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

Zekeriya BIYIKLIOĞLU*, Hüseyin BAŞ
Department of Chemistry, Karadeniz Technical University, Trabzon, Turkey

Received: 24.01.2020 • Accepted/Published Online: 27.03.2020 • Final Version: 01.06.2020

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.

*Correspondence: zekeriya@ktu.edu.tr

This work is licensed under a Creative Commons Attribution 4.0 International License.
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$_2$CO$_3$ 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≡N groups at 2230 (for 2), 2228 (for 3) cm$^{-1}$ occurred at expected frequencies, respectively. In the 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 13C-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]$^+$.

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 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 π→π* 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$^{-2}$] because of the redox active manganese metal ion [27]. Then second reduction
can be assigned to [Mn$^{II}$Pc$^{-2}$] / [Mn$^{I}$Pc$^{-2}$]$^{-1}$ couple [28]. After first reduction, [Cl-Mn$^{II}$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$_2$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 man-
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 |
|-----|------------|------------|
| 2a  | $aE_{1/2}$ 1.32$^c$ | -0.39 -1.54 |
|     | $b\Delta E_p$ (mV) - | 113 140 |
| 2b  | $aE_{1/2}$ 1.38$^c$ | -0.25 -1.29 |
|     | $b\Delta E_p$ (mV) - | 175 166 |
| 3a  | $aE_{1/2}$ 1.36$^c$ | -0.40 -1.57 |
|     | $b\Delta E_p$ (mV) - | 96 131 |
| 3b  | $aE_{1/2}$ 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 \( (5-\{(1E)-(4\text{-morpholin-4-ylphenyl})\text{methylene}\text{amino}\}-1\text{-naphthyl})\text{oxy} \) substituent was electropolymerized on GCE [20]. When compared with \( (5-\{(1E)-(4\text{-morpholin-4-ylphenyl})\text{methylene}\text{amino}\}-1\text{-naphthyl})\text{oxy} \) 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 electroosensing applications.

Acknowledgements
This work was supported by the Scientific Research Projects Coordination Unit of Karadeniz Technical University (project number: 7656).

References
1. Yıldırım Ö, Sevim AM, Gül A. Novel water-soluble metallophthalocyanines supported on cotton fabric. Coloration Technology 2012; 128: 236-243.
2. Olgaç R, Sogancı T, Baygu Y, Gök Y, Ak M. Zinc(II) phthalocyanine fused in peripheral positions octa-substituted with alkyl linked carbazole: Synthesis, electropolymerization and its electro-optic and biosensor applications. Biosensors Bioelectronics 2017; 98: 202-209.
3. Guillaud G, Simon J, Germain JP. Metallophthalocyanines: Gas sensors, resistors and field effect transistors. Coordination Chemistry Reviews 1998; 178-180: 1433-1484.
4. Amintha GS, Ameen MY, Reddy VS, Vasudevan S. Synthesis of peripherally tetra substituted neutral azophenoxy zinc phthalocyanine and its application in bulk hetero junction solar cells. Journal of Molecular Structure 2019; 1185: 425-431.
5. Yıldız B, Güzel E, Menges N, Şişman İ, Şener MK. Pyrazole-3-carboxylic acid as a new anchoring group for phthalocyanine-sensitized solar cells. Solar Energy 2018; 174: 527-536.
6. Platonova YB, Volov AN, Tomilova LG. Palladium(II) octaalkoxy- and octaphenoxyphthalocyanines: Synthesis and evaluation as catalysts in the Sonogashira reaction. Journal of Catalysis 2019; 373: 222-227.
7. Bıyıklıoğlu Z, Arslan T, Alawainati FA, Manaa H, Jaffar A et al. Comparative nonlinear optics and optical limiting properties of metallophthalocyanines. Inorganica Chimica Acta 2019; 486: 345-351.
8. Kawano SI, Yamada Y, Rongfang S, Ishihara Y, Tanaka K. Liquid-crystalline phthalocyanine with short inter-columnar distance and variation of the liquid crystallinity induced by square-planar metal ions. Chemistry Letters 2018; 47: 1262-1264.
9. Kamiloğlu AA, Acar İ, Bıyıklıoğlu Z, Saka ET. Peripherally tetra-{2-(2,3,5,6-tetrafluorophenoxy)ethoxy}substituted cobalt(II), iron(II) metallophthalocyanines: Synthesis and their electrochemical, catalytic activity studies. Journal of Organometallic Chemistry 2017; 828: 58-67.
10. Bıyıklıoğlu Z, Saka ET, Gökçe S, Kantekin H. Synthesis, characterization and investigation of homogeneous oxidation activities of peripherally tetra-substituted Co(II) and Fe(II) phthalocyanines: Oxidation of cyclohexene. Journal of Molecular Catalysis A Chemical 2013; 378: 156-163.
11. Mohammed I, Oluwole DO, Nemakal M, Sanmegwoda LK, Nyokong T. Investigation of novel substituted zinc and aluminium phthalocyanines for photodynamic therapy of epithelial breast cancer. Dyes and Pigments 2019; 170: 107592-107592.
12. Günesel A, Güzel E, Bilgiçi AT, Atmaca GY, Erdoğmuş A et al. Synthesis and investigation of photophysicochemical properties of novel ketone-substituted gallium (III) and indium (III) phthalocyanines with high singlet oxygen yield for photodynamic therapy. Journal of Luminescence 2017; 192: 888-892.
13. Shumba M, Nyokong Y. Electrocatalytic activity of nanocomposites of sulphur doped graphene oxide and nanosized cobalt phthalocyanines. Electroanalysis 2016; 28: 3009-3018.
14. Ipek Y, Dinger H, Koca A. Electrode modification based on "click electrochemistry" between terminal-alkynyl substituted cobalt phthalocyanine and 4-azidoaniline. Sensors and Actuators B Chemical 2014; 193: 830-837.
15. Nemakal M, Aralekkul S, Mohammed I, Swamy S, Sannegowda LK. Electropolymerized octabenzenimidazole phthalocyanine as an amperometric sensor for hydrazine. Journal of Electroanalytical Chemistry 2019; 839: 238-246.

16. Kobak RZU, Akyüz D, Koca A. Substituent effects to the electrochromic behaviors of electropolymerized metallophthalocyanine thin films. Journal of Solid State Electrochemistry 2016; 20: 1311-1321.

17. Zielinska A, Takai A, Sakurai H, Saeki A, Leonowicz M et al. Spin-active, electrochromic, solvent-free molecular liquid based on double-decker lutetium phthalocyanine bearing long branched alkyl chains. Chemistry: An Asian Journal 2018; 13: 770-774.

18. Ballarin B, Gazzano M, Cisneros JL, Tonelli D, Seeber R. Electro catalytic activity of cobalt phthalocyanine stabilized by different matrixes. Analytical and Bioanalytical Chemistry 2002; 374: 891-897.

19. Çakır V, Kantekin H, Bıyıklıoğlu Z, Koca A. Synthesis, electrochemistry, spectroelectrochemistry and electropolymerization of metal-free and metallophthalocyanines. Polyhedron 2014; 81: 525-533.

20. Keleş T, Akyüz D, Bıyıklıoğlu Z, Koca A. Electropolymerization of metallophthalocyanines carrying redox active metal centers and their electrochemical pesticide sensing application. Electroanalysis 2017; 29: 2125-2137.

21. Sehlotho N, Durmuş M, Ahsen V, Nyokong T. The synthesis and electrochemical behaviour of water soluble manganese phthalocyanines: Anion radical versus Mn(II) species. Inorganic Chemistry Communications 2008; 11: 479-483.

22. Tuncer S, Kaya K, Özşe neci İ, Burat AK. Non-peripherally tetrasubstituted phthalocyanines: Synthesis, characterization and, photophysical investigation. Journal of Organometallic Chemistry 2017; 827: 78-85.

23. Zheng BY, Ke MR, Lan WL, Hou L, Guo J et al. Mono- and tetra-substituted zinc(II) phthalocyanines containing-morpholinyl moieties: Synthesis, antifungal photodynamic activities, and structure-activity relationships. European Journal of Medicinal Chemistry 2016; 114: 380-389.

24. Keleş T, Bıyıklıoğlu Z, Gültekin E, Bekircan O. Synthesis and electrochemical properties of peripheral, non-peripheral tetra [2-(3,5-diphenyl-1H-1,2,4-triazol-1-yl)ethoxy] substituted cobalt(II), manganese(III) phthalocyanines. Inorganica Chimica Acta 2019; 487: 201-207.

25. Akinbulu IA, Nyokong T. The effects of point of substitution on the electrochemical behavior of new manganese phthalocyanines, tetra-substituted with diethylaminoethanethiol. Inorganica Chimica Acta 2010; 363: 3229-3237.

26. Çakır D, Arslan T, Bıyıklıoğlu Z. An effect of the substituent position and metal type on the electropolymerization properties of chalcone substituted metallophthalocyanines. Dalton Transactions 2015; 44: 20859-20866.

27. Nas A, Bıyıklıoğlu Z, Fandakhi S, Sarki G, Yalazan H et al. Tetra(3-(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)phenoxy) substituted cobalt, iron and manganese phthalocyanines: Synthesis and electrochemical analysis. Inorganica Chimica Acta 2017; 466: 86-92.

28. Orman EB, Altun S, Odabaş Z, Altündal A, Özkaya AR. Electrochemical, electrocatalytic dioxygen reducing and dielectric relaxation properties of non-peripheral tetra-2,3-dihydro-1H-inden-5-yl-oxy substituted phthalocyanines. Journal of the Electrochemical Society 2015; 162: H825-H840.

29. Demirbaş Ü, Akyüz D, Bayrak R, Barut B, Koca A et al. Synthesis, characterization and investigation of electrochemical and spectroelectrochemical properties of peripherally and non-peripherally tetra 2-methyl-5-benzothiazole substituted nickel(II), copper(II) and cobalt(II) phthalocyanines. Synthetic Metals 2017; 231: 112-119.

30. Çakır D, Bekircan O, Bıyıklıoğlu Z. 1,2,4-Triazole-substituted metallophthalocyanines carrying redox active cobalt(II), manganese(III), titanium(IV) center and their electrochemical studies. Synthetic Metals 2015; 201: 18-24.