

Synthesis and effect of substituent position, metal type on the electrochemical properties of (3-morpholin-4-ylpropoxy) groups substituted cobalt, manganese phthalocyanines

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Abstract: In this work, 4-(3-morpholin-4-ylpropoxy)phthalonitrile **2**, 3-(3-morpholin-4-ylpropoxy)phthalonitrile **3**, Co(II)Pc and Mn(III)Pcs containing (3-morpholin-4-ylpropoxy) groups at peripheral and nonperipheral positions were synthesized. Phthalonitrile derivatives (**2** and **3**), Co(II)Pc and Mn(III)Pcs (**2a**, **2b**, **3a**, **3b**) were characterized by using FT-IR, NMR (only for **2** and **3**), mass and UV-Vis (except **2** and **3**) spectral data techniques. Also, electrochemistry of (3-morpholin-4-ylpropoxy) group substituted Co(II)Pc and Mn(III)Pcs were inspected by using cyclic voltammetry. Electrochemical studies show that (3-morpholin-4-ylpropoxy) group substituted Co(II)Pc and Mn(III)Pcs electropolymerized on the Pt working electrode.

Key words: Synthesis, phthalocyanine, cobalt, manganese, voltammetry

1. Introduction

Peripheral or nonperipheral tetra-substituted phthalocyanines have been investigated in different areas owing to their chemical and thermal stability that possess physical and chemical properties [1,2]. Phthalocyanines and their derivatives have been used in many applications such as chemical and biosensor [3], solar cell, [4,5], catalyst [6], nonlinear optic [7], liquid crystal [8], catalyst [9,10], photosensitizers in photodynamic therapy (PDT) [11,12], because they have intense blue-green colour owing to the electronic delocalization of their 18- π electrons. On the other hand, electrochemical characterization of phthalocyanines is important for the electrocatalyst [13], electrosensing [14], electropolymerization [15,16], electrochromic fields [17].

Phthalocyanines bearing redox active metals (Co, Fe and Mn) have been investigated owing to their electrocatalytic properties [18]. The usage of cobalt phthalocyanines as an electrochemical sensor is of interest [19,20]. Also, Mn(III)Pcs exhibit exciting electrochemical response owing to different oxidation states of manganese ion [21]. In this work, we have synthesized Co(II)Pc and Mn(III)Pcs containing (3-morpholin-4-ylpropoxy) groups at peripheral and nonperipheral positions. It has been found that the attachment of -(3-morpholin-4-ylpropoxy) group to the phthalocyanine molecule in either a peripheral or nonperipheral position has a great effect on the electrochemical properties.

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2. Experimental design

All information about the used equipment, materials, synthesis, electrochemistry experiments is given in the Supplementary Information.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of Co(II)Pc and Mn(III)Pcs bearing (3-morpholin-4-ylpropoxy) groups was shown in Figure 1. Firstly, 4-(3-morpholin-4-ylpropoxy)phthalonitrile (**2**), 3-(3-morpholin-4-ylpropoxy)phthalonitrile (**3**) were synthesized from 3-morpholin-4-yl-propan-1-ol in the presence of available phthalonitrile by using K_2CO_3 in dry DMF [22,23]. Then, peripheral, nonperipheral tetra-(3-morpholin-4-ylpropoxy) group substituted Co(II)Pc and Mn(III)Pcs (**2a**, **2b**, **3a**, **3b**) were synthesized by cyclotetramerization from **2**, **3**. In the IR spectrum of **2**, **3**, stretching vibrations of $C\equiv N$ groups at 2230 (for **2**), 2228 (for **3**) cm^{-1} occurred at expected frequencies, respectively. In 1H -NMR spectrum of **2** and **3** in $CDCl_3$, aromatic protons appeared at 7.72–7.20 and 7.66–7.30 ppm. In the ^{13}C -NMR spectrum of **2** and **3**, nitrile carbon atoms were resonated at δ 115.75, 115.32 ppm (for **2**) and 116.98, 113.00 ppm (for **3**). The molecular ion peak of 4-(3-morpholin-4-ylpropoxy)phthalonitrile (**2**), 3-(3-morpholin-4-ylpropoxy)phthalonitrile (**3**) were found at m/z 272 $[M+H]^+$. The absence of the $C\equiv N$ stretches at 2230 (for **2**) and 2228 cm^{-1} (for **3**) in the IR spectra of the Co(II)Pc and Mn(III)Pcs bearing (3-morpholin-4-ylpropoxy) groups confirms that the cyclotetramerization consisted. The IR spectra of the Co(II)Pc and Mn(III)Pcs bearing (3-morpholin-4-ylpropoxy) groups are very similar. 1H -NMR and ^{13}C -NMR evaluations of the Co(II)Pc and Mn(III)Pcs were inhibited because of their paramagnetic characteristic [24]. MALDI-TOF mass spectra of Co(II)Pc and Mn(III)Pcs (**2a**, **2b**, **3a**, **3b**) confirmed the structures, with the molecular ion being easily identified at 1144.09 $[M]^+$, 1140.42 $[M-Cl]^+$ (Figure 2), 1144.12 $[M]^+$ and 1140.63 $[M-Cl]^+$, respectively. The UV-Vis spectra of Co(II)Pc and Mn(III)Pcs (**2a**, **2b**, **3a**, **3b**) in $CHCl_3$ are shown in Figure 3. UV-Vis spectra of Co(II)Pc and Mn(III)Pcs (**2a**, **2b**, **3a**, **3b**) showed single Q band absorption of $\pi \rightarrow \pi^*$ transitions at 673, 735, 694, 764 nm, respectively. B bands of Co(II)Pc and Mn(III)Pcs (**2a**, **2b**, **3a**, **3b**) were appeared in the UV region at 324, 384, 309, (355, 332) nm, respectively. On the other hand, **2b** and **3b** have an absorption band at 530 nm for **2b** and 542 nm for **3b**, interpreted as a charge transfer absorption [25].

3.2. Electrochemical studies

The electrochemistry of Co(II)Pc and Mn(III)Pcs (**2a**, **2b**, **3a**, **3b**) were obtained in DCM using a (DCM)/(TBAP) electrolyte system on a Pt working electrode. The electrochemical data were listed in Table. Figure 4a and Figure 4b show the CV responses of **2a**, **3a** in DCM/TBAP electrolyte system. **2a** and **3a** exhibited 2 reduction labelled as R_1 ($E_{1/2} = -0.39$ V for **2a**, $E_{1/2} = -0.40$ V for **3a**) and R_2 ($E_{1/2} = -1.54$ V for **2a**, $E_{1/2} = -1.57$ V for **3a**) in DCM/TBAP electrolyte system. Co^{II} can reduce before Pc ring, thus the R_1 process of **2a** and **3a** at $E_{1/2} = -0.39$ V and -0.40 V is easily assigned to the Co^{II}/Co^I reduction reaction of the complexes [26]. Figure 5a and Figure 5b show the CV responses of **2b**, **3b** in DCM/TBAP electrolyte system. **2b** and **3b** exhibited 2 reduction labelled as R_1 ($E_{1/2} = -0.25$ V for **2b**, $E_{1/2} = -0.21$ V for **3b**) and R_2 ($E_{1/2} = -1.29$ V for **2b**, $E_{1/2} = -1.09$ V for **3b**) in DCM/TBAP electrolyte system. The first reduction can be assigned to $[Cl-Mn^{III}Pc^{-2}] / [Cl-Mn^{II}Pc^{-2}]^{-1}$ because of the redox active manganese metal ion [27]. Then second reduction

can be assigned to $[\text{Mn}^{II}\text{Pc}^{-2}] / [\text{Mn}^I\text{Pc}^{-2}]^{-1}$ couple [28]. After first reduction, $[\text{Cl-Mn}^{II}\text{Pc}^{-2}]^{-1}$ species release axial chloride ion. Similar results were appeared for Co(II)Pc and Mn(III)Pcs in literature [29,30].

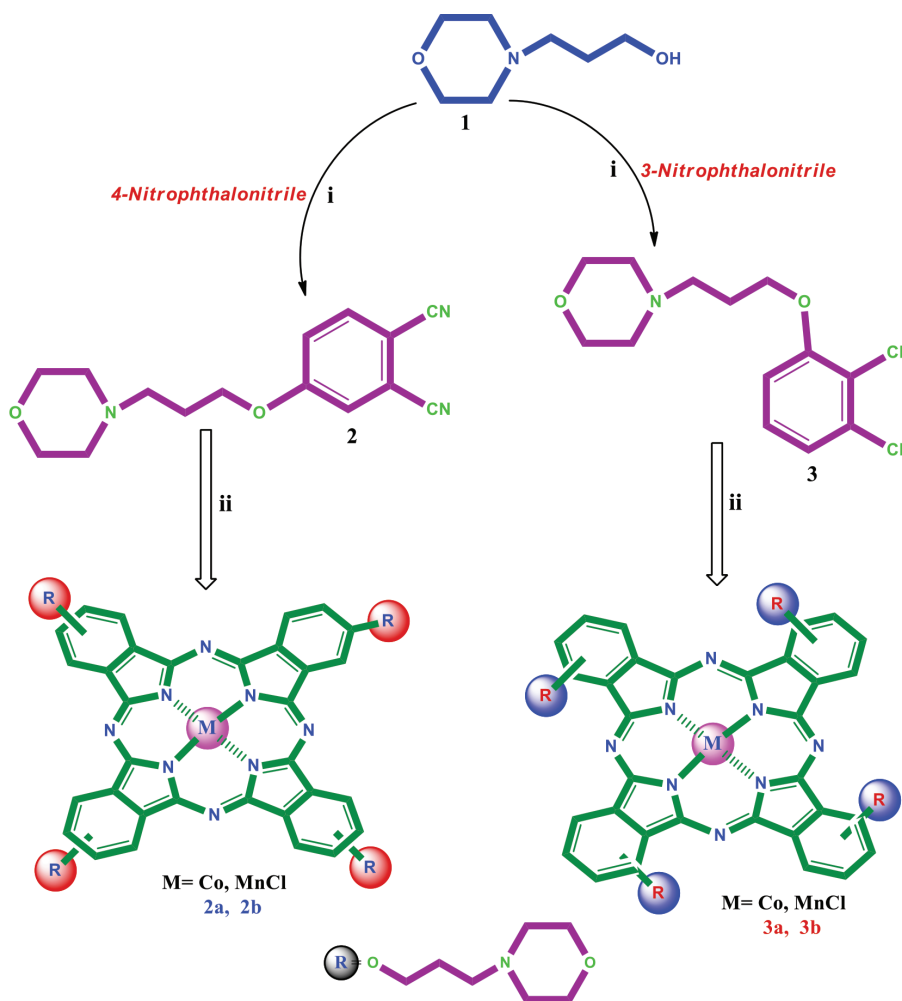


Figure 1. The synthesis of Co(II)Pc and Mn(III)Pcs bearing (3-morpholin-4-ylpropoxy) groups. (i) dry DMF, K_2CO_3 , 60 °C, 96 h.

While peripheral, nonperipheral tetra-(3-morpholin-4-ylpropoxy) group substituted Co(II)Pc and Mn(III)Pcs (**2a**, **2b**, **3a**, **3b**) illustrate widespread reduction reactions during the cathodic scans, Co(II)Pc and Mn(III)Pcs were electropolymerized on the working electrode during the anodic scans. Figure 6 shows the CV responses of peripheral, nonperipheral tetra-(3-morpholin-4-ylpropoxy) group substituted cobalt(II) phthalocyanines (**2a** and **3a**) during repetitive CV cycles. When Figure 6a is examined, the onset oxidation potential of peripheral tetra-(3-morpholin-4-ylpropoxy) group substituted cobalt(II) phthalocyanine **2a** at around 1.32 V is observed, whereas the onset potential of the nonperipheral tetra-(3-morpholin-4-ylpropoxy) group substituted cobalt(II) phthalocyanine **3a** has been determined at around 1.36 V (Figure 6b). In the following cycles, the oxidation peak currents raised and there was a small shift in the oxidation peaks. This suggests that the Co(II)Pc and Mn(III)Pcs incur polymerization in each scan and deposit onto the electrode surface. Figure 7 shows the CV responses of peripheral, nonperipheral tetra-(3-morpholin-4-ylpropoxy) group substituted man-

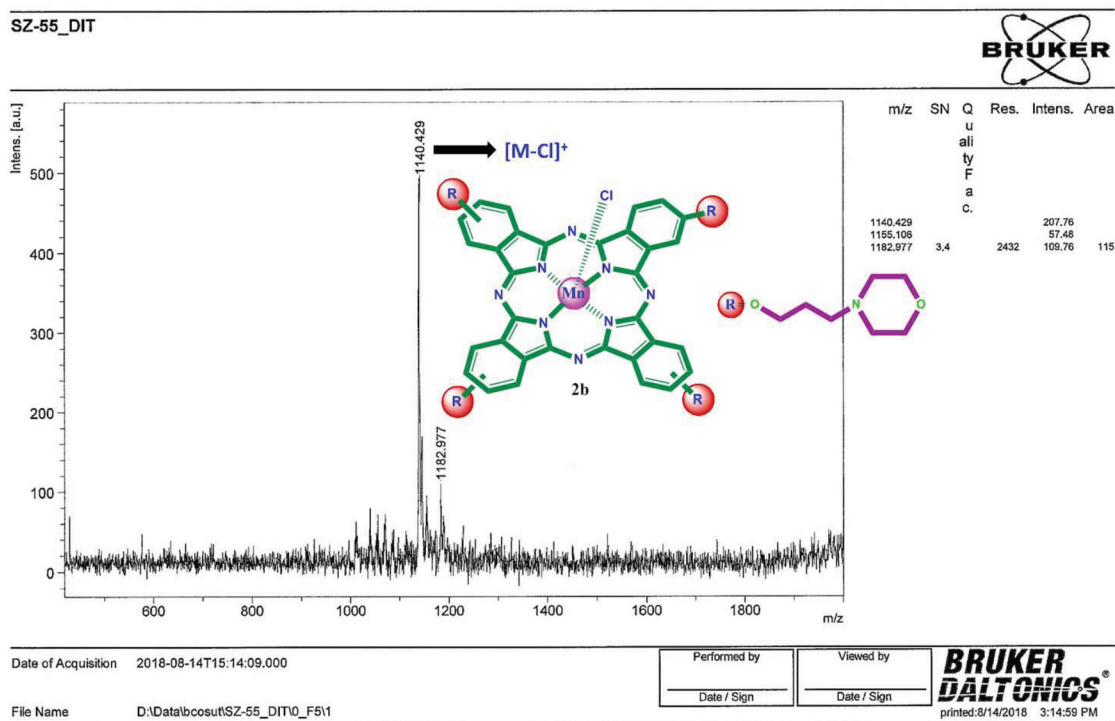


Figure 2. MALDI-TOF MS spectrum of **2b**.

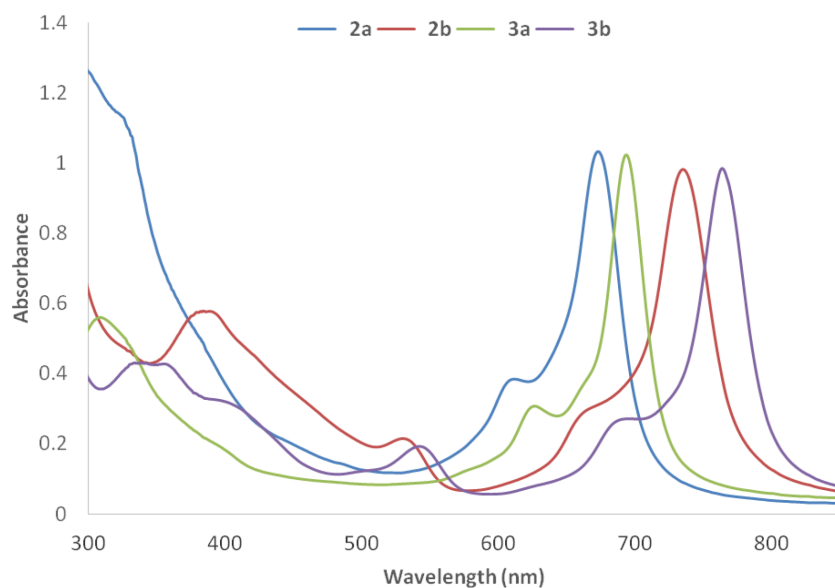


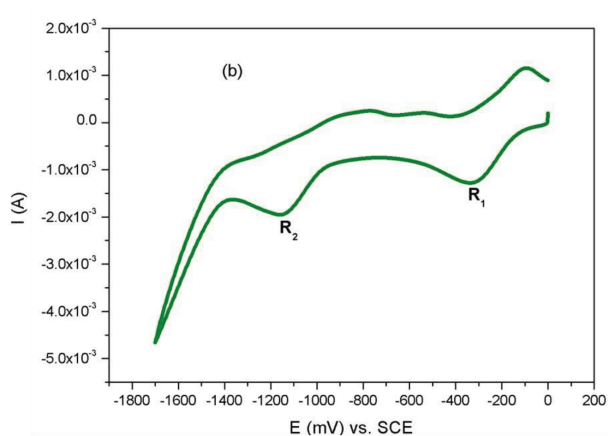
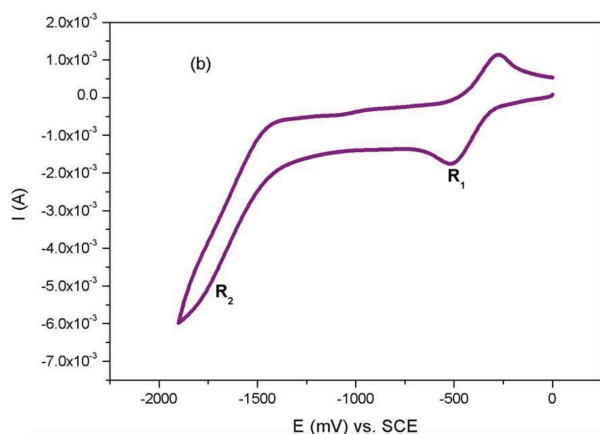
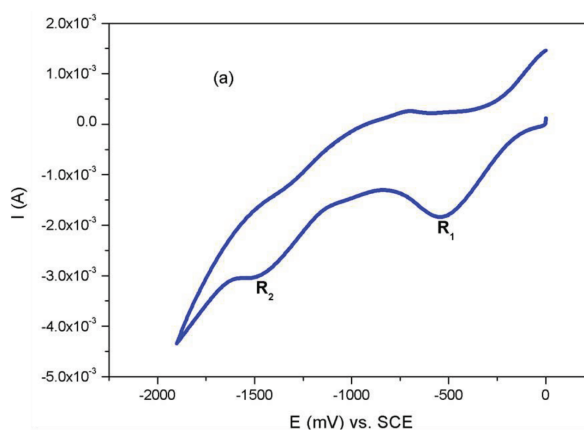
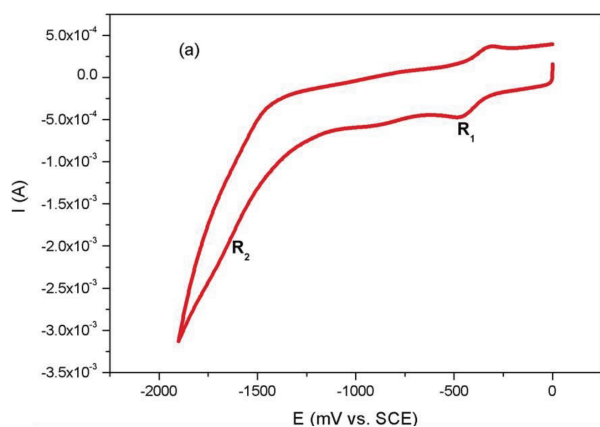
Figure 3. UV-Vis spectra of **2a**, **2b**, **3a**, **3b** in CHCl_3 . (Concentration: 1.00×10^{-5} M)

ganese(III) chloride phthalocyanines (**2b** and **3b**) during repetitive CV cycles. When Figure 7a is examined, the onset oxidation potential of peripheral tetra-(3-morpholin-4-ylpropoxy) group substituted manganese(III) chloride phthalocyanine **2b** at around 1.38 V is observed, whereas the onset potential of the nonperipheral

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

Pcs		Oxidations		Reductions	
		$^a E_{1/2}$	$^b \Delta E_p$ (mV)	$^a E_{1/2}$	$^b \Delta E_p$ (mV)
2a	$^a E_{1/2}$	1.32 ^c	-	-0.39	-1.54
	$^b \Delta E_p$ (mV)	-	-	113	140
2b	$^a E_{1/2}$	1.38 ^c	-	-0.25	-1.29
	$^b \Delta E_p$ (mV)	-	-	175	166
3a	$^a E_{1/2}$	1.36 ^c	-	-0.40	-1.57
	$^b \Delta E_p$ (mV)	-	-	96	131
3b	$^a E_{1/2}$	1.33 ^c	-	-0.21	-1.09
	$^b \Delta E_p$ (mV)	-	-	122	151

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

**Figure 4.** (a) CV graph of **2a**. (b) CV graph of **3a**.**Figure 5.** (a) CV graph of **2b**. (b) CV graph of **3b**.

tetra-(3-morpholin-4-ylpropoxy) group substituted manganese(III) chloride phthalocyanine **3b** has been determined at around 1.33 V (Figure 7b). Similar to **2a** and **3a**, peripheral, nonperipheral tetra-(3-morpholin-4-ylpropoxy) group substituted manganese(III) chloride phthalocyanines (**2b** and **3b**) show the electropolymerization process. Morpholine derivatives generally polymerize during the oxidation reaction. For example,

cobalt, titanium, manganese phthalocyanines bearing [(5-[(1E)-(4-morpholin-4-ylphenyl)methylene]amino)-1-naphthyl]oxy] substituent was electropolymerized on GCE [20]. When compared with [(5-[(1E)-(4-morpholin-4-ylphenyl)methylene]amino)-1-naphthyl]oxy cobalt, titanium, manganese phthalocyanines, redox processes of the studied phthalocyanines in present work, are generally compatible with a small potential difference. Because of the electropolymerization properties, peripheral, nonperipheral tetra-(3-morpholin-4-ylpropoxy) group substituted cobalt(II), manganese(III), phthalocyanines (**2a**, **2b**, **3a**, **3b**) may be a good nominee in electrochemical fields such as electrocatalysts, electrochromic applications.

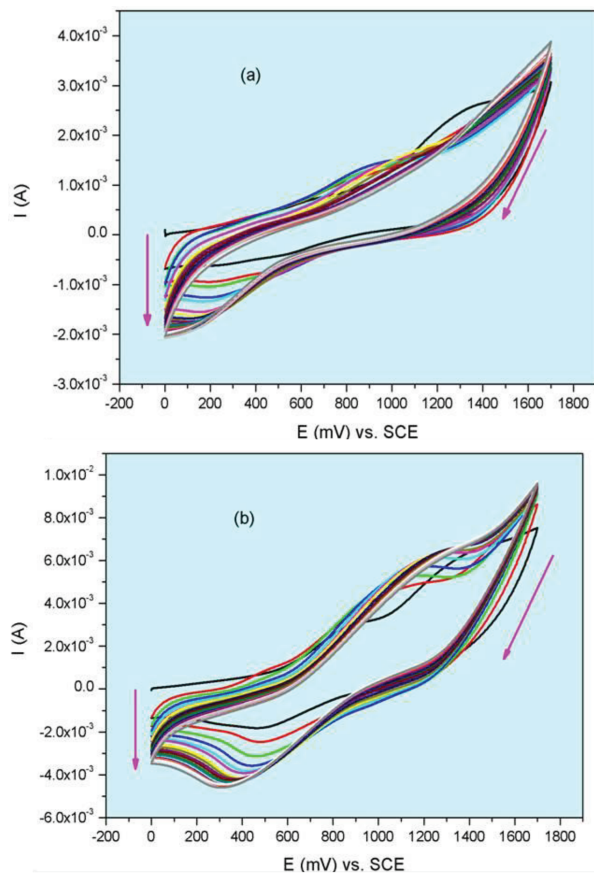


Figure 6. (a) Repetitive CVs of **2a**. (b) Repetitive CVs of **3a**.

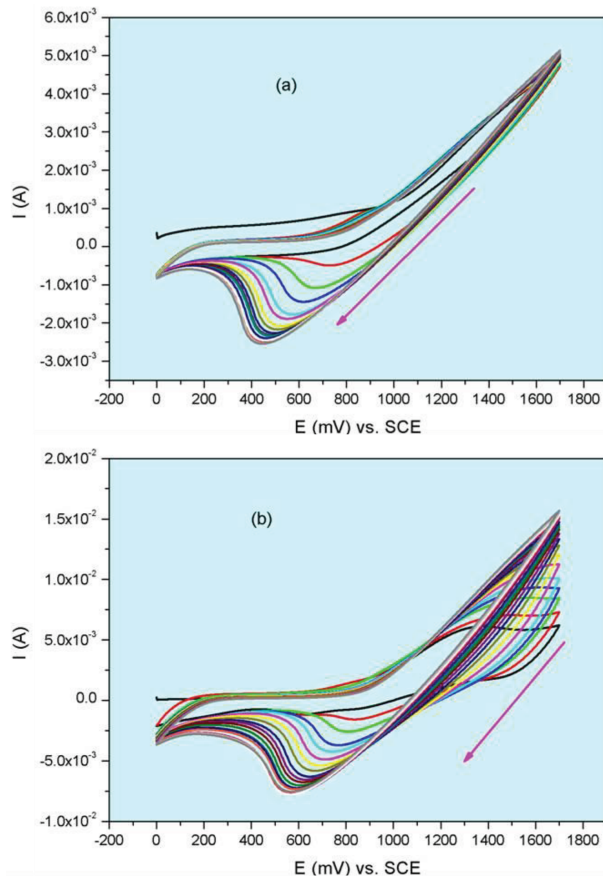


Figure 7. (a) Repetitive CVs of **2b**. (b) Repetitive CVs of **3b**.

Conclusion

As a conclusion, synthesis and electrochemistry of Co(II)Pc and Mn(III)Pcs containing (3-morpholin-4-ylpropoxy) groups at peripheral and nonperipheral positions have been presented in this study. Cyclic voltammetry was used in order to determine electrochemistry of Co(II)Pc and Mn(III)Pcs containing (3-morpholin-4-ylpropoxy) groups at peripheral and nonperipheral positions. According to the electrochemical results, Co(II)Pc and Mn(III)Pcs gave common reduction reactions. On the other hand, Co(II)Pc and Mn(III)Pcs containing (3-morpholin-4-ylpropoxy) groups at peripheral and nonperipheral positions were plated on Pt electrodes with the oxidation for polymerizable morpholino groups. Electropolymerization renders phthalocyanine, a valuable ma-

terial for the production of different electrochemical applications, for example electrocatalytic, electrochromic, and electro-sensing applications.

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