

Synthesis and electrochemical properties of copper(II), manganese(III) phthalocyanines bearing chalcone groups at peripheral or nonperipheral positions

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Abstract: In this study, new chalcone compound **1**, new phthalonitrile derivatives **2** and **3**, new copper(II), manganese(III) phthalocyanines bearing chalcone groups at peripheral or nonperipheral positions were synthesized. Electrochemistry of tetra-(4-((2*E*)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy) substituted Co(II)Pc and Mn(III)Pcs were studied with cyclic voltammetry (CV) to determine the redox properties of the phthalocyanines. According to the results, while the CuPcs **2a** and **3a** showed two Pc based reduction reactions and one Pc based oxidation reaction, MnPcs **2b** and **3b** gave two metal-based reduction reactions. All the redox processes are shifted toward positive potentials as a result of the increased electron-withdrawing ability of the trifluoromethyl substituents.

Key words: Synthesis, peripheral, nonperipheral, copper, manganese, voltammetry

1. Introduction

Since phthalocyanines (Pcs) have chemical, thermal stability and an 18 π electron system, they have been very important derivatives for researchers [1]. In addition to their usage as paint, phthalocyanines are preferred as functional materials in different technologies, such as electrochemical sensors [2,3], solar cells [4,5], gas sensors [6,7], nonlinear optics [8], semiconductors [9,10], liquid crystals [11,12], photovoltaics [13], catalysts [14], electrochromics [15,16], and photosensitizers in photodynamic therapy (PDT) [17–19].

Electrochemical properties of phthalocyanines depend on several factors, such as the type of the central metal ions, substituents, and solvent [20,21]. Owing to these properties, phthalocyanines have been used in different electrochemical technologies. Chalcones are the common core scaffolds of many naturally occurring compounds, from ferns to higher plants [22]. Their skeleton structure and functional groups also make them well-known intermediates for the synthesis of various heterocyclic and bioactive compounds [23]. In literature it is shown that the introduction of chalcone groups into the peripheral/nonperipheral positions of phthalocyanines increases the electrochemical properties of phthalocyanines [24–28]. Also, phthalocyanines bearing chalcone groups have efficient photocatalytic, photophysical, and photochemical properties [29,30]. We wondered how the presence of phthalocyanines in the peripheral or nonperipheral positions of the chalcone group affects the electrochemical properties of phthalocyanine compounds. For this reason, in this work we combined these two functional compounds (chalcone and phthalocyanine) into a single compound. Finally, we synthesized copper(II), manganese(III) phthalocyanines bearing (4-((2*E*)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy) groups at peripheral or nonperipheral positions and investigated their electrochemical properties.

2. Experimental

Materials, equipment, synthesis procedure, and electrochemistry experiments are given in the supplementary information.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of Pcs is given in Figure 1. Firstly, new chalcone compound (**1**) was obtained with the reaction between 2-fluoro-4-(trifluoromethyl)benzaldehyde and 4'-hydroxyacetophenone in alkaline conditions according to the known procedure of Claisen-Schmidt condensation [31]. Then, new phthalonitrile derivatives **2** and **3** were prepared with the

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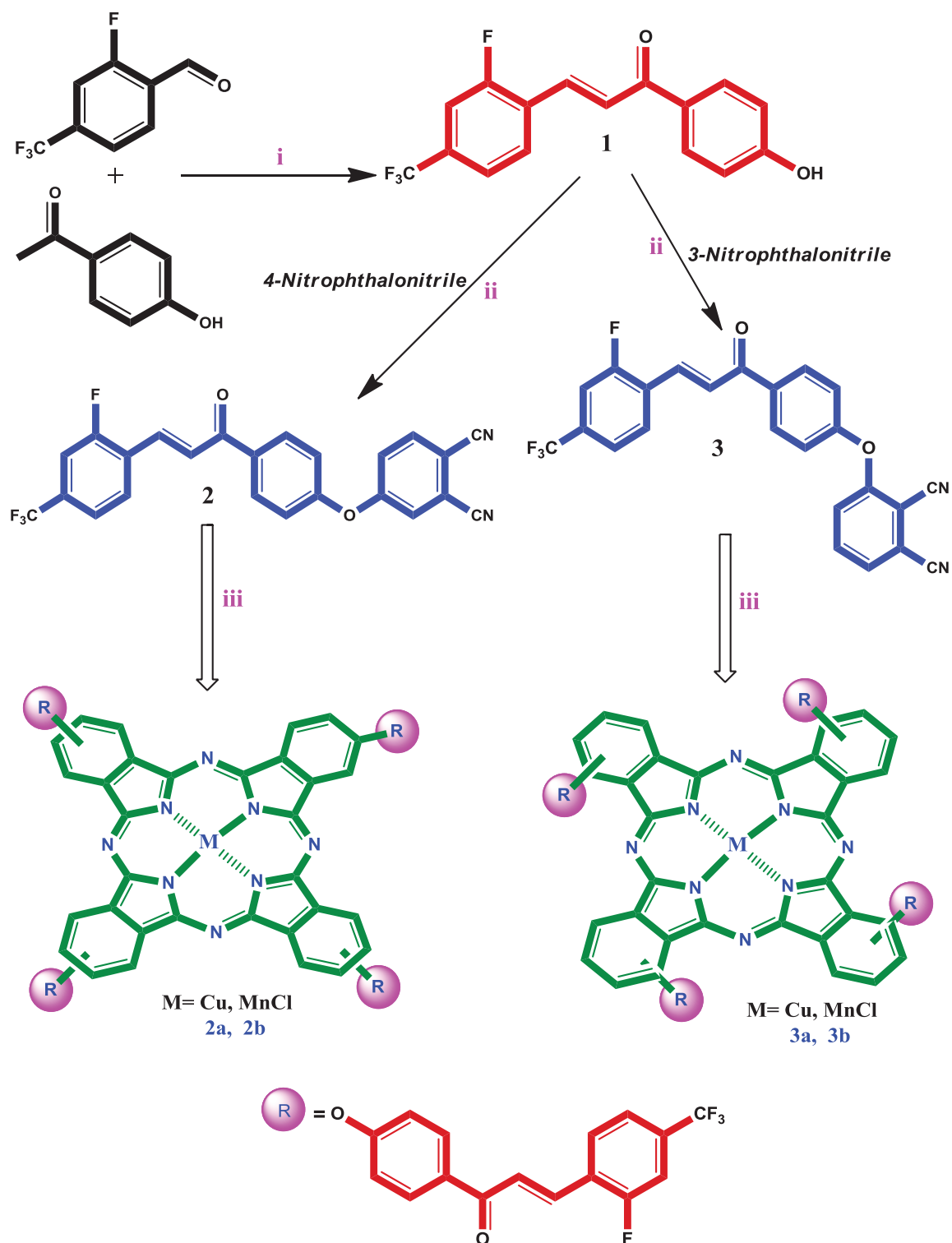


Figure 1. The synthesis of Cu(II)Pc and Mn(III)Pcs bearing 4-{(2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyloxy} groups. (i) NaOH, rt. (ii) DME, K_2CO_3 , 50 °C, 72 h. (iii) n-pentanol, DBU, 160 °C.

reaction between chalcone compound (1) and 4-nitro- and 3-nitrophthalonitrile, respectively. Then, new peripheral and nonperipheral tetra substituted Cu(II) and Mn(III) Pc derivatives were synthesized with the reaction of corresponding nitril derivatives (2 and 3) and metal salt presence of DBU in 1-pentanol. Infrared spectra of compound 1 exhibited

characteristic absorption bands of aliphatic C=C, C=O, and -OH groups at 1564 cm^{-1} , 1653 cm^{-1} , and 3328 cm^{-1} , respectively. The most important evidence observed in the $^1\text{H-NMR}$ spectrum of the formation of the chalcone compound is the peaks of the α,β -unsaturated moiety. It was most clear with the vicinal coupling constant values ($^3J_{\text{H}\alpha\text{-H}\beta} = 16.0/16.0$ Hz), that the configuration of these two protons was *trans*. Moreover, in the $^{13}\text{C-NMR}$, C-F coupling of aromatic and aliphatic carbons containing fluoro atoms doublets and multiplets peaks in the region of 163.1–108.2 ppm were formed. LC-MS/MS spectrum showed $m/z = 311$ $[\text{M}+\text{H}]^+$ as a molecular ion peak. In the IR spectra of phthalonitrile compound (**2**), and phthalonitrile compound (**3**) the vibrations belonging to C=N groups were observed at 2234, and 2230 cm^{-1} , respectively. In the $^1\text{H-NMR}$ spectrum (**2** and **3**), the new aromatic protons demonstrated that phthalonitriles (**2** and **3**) were prepared. The $m/z = 437$ $[\text{M}+\text{H}]^+$ mass peaks confirmed the structure of compounds (**2** and **3**). In the IR spectra of **2a**, **2b**, **3a**, and **3b**, sharp -C \equiv N vibrations of phthalonitrile compound (**2**), and phthalonitrile compound (**3**) disappeared as expected. Also, the IR spectra of the cobalt(II), manganese(III) Pcs (**2a**, **2b**, **3a**, and **3b**) were very similar. The $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ spectra of **2a**, **2b**, **3a**, and **3b** could not be measured due to the paramagnetic nature [32]. In MALDI-TOF MS spectra of **2a**, **2b**, **3a**, and **3b**, the presence of molecular ion peaks at $m/z = 1808.67$ $[\text{M}]^+$ for **2a**, 1800.69 $[\text{M-Cl}]^+$ for **2b**, 1808.04 $[\text{M}]^+$ for **3a**, and 1800.78 $[\text{M-Cl}]^+$ for **3b**, confirmed the structures. On the UV-Vis spectra of peripheral or nonperipheral tetra-chalcone substituted cobalt(II), manganese(III) Pcs (**2a**, **2b**, **3a**, and **3b**), the Q bands were observed as single and narrow bands at $\sim 1 \times 10^{-5}$ M (Figure 2). The absorption spectra of **2a**, **2b**, **3a**, and **3b** displayed Q bands at 674, 720, 690, and 741 nm. The B (Soret) bands of **2a**, **2b**, **3a**, and **3b** were observed at 337, 385, 329, and 330 nm. Furthermore, manganese(III) Pcs (**2b**, **3b**) have an absorption band at 497 nm for **2b** and 508 nm for **3b**, interpreted as a charge transfer absorption [33].

3.2. Electrochemical studies

Voltammetric responses of Pcs bearing (4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enyl}phenoxy) groups were carried out with CV in DCM/TBAP electrolyte on a Pt working electrode. The basic electrochemical data were tabulated in Table 1. Tetra-chalcone substituted copper(II) Pcs (**2a**, **3a**) bearing trifluoromethyl groups have redox inactive metal centers. Increasing the electron-withdrawing ability of the substituents generally causes a positive shift of the redox processes [34]. For this reason, **2a** and **3a** showed only Pc oriented electron transfer reactions. But, tetra-chalcone substituted manganese(III) Pcs (**2b**, **3b**) have redox active metal centers. For this reason, **2b** and **3b** showed metal based processes before the Pc processes. As shown in Figures 3a and 3b, tetra-chalcone substituted copper(II) Pcs (**2a**, **3a**) showed two reversible (for **2a**), two quasi-reversible (for **3a**) Pc based reductions at -0.82 V (R_1 for **2a**), -0.85 V (R_1 for **3a**) for $[\text{Cu}^{\text{II}}\text{Pc}^{2-}]/[\text{Cu}^{\text{II}}\text{Pc}^{3-}]^{1-}$, -1.16 V (R_2 for **2a**), -1.20 V (R_2 for **3a**) for $[\text{Cu}^{\text{II}}\text{Pc}^{3-}]^{1-}/[\text{Cu}^{\text{II}}\text{Pc}^{4-}]^{2-}$ processes and one oxidation at 0.93 V (O_1 for **2a**), 0.88 V (O_1 for **3a**) processes. These electrochemical responses of tetra-chalcone substituted copper(II) Pcs (**2a**, **3a**) are compatible with the literature [35]. Tetra-chalcone substituted manganese(III) Pcs (**2b**, **3b**) showed two metal-based reduction reactions and one oxidation reaction. As shown in Figures 4a and 4b, R_1 and R_2 processes at -0.17 V (for **2b**), -0.15 V (for **3b**), -0.94 V (for **2b**), and -0.96 V (for **3b**) are assigned to $[\text{Mn}^{\text{III}}\text{Pc}^{2-}]/[\text{Mn}^{\text{II}}\text{Pc}^{2-}]^{1-}$ and $[\text{Mn}^{\text{II}}\text{Pc}^{2-}]^{1-}/[\text{Mn}^{\text{I}}\text{Pc}^{2-}]^{2-}$

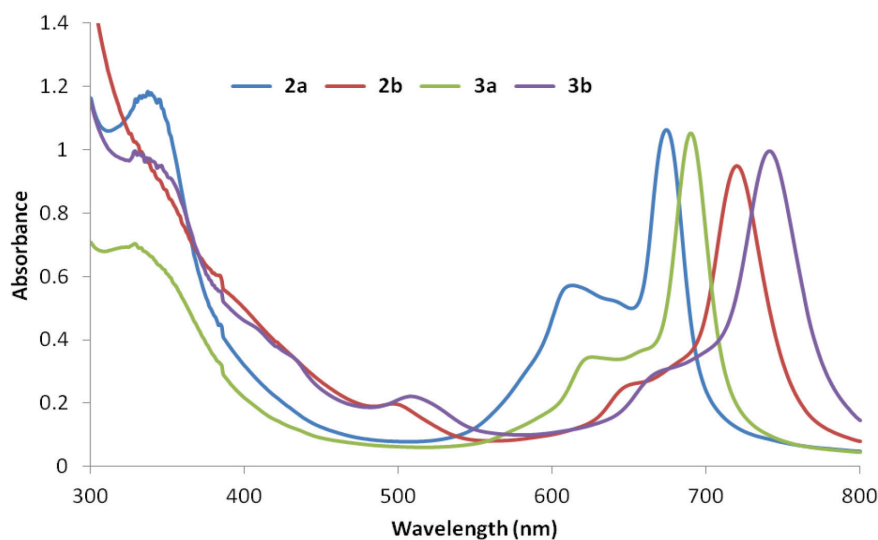
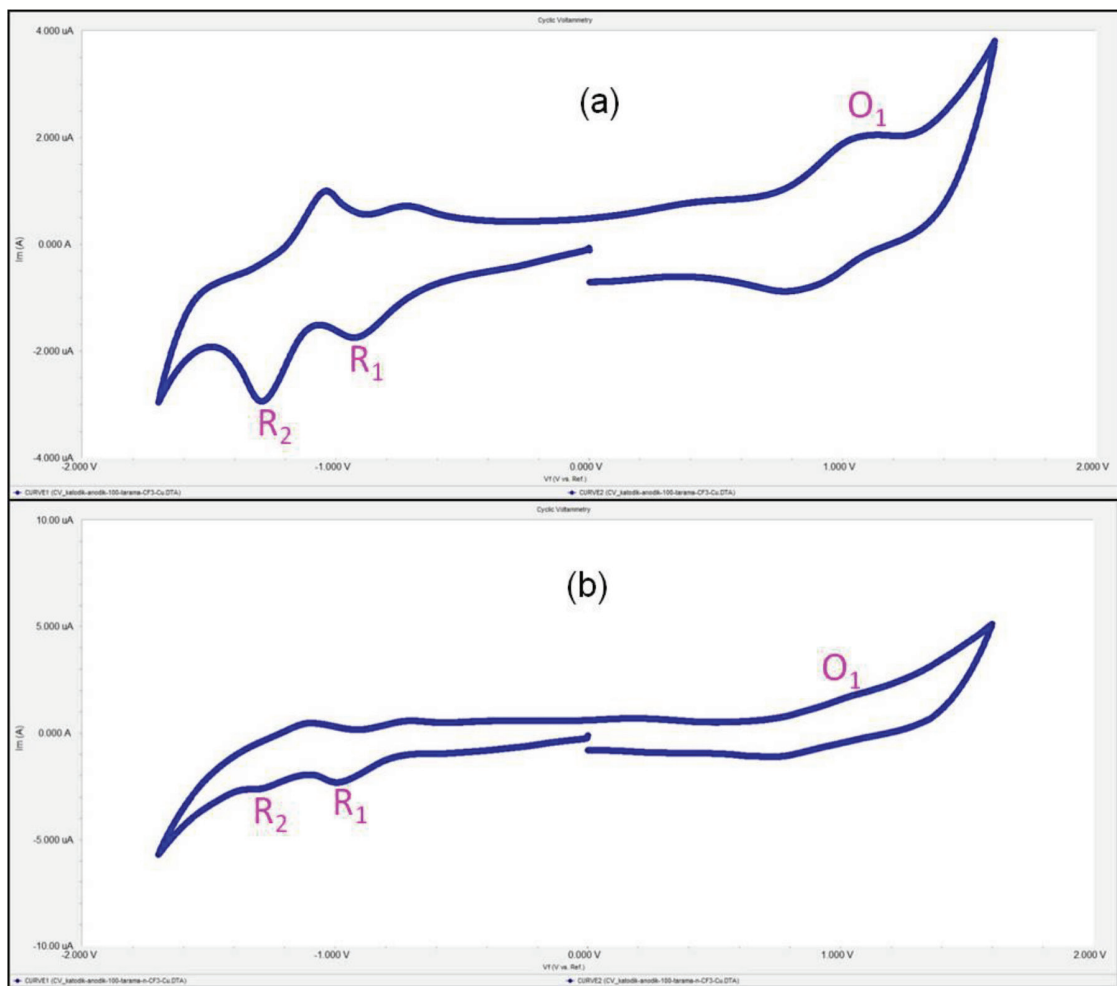


Figure 2. UV-Vis spectra of **2a**, **2b**, **3a**, and **3b** in THF. (Concentration: 1.00×10^{-5} M)

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

Pcs	Label	^a $E_{1/2}$	^b ΔE_p (mV)	^c $DE_{1/2}$
2a	R ₁	-0.82	98	1.75
	R ₂	-1.16	84	
	O ₁	0.93	88	
2b	R ₁	-0.17	134	1.33
	R ₂	-0.94	138	
	O ₁	1.16	140	
3a	R ₁	-0.85	123	1.73
	R ₂	-1.20	135	
	O ₁	0.88	140	
3b	R ₁	-0.15	138	1.28
	R ₂	-0.96	144	
	O ₁	1.13	140	

^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: $DE_{1/2} = E_{1/2}$ (first oxidation) - $E_{1/2}$ (first reduction).

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

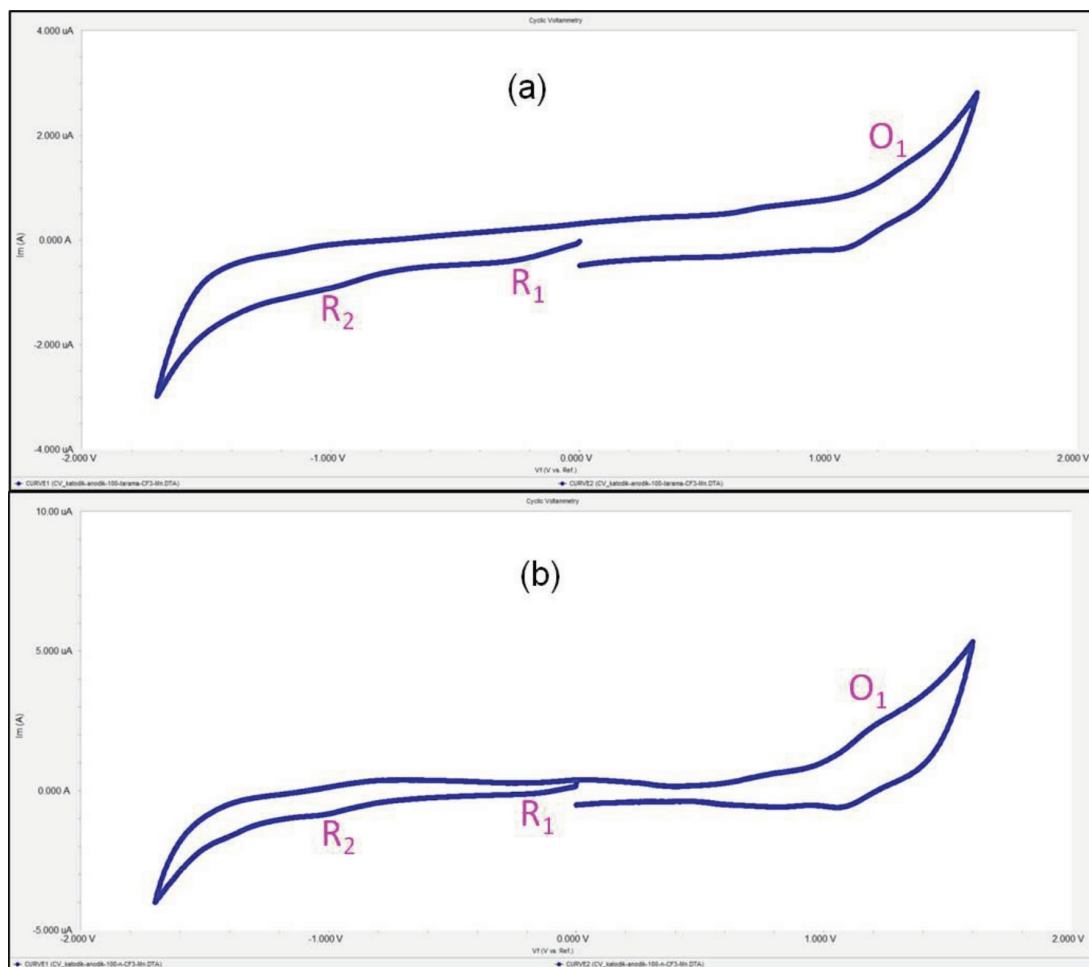


Figure 4. (a) CV graph of **2b**, (b) CV graph of **3b**.

respectively. Also, during the anodic potential scans, a quasi-reversible Pc oxidation reaction appeared at 1.16 V (for **2b**) and 1.13 V (for **3b**), for $[\text{Mn}^{\text{III}}\text{Pc}^{2-}]/[\text{Mn}^{\text{III}}\text{Pc}^{1-}]^{+}$ couple. These results are in agreement with the literature [36]. Moreover, as shown in Table 1, all the redox processes are shifted toward positive potentials as a result of the increased electron-withdrawing ability of the trifluoromethyl substituents with respect to MnPc bearing (2-{2-[4-(1H-pyrrol-1-yl)phenoxy]ethoxy}ethoxy) groups [37], and CuPc bearing 2-(9,10-dioxo-9,10-dihydro-anthracen-2-yl-methyl)-malonic acid diethyl ester [38], synthesized in previous studies. When we compared the results, it is clear that binding the trifluoromethyl substituents to the peripheral or nonperipheral positions causes shifting of the peak potentials to the positive sides.

4. Conclusion

In this paper, copper(II), manganese(III) Pcs bearing chalcone groups at peripheral or nonperipheral positions were successfully synthesized. The solubility of Pcs in organic solvents was increased by substitution of chalcone group to the peripheral or nonperipheral position of Pcs. Cyclic voltammetry was used to detect redox responses of Cu(II)Pcs and Mn(III)Pcs. Electrochemical measurements supported the suggested compounds. All Cu(II)Pcs and Mn(III)Pcs showed two reduction reactions during the cathodic potential scans. Results show that Mn(III)Pcs showed more redox activity than those of Cu(II)Pcs. The results demonstrated the usability of these Cu(II)Pcs and Mn(III)Pcs as functional materials owing to their rich redox responses. On the other hand, electrochemical measurements indicated that copper(II), manganese(III) Pcs bearing chalcone groups could be used for various electrochemical applications such as electrocatalytic, electrochromic and electroensing.

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Supplementary information

1. Materials and equipment

4'-Hydroxyacetophenone and 2-fluoro-4-(trifluoromethyl)benzaldehyde were purchased from commercial suppliers. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. The IR spectra were recorded on a Perkin Elmer 1600 FT-IR Spectrophotometer, using KBr pellets. ¹H and ¹³C-NMR spectra were recorded on Bruker Avance III 400 MHz spectrometers in DMSO-d₆ and chemical shifts were reported (δ) relative to Me₄Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. MALDI-MS of complexes were obtained in dihydroxybenzoic acid as MALDI matrix using nitrogen laser accumulating 50 laser shots (Bruker Microflex LT MALDI-TOF mass spectrometer Bremen, Germany). Optical spectra in the UV-Vis region were recorded with a Perkin Elmer Lambda 25 spectrophotometer.

2. Synthesis

2.1. (2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one (1): To a stirred solution of 4'-hydroxyacetophenone (5 mmol) in ethanol (30 mL), 5 mL alcoholic NaOH (10 mmol) solution was added dropwise at room temperature. After mixing the reaction for 30 min, 2-fluoro-4-(trifluoromethyl)benzaldehyde (5 mmol) was added to the medium in portions and the reaction mixture was stirred for 16 h. Completion of reaction was monitored by TLC and after completion it was poured into water and acidified with HCl solution (1 N) until pH = 6–6.5 [1]. The obtained solid was filtered, washed with water, and dried in the lyophilizer. The purity of product was checked by TLC and supporting structural information was obtained using spectroscopic methods. Yield: 84%. M.p.: 146--148 °C. IR (ATR), ν/cm^{-1} : 3328 (O-H), 3081 (Ar-H), 1653 (C=O), 1564 (HC=CH), 1111 (Aromatic C-F), 817 (Aliphatic C-F). ¹H NMR (400 MHz, DMSO-d₆, ppm), (δ): 10.6 (bs, 1H, -OH), 8.4 (d, 1H, Ar-H), 8.1 (AB, J=16.0 Hz, 1H, =CH), 8.0 (d, 2H, Ar-H), 7.8 (d, 1H, Ar-H), 7.7 (AB, J=16.0 Hz, 1H, =CH), 7.6 (m, 1H, Ar-H), 6.9 (d, 2H, Ar-H). ¹³C NMR (100 MHz, DMSO-d₆, ppm), (δ): 187.1, 163.1, 162.0, 159.5, 134.1, 132.6, 132.2, 132.0, 130.6, 130.5, 129.1, 129.0, 127.3, 127.1, 122.3, 122.1, 119.3, 116.0, 114.3, 114.0, 108.2. LC-MS/MS (ESI), (m/z): 311 [M+H]⁺.

2.2. 4-(4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy) phthalonitrile (2): (2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one **1** (0.8 g, 2.5 mmol) and 4-nitrophthalonitrile (0.45 g, 2.5 mmol) were dissolved in DMF (15 mL). Then, dry K₂CO₃ (1.1 g, 7.5 mmol) was added and stirred at 50 °C under N₂ atmosphere for 72 h. The mixture was cooled to room temperature and then poured into iced water (200 mL). After filtration under vacuum, the crude product was crystallized from ethanol. Yield: 0.44 g (40%), m.p. 159–160 °C. IR (ATR), ν/cm^{-1} : 3074 (Ar-H), 2921–2850 (Aliph. C-H), 2234 (C=N), 1665, 1603, 1587, 1564, 1502, 1484, 1428, 1329, 1275, 1247, 1210, 1165, 1111, 1067, 1009, 978, 854, 823, 743. ¹H NMR (400 MHz, DMSO-d₆, ppm), (δ): 8.40 (d, 1H, Ar-H), 8.31 (d, 2H, Ar-H), 8.18 (AB, 1H, =CH), 8.17 (d, 1H, Ar-H), 7.99 (d, 1H, Ar-H), 7.85 (AB, 1H, =CH), 7.84 (s, 1H, Ar-H), 7.73 (d, 1H, Ar-H), 7.60 (m, 1H, Ar-H), 7.37 (d, 2H, Ar-H). ¹³C NMR (100 MHz, DMSO-d₆, ppm), (δ): 187.96, 162.16, 159.63, 159.05, 139.91, 136.96, 134.35, 132.20, 132.12, 130.78, 130.75, 130.74, 126.98, 126.92, 124.51, 124.09, 122.30, 122.20, 120.25, 120.09, 117.39, 116.31, 115.81, 114.40, 114.11, 110.02, 109.93. LC-MS/MS (ESI), (m/z): 437 [M+H]⁺.

2.3. 3-(4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy) phthalonitrile (3): Synthesized similarly to **2** from 3-nitrophthalonitrile. Yield: 0.39 g (35%), m.p. 184–185 °C. IR (ATR), ν/cm^{-1} : 3096 (Ar-H), 2921–2851 (Aliph. C-H), 2230 (C=N), 1666, 1611, 1596, 1572, 1504, 1456, 1430, 1330, 1275, 1217, 1172, 1162, 1110, 1069, 1033, 1007, 980, 911, 830, 803, 745. ¹H NMR (400 MHz, DMSO-d₆, ppm), (δ): 8.40 (t, 1H, Ar-H), 8.32 (d, 2H, Ar-H), 8.18 (AB, 1H, =CH), 7.97 (d, 1H, Ar-H), 7.92 (d, 1H, Ar-H), 7.84 (AB, 1H, =CH), 7.83 (d, 1H, Ar-H), 7.72 (d, 1H, Ar-H), 7.54 (m, 1H, Ar-H), 7.41 (d, 2H, Ar-H). ¹³C NMR (100 MHz, DMSO-d₆, ppm), (δ): 187.91, 162.14, 159.62, 159.23, 158.77, 136.71, 134.41, 133.93, 133.89, 132.09, 130.76, 130.72, 130.31, 129.92, 126.96, 126.91, 124.38, 123.33, 122.35, 122.27, 119.81, 116.63, 16.04, 114.40, 114.10, 113.67, 113.60, 107.06. LC-MS/MS (ESI), (m/z): 437 [M+H]⁺.

2.4. 2(3),9(10),16(17),23(24)-Tetrakis-(4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy)-phthalocyaninato copper(II) (2a): 4-(4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy) phthalonitrile (**2**) (100 mg, 0.23 mmol), CuCl₂ (16 mg, 0.11 mmol), 1-pentanol (2 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3 drops) was stirred at 160 °C for 24 h. The mixture was precipitated with ethanol. The green product was obtained by column chromatography using basic aluminum oxide and CHCl₃ as eluent. Yield: 25 mg (25%), m.p. > 300 °C. IR (ATR), ν/cm^{-1} : 3066 (Ar-H), 2918–2849 (Aliph. C-H), 1682, 1595, 1504, 1463, 1429, 1328, 1259, 1235, 1164, 1121, 1092, 1012, 950, 876, 800. UV-Vis (THF) λ_{max} nm (log e): 674 (4.02), 613 (4.75), 337 (5.07). MALDI-TOF-MS m/z: 1808.67 [M]⁺.

2.5. 2(3),9(10),16(17),23(24)-Tetrakis-(4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy)-phthalocyaninato manganese(III)chloride (2b): Synthesized similarly to **2a** by using MnCl₂ instead of CuCl₂. Yield: 21

mg (20%), m.p. > 300 °C. IR (ATR), ν/cm^{-1} : 3078 (Ar-H), 2918–2849 (Aliph. C-H), 1684, 1595, 1526, 1504, 1463, 1407, 1330, 1259, 1234, 1165, 1119, 1072, 1013, 954, 910, 797. UV-Vis (THF) λ_{max} nm (log ϵ): 720 (4.97), 652 (4.41), 497 (4.29), 385 (4.78). MALDI-TOF-MS m/z : 1800.69 [M-Cl]⁺.

2.6. 1(4),8(11),15(18),22(25)-Tetrakis--(4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy)-phthalocyaninato copper(II) (3a) : Synthesized similarly to 2a by using 3-(4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy)phthalonitrile (3) instead of 4-(4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy)phthalonitrile (2). Yield: 22 mg (22%), m.p. > 300 °C. IR (ATR), ν/cm^{-1} : 3068 (Ar-H), 2919–2850 (Aliph. C-H), 1680, 1582, 1503, 1483, 1427, 1328, 1244, 1214, 1164, 1120, 1089, 1065, 1006, 911, 877, 799, 743. UV-Vis (THF) λ_{max} nm (log ϵ): 690 (5.02), 625 (4.53), 329 (4.4). MALDI-TOF-MS m/z : 1808.04 [M]⁺.

2.7. 1(4),8(11),15(18),22(25)-Tetrakis--(4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy)-phthalocyaninato manganese(III)chloride (3b) : Synthesized similarly to 2b by using 3-(4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy)phthalonitrile (3) instead of 4-(4-((2E)-3-[2-fluoro-4-(trifluoromethyl)phenyl]prop-2-enoyl)phenoxy)phthalonitrile (2). Yield: 18 mg (17%), m.p. > 300 °C. IR (ATR), ν/cm^{-1} : 3073 (Ar-H), 2927–2857 (Aliph. C-H), 1682, 1580, 1503, 1484, 1424, 1327, 1242, 1211, 1163, 1138, 1067, 1010, 984, 911, 825, 743. UV-Vis (THF) λ_{max} nm (log ϵ): 741 (4.99), 670 (4.47), 508 (4.34), 330 (4.99). MALDI-TOF-MS m/z : 1800.78 [M-Cl]⁺.

3. Electrochemical measurements

The cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Interface 1000 potentiostat/galvanostat controlled by an external Pc and utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm². A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade TBAP in extra pure DCM was employed as the supporting electrolyte at a concentration of 0.10 mol dm⁻³.

References

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