coated on the working electrode as a polymeric film as a result of the electropolymerization reaction. Electropolymerization of the complex was well reflected by the consecutive CV responses of the system. During the consecutive second CV cycle, a new anodic wave was recorded at 0.87 V, assigned to the polymerized complex. This new wave decreases in current intensity with a positive potential shift, as a result of consecutive CV cycles. Similarly the cathodic wave at 0.60 V decreases with current intensity, while a small wave is observed at around 0.20 V. These CV changes illustrate coating of the complex on the working electrode with an electropolymerization process. The film on the electrode surface was seen easily with the naked eye, as shown in the photograph of the film in Fig. 5. IR analysis of the CoPc film has been recorded, as given below and in the Supplementary material file as Fig. S3. The peaks at around 3000 cm^{-1} are characteristic aromatic hydrogen peaks of the Pc ring. The disappearance of the peaks of the groups on the substituent indicated that the electropolymerization of the complexes significantly affected the behavior of the substituents.

The CoPc film on the electrode surface was characterized by CV and UV-Vis measurements (Fig. S4 in the Supplementary file). The ITO/CoPc film gave two quasi-reversible oxidation reactions and the characters of these peaks are completely different than those of monomeric CoPc. Both the ITO/CoPc film and monomeric CoPc gave a Q band at the same wavelength, 675 nm, which indicates that the electropolymerization reaction did not significantly affect the electronic behavior of the Pc ring. It is well known that electropolymerization reactions occur from the cationic polymerization of amino groups. Except the amino groups, there is no polymerization side for these complexes.

The effects of the metal ions in the Pc cores of the complexes are well reflected with the CVs of the complexes. As shown in Fig. 6, H_2Pc , CuPc, and NiPc give very similar reduction processes during the cathodic potential scans. All of these complexes give two reversible reduction couples. The only difference between the CV and SWV of the complexes is the peak potentials of the redox processes. The reduction reactions shift to negative potentials with respect to the decreasing effective nuclear charge of the central ions. The order of the easy of reduction is observed as: H_2Pc ($E_{1/2}$ of R_1 : -0.9087 V) > NiPc ($E_{1/2}$ of R_1 : -0.90 V) > CuPc ($E_{1/2}$ of R_1 : -0.93 V). For the analyses of the complexes, the CVs of the complexes were recorded at different scan rates and the results are given in the Supplementary file. The ΔE_p and I_{pa}/I_{pc} values of the redox couples indicate electrochemical and chemical reversibility of all the reduction processes of the complexes [31].

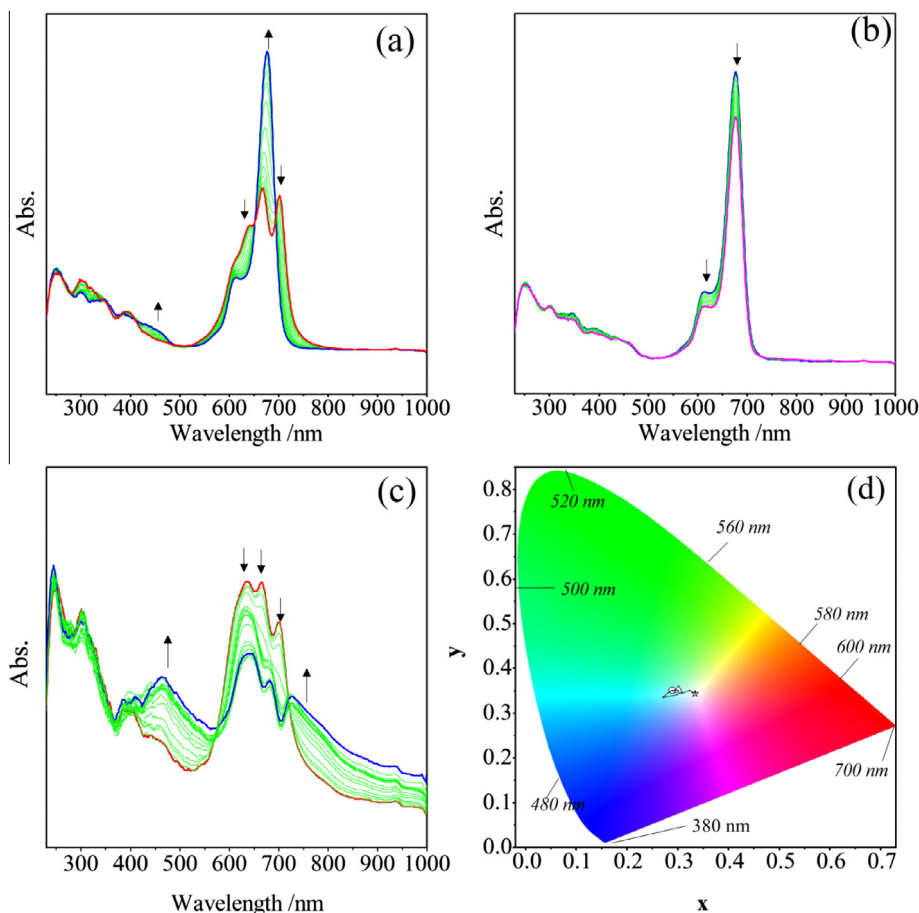


Fig. 9. *In situ* UV-Vis spectral changes of H₂Pc in DCM/TBAP. (a) $E_{\text{app}} = -0.80$ V. (b) $E_{\text{app}} = -1.30$ V. (c) $E_{\text{app}} = 1.50$ V. (d) Chromaticity diagram (each symbol represents the color of the electro-generated species; \square : [H₂Pc⁻²], \circ : [H₂Pc⁻³]⁻¹, \triangle : [H₂Pc⁻⁴]⁻², \star : polymer. (Color online.)

Like CoPc, the compound H₂Pc, CuPc and NiPc were also electropolymerized on the working electrode in similar manners. However, when central ion of the Pc core changed, the CV responses of the electropolymerization processes also changed. Generally the peak potentials of the polymers, peak current changes and/or shifting trends of the peaks differed when the metal centers were changed. Fig. 7 represents the repetitive CVs of H₂Pc, CuPc and NiPc recorded during the anodic CV cycles. As shown in Fig. 7, while the peak current of the electropolymerization reaction starts to decrease after the third CV cycle for H₂Pc, it increases until the 12th CV cycle for NiPc and it continuously increases for CuPc. Thus CuPc can form a more electroactive and thicker polymeric film than the other complexes. When we compared the peak potential of the electropolymerization waves of the complexes, we can list the complexes with respect to the ease of oxidation as: H₂Pc (E_{pa} : 0.97 V) > CuPc (E_{pa} : 0.90 V) > NiPc (E_{pa} : 0.88 V). Modification of the working electrodes on electropolymerization of these complexes is a desired factor for the usage of an active species in different electrochemical application fields. It is possible to control all the parameters of a modified electrode by controlling the potential, concentration and or CV cycle numbers of the electropolymerization reactions [32–36].

3.3. Spectroelectrochemistry

The *in situ* spectroelectrochemical measurements of MPcs having a redox inactive Pc core are well characterized from our previous studies. For this type of complex, general UV-Vis spectral changes during redox reactions are a decrease of the Q band

without a shift and observation of new bands at ligand to metal charge transfer (LMCT) and/or metal to ligand charge transfer (MLCT) regions. The complexes H₂Pc and CuPc gave similar spectral changes to similar complexes reported in the literature [37–41]. However NiPc gives different spectral changes than those reported in the literature [42,43]. As shown in Fig. 8, NiPc also gives Pc based electron transfer processes, but the spectral changes are different from those recorded for the Pc based reduction reactions. In the neutral state, NiPc gives a Q band at 670 nm with a shoulder at 623 nm. The shoulder is assigned to the aggregated NiPc species. When -0.90 V was applied, the Q band decreases in intensity and a new sharp band is recorded at 580 nm (Fig. 8a). These spectral changes are inconsistent with the spectral changes of a Pc based reduction reaction. However under -0.90 V application, different spectral changes are also observed. During this process, a new sharp band is also observed at 932 nm and the band at 623 nm shifts to 637 nm, in addition to the Pc reduction based spectral changes. These different spectral responses also alter the color of the neutral and anionic forms of the complex, as shown in Fig. 8b. During the oxidation reaction at 1.40 V, first of all the intensity of all the bands decreases and then small bands start to increase in LMCT regions (at around 470 and 800 nm). Finally all the bands increase in intensity. These spectral changes support the electropolymerization process. Due to the electropolymerization, the concentration of the monomeric species decreases, which diminishes the intensity of the bands of the monomeric NiPc. The electropolymerized film then starts to plug the pores of the Pt gauze working electrode, which prevents penetrating light and causes an increase of the band intensities.

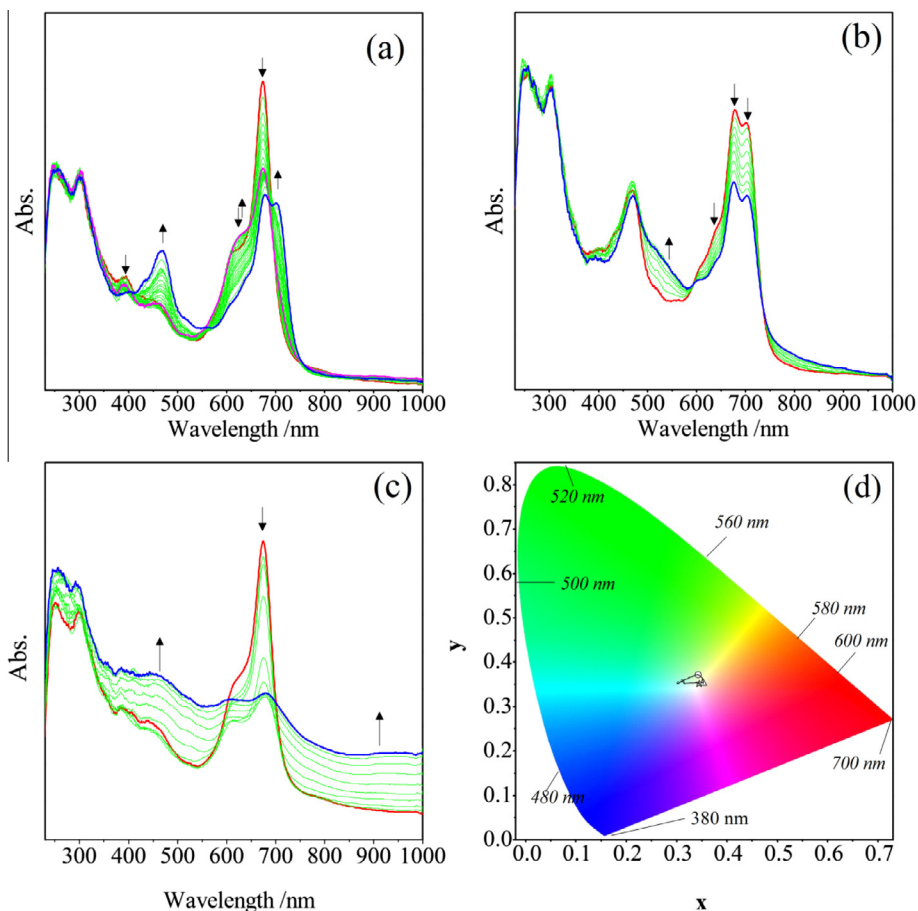


Fig. 10. *In situ* UV-Vis spectral changes of CoPc in DCM/TBAP. (a) $E_{app} = -0.50$ V. (b) $E_{app} = -1.50$ V. (c) $E_{app} = 1.50$ V. (d) Chromaticity diagram (each symbol represents the color of the electro-generated species; \square : $[\text{Co}^{\text{II}}\text{Pc}^{-2}]$, \circ : $[\text{Co}^{\text{I}}\text{Pc}^{-2}]^{-1}$, Δ : $[\text{Co}^{\text{I}}\text{Pc}^{-3}]^{-2}$, \star : polymer. (Color online.)

The general trend in the spectral changes of H_2Pc is different from those of the MPc complexes. H_2Pc gives a characteristic split Q band at 666 and 702 nm. Due to the aggregation, a band as a shoulder of the Q band is observed at 640 nm (Fig. 9a). This spectral response is in harmony with the metal free Pc complexes reported in the literature [44–47]. During the first reduction reaction, the split Q band turns into a sharp single band at 676 nm (Fig. 9a), which is the characteristic spectral change of the Pc based reduction of metal free Pc complexes. During the second reduction reaction, the Q band at 676 nm decreases in intensity without a shift, which indicates the formation of dianionic H_2Pc species (Fig. 9b). When 0.0 V was applied to the working electrode after the reduction reactions, approximately the same spectrum of H_2Pc was obtained, which indicates the chemical reversibility of the reduction reactions. Spectral changes of H_2Pc recorded during the oxidation reaction support electropolymerization of the complex, since while the bands of the monomer immediately decrease in intensity, new bands of the polymeric species are observed at 460 and 730 nm (Fig. 9c). The colors of the neutral anionic and polymeric H_2Pc are represented in the chromaticity diagram of the complex (Fig. 9d).

CoPc shows different *in situ* spectroelectrochemical responses to the other complexes, due to the redox activity of the Co^{II} center of the complex. Whilst all the reduction processes of H_2Pc , NiPc and CuPc are Pc based reduction reactions, the first reduction reaction of CoPc is a metal based electron transfer process. This different behavior of the complex is well reflected by the *in situ* spectroelectrochemical measurements. While the Q band of NiPc and CuPc change without a shift, the Q band of CoPc shifts from 674 to 704 nm. At the same time, a new band is recorded at 468 nm

(Fig. 10a). Shifting of the Q band and the observation of a new band between 450 and 500 nm characterize a metal based electron transfer reaction. The spectral changes represented in Fig. 10a show that the first reduction reaction of CoPc is a metal based process and is assigned to the $[\text{Co}^{\text{II}}\text{Pc}^{-2}]/[\text{Co}^{\text{I}}\text{Pc}^{-2}]^{-1}$ reaction [48–54]. The bluish green color ($x = 0.3034$ and $y = 0.3567$) of the complex changes to light orange ($x = 0.343$ and $y = 0.3711$) after the first reduction reaction, as shown in Fig. 10d. Fig. 10b shows the spectral changes recorded during the second reduction reaction of CoPc. During this process, while the Q band at 704 nm decreases without a shift, a new broad band is observed at 550 nm. These spectral changes indicate the reduction of $[\text{Co}^{\text{I}}\text{Pc}^{-2}]^{-1}$ to $[\text{Co}^{\text{I}}\text{Pc}^{-3}]^{-2}$ during the R_2 redox reaction. An orange color ($x = 0.3524$ and $y = 0.352$) is obtained after the second reduction reaction, as shown in Fig. 10d. During the oxidation reaction, CoPc gives similar spectral changes to H_2Pc , NiPc and CuPc due to the electropolymerization of the complex. During this process, the band of monomeric CoPc immediately decreases and then the intensity of all the bands increase due to coating of the electrode surface with the polymer. Fig. 10c shows the spectral changes recorded during the oxidation reaction of CoPc. A decrease of the Q band and the observation of new bands at 530 and 745 nm are characteristic changes for the Pc oxidation reaction of CoPc during the R_1 redox reaction. A light orange color is recorded for the cationic species of CoPc, obtained after the oxidation reaction ($x = 0.3484$ and $y = 0.3506$).

4. Conclusion

In this study, the syntheses, spectral and electrochemical properties of soluble peripheral substituted metal-free, nickel(II),

cobalt(II) and copper(II) phthalocyanines (4–7) are discussed. The target symmetrical phthalocyanines were separated by column chromatography, using aluminium oxide. All the compounds were characterized by standard methods (UV–Vis, IR, ¹H NMR, ¹³C NMR and MS spectroscopic data). Electrochemical responses of the complexes support the proposed structures of the complexes. The presence of alkyl amino groups on the substituents of the complexes causes the coating of the complexes on the working electrode with an oxidative electropolymerization process. Modification of the working electrode with thin films upon electropolymerization increases the usage potential of the complexes in various electrochemical devices, such as electrocatalytic, electrochromic and electroensing applications. The more distinctive color changes during the redox reactions of CoPc most probably result from the redox active character of the metal center. Thus metal based redox reactions alter the spectrum of the complex more than those of the Pc based electron transfer reactions. The distinct color changes of CoPc illustrate its possible usage as an electrochromic material.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2014.07.009>.

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