



Synthesis and electrochemistry of metallophthalocyanines bearing {4-[(2E)-3-(3,4,5-trimethoxyphenyl)prop-2-enoyl]phenoxy} groups

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ABSTRACT

In this study, metallophthalocyanines **4**, **5**, **6** was carried out by the cyclotetramerization of 4-{3-[(2E)-3-(3,4,5-trimethoxyphenyl)prop-2-enoyl]phenoxy}phthalonitrile **3**. The synthesis of metallo derivatives [Zn(II), Co(II), Cu(II)] of phthalocyanines obtained from corresponding phthalonitrile derivative and in the presence of the anhydrous divalent metal salts (Zn(CH₃COO)₂, CoCl₂ and CuCl₂) was described. These phthalocyanines showed good solubility in organic solvents such as chloroform, tetrahydrofuran, DMSO and DMF. The newly synthesized Pcs were verified by IR, ¹H NMR, ¹³C NMR, UV–vis and MS spectral data. The electrochemical properties of the zinc(II), copper(II) and cobalt(II) phthalocyanines were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods. The cobalt complex showed a metal based reduction process, while zinc phthalocyanines were giving ligand based electron transfer processes.

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1. Introduction

Phthalocyanines (Pcs) have 18- π electron system, known as aromatic macrocyclic compounds, which don't occur in nature. They have attracted great interest for the first time since their accidental discovery in Scotland in 1928. Their considerable properties that include flexibility, thermal and chemical properties, photoconductivity and semiconductivity [1] have been of huge attention in research. In many fields, phthalocyanines have been remarkably used because of their magnificently industrial and technological properties such as for optical read-write discs [2], medical applications [3], chemical sensors in photocopying machines [4,5], solar cells for high energy batteries [6] and photocatalysis [7]. In recent years, especially metallophthalocyanines have been remarkably used photodynamic reagents for cancer therapy [8–11] because of their good singlet oxygen generation ability.

Low solubility of phthalocyanines in organic solvents and water restricts for the investigations of their chemical and physical behaviours in many fields [12]. It is synthesized soluble metal-free or

metallophthalocyanines which linked long chain aliphatic groups, amide groups and carboxylic acid groups [13,14] or crown ether groups [15–19], etc. at the peripheral and non-peripheral positions of phthalocyanine ring. On the other hand, tetra-substituted Pcs are more soluble than octa-substituted Pcs due to the high dipole moment which derives from the unsymmetrical arrangement of the substituents at the periphery [20,21].

The chalcone moieties are of great interest and significance since this sub-unit is found in numerous natural compounds [22,23]. Therefore, intense efforts have been dedicated to the development of efficient methods for the synthesis of functionalized chalcones. They have attracted prominent current interest for several years because of their broad range of biological properties such as anticancer, antiinflammatory, antioxidant, cytotoxic, antimicrobial, analgesic and antipyretic [24]. Furthermore, chalcones are useful in various applications such as non-linear optics (NLO), electrochemical sensing, optical limiting, Langmuir films and photoinitiated polymerization [25–28].

Microwave assisted synthesis of phthalocyanines not only reduces chemical reactions times from hours to minutes but also improves reactions yield and their reproducibility [29–34]. The redox properties of phthalocyanines are critically related to most of their industrial applications. Redox process depend on various factors such as the type of metal, solvent, axial ligands and

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substituents. Cyclic voltammetry is the most widely used method to determine electrochemical properties in solution. Electrochemical properties of metallophthalocyanines have been intensively studied [35,36]. Electrochemical analyses of the newly synthesized metallophthalocyanine complexes are necessary to determine their possible applications in different electrochemical technologies such as chemical sensors, electrocatalysts and electrochromic materials. Therefore, we have synthesized, characterized and investigated the electrochemical properties of these novel metallophthalocyanine complexes substituted with (2E)-1-(3-Hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one groups on peripherally position.

2. Experimental

2.1. Synthesis

2.1.1. Synthesis of 4-{4-[(2E)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-yl]phenoxy}phthalonitrile (**3**)

(2E)-1-(4-Hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (**1**) (1 g, 3.18×10^{-3} mol) was dissolved in dry DMF (0.010 L) and 4-nitrophthalonitrile (0.55 g, 3.18×10^{-3} mol) was added under nitrogen atmosphere. To this reaction mixture finely ground anhydrous potassium carbonate (1.31 g, 9.54×10^{-3} mol) was added in 8 portions every 15 min. The reaction mixture was stirred under N_2 at 50 °C for 4 days. Then the solution was poured into ice-water (100 g). Solid product was filtered, washed water and dried in vacuo over P_2O_5 . The crude product **3** was crystallized from ethanol. Yield: 0.70 g (50%), mp: 151–153 °C. IR (KBr pellet), $\nu_{\max}/\text{cm}^{-1}$: 3071 (Ar–H), 2939–2840 (Aliph. C–H), 2232 (C≡N), 1663, 1580, 1504, 1420, 1319, 1280, 1249, 1127, 1001, 957, 832, 754, 666, 608, 524. ^1H NMR (400 MHz, CDCl_3): δ 7.97 (d, $J = 8$ Hz, 2H, Ar–H), 7.78 (d, $J = 8$ Hz, 2H, Ar–H), 7.75 (s, 1H, Ar–H), 7.64 (t, $J = 8$ Hz, 1H, Ar–H), 7.40 (d, $J = 16$ Hz, 1H, α -H), 7.34 (bt, 1H, Ar–H), 7.28 (d, $J = 16$ Hz, 1H, β -H), 6.88 (s, 2H, Ar–H), 3.92 (s, 6H, O–CH₃), 3.90 (s, 3H, O–CH₃). ^{13}C NMR (100 MHz, CDCl_3): δ 188.87, 161.26, 154.17, 153.54, 146.16, 140.97, 135.57, 130.98, 129.96, 126.08, 124.68, 121.79, 121.71, 120.58, 120.35, 117.79, 115.26, 114.85, 109.41, 106.01, 61.00, 56.30, 56.24 MS (ES^+), (m/z): 459 [$\text{M} + \text{H}_2\text{O} + \text{H}$] $^+$.

2.1.2. Synthesis of zinc(II) phthalocyanine (**4**)

A mixture of 4-{3-[(2E)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-yl]phenoxy}phthalonitrile **3** (0.25 g, 0.57×10^{-3} mol), anhydrous $\text{Zn}(\text{CH}_3\text{COO})_2$ (53×10^{-3} g, 0.29×10^{-3} mol) 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_2O_5 . The obtained green solid product was purified from the column chromatography which is placed aluminium oxide using only chloroform:methanol (100:3) as solvent system. Yield: 0.115 g (44%). IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3068 (Ar–H), 2933–2835 (Aliph. C–H), 1660, 1578, 1465, 1432, 1317, 1275, 1234, 1124, 1088, 1043, 1000, 826, 795, 746. ^1H NMR (400 MHz, CDCl_3) (δ : ppm): 7.77–7.71 (m, 16H, Ar–H), 7.62–7.53 (m, 12H, Ar–H), 7.36–7.31 (m, 8H, Ar–H), 6.86 (m, 8H, Ar–H), 3.92 (m, 24H, O–CH₃), 3.79 (m, 12H, O–CH₃). UV–vis (chloroform): $\lambda_{\max}$, nm (log ϵ): 349 (4.90), 615 (4.16), 680 (4.83). MALDI-TOF-MS m/z : 1826 [$\text{M} + \text{H}$] $^+$.

2.1.3. Synthesis of cobalt(II) phthalocyanine (**5**)

The reaction was carried out by the compound **4** procedure using compound **3** (0.2 g, 0.45×10^{-3} mol) anhydrous CoCl_2 (30×10^{-3} g, 0.23×10^{-3} mol) and 2-(dimethylamino)ethanol (0.002 L). The obtained green solid product was chromatographed on preparative silicagel plate with chloroform:methanol (100:5) as eluents. Yield: 0.1 g (49%). IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3065 (Ar–H), 2924–2852 (Aliph. C–H), 1661, 1579, 1503, 1462, 1377, 1320, 1275,

1241, 1126, 1098, 1001, 828, 752. UV–vis (chloroform): $\lambda_{\max}$, nm (log ϵ): 334 (5.13), 611 (4.32), 672 (4.69). MALDI-TOF-MS m/z : 1819 [$\text{M} + \text{H}$] $^+$.

2.1.4. Synthesis of copper(II) phthalocyanine (**6**)

The reaction was carried out by the compound **4** procedure using compound **3** (0.2 g, 0.45×10^{-3} mol) anhydrous CuCl_2 (30×10^{-3} g, 0.23×10^{-3} mol) and 2-(dimethylamino)ethanol (0.002 L). The obtained green solid product was chromatographed on preparative silicagel plate with chloroform:methanol (100:5) as eluents. Yield: 0.105 g (51%). IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3065 (Ar–H), 2928–2836 (Aliph. C–H), 1661, 1579, 1503, 1432, 1419, 1313, 1275, 1242, 1185, 1124, 1051, 952, 828, 796, 747. UV–vis (chloroform): $\lambda_{\max}$, nm (log ϵ): 338 (5.16), 622 (4.21), 682 (4.61). MALDI-TOF-MS m/z : 1824 [$\text{M} + \text{H}$] $^+$.

3. Results and discussion

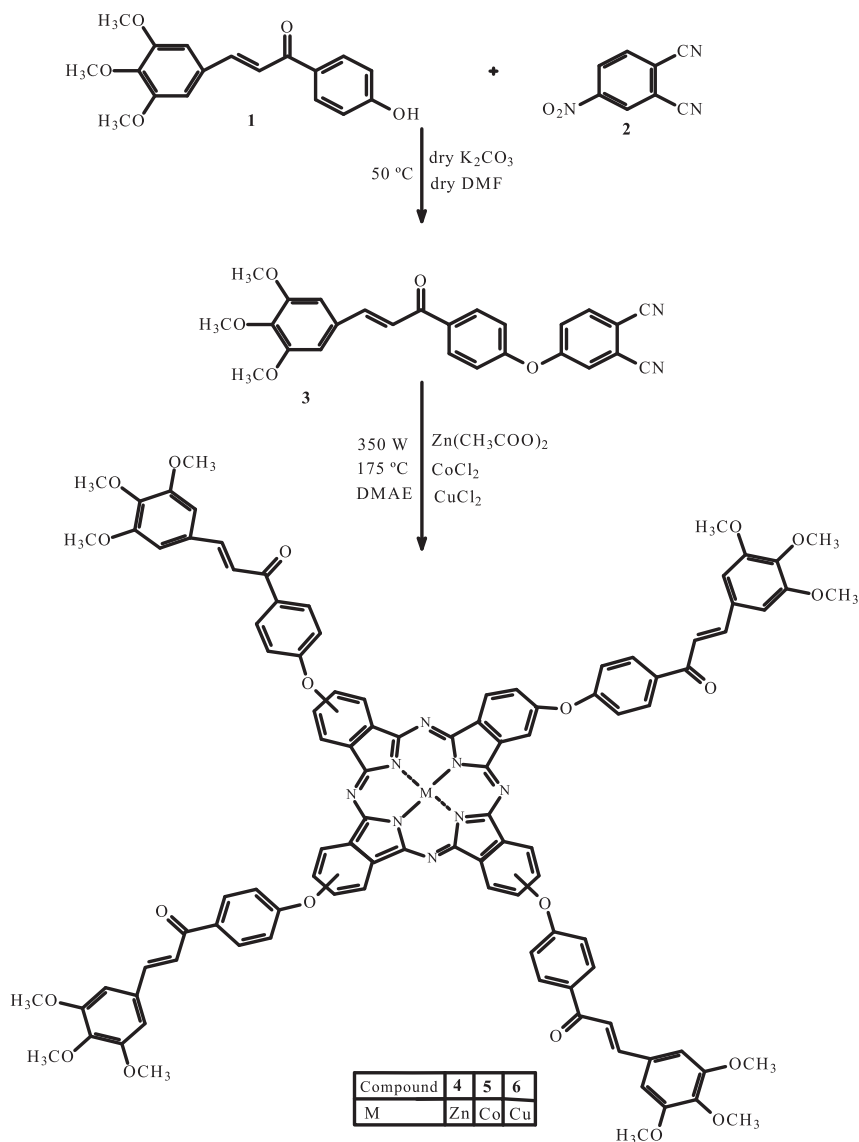
3.1. Syntheses and characterization

Starting from (2E)-1-(3-Hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one **1** and 4-nitrophthalonitrile **2**, the general synthetic route for the synthesis of new metallophthalocyanines are given in Scheme 1. The synthesis of peripheral substituted phthalonitrile derivative **3** is based on the reaction of (2E)-1-(3-Hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one with 4-nitrophthalonitrile (in dry DMF and in the presence of dry K_2CO_3 as base, at 50 °C in 96 h). The metallophthalocyanines **4–6** were obtained by the anhydrous metal salts [$\text{Zn}(\text{CH}_3\text{COO})_2$, CoCl_2 and CuCl_2] in 2-(dimethylamino)ethanol by microwave irradiation. The structures of the target compounds were confirmed using IR, ^1H NMR, ^{13}C NMR and MS spectral data. The characterization data of the new compounds are consistent with the assigned formula.

The IR spectra of the phthalonitrile compound **3** clearly indicate the presence of C≡N group by the intense stretching bands at 2232 cm^{-1} . The ^1H NMR spectra of phthalonitrile compound **3** were recorded in CDCl_3 . In the ^1H NMR spectrum of compound **3**, OH group of (2E)-1-(3-Hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one disappeared as expected. In the ^1H NMR spectrum of **3** the aromatic protons appear at 7.97 (d), 7.78 (d), 7.75 (s), 7.64 (t), 7.34 (bt), 6.88 (s) ppm. In the ^{13}C NMR spectrum of compound **3** indicated the presence of nitrile carbon atom at $\delta = 115.26$, 120.58 ppm. In the mass spectra of phthalonitrile compound **3**, the molecular ion peak was observed at m/z 459 [$\text{M} + \text{H}_2\text{O} + \text{H}$] $^+$.

The IR spectrum of the zinc phthalocyanine **4**, cobalt phthalocyanine **5** and copper phthalocyanine **6** clearly indicates the cyclotetramerization of the phthalonitrile derivatives **3** with the disappearance of the C≡N peaks at 2232 cm^{-1} . The IR spectra of ZnPc , CoPc and CuPc are also very similar. ^1H NMR spectrum of compound **4** the aromatic protons appeared at 7.77–7.71, 7.62–7.53, 7.36–7.31, 6.86 ppm, aliphatic CH_3 protons at 3.92, 3.79 ppm. ^1H NMR measurement of the cobalt and copper phthalocyanines **5–6** were precluded owing to its paramagnetic nature. The mass spectra of tetra-substituted phthalocyanines **4**, **5** and **6** confirmed the proposed structure, with the molecular ion being easily identified at 1826 [$\text{M} + \text{H}$] $^+$, 1819 [$\text{M} + \text{H}$] $^+$ and 1824 [$\text{M} + \text{H}$] $^+$ respectively.

The metal-free and metallophthalocyanine complexes exhibit distinctive 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]. UV–Vis spectra of metallophthalocyanines **4–6** in chloroform displayed an intense single Q band absorption of $\pi \rightarrow \pi^*$ transitions around 672–682 nm. The maximum absorption band of ZnPc



Scheme 1. The synthesis of metallophthalocyanines 4, 5 and 6.

derivative **4** appeared at 680 nm, while the Q bands of CoPc **5** and CuPc **6** centred at 672 and 682 nm (Fig. 1).

3.2. Electrochemical measurements

The solution redox properties of the phthalocyanines were studied by CV and DPV on a platinum working electrode in DCB containing 0.1 M Tetrabutylammonium hexafluorophosphate (TBAHFP). Table 1 lists the assignments of the couples recorded and the estimated electrochemical parameters, which includes the half-wave potentials ($E_{1/2}$), the ratio of anodic to cathodic peak currents (I_{pa}/I_{pc}), peak to peak potential separations (ΔE_p) and the difference between the first reduction and oxidation processes ($\Delta E_{1/2}$). The potentials are given versus Ag/AgCl reference electrode.

Reduction of an electroactive species is associated to energy level of its LUMO and whereas oxidation of an electroactive species depends on the energy level of HOMO. Redox processes of phthalocyanines occur via successive one-electron transfer between working electrode and π -conjugated system of the phthalocyanine ring system. A typical redox reaction yields a long lived anion or

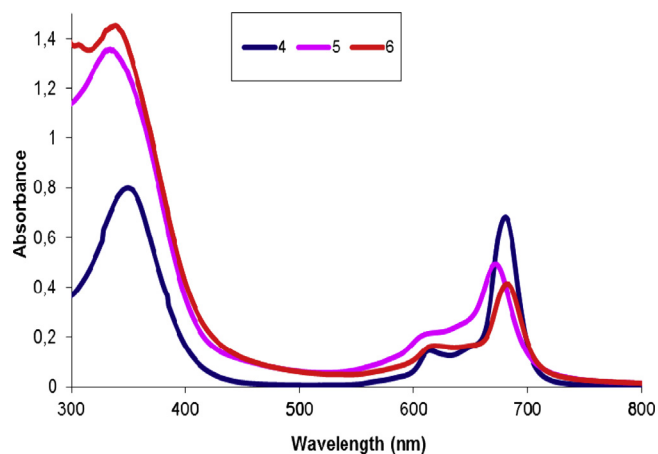
Fig. 1. UV-vis spectrum of 4, 5 and 6 in CHCl_3 .

Table 1
The electrochemical data of the phthalocyanines.

Compound	Redox step	E_p (V)	$E_{1/2}$	ΔE_p mV	I_{pa}/I_{pc}	$\Delta E_{1/2}$ (V)
ZnPc	R ₁	−1.230 (−1.020)	−1.125	210	0.44	1.718
	R ₂	−1.440 (−1.340)	−1.390	100	1.00	
	R ₃	−1.680 (−1.610)	−1.645	70	1.02	
	O ₁	0.655 (0.532)	0.593	132	0.58	
	O ₂	1.050 (0.869)	0.960	181	0.57	
	O ₃	1.400 (1.290)	1.345	110	0.39	
CoPc	R ₁	−0.294 (−0.274)	−0.284	20	0.93	1.018
	R ₂	−1.280 (−1.180)	−1.230	100	0.55	
	R ₃	−1.460 (−1.240)	−1.350	220	0.94	
	O ₁	0.734 (–)	–	–	–	
	O ₂	1.410 (–)	–	–	–	
	O ₃	–	–	–	–	
CuPc	R ₁	−0.813 (−0.735)	−0.774	78	0.93	2.139
	R ₂	−1.190 (−1.140)	−1.165	50	0.73	
	R ₃	−1.460 (−1.360)	−1.410	100	0.49	
	O ₁	1.410 (1.320)	1.365	90	0.48	
	O ₂	–	–	–	–	

Scan rate 100 mV/s.

cation radical in non-aqueous solutions. The redox processes in metallophthalocyanines depend on the central metal ion, whether possessing an energy level between HOMO and LUMO of the phthalocyanine. The complexes with Co, Fe and Mn possessing this type orbitals, in general, exhibit redox processes via central metal ion. In contrast to Co and Fe complexes Zn, Cu or Ni complexes undergo reduction and oxidation to yield cation and anion radicals, respectively [38–42]. The first reduction of cobalt(II) phthalocyanine is always on the Co(II) centre and the first oxidation is dependent on the solvent used.

The cyclic voltammogram and differential pulse voltammogram of ZnPc **4** exhibited six redox processes in the −1.75 to +1.65 V range as shown in Fig. 2. It gives three reduction processes, which are appeared at −1.230 V, −1.440 V and −1.680 V. Three oxidation peaks resulted at 0.655 V, 1.050 V and 1.400 V. The anodic to cathodic peak separations of the electrochemical couples varied from 70 to 210 mV showed that reversible and quasi-reversible nature of the electrode processes. The anodic to cathodic peak current ratio of reduction peaks and cathodic to anodic peak current ratio of the oxidation peaks varied from 0.39 to 1.02 support reversible and quasi-reversible nature of the processes.

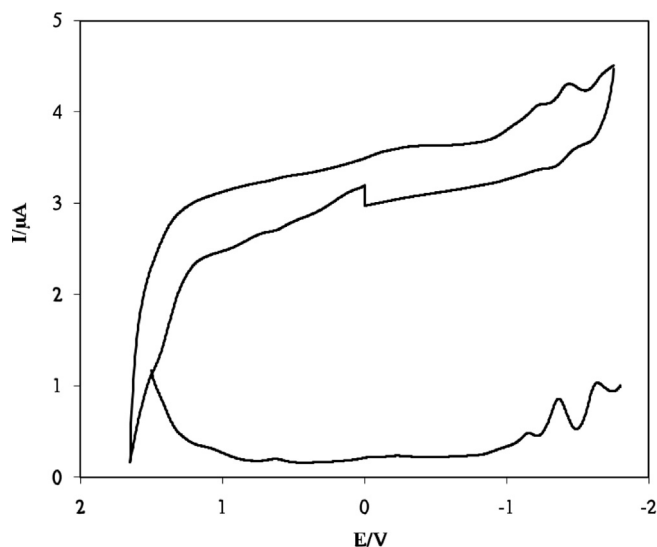


Fig. 2. Cyclic and differential pulse voltammograms of zinc(II) phthalocyanine **4** at 0.100 V s^{−1} scan rate on Pt in DCB/TBAHFP (ZnPc 1·10^{−4} mol dm^{−3}, Pulse width = 50 ms, pulse height = 50 mV, step height = 4 mV, step time = 200 ms).

Cyclic voltammogram and differential pulse voltammogram of copper(II) phthalocyanine **6** are illustrated in Fig. 3. The copper(II) phthalocyanine gave very similar voltammograms with zinc(II) derivative except potential shifts. The reduction peak potential of the zinc derivative was more negative (−1.125 V) than the copper(II) phthalocyanine (−0.813 V) corresponding to electropositivity of central metal ion. The separation between the first and second ring reductions was found 0.21 V for zinc(II) and 0.38 V for copper(II) phthalocyanine in accord with literature values obtained for the complexes which have redox inactive metal centre. The introduction of zinc ion into phthalocyanine ring can be considered as a perturbation of the frontier MOs of the phthalocyanine molecule. The introduction of metal ion results an increase in negative charge of the ring system thus the system become harder to reduction.

The cyclic voltammogram of the cobalt(II) phthalocyanine **5** exhibited five redox processes (Fig. 4). Scanning the potential to the negative side, three reversible reduction processes at −0.294 V, −1.280 and −1.460 V and upon scanning anodically, two oxidation processes at 0.734 V and 1.140 V were recorded. The peak ratios and ΔE_p values of cathodic peaks indicate one-electron transfer reactions. The first and second reduction of the CoPc had a potential difference of an approximately 0.946 V, which was in agreement with other CoPc complexes. The lower $\Delta E_{1/2}$ gap suggested that the first reduction of the CoPc originated from the redox couple [Co(II)Pc(−2)]/[Co(I)Pc(−2)] in DCB [43].

4. Conclusion

The novel phthalonitrile derivative **3** substituted with (2E)-1-(3-Hydroxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one group and their peripherally zinc(II), cobalt(II) and copper(II) phthalocyanine complexes **4–6** have been synthesized for the first time in this study. The new phthalonitrile compound and metallophthalocyanines have been characterized by UV–vis, IR, ¹H NMR, ¹³C NMR, ES-MS mass spectroscopies and LT MALDI-TOF mass spectrometer. All these new phthalocyanine complexes showed excellent solubility in many organic solvents such as chloroform, tetrahydrofuran, DMSO and DMF. The electrochemical studies of the metal complexes showed that the reduction potential of ZnPc shifted more negative potential as a result of coordination to zinc ion causes electron enrichment of the ring system. Electrochemical behaviour of CoPc is departed from CuPc and ZnPc with a metal based reduction.

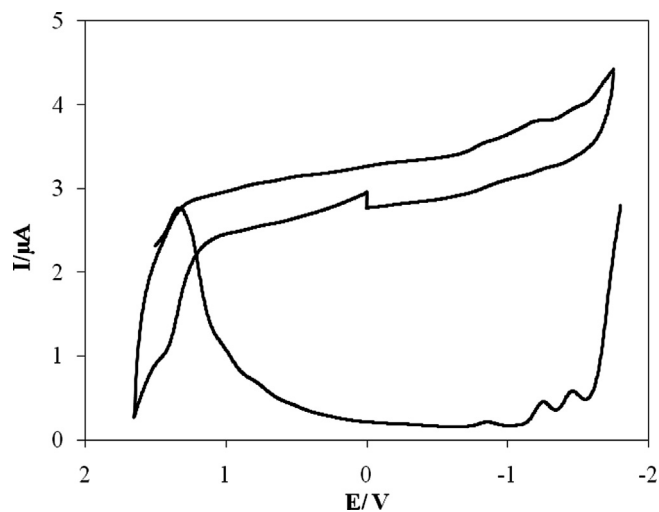


Fig. 3. Cyclic and differential pulse voltammograms of Cu(II) phthalocyanine **6** at 0.100 V s^{−1} scan rate on Pt in DCB/TBAHFP (CuPc 1·10^{−4} mol dm^{−3}, Pulse width = 50 ms, pulse height = 50 mV, step height = 4 mV, step time = 200 ms).

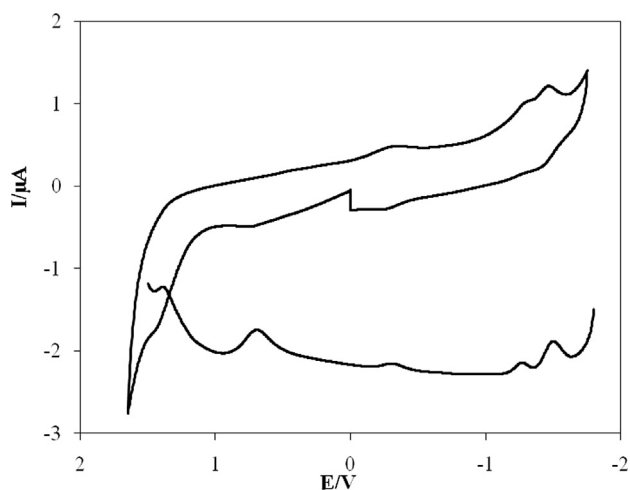


Fig. 4. Cyclic and differential pulse voltammograms of Co(II) phthalocyanine **5** at 0.100 V s^{-1} scan rate on Pt in DCB/TBAHFP (CoPc $1 \cdot 10^{-4} \text{ mol dm}^{-3}$, Pulse width = 50 ms, pulse height = 50 mV, step height = 4 mV, step time = 200 ms).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorgchem.2013.11.021>.

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