

## 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- $\pi$  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

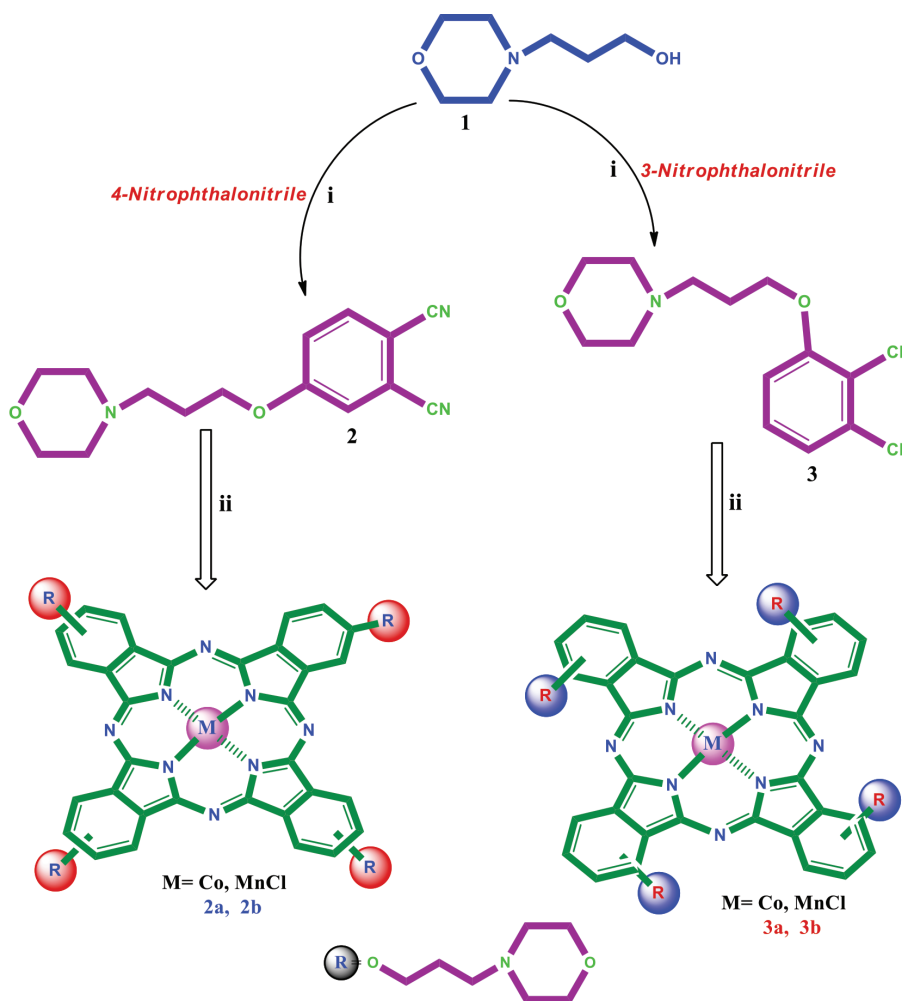
### 3.1. Synthesis and characterization

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  $\delta$  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,  $\text{K}_2\text{CO}_3$ , 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 manganese(III) chlo-

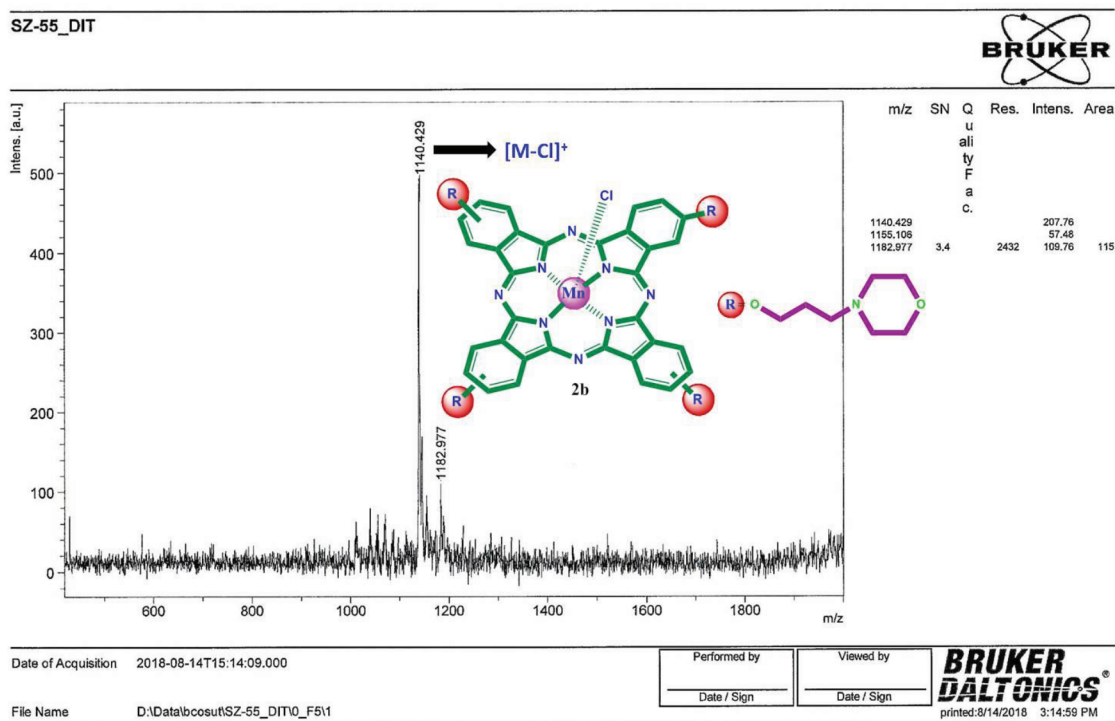


Figure 2. MALDI-TOF MS spectrum of **2b**.

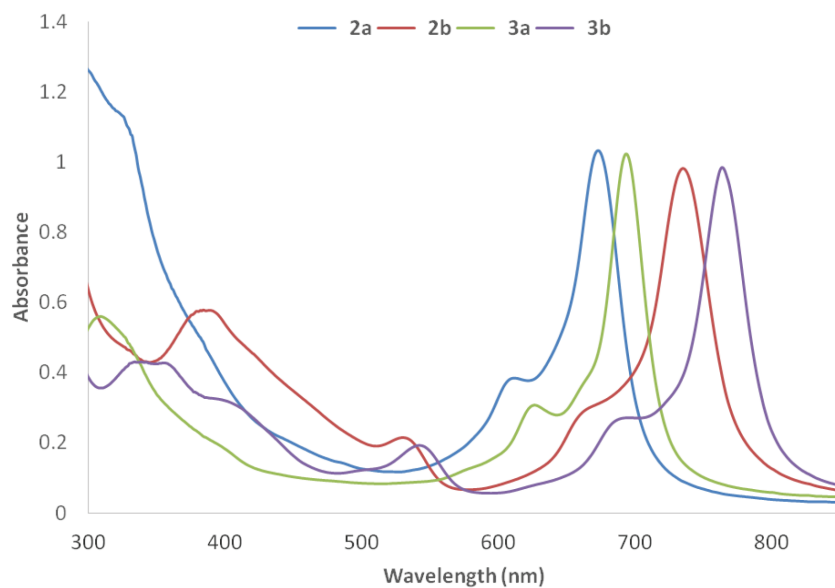


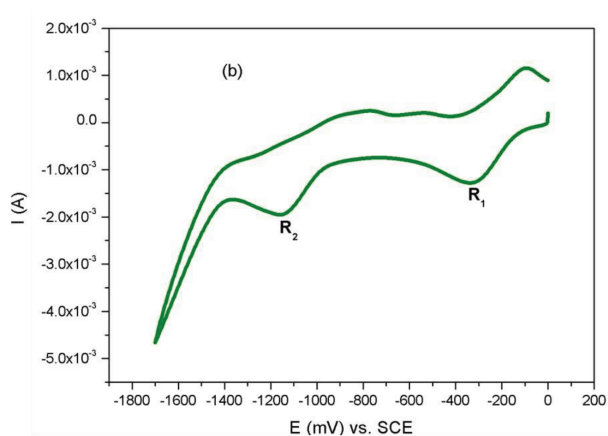
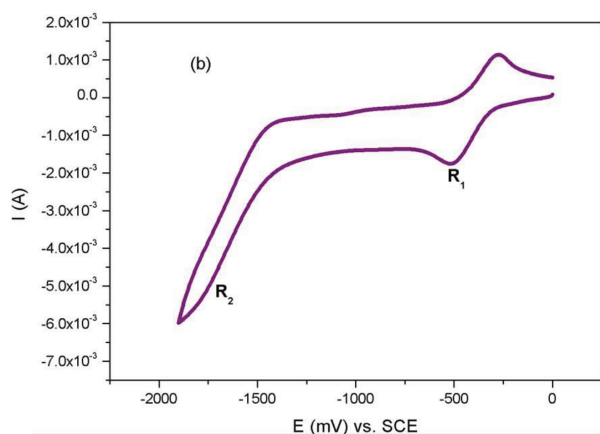
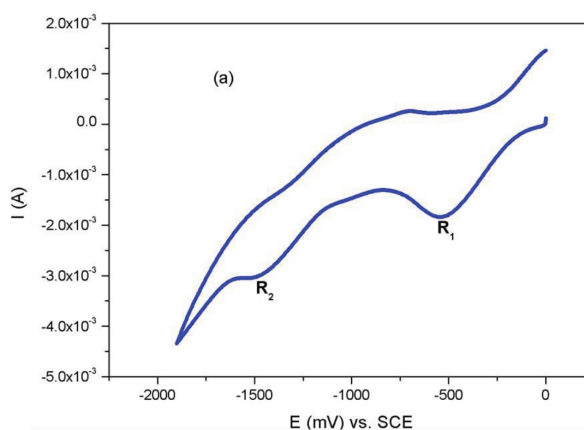
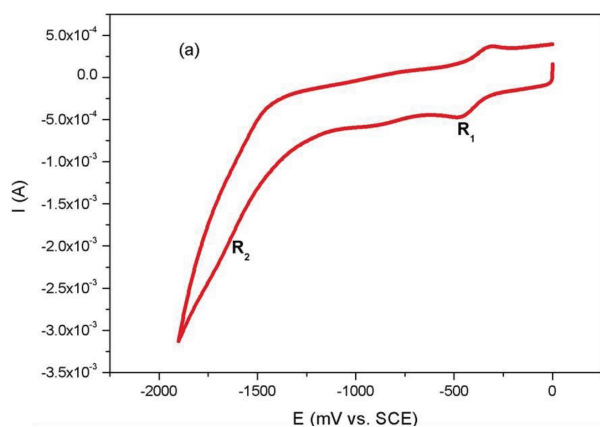
Figure 3. UV-Vis spectra of **2a**, **2b**, **3a**, **3b** in  $\text{CHCl}_3$ . (Concentration:  $1.00 \times 10^{-5}$  M)

ride 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 tetra-(3-morpholin-4-

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

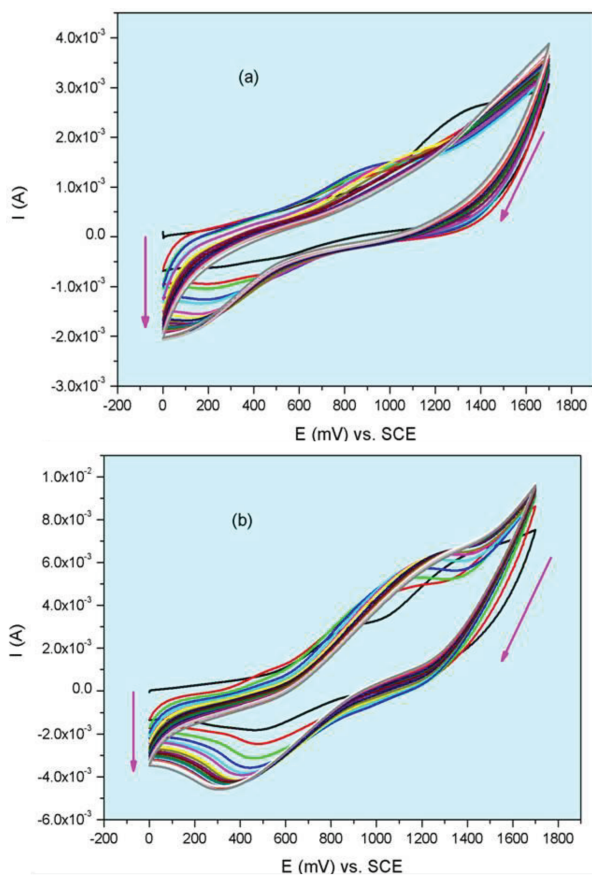
Pcs		Oxidations	Reductions	
	<b>2a</b>	<sup>a</sup> $E_{1/2}$	1.32 <sup>c</sup>	-0.39
	<sup>b</sup> $\Delta E_p$ (mV)	-	113	140
<b>2b</b>	<sup>a</sup> $E_{1/2}$	1.38 <sup>c</sup>	-0.25	-1.29
	<sup>b</sup> $\Delta E_p$ (mV)	-	175	166
<b>3a</b>	<sup>a</sup> $E_{1/2}$	1.36 <sup>c</sup>	-0.40	-1.57
	<sup>b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

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

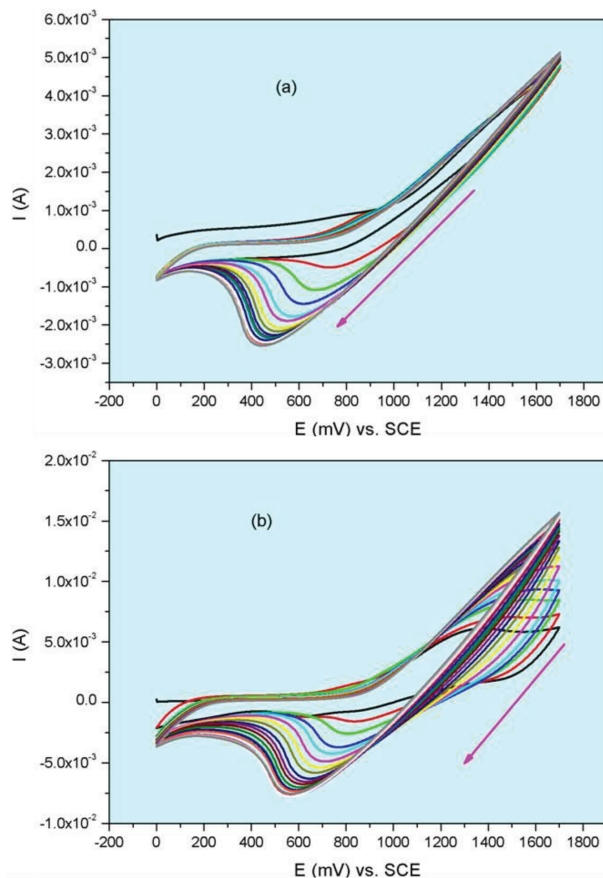
**Figure 4.** (a) CV graph of **2a**. (b) CV graph of **3a**.**Figure 5.** (a) CV graph of **2b**. (b) CV graph of **3b**.

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 electroensing applications.

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