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ARTICLE TYPE

Effect of substituent position and metal type on the electropolymerization properties of chalcone substituted metallophthalocyanines

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Cobalt(II) and manganese(III) phthalocyanines bearing peripherally and non-peripherally tetra substituted {(2E)-3-[4-(dimethylamino)phenyl]prop-2-enoyl}phenoxy) groups were synthesized by cyclotetramerization of the phthalonitrile derivatives and their electrochemical properties were examined with CV and SWV techniques by the first time. The novel compounds were characterized by using IR, ^{1}H-NMR, ^{13}C-NMR, UV-Vis and MS spectral data. Cyclic and square wave voltammetry revealed well-defined metal-based and ligand-based reduction processes within the complexes. Electrochemical measurements exhibit that all complexes oxidatively electropolymerized on the Pt working electrode during repetitive cyclic voltammetry measurements. This study is the first example of electropolymerization of peripherally and non-peripherally tetra chalcone substituted cobalt(II) and manganese(III) phthalocyanines. Types of the metal center of the complexes and position of substituents affect the character of the polymerization processes.

1. Introduction

Metallophthalocyanines (MPcs) are a class of macrocyclic compounds which are very versatile because they possess a highly conjugated π-electron system. They were first developed as industrial pigments, and have been diversely applied in various fields, including electrochromism,[1] gas sensors,[2] catalysis,[3] nanotechnology,[4] liquid crystal,[5] non-linear optical devices,[6] photochromic materials,[7] medicine[8] and photodynamic therapy (PDT).[9-10]

Most of the recent uses of phthalocyanines (Pcs) have focused on the electronic properties of the π-electron system of the macrocycles. These properties can be chemically tuned by changing the peripheral or non-peripheral substituents and/or the central metal. MPc complexes containing electroactive metals such as cobalt, iron and manganese have been well studied because of their electrocatalytic properties towards many analytes.[11] The potential use of cobalt phthalocyanine (CoPc) complexes in the design of electrochemical sensors has attracted extensive research interest.[12,13] The electrochemical properties of manganese phthalocyanine (MnPc) complexes have also generated considerable attention.[14,15] MnPc complexes show interesting electrochemical behavior with oxidation states of the central Mn ion ranging from Mn^{I} to Mn^{IV},[16,17] thus enhancing the detection of analytes involving multi-electron transfer processes. Although a substantial number of chalcone substituted phthalocyanine derivatives have been reported rare[18-20] to date, electropolymerizable peripherally and non-peripherally tetra chalcone substituted cobalt and manganese phthalocyanine complexes has not been reported in the literature. For these reasons, in this article, we designed and synthesized a novel series of peripherally and non-peripherally tetra chalcone substituted cobalt and manganese phthalocyanine bearing electropolymerizable ligand for the first time. The effect of substituent position and metal type on the electropolymerization properties were investigated.

2. Experimental Section

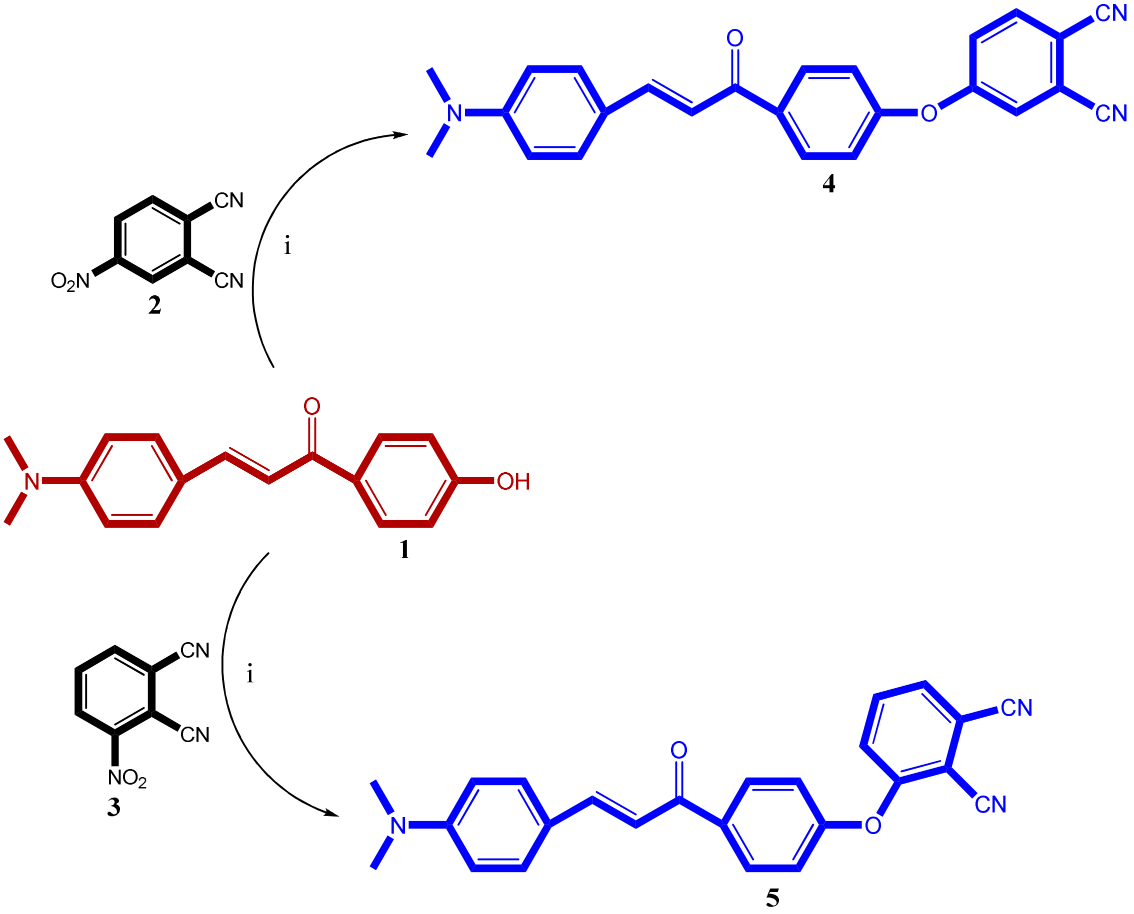

Figure 1. The synthesis of compounds 4 and 5. Reagent and condition: (i) dry DMF, K_2CO_3, 60 °C, 96 h.

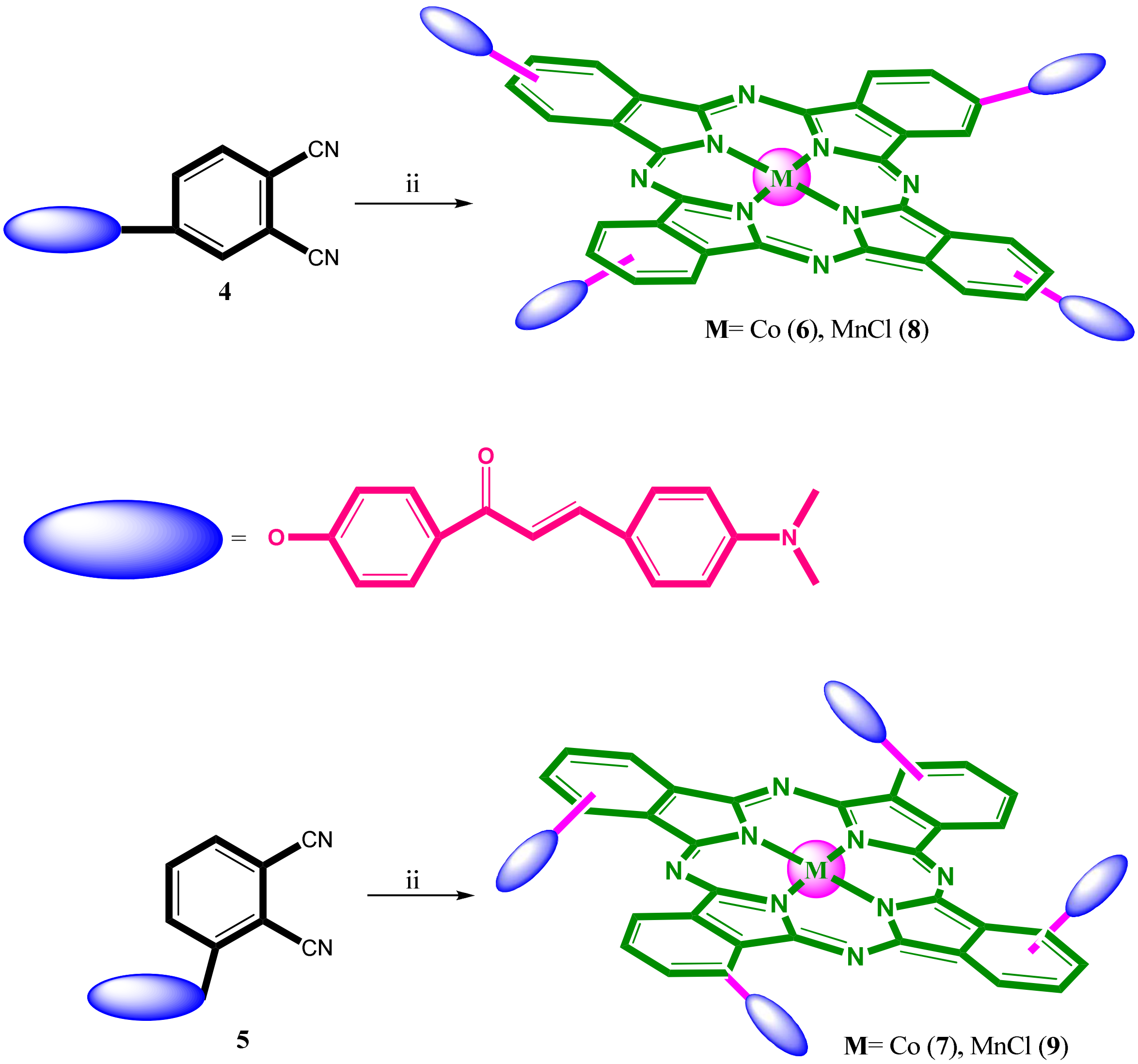

Figure 2. The synthesis peripherally and non-peripherally tetra substituted metallophthalocyanines. Reagent and condition: (ii) $CoCl_2$, $MnCl_2$, n-pentanol, DBU, 160 °C.

2.1. Materials and methods

The used materials, equipments and the electrochemical measurements were supplied as supplementary information.

2.2. Synthesis

2.2.1. *4-(4-{(2E)-3-[4-(Dimethylamino)phenyl]prop-2-enoyl}phenoxy)phthalonitrile (4)*

4-Nitrophthalonitrile (**2**) (0.6 g, 3.37 mmol) was dissolved in 8 mL dry DMF under N_2 atmosphere and of (2E)-3-[4-(dimethylamino)phenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one (**1**) (0.9 g, 3.37 mmol) was added to this mixture. After stirring for 30 minutes at 60 °C, finely ground anhydrous K_2CO_3 (1.40 g, 10.11 mmol) was added portion wise within 2 h. The reaction mixture was stirred under N_2 at 60 °C for 4 days. At the end of this time, the reaction mixture was poured into ice-water (150 g) and stirred at room temperature for 2 h to yield a crude product. Then, this precipitate was isolated by filtration and washed with distilled water and cold ethanol. The crude product was crystallized from ethanol to give pure product and then dried in vacuo (P_2O_5). Yield: 0.70 g (53%), m.p. 208-209 ºC. IR (KBr Pellet), ν/cm^{-1} : 3061 (Ar-H), 2902-2826 (Aliph. C-H), 2233 (C≡N), 1642, 1584, 1556, 1544, 1520, 1498, 1489, 1434, 1364, 1342, 1250, 1226, 1208, 1154, 1027, 1001, 988, 943, 860, 806, 755, 678, 628. ^{1}H-NMR. (400 MHz, $CDCl_3$), (δ:ppm): 8.14 (d, 2H, *J*= 8.2, Ar-H), 7.86-7.77 (m, 2H, Ar-H), 7.59 (d, 2H, *J*= 8.4, -CH=), 7.39-7.28 (m, 3H, Ar-H), 7.19 (d, 2H, *J*= 8.2, Ar-H), 6.73 (d, 2H, *J*= 8.4, Ar-H), 3.08 (s, 6H, CH_3-N). ^{13}C-NMR (100 MHz, $CDCl_3$), (δ:ppm): 188.77, 160.83, 160.81, 156.82, 152.26, 146.55, 136.96, 135.56, 135.54, 131.05, 1331.03, 130.61, 130.59, 122.33, 122.03, 120.06, 116.06, 111.84, 111.81, 40.12. MS (ESI), (m/z) calc. 393.43; found: 394.39 $[M+H]^+$.

2.2.2. *3-(4-{(2E)-3-[4-(Dimethylamino)phenyl]prop-2-enoyl}phenoxy)phthalonitrile (5)*

The synthetic method to that of compound **4** was used to obtain compound **5** by using a mixture of compound **3** (0.6 g, 3.37 mmol), compound 1 (0.9 g, 3.37 mmol) and anhydrous K_2CO_3 (1.40 g, 10.11 mmol). Yield: 1.05 g (80%), m.p. 148-149 ºC. IR

(KBr Pellet), ν/cm^{-1} : 3099 (Ar-H), 2900-2803 (Aliph. C-H), 2233 (C≡N), 1650, 1582, 1561, 1549, 1523, 1501, 1452, 1412, 1367, 1341, 1273, 1225, 1204, 1186, 1031, 1010, 978, 945, 866, 797, 753, 666, 628. ^{1}H-NMR. (400 MHz, $CDCl_3$), (δ:ppm): 8.13 (d, 2H, *J*= 8.7, Ar-H), 7.85 (d, 1H, *J*= 12.4, -CH=), 7.64 (t, 1H, *J*= 8.5, Ar-H), 7.58-7.53 (m, 3H, Ar-H), 7.34 (d, 1H, *J*= 12.2, -CH=), 7.21-7.19 (d, 3H, *J*= 8.7, Ar-H), 6.72 (d, 2H, *J*= 8.8, Ar-H), 3.07 (s, 6H, CH_3-N). ^{13}C-NMR (100 MHz, $CDCl_3$), (δ:ppm): 188.86, 159.87, 157.04, 152.24, 146.52, 136.82, 134.52, 130.94, 130.58, 130.50, 127.78, 122.36, 121.49, 121.46, 119.74, 116.09, 114.95, 114.93, 111.82, 40.10. MS (ESI), (m/z) calc. 393.43; found: 394.39 $[M+H]^+$.

2.2.3. *2(3),9(10),16(17),23(24)-Tetrakis-(4-{(2E)-3-[4-(dimethylamino)phenyl]prop-2-enoyl}phenoxy) phthalocyaninato cobalt(II) (6)*

A mixture of 4-(4-{(2E)-3-[4-(dimethylamino)phenyl]prop-2-enoyl}phenoxy)phthalonitrile **4** (0.15 g, 0.38 mmol), anhydrous $CoCl_2$ (0.024 g, 0.19 mmol) and catalytic amount of DBU (5 drops) in 2 mL of n-pentanol was heated and stirred at 160 °C in a sealed glass tube for 12 h under N_2 atmosphere. After cooling to room temperature, the reaction mixture was precipitated by the addition of ethanol. The obtained green product was filtered off, washed with ethanol and diethyl ether and then dried in vacuo. Purification of the crude product was accomplished by column chromatography which was placed aluminum oxide using $CHCl_3$:CH_3OH (100:1) solvent system as eluent. Yield: 0.056 g (36%), m.p. > 250 ºC. IR (KBr Pellet) ν_{max}/cm^{-1}: 3054 (Ar-H), 2970-2854 (Aliph. C-H), 1650, 1582, 1520, 1500, 1467, 1432, 1363, 1335, 1260, 1224, 1207, 1156, 1027, 1009, 976, 944, 877, 807, 749, 676, 616. UV-vis (Chloroform): λ_{max}, nm (log ε): 406 (5.28), 600 (4.53), 662 (5.05). MALDI-TOF-MS m/z calc. 1632.68; found: 1633.14 $[M+H]^+$.

2.2.4. *1(4),8(11),15(18),22(25)-Tetrakis-(4-{(2E)-3-[4-(dimethylamino)phenyl]prop-2-enoyl}phenoxy) phthalocyaninato cobalt(II) (7)*

A similar preparation method to that of complex **6** was used to obtain cobalt(II) phthalocyanine **7** by using a mixture of compound **5** (0.15 g, 0.38 mmol), anhydrous $CoCl_2$ (0.024 g, 0.19 mmol), n-pentanol (2 mL) and 1,8-diazabycyclo[5.4.0]undec-7-ene (DBU) (5 drops). Finally, pure cobalt(II) phthalocyanine (**6**) was obtained by column chromatography which is placed aluminium oxide using $CHCl_3$:CH_3OH (100:1) as solvent system. Yield: 0.048 g (30%), m.p. > 250 ºC. IR (KBr Pellet) ν_{max}/cm^{-1}: 3044 (Ar-H), 2977-2858 (Aliph. C-H), 1650, 1580, 1520, 1501, 1475, 1432, 1360, 1332, 1260, 1227, 1207, 1157, 1028, 1008, 977, 945, 877, 807, 746, 676, 621. UV-vis (Chloroform): λ_{max}, nm (log ε): 414 (5.08), 620 (4.41), 688 (4.97). MALDI-TOF-MS m/z calc. 1632.68; found: 1632.55 $[M]^+$.

2.2.5. *2(3),9(10),16(17),23(24)-Tetrakis-(4-{(2E)-3-[4-(dimethylamino)phenyl]prop-2-enoyl}phenoxy) phthalocyaninato manganese(III)chloride (8)*

A mixture of compound (**4**) (0.15 g, 0.38 mmol), $MnCl_2$ (0.023 g, 0.19 mmol), 5 drops of 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) in n-pentanol (2 mL) was heated to 160 ºC with stirring for 12 h under N_2. The brownish reaction mixture was cooled to room temperature and then diluted with ethanol until the crude product precipitated. The precipitate was filtered and dried in vacuo. Finally, crude product was purified by column chromatography on aluminium oxide using $CHCl_3$:CH_3OH (100:1) as solvent system. Yield: 0.080 g (50%), m.p. > 250 ºC. IR (KBr Pellet) ν_{max} / cm^{-1}: 3044 (Ar-H), 2968-2852 (Aliph. C-H), 1650, 1581, 1520, 1499, 1466, 1432, 1363, 1334, 1259, 1224, 1206, 1155, 1026, 1009, 979, 944, 892, 807, 742, 676, 614. UV-vis (Chloroform): λ_{max}, nm (log ε): 405(5.28), 500 (4.31), 644 (4.59), 718 (4.96). MALDI-TOF-MS m/z calc. 1664.14; found: 1636.36 $[M-2CH_3+2H]^+$.

2.2.6. *1(4),8(11),15(18),22(25)-Tetrakis-(4-{(2E)-3-[4-(dimethylamino)phenyl]prop-2-enoyl}phenoxy) phthalocyaninato manganese(III)chloride (9)*

A similar preparation method to that of complex **8** was used to obtain manganese(III) phthalocyanine **9** by using a mixture of compound **5** (0.15 g, 0.38 mmol), $MnCl_2$ (0.023 g, 0.19 mmol), n-pentanol (2 mL) and DBU (5 drops). Finally, pure cobalt(II) phthalocyanine (6) was obtained by column chromatography which is placed aluminium oxide using $CHCl_3$:CH_3OH (100:1) as solvent system. Yield: 0.062 g (39%), m.p. > 250 ºC. IR (KBr Pellet) ν_{max}/cm^{-1}: 3040 (Ar-H), 2980-2854 (Aliph. C-H), 1647, 1580, 1520, 1501, 1482, 1434, 1360, 1327, 1244, 1227, 1206, 1157, 1029, 1009, 974, 945, 894, 807, 741, 676, 617. UV-vis (Chloroform): λ_{max}, nm (log ε): 412 (5.03), 531 (4.25), 679 (4.43), 754 (5.03). MALDI-TOF-MS m/z calc. 1664.14; found: 1635.55 $[M-2CH_3+H]^+$.

3. RESULTS AND DISCUSSION

3.1. Characterization

The synthesis of peripherally and non-peripherally tetra-chalocone substituted cobalt(II) and manganese(III) phthalocyanines are shown in Figure 1 and 2. Phthalonitrile derivatives **4** and **5** were obtained from the reaction of (2E)-3-[4-(dimethylamino)phenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one (**1**) with 4-nitrophthalonitrile (**2**) and 3-nitrophthalonitril (**3**) in dry DMF/dry K_2CO_3 under N_2 atmosphere at 60 °C for 4 days, respectively. All spectral data support the proposed structures of compounds **4** and **5**.

According to IR spectroscopy data, new vibration appeared at 2233 cm^{-1}, which belongs to the C≡N groups, supported the proposed structures of compounds **4** and **5**. In ^{1}H-NMR spectra of phthalonitrile compounds (**4** and **5**) the OH group of compound **1** disappeared, as expected. Presence of additional aromatic protons indicated that substitution was accomplished. In the ^{13}C-NMR spectrum of **4** and **5**, the presence of nitrile carbon atoms were indicated, with peaks at δ 116.06, 111.84 ppm (for **4**) and 119.74, 116.09 ppm (for **5**). Molecular ion $[M+H]^+$ peaks m/z at 394 in the mass spectra of compounds **4** and **5** were showed that target compounds were successfully prepared.

The synthesis of new peripherally and non-peripherally tetrasubstituted cobalt(II) and manganese(III) phthalocyanines (**6**, **7**, **8** and **9**) is described in this work. The cyclotetramerization of the phthalonitrile derivative **4** in the presence of anhydrous $CoCl_2$ and $MnCl_2$ in n-pentanol and a few drops 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at reflux temperature under a nitrogen atmosphere afforded the peripherally cobalt(II) and manganese(III) phthalocyanines (**6** and **8**). Cyclotetramerization of the phthalonitrile derivative **5** to the non-peripherally tetra-substituted cobalt(II) and manganese(III) phthalocyanines (**7** and **9**) were accomplished in the presence of anhydrous $CoCl_2$ and $MnCl_2$ in n-pentanol and DBU at reflux temperature under a nitrogen atmosphere.

All newly synthesized compounds (**6**, **7**, **8** and **9**) were characterized by UV-vis, FT-IR, MS spectroscopic data. ^{1}H-NMR and ^{13}C-NMR measurements of the peripherally and non-peripherally tetrasubstituted cobalt(II) and manganese(III) phthalocyanines (**6**, **7**, **8** and **9**) were precluded due to their paramagnetic nature.[21] All obtained results were compatible with the proposed structures. The IR spectra of the peripherally and non-peripherally tetrasubstituted cobalt(II) and manganese(III) phthalocyanines (**6**, **7**, **8** and **9**) clearly indicate the cyclotetramerization of the phthalonitrile derivatives **4** and **5**, with the disappearance of the C≡N peak at 2233 cm^{-1}. The MALDI-TOF mass spectra of the tetra-substituted phthalocyanines **6**, **7**, **8** and **9** confirmed the proposed structures, with the molecular ion being easily identified at 1633 $[M+H]^+$, 1632 $[M]^+$, 1636 $[M-2CH_3+2H]^+$ and 1635 $[M-2CH_3+H]^+$, respectively. The metallophthalocyanines display typical electronic spectra with two strong absorption regions, one of them in the UV region at around 300-350 nm (B band) and the other one in the visible region at around 600-700 nm (Q band). The electronic absorption spectra of metallophthalocyanines **6**, **7**, **8** and **9**, in chloroform at room temperature are shown in Figure 3. UV-Vis spectra of metallophthalocyanines **6**, **7**, **8** and **9** (in $CHCl_3$) exhibit intense single Q band absorption of $\pi\rightarrow\pi^*$ transitions at 662, 688, 718 and 754 nm, respectively. B bands of metallophthalocyanines (**6**, **7**, **8** and **9**) were observed in the UV region at 406, 414, 405 and 412 nm, respectively. The peaks at 500 (complex **8**) and 531 (complex **9**) are associated with charge transfer in MPc complexes.[22] The UV–Vis spectrum of non-peripheral substituted MPc complexes show a red-shifted Q-band with respect to peripheral substituted MPc complexes. Red-shifting of the Q-band is normal with non-peripheral substitution in MPc complexes. Increase in steric limitations, caused by non-peripheral substitution, increases the conformational stress on MPc complexes. Such conformational stress results in shift in position of Q-band.[22]

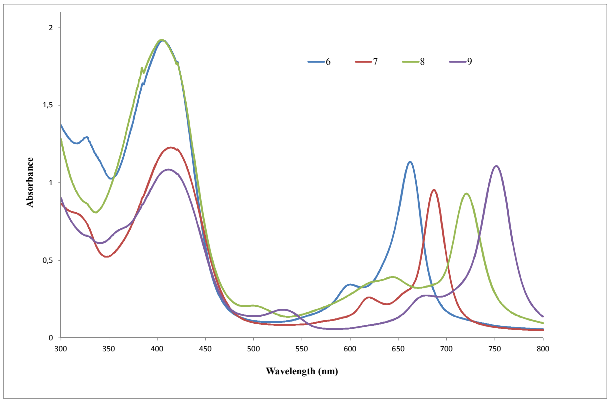

Fig. 3. UV-Vis spectrum of **6**, **7**, **8** and **9** in $CHCl_3$.

3.2. Electrochemical studies

Electrochemical feature of MPcs were performed to derive basic electrochemical parameters of the complexes which are need to decide their usage in different electrochemical technologies such as, electrocatalytic, electrochromic and electrosensing applications.[23-25] To propose possible application of peripherally and non-peripherally tetrasubstituted cobalt(II) and manganese(III) phthalocyanines (**6**, **7**, **8** and **9**) in the electrochemical technologies, redox behaviors of the complexes (**6**, **7**, **8** and **9**) were performed in DCM/TBAP electrolyte system on a Pt working electrode with CV and SWV techniques. Results of the CV and SWV analysis are tabulated on Table 1. Table 1 lists the assignments of the redox couples and the electrochemical parameters, which included half-wave peak potentials ($E_{1/2}$), anodic to cathodic peak potential separation (ΔE_p), and difference between the first oxidation and reduction potentials ($\Delta E_{1/2}$).[26] CVs of all complex were recorded at different scan rates and given in the "supplementary material" file.

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

MPcs		Ring Oxidation	M^{III}/M^{II}	M^{II}/M^{I}	Ring Reductions	$^c\Delta E_{1/2}$
6	$^aE_{1/2}$	1.14^d $(0.80)^e$	-	-0.57	-1.30	0.73
	$^b\Delta E_p$ (mV)	-	-	100	115	
7	$^aE_{1/2}$	1.05^d $(0.71)^e$	-	-0.19	-1.31	1.12
	$^b\Delta E_p$ (mV)	-	-	130	110	
8	$^aE_{1/2}$	1.05^d $(1.13)^e$	-0.20	-0.95	-1.30	0.75
	$^b\Delta E_p$ (mV)	-	30	100	40	
9	$^aE_{1/2}$	1.01^d $(1.11)^e$	-0.08	-0.90	-1.31	0.82
	$^b\Delta E_p$ (mV)	-	160	90	90	

[a]: $E_{1/2}$ values $((E_{pa}+E_{pc})/2)$ were given versus SCE and Fc/Fc^+ (in parenthesis) at 0.100 Vs^{-1} scan rate. [b]: $\Delta E_p = E_{pa} - E_{pc}$. [c]: $\Delta E_{1/2} = E_{1/2}$ (first oxidation)- $E_{1/2}$ (first reduction). [d]: E_{pa} of the polymerization process recorded during the first CV cycle. [e]: E_{pc} of the polymerization process recorded during the first CV cycle.

Figure 4 and Figure 5 represent the CV and SWV responses of peripherally and non-peripherally tetrasubstituted cobalt(II) phthalocyanines (**6** and **7**), respectively. The CV and SWV responses recorded in the cathodic potential side of the TBAP/DCM electrolyte system on a Pt working electrode. Complexes **6** and **7** give a reversible metal based reduction couple (R_1) at $E_{1/2}$= -0.57 V and -0.19 V, respectively. This uncommon redox behavior of complex **6** and **7** is resulted from the redox activity of Co^{II} metal ion of the complexes. Due to the existence of the empty "d" orbital of Co^{II} metal ion between the energy level of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Pc ring, Co^{II} can reduce before Pc ring, thus the R_1 process of complexes **6** and **7** at $E_{1/2}$= -0.57 V and -0.19 V is easily assigned to the Co^{II}/Co^{I} reduction reaction of the complexes. Peripherally and non-peripherally tetrasubstituted cobalt(II) phthalocyanines (**6** and **7**) also give a reversible Pc based reduction couple (R_2) at $E_{1/2}$= -1.30 V and -1.31 V, respectively, during the cathodic potential scans. SWVs clearly show the reversibility of the redox processes. Derived electrochemical parameters of the complexes tabulated on Table 1 are in agreements with the similar complexes in the literature.[27-29]

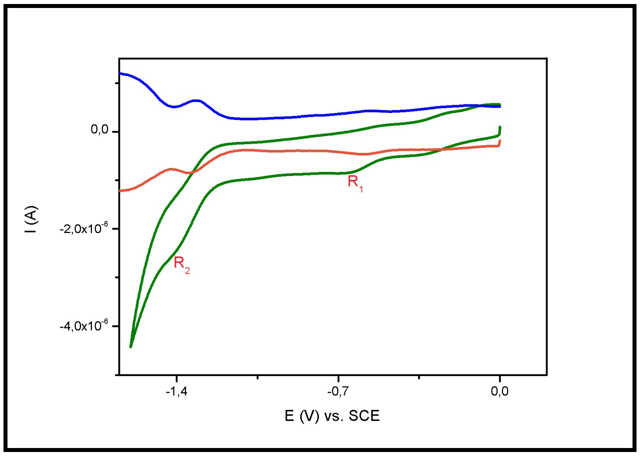

Fig. 4. CVs and SWVs of CoPc **6** at 0.100 V.s^{-1} in TBAP/DCM.

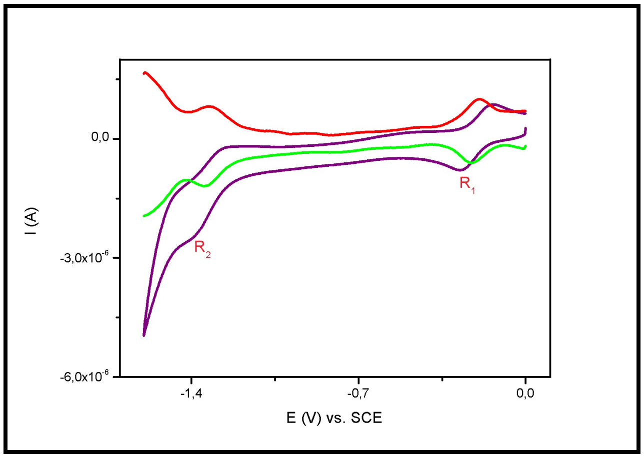

Fig. 5. CVs and SWVs of CoPc **7** at 0.100 V.s^{-1} in TBAP/DCM.

While complexes **6** and **7** illustrate common metal and Pc ring based reduction reactions during the cathodic potential scans, they give extraordinary redox responses during the anodic potential scans. Figure 6 and Figure 7, respectively, illustrate CV responses of peripherally and non-peripherally tetrasubstituted cobalt(II) phthalocyanines (**6** and **7**) during repetitive CV cycles. During the first anodic scan for complex **6**, an huge anodic wave at 1.14 V and its reverse cathodic couple are recorded at 0.80 V. This CV behavior indicates oxidation of 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 polymeric film as results of electropolymerization reaction. Electropolymerization of the complex was well reflected with the consecutive CV responses of the system. During the consecutive second CV cycle a new anodic wave is recorded at 1.23 V assigned to the polymerized complex. This new wave decreases in current intensity with a positive potential shift during 3. CV cycle. Then its peak current decreases continuously with a potential shift until the 20. CV cycle. Similar CV responses were recorded for the cathodic wave. During the first anodic scan for complex **7**, an anodic wave at 1.05 V and its reverse cathodic couple are recorded at 0.71 V. During the consecutive second CV cycle a new anodic wave is recorded at 1.10 V assigned to the polymerized complex. This new wave current decreases continuously with a positive potential shift until the 20. CV cycle. Similar CV responses were recorded for the cathodic wave. These voltammetric responses of the complex illustrate coating of the complex on the working electrode with an electropolymerization process. The film on the electrode surface was seen easily with naked eyes. Complexes **6** and **7** were electropolymerized on the working electrode with similar manners. But peak potentials or shifting trends of the peaks differed when position of substituent was changed.

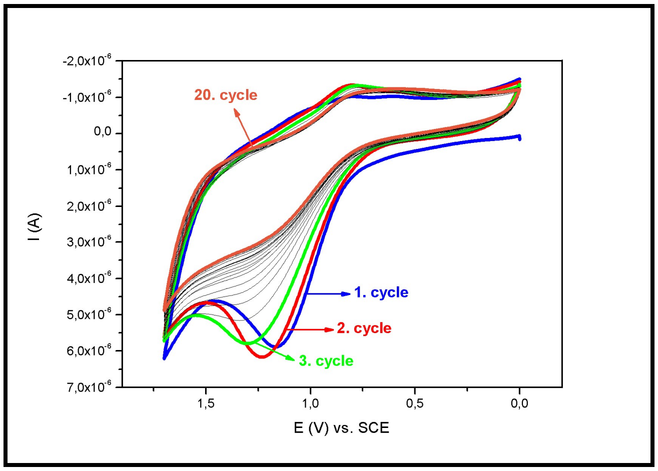

Figure 6. Repetitive CVs of CoPc **6** recorded at anodic potential windows of DCM/TBAP electrolyte system at 0.100 Vs^{-1} scan rate on a Pt working electrode.

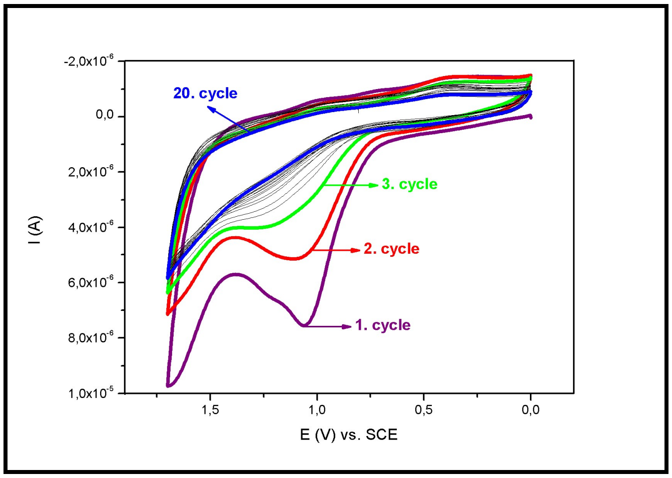

Figure 7. Repetitive CVs of CoPc **7** recorded at anodic potential windows of DCM/TBAP electrolyte system at 0.100 Vs^{-1} scan rate on a Pt working electrode.

Figs. 8 and 9 show the cyclic voltammetry profiles complexes **8** and **9**, respectively, in DCM containing 0.1 M TBAP as supporting electrolyte. It is well known that Mn^{III} metal center can be easily reduced to the more stable Mn^{II} form at around 0.0 V. In the literature, the second metal based reduction reaction Mn^{II}ClPc^{-2}/Mn^{I}ClPc^{-2} is observed after ca. -0.80 V than the first reduction reaction Mn^{III}ClPc^{-2}/Mn^{II}ClPc^{-2}.[30,31] Complex **8** gives three redox processes (Figure 8). Process I (R$_1$ couple) and process II (R$_2$ couple) are reversible metal reduction processes, assigned to Mn^{III}ClPc^{-2}/Mn^{II}ClPc^{-2} ($E_{1/2}$ = -0.20 V vs. Pt for R$_1$) and Mn^{II}ClPc^{-2}/Mn^{I}ClPc^{-2} ($E_{1/2}$ = -0.95 V vs. Pt for R$_2$) species, respectively. Process III (R$_3$ couple) is a reversible ring reductions, assigned to Mn^{I}ClPc^{-2}/Mn^{I}ClPc^{-3} ($E_{1/2}$ = -1.30 V vs. Pt) species. Similarly, three redox processes can be identified for complex **9** (Figure 9). Process I (R$_1$) is a irreversible metal reduction process, assigned to Mn^{III}ClPc^{-2}/Mn^{II}ClPc^{-2} (E$_{1/2}$ = -0.08 V vs. Pt) species. Process II (R$_2$) is a reversible metal reduction process, assigned to Mn^{II}ClPc^{-2}/Mn^{I}ClPc^{-2} (E$_{1/2}$ = -0.90 V vs. Pt) species. Process III (R$_3$ couple) is a reversible ring reductions, assigned to Mn^{I}ClPc^{-2}/Mn^{I}ClPc^{-3} (E$_{1/2}$ = -1.31 V vs. Pt) species.

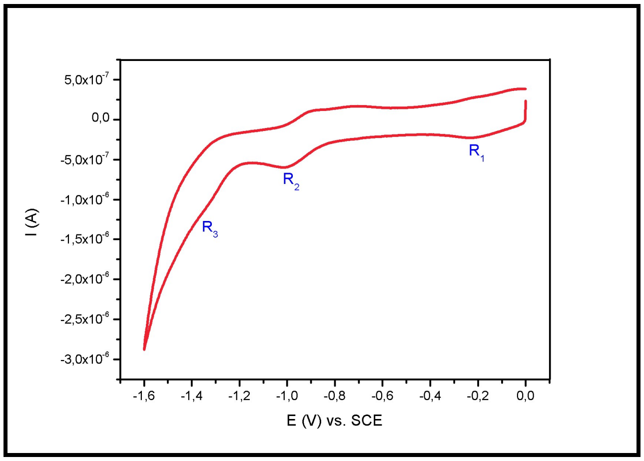

Figure 8. CV of **MnPc** (**8**) (5.0 10^{-4} mol dm^{-3}) recorded at cathodic potentials at 0.100 Vs^{-1} scan rate on a Pt working electrode in DCM/TBAP.

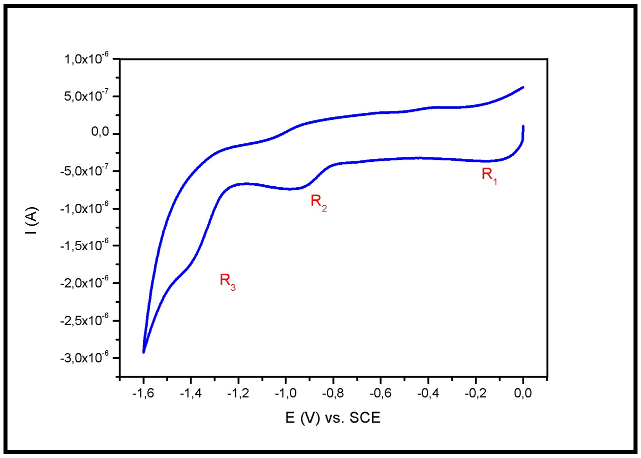

Figure 9. CV of **MnPc** (**9**) (5.0 10^{-4} mol dm^{-3}) recorded at cathodic potentials at 0.100 Vs^{-1} scan rate on a Pt working electrode in DCM/TBAP.

During the oxidation processes, complexes **8** and **9** are electropolymerized on the working electrode. When only anodic potentials are scanned (from 0.0 V to 1.60 V), polymerization process of the complex **8** is seen in Figure 10. As shown in Figure 10, an anodic wave was recorded at 1.05 V and its reverse couple is recorded at 1.13 V during the first CV cycle. During the repetitive potential scans, the anodic wave increase up to 20. cycles with a potential shift at 1.30 V. Similar CV responses were recorded for the cathodic wave with a potential shift at 0.95 V. These voltammetric data shows electropolymerization of the complex **8** on the working electrode. On the other hand, electropolymerization behavior of complex **9** is seen in Figure 11. As shown in Figure 11, during the first anodic scans, complex **9** gives an anodic wave at 1.01 V and its reverse cathodic wave at 1.11 V. During the third anodic scans, a new huge anodic wave and its reverse cathodic couple are recorded at 1.20 V and 1.06 V, respectively. After 3. CV cycles these waves starts to increase to 20. cycle with potential shift, indicating electropolymerization of the complex **9** on the working electrode. Like complexes **6** and **7**, the compounds **8** and **9** 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. In previous papers, authors reported electropolymerization of peripherally tetra-substituted metallophthalocyanines bearing various amino moieties,[32-34] ethylenedioxythiophene,[35] hydroquinoline[36], pyrrol[37] groups. But this study is the first example of electropolymerization of peripherally and non-peripherally tetra chalcone substituted cobalt(II) and manganese(III) phthalocyanines.

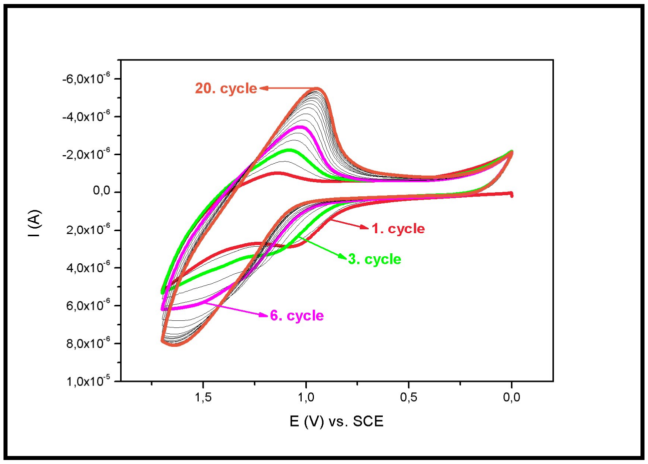

Figure 10. Repetitive CVs of MnPc **8** recorded at anodic potential windows of DCM/TBAP electrolyte system at 0.100 Vs^{-1} scan rate on a Pt working electrode.

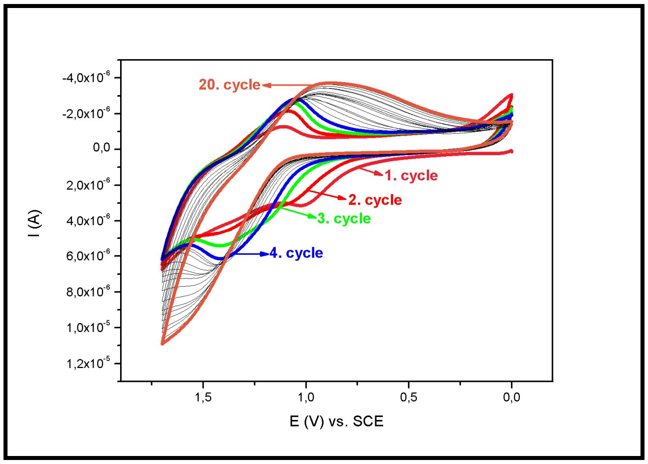

Figure 11. Repetitive CVs of MnPc **9** recorded at anodic potential windows of DCM/TBAP electrolyte system at 0.100 Vs^{-1} scan rate on a Pt working electrode.

4. Conclusion

The spectral and electrochemical properties of newly synthesized peripherally and non- peripherally tetra-substituted cobalt(II) and manganese(III) phthalocyanines have been presented in this work. The target symmetrical phthalocyanines were separated by column chromatography which is placed aluminium oxide and characterized by a combination of IR, UV-Vis and MS spectral data. The cobalt and manganese complexes showed metal-based and ring-based redox processes. When the complexes are over-oxidized, electropolymerization of the complexes on the working electrode is recorded. All complexes were electropolymerized on the working electrode with similar manners. But peak potentials or shifting trends of the peaks differed when metal centers and substituents were changed. As a result, this study is the first example of electropolymerization of peripherally and non-peripherally tetra chalcone substituted cobalt(II) and manganese(III) phthalocyanines. Electropolymerization behavior of the complexes are the desired properties of the electrochemical applications, especially, electrocatalytic, electrochromic and electrosensing applications.

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Notes and references

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

MPcs		**Ring Oxidation**	**M^{III}/M^{II}**	**M^{II}/M^{I}**	**Ring Reductions**	**$^{c}\Delta E_{1/2}$**
6	$^{a}E_{1/2}$	1.14^{d} 0.80)^{e}	-	-0.57	-1.30	0.73
	$^{b}\Delta E_{p}$ (mV)	-	-	100	115	
7	$^{a}E_{1/2}$	1.05^{d} (0.71)^{e}	-	-0.19	-1.31	1.12
	$^{b}\Delta E_{p}$ (mV)	-	-	130	110	
8	$^{a}E_{1/2}$	1.05^{d} (1.13)^{e}	-0.20	-0.95	-1.30	0.75
	$^{b}\Delta E_{p}$ (mV)	-	30	100	40	
9	$^{a}E_{1/2}$	1.01^{d} (1.11)^{e}	-0.08	-0.90	-1.31	0.82
	$^{b}\Delta E_{p}$ (mV)	-	160	90	90	

[a]: $E_{1/2}$ values $((E_{pa}+E_{pc})/2)$ were given versus SCE and Fc/Fc^{+} (in parenthesis) at 0.100 Vs^{-1} scan rate. **[b]:** $\Delta E_{p}= E_{pa}-E_{pc}$. [c]: $\Delta E_{1/2} = E_{1/2}$ (first oxidation)- $E_{1/2}$ (first reduction). [d]: E_{pa} of the polymerization process recorded during the first CV cycle. [e]: E_{pc} of the polymerization process recorded during the first CV cycle.

Graphical Abstract