ORIGINAL ARTICLE



Synthesis and investigation of spectroelectrochemical properties of peripherally tetra-substituted phthalocyanine bearing 3-(4-{[3-(trifluoromethyl)benzyl]oxy}phenyl)propan-1-ol and its metallo compounds

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Abstract

In this study, the new compounds; 3-(4-[[3-(trifluoromethyl)benzyl]oxy]phenyl)propan-1-ol**3**was prepared by the reaction of 4-(3-hydroxypropyl)phenol**1**with 1-(bromomethyl)-3-(trifluoromethyl)benzene**2** $and 4-[3-(4-{[3 (trifluoromethyl)benzyl] oxy}phenyl)propaxy] phthalonitrile$ **5**was synthesized by the reaction of 4-nitrophthalonitrile**4** $with 3-(4-{[3-(trifluoromethyl)benzyl]oxy}phenyl)propan-1-ol$ **3**. Novel peripherally tetra substituted H₂Pc**6**, Co(II)**7**, Cu(II)**8**, Ni(II)**9**and Fe(II)**10** $phthalocyanines, which have peripheral positions with 4-[3-(4-{[3 (trifluoromethyl)benzyl]oxy}phenyl)propoxy] groups, were synthesized and all of the new compounds characterized by IR, ¹H NMR, ¹³C NMR, UV–Vis, mass spectroscopies and elemental analysis. The electrochemical and spectroelectrochemical investigation of the phthalocyanines carrying 4-[3-(4-{[3 (trifluoromethyl)benzyl]oxy}phenyl)propoxy] groups were studied using various electrochemical techniques in DMF on a glassy carbon electrode. Cyclic voltammetry and square wave voltammetry studies show that the complexes have either metal based or ligand-based diffusion controlled electron transfer properties. To shed more light on the electron-transfer steps of the complexes and assignments of the redox couples were carried out by spectroelectrochemical measurements. The color changes during spectral changes of redox species were recorded with in situ electrocolorimetric measurements. The electrochemical and in situ UV–Vis spectral change of complexes indicated their applicability in the fields of the electrochemical technologies.$

Keywords Phthalocyanine · Synthesis · Electrochemistry · Voltammetry

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Introduction

In recent years, phthalocyanines (Pcs) have been generally studied since they have been applied to many scientific field applications such as chemical sensors [1], catalysts [2, 3], photodynamic therapy [4, 5], electrochromic agent [6], dyes and pigments [7], liquid crystal [8], electrocatalytic [9] and solar energy conversion [10].

A major deficiency of the metal-free and metallo Pcs is that their solubility organic solvents is very poor [11]. The lower solubility of Pcs prevents from their application in many areas. The solubility of Pcs can be increased by the affiliation with various alkyl, aryloxy, macrocyclic, alkoxy and phenoxy groups on the peripheral and non-peripheral positions.

Metallophthalocyanines are a member of transition metal complexes known as macrocyclic complexes. They have an

inner structure that is common in naturally occurring molecules such as heme groups in hemoglobin, chlorophyll, cytochrome c, vitamin B12 [12–14]. The reason why these molecules are unusual in many areas, besides their strong absorption in the UV-Vis region and their electrical properties, Pcs are also thermally and chemically stable compounds, and can support intense electromagnetical radiations [15]. In addition, they have properties such as being in combination with different metals and various substituents, thanks to these features can make fine adjustment of the physical properties [16]. Recently, Pcs have appeared as charming molecule for their arrangement into molecular materials and for fabricating materials at the nanometer scale. Thus, Pcs can be used successfully as active components of organic field effect transistors, electrochromic materials and solar cells, etc [15, 17].

The electrochemical properties of Pcs are generally determined by voltammetric techniques such as cyclic voltammetry (CV), differential pulse voltammetry and square-wave voltammetry (SWV). In addition, the nature of the redox process can be clarified with the in situ spectroelectrochemical measurements [18–20].

In this study, we reported the synthetic procedures of 3-(4-{[3-(trifluoromethyl)benzyl]oxy}phenyl)propan-1-ol **3**, phthalonitrile compound **5** and peripherally tetra substituted metal-free **6**, cobalt(II) **7**, copper(II) **8**, nickel(II) **9** and iron(II) **10** Pcs. The structures of the synthesized new compounds were identified by several spectroscopic methods. The electrochemistry and in situ spectroelectrochemistry of metal-free and metallophthalocyanine containing 4-[3-(4-{[3 (trifluoromethyl)benzyl]oxy}phenyl)propoxy] groups on the peripheral positions have been investigated by CV, SWV and in situ spectroelectrochemistry for understanding of their redox behaviors.

Experimental

Materials

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

Synthesis

Synthesis of 3-(4-{[3-(trifluoromethyl)benzyl]oxy}phenyl) propan-1-ol (3)

4-(3-Hydroxypropyl)phenol **1** (1 g, 6.57 mmol) was dissolved 50 ml of acetone under N₂ atmosphere. Anhydrous K₂CO₃ (1.03 g, 7.49 mmol) was added to reaction mixture then stirring at 60 °C for 15 min. 2 ml 1-(bromomethyl)-3-(trifluoromethyl)benzene **2** (1.79 g, 7.49 mmol) and

18-crown-6 (0.19 g, 0.73 mmol) was added to this solution. The reaction mixture was refluxed under nitrogen for 48 h. After the mixture was cooled, the solvent was removed under vacuum, and the resulting crude product was dissolved in 70 ml of chloroform (CHCl₃). The mixture was washed with 35 ml of water. The organic phase was dried over magnesium sulphate (MgSO₄), filtered and rotary evaporated. The obtained oily crude product was purified using column chromatography with basic aluminium oxide as the column material and a chloroform/methanol (10:2) solvent system. Yield: 1.72 g (84.72%). IR (KBr tablet), ν_{max}/cm^{-1} : 3371 (Aliph-OH), 3031 (Ar-H), 2933-2868 (Aliph. C-H), 1611 (C=C), 1328, 1119-1072 (C-O-C), 906 (C-H), 798, 698. ¹H–NMR. (CDCl₃), (δ: ppm): 7.74 (s, 2H, Ar–H), 7.63–7.51 (m, 2H, Ar-H), 7.27 (d, 2H, Ar-H), 6.95 (d, 2H, Ar-H), 5.09 (s, 2H, -O-CH₂-Ar), 3.71 (m, 2H, -O-CH₂), 3.54 (s, 1H, O-H), 2.70 (t, 2H, -CH₂), 1.93 (m, 2H, -CH₂) (Fig. 1). ¹³C NMR. (CDCl₃), (δ: ppm): 156.73 (C=C), 138.27 (C=C), 134.56 (C=C), 132.38 (C=C), 131.07 (C=C), 130.63(C=C), 129.47 (C=C), 129.06 (C=C), 124.73 (C=C), 124.09 (C=C), 122.77 (C=C), 114.81 (C=C), 69.26 (F₃-C-Ar), 64.24 (O-CH₂-Ar), 62.16 (O-CH₂), 34.19 (CH₂-Ar), 31.13 (CH₂-CH₂). MS (ESI), (m/z): Calculated: 310.32 ; Found: 310.19 [M]⁺. Elemental Analysis, Anal, calc. for C₁₇H₁₇O₂F₃: C, 65.78; H, 5.48; Found: C, 65.90; H, 5.00%.

Synthesis of 4-[3-(4-{[3(trifluoromethyl)benzyl]oxy}phenyl) propoxy] phthalonitrile (5)

Compound 3 (1.0 g, 3.22 mmol) and 4-nitrophthalonitrile 4 (0.57 g, 3.22 mol) were dissolved in dry DMF (20 ml) and the solution was stirred at 55-60 °C. Then, powdered dry K_2CO_3 (0.16 g, 1.16 mmol) was added to the system in eight equal portions at 15 min intervals over 2 h. The system was stirred under N_2 at same temperature for 5 days. After this time, the reaction mixture was poured into ice-water and stirred at room temperature for 3 h to yield a crude product. The mixture was filtered and washed with water then dried in vacuum over P_2O_5 for 4 h and recrystallized from ethanol but product didn't crystallize. Obtained orange oily product was purified using column chromatography with silicon dioxide as the column material and a chloroform solvent. Yield: 1.2 g (85%). IR (KBr tablet), $\nu_{\text{max}}/\text{cm}^{-1}$: 3074 (Ar–H), 2919–2849 (Aliph. C-H), 2231 (C=N), 1671-1510 (C=C), 1162-1073 (C–O–C), 968, 827, 798, 700, 660. ¹H NMR. (CDCl₃), (δ: ppm): 7.72 (m, 6H, Ar-H), 7.37 (m, 1H, Ar-H), 7.24 (m, 2H, Ar-H), 6.94 (m, 2H, Ar-H), 5.11 (s, 2H, -O-CH₂-Ar), 4.15 (t, 2H, -O-CH₂), 2.97 (m, 2H, -CH₂-Ar), 2.16 (m, 2H, -CH₂-CH₂) (Fig. 2). ¹³C NMR. (CDCl₃), (δ: ppm): 162.09, 156.97, 138.12, 135.20, 133.28, 130.59, 129.49, 129.45, 129.07, 124.77, 124.08, 128.47, 119.51, 119.35, 117.44, 115.72 (C≡N), 115.29 (C≡N), 114.97, 114.79, 107.16, 69.28 (F₃-C-Ar), 68.08 (O-CH₂-Ar), 62.24 (O-CH₂), 34.38



Fig. 1 a ¹H NMR spectrum of compound 3, b ¹H NMR spectrum of compound 3 with D_2O





(CH₂–Ar), 30.90 (CH₂–CH₂). MS (ESI), (m/z): Calculated: 436.43; Found: 437.00 [M+H]⁺. Elemental Analysis, Anal, calc. for $C_{25}H_{19}N_2O_2F_3$: C, 68.81; H, 4.36; N, 6.42; Found: C, 65.90; H, 5.00; N, 6.85%.

General procedure for synthesis of metalfree (6), metallophthalocyanines (7–10)

Substituted phthalonitrile **5** and for metallophthalocyanines corresponding anhydrous metal salts (CoCl₂ (14.25 mg, 0.11 mmol); CuCl₂ (14.79 mg, 0.11 mmol); NiCl₂ (14.26 mg, 0.11 mmol); Fe(Ac)₂ (19.12 mg, 0.11 mmol)) were dissolved in 2 ml of DMAE. Then the temperature was raised to 160 °C and stirred for 4 h under nitrogen atmosphere. Methanol was added to the medium and the green raw products were filtrated and washed with hot ethanol, methanol, *n*-hexane and diethyl ether. The pure green product was purified on silica gel column. with chloroform–methanol (5:1) for compound **6**, (5:2) for compound **7**, (5:1) for compound **8**, (5:2) for compound **9** and **10** solvent system as eluent. Spectral data of these products are given below.

Metal-free phthalocyanine (6) Yield: 5 mg, (2.5%), mp > 300 °C. IR (KBr tablet) ν_{max} /cm⁻¹: 3292 (–NH), 3034 (Ar–CH), 2919–2850 (Aliph. CH), 1610–1510 (C=C), 1486–1463 (HC=N), 1328, 1233–1161 (C–N), 1117–1096 (C–O–C), 957 (C–H), 796, 697. ¹H NMR. (CDCl₃), (δ: ppm): 7.73–7.29 (m, 22H, Ar–H), 7.04–6.99 (m, 22H, Ar–H), 5.11–5.09 (m, 8H, –O–CH₂–Ar), 2.40 (m, 8H, –O– CH₂), 2.30 (m, 16H, CH₂). UV–Vis (CHCl₃): λ_{max} , nm (log ε): 702 (6.00), 685 (5.81), 608 (5.54), 390 (5.80). MALDI– TOF–MS m/z: Calculated: 1747.72 ; Found: 1747.50 $[M]^+$. Elemental Analysis, Anal, calc. for $C_{100}H_{78}N_8O_8F_{12}$: C, 68.68; H, 4.46; N, 6.41; Found: C, 68.02; H, 4.75; N, 6.52%.

Cobalt(II) phthalocyanine (7) Yield: 20 mg (10%). mp: >300 °C. IR (KBr tablet) ν_{max} /cm⁻¹: 3068 (Ar–CH), 2920–2850 (Aliph. CH), 1609–1510 (C=C), 1462–1410 (HC=N), 1329, 1231–1161 (C–N), 1117–1071 (C–O–C), 912 (C–H), 795, 660. UV–Vis (CHCI₃): λ_{max} , nm (log ϵ): 666 (5.91), 607 (5.45), 329 (5.86). MALDI–TOF–MS m/z: Calculated:1804.65; Found: 1805.14 [M+H]⁺. Elemental Analysis, Anal, calc. for C₁₀₀H₇₆N₈O₈F₁₂Co: C, 66.49; H, 4.21; N, 6.20; Found: C, 66.74; H, 4.02; N, 6.57%.

Copper(II) phthalocyanine (8) Yield: 15 mg (7.5%). mp: >300 °C. IR (KBr tablet) ν_{max} /cm⁻¹: 3047 (Ar–CH), 2928–2860 (Aliph. CH), 1595–1509 (C=C), 1484–1460 (HC=N), 1328, 1230–1161 (C–N), 1116–1094 (C–O–C), 879 (C–H), 795, 699. UV–Vis (CHCI₃): λ_{max} , nm (log ε): 677 (5.93), 617 (5.50), 329 (5.86). MALDI–TOF–MS m/z: Calculated: 1809.26; Found: 1810.74 [M+H]⁺. Elemental Analysis, Anal, calc. for C₁₀₀H₇₆N₈O₈F₁₂Cu: C, 66.33; H, 4.20; N, 6.19; Found: C, 66.50; H, 4.33; N, 6.36%.

Nickel(II) phthalocyanine (9) Yield: 12 mg (6%). mp: > 300 °C. IR (KBr tablet) ν_{max}/cm^{-1} : 3056 (Ar–CH), 2926–2860 (Aliph. CH), 1610–1510 (C=C), 1484–1463 (HC=N), 1328, 1232–1161 (C–N), 1117–1095 (C–O–C), 919 (C–H), 796, 660. ¹H NMR. (CDCl₃), (8: ppm): 7.72–7.00 (m, 22H, Ar–H), 6.99–6.93 (m, 22H, Ar–H), 5.07–5.06 (m, 8H, –O–CH₂–Ar), 4.12 (m, 8H, –O–CH₂), 1.57 (m, 16H, CH₂).

UV–Vis (CHCI₃): λ_{max} , nm (log ε): 675 (6.02), 615 (5.64), 384 (5.75), 332 (5.87). MALDI–TOF–MS m/z: Calculated: 1804.41; Found: 1805.46 [M+H]⁺. Elemental Analysis, Anal, calc. for C₁₀₀H₇₆N₈O₈F₁₂Ni: C, 66.50; H, 4.21; N, 6.21; Found: C, 66.09; H, 4.73; N, 6.45%.

Iron(II) phthalocyanine (10) Yield: 10 mg (5%). mp: > 300 °C. IR (KBr tablet) ν_{max} /cm⁻¹: 3054 (Ar–CH), 2921–2850 (Aliph. CH), 1608–1510 (C=C), 1485–1450 (HC=N), 1328, 1231–1161 (C–N), 1117–1096 (C–O–C), 960 (C–H), 796, 699. ¹H NMR. (CDCl₃), (δ: ppm): 7.63–7.57 (m, 22H, Ar–H), 7.56–7.27 (m, 22H, Ar–H), 5.07 (m, 8H, –O–CH₂–Ar), 4.09 (m, 8H, –O–CH₂), 1.53 (m, 16H, CH₂). UV–Vis (CHCI₃): λ_{max} , nm (log ε): 677 (6.00), 622 (5.81). MALDI–TOF–MS m/z: Calculated: 1801.56; found: 1802.50 [M+H]⁺. Elemental Analysis, Anal, calc. for C₁₀₀H₇₆N₈O₈F₁₂Fe: C, 66.61; H, 4.22; N, 6.22; Found: C, 66.94; H, 4.61; N, 6.83%.

Results and discussion

Synthesis and characterization

The general synthetic pathway for the synthesis of 3-(4-{[3-(trifluoromethyl)benzyl]oxy}phenyl)propan-1-ol 3, phthalonitrile compound 5 and its metalfree 6, cobalt(II) 7, copper(II) 8, nickel(II) 9 and iron(II) 10 phthalocyanine complexes were given in Fig. 3. All new compounds (3, 5, 6-10) were fully characterised by IR, ¹H NMR, ¹³C NMR (only 3 and 5), UV-Vis (for compounds 6-10) and MS spectral data. 3-(4-{[3-(trifluoromethyl)benzyl]oxy}phenyl) propan-1-ol 3 was prepared through base catalyzed reaction of 4-(3-hydroxypropyl)phenol 1 with 1-(bromomethyl)-3-(trifluoromethyl)benzene 2 in acetone. The formation of compound 3 was confirmed by the combination of spectroscopic data. In the IR spectra of compound 3, the peak due to phenolic O-H vibration (3400 cm⁻¹) of 4-(3-hydroxypropyl)phenol disappeared and -CH2-OH and aliphatic C-H bands (3371 cm⁻¹) appeared, confirming the formation of compound **3**. In the ¹H NMR spectra of **3**, the phenolic OH group (δ =4.5 ppm) of compound **3** disappeared, as expected and showed new signal at $\delta = 5.10$ ppm (Ar–CH₂–O) and $\delta = 3.54$ ppm (Aliph OH group) (Fig. 1). The characteristic ¹³C NMR signals of aromatic carbon atoms at δ : 156.73, 138.27, 134.56, 132.38, 131.07, 130.63, 129.47, 129.06, 124.73, 124.09, 122.77, 114.81; carbon atom belonging to CF₃ group at $\delta = 69.26$ and carbon atoms belonging to methyl groups at $\delta = 64.24$, 62.16, 34.19 and 31.13 ppm, supported the structure. The mass spectra of compound 3 confirmed the structure proposed, with the molecular ion at 310.19 [M]⁺.

The synthesis of 4-[3-(4-{[3 (trifluoromethyl)benzyl]oxy} phenyl)propoxy] phthalonitrile 5 was obtained in 85% yield through base-catalyzed aromatic displacement of 4-nitrophthalonitrile with compound 5 using K_2CO_3 as the base in dry DMF. In the IR spectrum of phthalonitrile compound 5 was clearly verified with the disappearance of the OH group of **3** and the presence of $C \equiv N$ group by the sharp stretching bands at 2231 cm⁻¹. Other IR stretching vibrations of 5 were similar to compound 3. In the ¹H NMR spectrum of compound 5 at $\delta = 4.5$ ppm (OH group) was disappeared and the aromatic protons appear at $\delta = 7.72$ (m), 7.37 (m), 7.24 (m), 6.94 (m) ppm (Fig. 2). In the 13 C NMR spectrum of compound 5 indicated the presence of nitrile carbon atom $(C \equiv N)$ at $\delta = 115.72 - 115.29$ ppm. In the mass spectra of phthalonitrile compound 5, the molecular ion peak was observed at m/z: 437.00 [M+H]⁺, confirmed the proposed chemical structure.

The reaction of phthalonitrile 5 with DMAE gave to the metal-free phthalocyanine complex 6 and cyclotetramerization of compound 5 to the peripherally tetra-substituted metallophthalocyanines (7-10) were accomplished in the presence of metal salts (CoCl₂, CuCl₂, NiCl₂ and FeCl₂) at 160 °C in DMAE in 4 h under inert atmosphere. These reactions spoiled under 160 °C in long time such as 12 h, 24 h. We accomplished these reactions in 4 h. In the IR spectra, the formation of phthalocyanine compounds 6–10 was clearly confirmed by the disappearance of the $C \equiv N$ band. IR spectrum of Pcs 6-10 was very similar to each other. The metal-free phthalocyanine 6 was showed an additional absorption band at 3292 cm⁻¹ assigned to the NH stretching vibrations. In the ¹H NMR spectrum of metal-free phthalocyanine 6 in CDCl₃ the aromatic protons resonated between 7.73 and 6.99 ppm as multiplet and aliphatic protons were observed at $\delta = 5.11 - 5.09$ (m, 8H, $-O-CH_2-Ar$), 2.40 (m, 8H, -O-CH₂), 2.30 (m, 16H, CH₂) ppm. The ¹H NMR spectrum, the NH protons of compound 6 could not be observed because of the strong aggregation of the molecules [21]. The MALDI-TOF mass spectrum of compound 6, which showed a peak at $m/z = 1747.50 [M]^+$, confirmed the proposed formula for this compound. showed similar signals because of the same ring systems. In addition, ¹H NMR spectra of the compound 9 and 10 showed similar signals with compound 6 because of the same ring systems. But, the ¹H NMR spectra of complexes 7 and 8 could not be determined owing to the paramagnetic nature [22]. The MALDI-TOF mass spectrum of CoPc 7, CuPc 8, NiPc 9 and FePc 10, the presence of molecular ion peaks at $m/z = 1804.65 [M+H]^+$, 1810.74 [M+H]⁺, 1804.41 [M+H]⁺ and 1801.56 [M+H]⁺ respectively, are in accordance with the expected values.

The UV–Vis spectra of the metal-free Pc 6 and MPcs 7–10 show typical electronic spectra with two strong absorption regions (Q and B bands). In the electronic



Fig. 3 The synthesis route of compounds 3, 5–10

spectra disunited two bands for the metal-free Pc compound **6** and a single Q band for the metallo Pc complexes (**7–10**) in CHCl₃ at 1×10^{-6} mol dm⁻³. Characteristic absorptions in the Q band region were 702/685 nm for H₂Pc **6**, 666 nm for compound CoPc **7**, 677 for compound CuPc **8**, 675 nm for compound NiPc **9** and 677 nm for compound FePc **10** in CHCl₃. B band absorptions of the H₂Pc **6** and metallophthalocyanines **7–9** were observed at 390, 329, 329, 384–332 nm, respectively (Fig. 4a, b). B band absorptions of the FePc **10** were not observed and FePc was aggregation in solvent (Fig. 4).

Voltammetric characterization

The electrochemical behavior of MPcs (Co²⁺, Cu²⁺, Fe²⁺ and Ni²⁺) to illustrate the effects of metal center of phthalocyanine to the redox properties was investigated via CV and SWV in DMF involving TBAP as supporting electrolyte. All of the compounds in the series showed three reductions and one oxidation (except CoPc and FePc) in determined the potential window versus Ag/AgCl provided by DMF (Figs. 5, 6, 7). Different scan rates were performed at CV measurement (from 25 to 500 mV s⁻¹) for each sample in series. Half-wave potentials ($E_{1/2}$), peak to peak separation





 $(\Delta E_{\rm p})$ and ratio of anodic to cathodic peak currents $(I_{\rm p,a}I_{\rm p,c})$ were recorded from CV with a scan rate of 100 mV s⁻¹. The obtained electrochemical data of the complexes are listed in Table 1.

CoPc gives a metal center based one-electron reduction, R_1 and two ring based reductions, R_2 and R_3 during the cathodic potential scans. Moreover, during the anodic scans, a metal based O_1 and a Pc based O_2 are also observed (Fig. 5). The first reduction and oxidation reactions of CoPc occur at small potentials with respect to those of the Pc based processes (Table 1). It is likely that d-energy levels of CoPc complex fall between the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) energy levels, and thus it exhibits metalbased redox processes. The first reduction and the first oxidation processes of CoPc in DMF could be assigned to the $Co^{II}Pc^{-2}/[Co^{I}Pc^{-2}]^{-}$ and $Co^{II}Pc^{-2}/[Co^{III}Pc^{-2}]^{+}$ redox couples respectively, and the remaining processes to the Pc ring. The second and third reduction couples labelled R_2 and R_3 are observed at -1.46 V versus Ag/AgCl and -2.12 V versus Ag/AgCl, respectively, may be assigned to $[Co^{I}Pc^{-2}]^{-/}[Co^{I}Pc^{-3}]^{2-}$ and to $[Co^{I}Pc^{-3}]^{2-/}[Co^{I}Pc^{-4}]^{3-}$ in comparison with literature data [23, 24]. For these redox couples, the cathodic to anodic peak current ratios are near unity, but the cathodic to anodic peak separations are 130 mV (R₁) and 100 mV (R₃), suggesting quasi-reversible behavior, whereas R2 behaves reversible. In addition, the peak currents for all processes increase linearly with the square root of scan rates, for scan rates ranging from 25 to 500 mV s⁻¹ which illustrated diffusion controlled mass transfers during the redox reactions. To shed more light on the electron-transfer steps of the complexes, UV-Vis





(a) \overline{O}_{i} 20 0 I (μA) Scan rates: 25 mVs 50 mVs -40 100 mVs 250 mVs 500 mVs -60 -0.5 -2.0 -1.5 -1.0 0.0 0.5 1.0 E (V) vs. Ag/AgCl **(b)** 5.0 2.5 I (μA) 0 0.0 Ŕ -2.5 -5.0 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 -2.5 1.5 E (V) vs. Ag/AgCl

Fig. 5 a CVs of CoPc recorded at various scan rates and b SWVs of CoPc recorded at 0.100 V s⁻¹ scan rate on a GCE working electrode in DMF/TBAP electrolyte

spectroelectrochemical measurements were carried out. Figure 8a represents in situ UV–Vis spectral changes during the first reduction of CoPc at -0.55 V versus Ag/AgCl, corresponding to the redox process labeled R₁ in Fig. 5. CoPc complex displays the O band at 666 nm with a shoulder at 606 nm in the Vis-region and the B band at 320 nm in the UV-region. The Q band shifts to 671 nm, while new bands at 464 nm and 707 nm appears during the first reduction process. The band at 464 nm and the shifting of the Q band indicate formation of [Co^{II}Pc⁻²]⁻ species, confirming the CV assignment of the couple R_1 process [25–28]. During the second (Fig. 8b) reduction, the Q band at 707 nm continues to decrease and the absorption between 474 and 946 nm increases. These spectral changes at the potential of the couples R₂ are characteristics for a ring-based reduction in CoPc complex. Spectral changes observed during the third reduction process also illustrated the Pc based character of this process. Figure 8c shows spectral changes of oxidation processes. The Q band at 666 nm increases in intensity with red shift to 676 nm. The increase of the Q band with red shift is characteristic of a metal-based oxidation in CoPc complexes [29]. Therefore, the oxidation process, O_1 is easily assigned to $Co^{II}Pc^{-2}/[Co^{III}Pc^{-2}]^+$ process for couple O_1 of CoPc in Fig. 5. Figure 8c (inset of graph) also shows second oxidation process. During the second

Fig. 6 a CVs of CuPc recorded at various scan rates and b SWVs of CuPc recorded at 0.100 V s^{-1} scan rate on a GCE working electrode in DMF/TBAP electrolyte

oxidation reaction, the Q band decreases at 676 nm. These changes indicate Pc-based oxidation process ($[Co^{III}Pc^{-2}]^+/$ $[Co^{III}Pc^{-1}]^{2+}$) for couple O₂ of CoPc in Fig. 5. Chromaticity diagram recorded color changes as a result of spectral change during the redox processes is represented in Fig. 8d. The cyan color (x = 0.2665 and y = 0.3304) of CoPc complex turns to light green (x = 0.3446 and y = 0.4064), then yellow (x = 0.4137 and y = 0.4275) and at last orange (x = 0.4336 and y = 0.4048) during the reduction processes. During the oxidation reaction, cyan color of CoPc turns to greenish cyan (x = 0.3013 and y = 0.3572) and then yellow color (x = 0.3466 and y = 0.3608). These multi-color change properties of CoPc indicates a potential candidate for use as electrochromic material in window applications [19, 30, 31].

The general voltammetric behaviours of CuPc and NiPc are like each other [32]. CuPc and NiPc complexes display three reductions and one oxidation couples as given for CuPc in Fig. 6. Voltammetric responses of the complex (CuPc and NiPc) are completely different than those of FePc and CoPc because just give common Pc based electron transfer reactions [33, 34]. This similarity proposes that all redox processes of these complexes are Pc ring-based, having redox inactive metal center.

The first reduction of the phthalocyanine ligand is equal to the position of LUMO, while the first oxidation of the



Fig. 7 a CVs of FePc recorded at various scan rates and b SWVs of FePc recorded at 0.100 V s⁻¹ scan rate on a GCE working electrode in DMF/TBAP electrolyte

ligand is equal to the position of HOMO. In the light of this information, $\Delta E_{1/2}$ values represent the HOMO–LUMO gap in MPc species involving redox-inactive metal center.

Table 1 Voltammetric data of

the complexes

 $\Delta E_{1/2}$ values of redox-inactive metal center having CuPc and NiPc are in harmony with the literature [29, 33]. Although CuPc and NiPc illustrated similar voltammetric responses and had similar redox parameters as shown in Table 1, there were slight differences between $\Delta E_{1/2}$ values of the complexes. This difference is possibly stemmed from the strong withdraw of electrons with increase effective nuclear charge of metal center of Pc rings. Aggregation of Pcs in solution to form dimers and higher aggregated forms is based on the concentration, nature of the solvent, nature of the substituents, metal ion complexes, and temperature [35, 36]. In comparison with CoPc, CuPc and NiPc showed more tendency to aggregate in DMF solution. The aggregation tendency was observed clearly in situ UV-Vis spectral changes of CuPc. The spectral changes monitored during the redox processes of CuPc and NiPc in DMF/TBAP, were similar to each other. When examined, spectral change of CuPc gives the Q band at 678 nm with a strong aggregation band at 618 nm. This aggregation is H-aggregation, since it was observed at the higher energy side of the Q band [37]. Upon the first reduction of CuPc, the O band absorption decreases without shift and the appearance of a new absorption bands were observed at 571 and 950 nm simultaneously during the redox processes of these complexes (Fig. 9a). These spectral changes are characteristic for Pc ring-based redox processes and so, they support the ligand-based nature of the redox processes of CuPc and NiPc complexes. During the second reduction, new bands appear in the range of 500-700 nm, while the Q band decreases with broken of aggregation band (Fig. 9b). Figure 9c shows spectral

Complexes	Parameters	Redox processes						
		$\overline{O_2}$	O ₁	R ₁	R_2	R ₃	R_4	$\Delta E_{1/2} \left(\mathbf{V} \right)$
CoPc (in DMF)	E _{1/2} (V) ^a	1.42	0.38	-0.34	-1.42	-2.00	_	
	$\Delta E_{p} (mV)^{b}$	200	60	130	60	100	-	0.72
	$I_{p,a}/I_{p,c}$ ^c	0.25	0.62	1.00	1.00	0.67	-	
CuPc (in DMF)	$E_{1/2}(V)^{a}$	_	0.73	-0.76	-1.15	-1.87	-	
	$\Delta E_{p} (mV)^{b}$	-	200	60	69	110	-	1.49
	$I_{p,a}/I_{p,c}$ c	_	0.49	0.99	0.94	1.00	-	
FePc (in DMF)	$E_{1/2}(V)^{a}$	_	0.90	0.25	-0.54	-1.09	-1.46	
	$\Delta E_{p} (mV)^{b}$	-	80	60	110	80	70	0.84
	$I_{p,a}/I_{p,c}$ c	-	0.93	1.53	1.00	0.87	1.00	
NiPc (in DMF)	$E_{1/2}(V)^{a}$	_	0.90	-0.76	-1.17	-1.89	-	
	$\Delta E_p (mV)^b$	_	130	60	60	110	-	1.66
	I _{p,a} /I _{p,c} ^c	-	0.51	0.87	0.50	1.00	_	

All data were given versus Ag/AgCl

 $\Delta E_{1/2} = E_{1/2}$ (first oxidation) – $E_{1/2}$ (first reduction). HOMO–LUMO gap of complexes

 ${}^{a}E_{1/2}$ values $(E_{pa} + E_{pc})/2$ were recorded at 0.100 V s⁻¹ scan rate

$$^{b}\Delta E_{p} = E_{pa} - E_{pc}$$

 $^{c}I_{p,a}/I_{p,c}$ for reduction, $I_{p,c}/I_{p,a}$ for oxidation processes





changes during the oxidation of the CuPc species, all bands decrease in intensity due to the decomposition of the oxidized species of the complex.

Color changes recorded during the reduction and oxidation reactions of CuPc, are also represented by the chromaticity diagram in Fig. 9d. The color of the solution changes from light green (x = 0.2645 and y = 0.3484) to blue (x = 0.2467 and y = 0.2865) during the first reduction process R₁. Upon the second reduction, it goes to purple (x = 0.2849and y = 0.2433). On the other hand, the spectral changes recorded during oxidation process of CuPc are accompanied by the color changes from green (x = 0.2645 and y = 0.3484) to greenish cyan (x = 0.3057 and y = 0.3380) (Fig. 9d).

Pcs bearing Fe²⁺ metal centers are rare in the literature due to the difficulty of the syntheses and instability of these complexes [38–40], although there are a few papers on the electrochemistry of Pc bearing Fe³⁺ metal centers [41–43]. In Fig. 7 shows the CV and SWV for Fe^{II}Pc complex in DMF/TBAP electrolyte system. The complex gives four reduction and one oxidation processes. The reductions of metal center of Fe^{II}Pc complex indicated a different behavior from the other [44]. Compared to the literature, Fe^{II}Pc can give reduction couples at more positive potentials [45, 46]. Although, R_1 is observed at positive potentials (at 0.25 V), Fe^{II}Pc illustrates the second metal based process R_2 at -0.54 V. Moreover, at more negative potential, it gives ring based reduction reactions, R_3 at -1.09 V and R_4 at -1.46 V. During the anodic scans, a quasi-reversible oxidation couple (O₁ at 0.90 V) is observed. All redox couples are well recorded also with SWVs (Fig. 7b).

Spectroelectrochemical measurement for FePc complex are given in Fig. 10. Upon the first reduction, the Q band shifts to shorter wavelengths with increasing in the current intensity (Fig. 10a). Generally, the shifting of the Q band on the reduction or oxidation suggests a metal-based process [47]. Thus the spectral changes shown in Fig. 10a are typical of a metal-based reduction, assigned to reduction state of the central Fe(II) to Fe(I). Figure 9b represents the spectral changes under the applied potential of -1.20 V and then -1.80 V. While, the intensity of Q band from 665 to 668 nm decreases by shifting, new peaks appear in charge transfer region at 522 nm and 812 nm. The shift of Q band and the peak at 526 nm characterize a metal-based reduction of [Fe^{II}Pc⁻²]⁰ to [Fe^IPc⁻²]^{1–} species. Further reductions are Fig. 9 In situ UV–Vis spectral changes of CuPc in DMF/TBAP electrolyte. **a** $E_{app} = -0.90$ V, **b** $E_{app} = -2.10$ V, **c** $E_{app} = 1.20$ V, **d** Chromaticity diagram (each symbol represents the color of electro-generated species; square: [Cu^{II}Pc²⁻]; circle: [Cu^{II}Pc³⁻]¹⁻; triangle: [Cu^{II}Pc⁴⁻]²⁻; star: [Cu^{II}Pc¹⁻]¹⁺)



expected to occur on the ring because of $[Fe^{I}Pc^{-3}]^{2-}$ species. Moreover, intensity of Q band at 668 nm continues to decrease and new peak observed at 474 nm (inset of Fig. 10b). Color changes of the complex in solution during the redox processes were recorded with in situ electrocolorimetric measurements as shown Fig. 10c. Without any potential application, the solution of $Fe^{II}Pc^{-2}$ is green (x=0.3395 and y=0.3724). As the potential is declined from 0.00 to -1.80 V, the color of the complex starts to change and a light yellow (x=0.3432 and y=0.3388). Color of the complex during oxidation reaction turns to yellow (x=0.3626 and y=0.3672).

Conclusion

In this paper, we reported the synthetic procedures of 3-(4-{[3-(trifluoromethyl)benzyl]oxy}phenyl)propan-1-ol 3, new group substituted phthalonitrile compound 5 and its metal free 6, cobalt(II) 7, copper(II) 8, nickel(II) 9 and iron(II)10 phthalocyanine. The obtained new compounds were characterized by standard spectroscopic methods (IR, UV-Vis, ¹H NMR, ¹³C NMR, mass spectrometry) and elemental analysis. Electrochemical characterizations were performed in order to support the proposed structure of the complexes and to investigate the effects of the metal centers and substituents to the general redox behaviors of these complexes. Multiple reversible and quasi-reversible electron transfer processes of the complexes at low potentials (especially for CoPc and FePc) indicate the possible application of the complexes in different electrochemical technologies such as electrochromic, electrocatalytic and electrosensor applications.



Fig. 10 In situ UV–Vis spectral changes of FePc in DMF/TBAP electrolyte. **a** $E_{app} = -0.80$ V, **b** $E_{app} = -1.20$ V (inset of graph $E_{app} = -1.80$ V), **c** Chromaticity diagram (each symbol represents the color of electro-generated species; square: [Fe^{II}Pc⁻²]¹⁻; triangle: [Fe^IPc⁻³]²⁻; star: [Fe^{III}Pc⁻²]⁺²)

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