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FULL PAPER

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Anthracene Substituted Co (II) and Cu (II) phthalocyanines; Preparations, Investigation of Catalytical and Electrochemical Behaviors

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An approach to investigation of catalytical behaviors of Co (II) and Cu (II) phthalocyanines is reported that is based on changing any parameter to effect these behaviors. Towards this end, new anthracene substituted Co (II) and Cu (II) phthalocyanines were prepared and characterized spectroscopic methods. New cobalt (II) and copper (II) phthalocyanines were used as catalyst for oxidation of different phenolic compounds (such as 2,3-dichlorophenol, 4-methoxyphenol, 4-nitrophenol, 2,3,6-trimethylphenol) with different oxidants. Then, electrochemical characterization of cobalt (II) and copper (II) phthallocyanines were determined by using cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. Although copper (II) phthalocyanine showed similar Pc based electron transfer processes, cobalt (II) phthalocyanine showed metal and ligand based reduction reactions as expected.

KEYWORDS
electrochemistry, oxidation, phenolic compounds, phthalocyanine

1 | INTRODUCTION

Pollution is a rising cause of concern brought about by an increasing global population and rapid industrialization. Waste generated from industries and households have reciprocal effects on the environment if mismanaged and would hence limit access to clean water. Among the broad number of water pollutants, phenols and its substituents are highly toxic and can cause harm to human health.[1,2] It is used as a raw material in industries for the manufacture of plastics and dyes. Phenol can also be found as a component of cosmetics and pesticides, as well as antiseptic in pharmaceutical products.[3] Consequently, it is commonplace to find phenol discarded into water bodies as industrial waste. As a result of its high toxicity, both the United States Environmental Protection Agency (EPA) and the European Union (EU) list phenol as a priority pollutant.[4]

Phthalocyanines (Pcs) have had wide usage in different areas such as press inks, dyes, pigments and laser technology, beginning from their first synthesis early in the last century.[5–10] Other areas of current interest include applications in liquid crystals,[9,10] catalysis,[11,12] dye-sensitized solar cells,[13] photodynamic therapy (PDT),[14–18] biomedicine, electronic and optoelectronic devices,[18,19] chemical sensors,[20,21] nonlinear optical (NLO) materials.[22]

In this paper, 4-((anthracen-9-ylmethylene)amino) phenoxy substituted cobalt (II) **4** and copper (II) **5** phthalocyanine have been synthesized. Solubility of pthalocyanine in industrial organic solvents causes problems for different type of applications; because of this reason synthesis of soluble phthalocyanine derivatives is an important task. The solubility of Pcs has been increased by using substituents such as alkyl, alkoxy, aryloxy, and alkylthio chains and bulky groups. Thanks

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to the substituent groups, Co (II) and Cu (II) phthalocyanine complexes **6** and **7** can readily dissolve in common organic solvents.[23] Herein, it has been reported that the successfull application of Co (II) and Cu (II) phthalocyanines as oxidation catalysts for oxidation of 2,3-dichlorophenol, 4-methoxyphenol, 4-nitrophenol, 2,3,6-trimethylphenol. The electrochemical properties of phthalocyanines depends on diverse factors such as the solvent, axial ligands and type of metal center. The industrial application of phthalocyanines is related to their redox properties.[24–26] In order to determine redox properties of cobalt (II) and copper (II) phthallocyanines, generally voltammetric methods such as cyclic voltammetry (CV), square wave voltammetry (SWV) are used. Although copper (II) phthalocyanine showed similar Pc based electron transfer processes, cobalt (II) phthalocyanine showed metal and ligand based reduction reactions as expected.

2 | EXPERIMENTAL

2.1 | Materials

All reactions were carried under a dry nitrogen atmosphere using Standard Schlenk techniques. All chemicals, solvents, and reagents were of reagent grade quality and were used as purchased from commercial sources. All solvents were dried and purified as described by reported procedure.[27] 4-Nitrophthalonitrile **4**[28] were prepared according to the literature procedure. 9-anthraldehyde **1,** 4-aminophenol **2** 2,3-dichlorophenol, 4-methoxyphenol, 4-nitrophenol, 2,3,6-trimethylphenol were purchased from Sigma-Aldrich and used without further purification and chemical treatment.

2.2 | Equipment

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer using KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer in $CDCl_3$. Chemical shifts were reported (δ) relative to Me_4Si as internal standard. MALDI-MS of complexes were obtained in dihydroxybenzoic acid as MALDI matrix using nitrogen laser accumulating 50 laser shots using Bruker Microflex LT MALDI-TOF mass spectrometer. Optical spectra in the UV–vis region were recorded with a Perkin Elmer Lambda 25 spectrophotometer. GC Agilent Technologies 7820A equipment (30 m x 0.32 mm x 0.50 μm DB Wax capillary column, FID detector) was used GC measurements.

2.3 | Electrochemical measurements

All electrochemical measurements were carried out with Gamry Interface 1000 potentiostat/galvanostat utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm^2. A Pt wire was served as the counter electrode and saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabuthylammonium perchlorate (TBAP) in extra pure dichloromethane (DCM) was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}.

2.4 | General procedure for the oxidation of phenolic compounds

Experiments were carried out in a thermostated Schlenk vessel equipped with a condenser and stirrer. The solution of phenolic compounds and catalyst in solvent was purified with bubbling nitrogen gas to remove the oxygen. A mixture of phenolic compounds (1.41×10^{-3} mol), catalyst (2.83×10^{-6} mol) and solvent (0.01 l) was stirred in a Schlenk vessel for few minutes at room temperature. The oxidant TBHP (2.26×10^{-3} mol) was then added and the reaction mixture was stirred for the desired time. The samples (0.5 ml) were taken at certain time intervals. Each sample was injected at least twice in the GC, 1 μL each time. Formation of products and consumption of substrates were monitored by GC. Each run was repeated three or four times. The structure of the reaction products was confirmed by ^{1}H-NMR spectroscopy.

2.5 | Synthesis

2.5.1 | Synthesis of (E)-4-((anthracen-9-ylmethylene)amino) phenol (3)

9-Anthraldehyde **1** (2.0 g, 9.70 mmol) and 4-aminophenol (1.06 g, 9.70 mmol) **2** were dissolved in dry ethanol (80 ml). Then, 6 drops of acetic acid was added to the solution. The reaction mixture was refluxed for 24 h under N_2. The reaction was monitored by thin layer chromatography. At the end of this period, the mixture was cooled to room temperature, evaporated until it was completely dry under reduced pressure. The raw material was recrystallized from ethanol to give a yellow crystalline powder and dried in a vacuum over P_2O_5. Yield: 2.20 g, (76.65%), mp: 256–258 C. IR (KBr tablet) max/cm^{-1}: 3440 (—OH), 3089 (Ar—CH), 2988 (Alip-H), 1614 (C=N), 1445, 1382, 1277, 1190, 1154, 870,744. ^{1}H NMR (CDCl3), (d: ppm): 12.43 (s, H, OH/D2O exchangeable), 8.44 (s, 2H, CH=N), 7.74–7.55 (m, 4H, Ar—H), 7.46–

7.37 (m, 4H, Ar—H), 7.30–7.15 (m, 4H, Ar—H), 7.10 (s, H, Ar—H). 13C NMR (CDCl3), (d: ppm): 162.10 (CH=N), 161.09 (ArC—O), 148.05 (ArC—N), 134.51, 133.66, 132.25, 131.98, 130.68, 129.68, 128.60, 128.53, 127.66, 126.55, 125.80, 124.77, 123.61, 122.44, 120.18, 118.55, 117.33, 116.47. MS (ESI), (m/z): $C_{21}H_{15}NO$ Calculated: 296.35; Found: 297.48 $[M + H]^+$.

2.5.2 | Synthesis of (E)-4-(4-((anthracen-9-ylmethylene)amino)phenoxy) phthalonitrile (5)

4-Nitrophthalonitrile **4** (1.10 g, 6.41 mmol) was dissolved in 10 ml dry DMF under N_2 atmosphere, and of (E)-4-((anthracen-9-ylmethylene)amino) phenol **3** (1.19 g, 6.41 mmol) added to mixture. After stirring for 30 min at 60 °C, finely ground anhydrous K_2CO_3 (2.65 g, 19.23 mmol) was added portion wise within 2 h. The reaction mixture was stirred under N_2 at 60 °C for 3 days. At the end of 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 dried in vacuum over P_2O_5 for 4 h and recystallized from ethanol to give bright brown crystalline powder. Yield: 1.95 g (72%). mp: 144-145 °C. Anal.calc. For $C_{29}H_{17}N_3O$ IR (KBr pellet), ν_{max}/cm^{-1}: 3085, 3040 (Ar-H), 2926, 2860 (Aliph. C-H), 2231 (C°N), 1672 (C-O), 1627, 1561, 1588, 1484, 1444, 1285, 1251, 1196, 1161, 1099, 1087, 969, 953, 926, 796, 777, 731, 655. ^{1}H-NMR. ($CDCl_3$), (δ:ppm): 7.96–7.88 (m, 4H, Ar-H), 7.80–7.68 (m, 4H, Ar-H), 7,62–7.48 (m, 4H, Ar-H), 7.38–7.25 (m, 3H, Ar-H) 7.14 (s, H, Ar-H), 7.10 (s, H, CH=N). ^{13}C-NMR. ($CDCl_3$), (δ:ppm): 161.90 ($C_{15} = N$), 154.39 (C_{22}-O), 150.86 (C_{19}-O), 141.40 (C_{16}), 140.59 (C_1), 136.44 (C_{23}), 135.56 (C_{27}), 134.49 (C_{24}), 133.72 (C_{25}) 132.80 (C_{26}), 131.28 (C_{20}), 130.67 (C_{21}), 129.66 (C_{17}), 128.80 (C_8), 127.46 (C_{18}), 126.57 (C_5-C_4), 125.33 (C_3-C_6), 124.68 (C_7-C_2), 122.38 (C_9-C_{14}), 121.80 (C_{10}-C_{13}), 120.43 (C_{11}-C_{12}), 117.51 ($C_{28} \equiv N$), 115.61 ($C_{29} \equiv N$). MALDI-TOF-MS, (m/z): Calculated: 423.46; Found: 441.36 $[M + H_2O]^+$ $C_{29}H_{17}N_3O$.

2.5.3 | General Procedure of Metal Phthalocyanines 6–7

To give the metal phthalocyanies, the mixture of phthalonitrile compound **5** (0.5 g, 1.18 mmol), the related anhydrous metal salt ($CoCl_2$) (38.19 mg, 0.295 mmol) for compound **6**, $CuCl_2$ (39.69 mg, 0.295 mmol) for compound **7** and two drops of DBU was heated at 160 °C in dry n-pentanol (3 mL) in a sealead tube, and stirred for 24 h. At the end of the reaction, green product was precipitated by addition of ethanol (20 ml) and filtered off. Along 2 hours, the green solid product was refluxed with ethanol (30 ml), filtered off again and washed with hot ethanol, distilled water and diethyl ether. After drying under vacuum, the product was purified on basic alumina column with chloroform–methanol (92:8) for compound **6**, (95:5) for compound **7** solvent system as eluent.

2.5.4 | Synthesis of Cobalt (II) phthalocyanine (6)

Yield: 200 mg (38%). Mp >300 °C. Anal.calc. For $C_{117}H_{72}O_4N_{12}Co$ FT-IR ν_{max}/cm^{-1} (KBr pellet): 3088, 3045 (Ar-H), 2992, 2866 (Aliph. C-H), 1732, 1644, 1506, 1488, 1451, 1388, 1326, 1287, 1266, 1179, 1098, 1022, 986, 956, 872, 765, 721, 703, 699. UV–Vis ($CHCl_3$): λ_{max}, nm (log ε): 676 (4.72), 610 (4.45), 330 (4.88). MALDI-TOF-MS, (m/z): Calculated: 1768.83; Found:1769.38 $[M + H]^+$ $C_{117}H_{72}O_4N_{12}Co$: calcd. C 79.45; H 4.10; N 9.50%; found: C 79.50; H 4.15; N 9.55.

2.5.5 | Synthesis of Copper (II) phthalocyanine (7)

Yield: 220 mg (42%). Mp >300 °C. Anal.calc. For $C_{117}H_{72}O_4N_{12}Cu$ FT-IR ν_{max}/cm^{-1} (KBr pellet): 3092, 3045, 3002 (Ar-H), 2986, 2923, 2860 (Aliph. C-H), 1740, 1605, 1522, 1455, 1440, 1386, 1365, 1288, 1233, 1162, 1089, 1026, 988, 923, 879, 853, 772, 744. UV–Vis ($CHCl_3$): λ_{max}, nm (log ε): 672 (4.98), 617 (4.44), 327 (4.62). MALDI-TOF-MS, (m/z): Calculated:1773.44; Found: 1174.20 $[M + H]^+$ $C_{117}H_{72}O_4$N12Cu: calcd. Calcd. C 79.24; H 4.09; N 9.48%; found: C 77.36; H 4.12; N 10.00.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and characterization

All synthetic pathways for new cobalt (II) and copper (II) phthalocyanine compounds were outlined in Figure 1. The condensation of 9-anthraldehyde **1** with 4-aminophenol **2** in dry ethanol at 1:1 ratio gave the expected (E)-4-((anthracen-9-ylmethylene)amino) phenol **3** (Schiff base) in a high yield (76.65%).[29] In the IR spectrum of **3**, the disappearing of the intense absorption bands at 3388 and 3360 cm^{-1}, corresponding to the $-NH_2$ groups of **2**, after the conversion to substituted Schiff base and the appearance of a new band at 1612 cm^{-1} corresponding to CH=N group, indicated that the combining has occurred. Moreover, in the same spectrum of **3**, the disapearing of sharp absorbtion band at 1700 cm^{-1} (C=O) of **1**and the appearance of new band at 1612 cm^{-1} indicated that the combining has successfully occured. The rest of the spectrum of the Schiff base **3** resembles closely that of starting reactants **1** and **2** including the

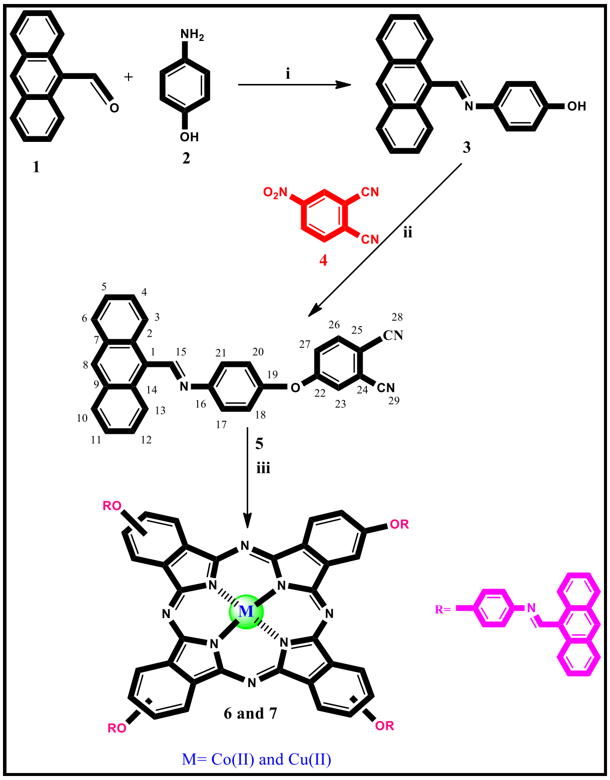


FIGURE 1 The synthetic route of the phthalonitrile, cobalt phthalocyanine and copper phthalocyanine. Reagents and conditions: i: dry ethanol, 6 drops of acetic acid, N_2, 24 h; ii: dry DMF, dry K_2CO_3, N_2, 55–60 °C dry DMF, K_2CO_3, 60 °C, 96 h; (iii) n-pentanol, DBU, 160 °C, $CoCl_2$, $CuCl_2$

characteristic stretching/deformation vibrations of aliphatic, aromatic/aliphatic and phenolic groups. The difference between two H-NMR spectra of substituted phenol **2** and the Schiff base **3** is due to the presence of iminic carbon CH=N at 8.44 ppm. Moreover, ^{13}C NMR spectrum of compound **3** clearly indicates the presence of CH=N group (162.10 ppm). The MS mass spectrum of compound **3** shows a molecular ion peak at m/z = 297.48 $[M + H]^+$, supporting the proposed formula of this compound.

The compound **5** was obtained from the reaction of compound **3** to 4-nitrophthalonitrile **4** in dry K_2CO_3/dry DMF under N_2 atmosphere at 55–60 °C for 3 days. This is accomplished by a base catalyst nucleophilic displacement aromatic nitro group of 4-nitrophthalonitrile with the Schiff base **3**.[30] Similarly, comparison of the IR spectral data clearly indicated the presence of compound **5**. The —OH stretching/deformation of compound **3** at 3440/1382 cm^{-1} and NO_2 stretching of compound **4** at 1519 and 1333 cm^{-1} disappeared, and a new absorption band appeared at 2231 cm^{-1} ($C \equiv N$), indicating the reaction took place. In the ^{1}H NMR spectrum of dinitrile **5** a singlet at 12.43 ppm belonging to the phenolic —OH **3** disappeared after the conjunction reaction. The spectral data belonging to new formation indicated that the joining has occurred as predicted by the proposed structure. The ^{13}C-NMR spectra of compound **5** indicated carbon atoms between at 161.90–115.61 ppm. The nitrile carbon atoms for compound **5** were also observed at 117.51 and 115.61 ppm. In the mass spectum of compound **5**, the presence of molecular ion peak at m/z = 441.36 $[M + H_2O]^+$, confirmed the proposed structures.

The cyclotetramerization of the phthalonitrile compound **5** to the cobalt (II) and copper (II) phthalocyanine **6** and **7** can be seen clearly by the disappearance of the peaks at 2231 cm^{-1} belonging to the C≡N vibrations. The IR spectra of **6** and **7** showed similar characteristics. The NMR spectra of peripherally tetra-substituted cobalt (II) and copper (II) phthalocyanines **4** and **5** were not be able to take into precluded owing to their paramagnetic nature.[31] The mass spectra of compounds **6** and **7**, which showed peaks at m/z = 1769.38 $[M + H]^+$ and 1174.20 $[M + H]^+$ respectively support the proposed formula for these compounds. The results of the elemental analysis also confirmed the structure of complexes **6** and **7.**

The electronic spectra of the phthalocyanines have two strong absorption bands in UV/Vis spectroscopy. One of them is in the visible region at 600–700 nm (Q Band) due to electronic transitions from π-highest occupied molecular orbital (HOMO) to π^*-lowest unoccupied molecular orbital (LUMO) energy levels, and the other one is in the UV region at about 300–500 nm (B or Soret Band) due to transitions from deeper π-HOMO and π^*-LUMO energy levels.[32] The Q-band of the phthalocyanines is more intense than Soret band. While the Q bands of the metal-free phthalocyanines are splitted two bands, owing to D_{2h} symmetry and the lifting of degeneracy of the LUMO level, as Q_x, Q_y bands that of metallophthalocyanines are observed as a single band owing to D_{4h} symmetry.[33] The Q-band absorptions of π-π^* transition for both phthalocyanines in chloroform were observed as a single band of high intensity at 676 nm for **6**, 672 nm for **7**. There was also a shoulder at the slightly higher energy side of the Q band for each phthalocyanine. B band absorptions of the metallophthalocyanines **6–7** were observed at 330, 327 nm respectively (Figure 2).

Redox properties of phthalocyanines were performed with CV and SWV measurements in dichloromethane (DCM)/tetrabutylammoniumperchlorate (TBAP) electrolyte system on a Pt working electrode. Basic electrochemical parameters, the assignments of the redox couples and estimated electrochemical parameters including the half-wave potentials ($E_{1/2}$), peak to peak potential separations (ΔE_p), and difference between the first oxidation and reduction processes ($\Delta E_{1/2}$), are derived from the analyses of the complexes and these data are shown in Table 1.

While CoPc type complexes were reported as MPcs having redox active metal center, CuPc ise known as MPcs

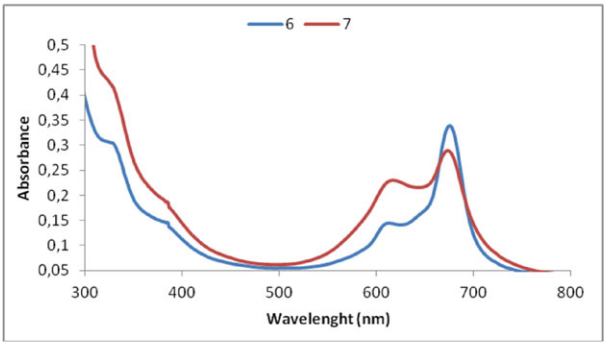


FIGURE 2 UV–Vis spectrum of complexes **6** and **7** in chloroform

having redox inactive Pc core. Therefore, voltammeric results of CuPc and CoPc were discussed here as examples for MPcs having redox inactive and redox active metal centers respectively. Figure 3 represents CV responses of CoPc in DCM/TBAP electrolyte on a Pt working electrode. CoPc undergoes one reduction reaction, at −0.41 V and two oxidation reactions at 0.71 V and 1.31 V within the potential window of DCM/TBAP electrolyte system. While the reduction reaction is reversible, two oxidation reductions have quasi-reversible character. It is well known that the central metal ion can reduce when d orbitals of the metal ion locate between HOMO and LUMO of the ring.[34] This phenomenon occurs in the MPcs involving only redox active metals, such as Mn, Fe or Co.[35] As a consequence, R_1 process ($[Co^{II}Pc^{2-}]$ / $[Co^{I}Pc^{2-}]^-$) could be assigned to the cobalt-based redox couple and the remaining redox couples to the ring. But the first and second oxidation processes of $Co^{II}Pc$ is assigned to ligand-based processes, $\mathbf{O_1}$→$[Co^{II}Pc^{2-}]$ / $[Co^{II}Pc^{-}]^+$, $\mathbf{O_2}$→$[Co^{II}Pc^{-}]^+$/ $[Co^{II}Pc]^{2+}$. On the other hand, ($\Delta E_{1/2}$ value (1.12 V) of CoPc is in agreement with the cobalt phthalocyanines in the literature,[36,37] which supports the proposed structure of the complex. Also, HOMO-LUMO gap of CoPc ($\Delta E_{1/2}$ = 1.12 V) is in compliance with the CoPc reported in the literature.[38]

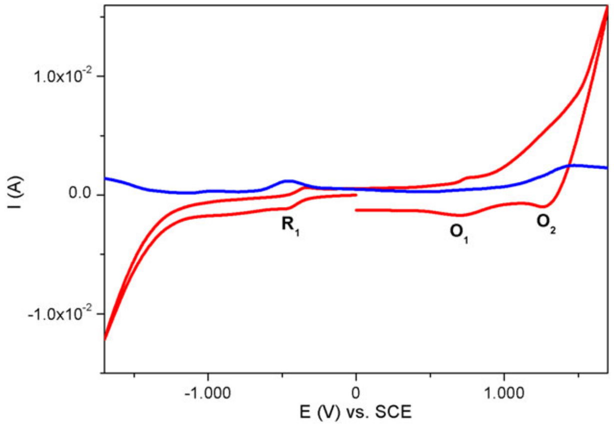


FIGURE 3 CV and SWV of CoPc

Figure 4a and 4b represents CV and SWV responses of CuPc in DCM/TBAP electrolyte on a Pt working electrode. As shown in Figure 4, electrochemical behavior of CuPc is different than that of CoPc. Complex **7** has redox inactive metal center (Cu) thus indicating phthalocyanine ring-based behaviors for all redox processes since the energy level of the d orbitals of this metal ion is placed out of the HOMO-LUMO energy levels. The first reduction of the Pc ligand is associated to the position of the lowest occupied molecular orbital (LUMO) whereas the first oxidation of the ligand is associated to the position of the highest occupied molecular orbital (HOMO). For this reason, ($\Delta E_{1/2}$ values related with the HOMO–LUMO gap in CuPc species having redox inactive metal centers and for CuPc, is generally consistent with the values reported in the literature.[39,40] CuPc gives two quasi-reversible reductions, R_1 at −0.86 V (ΔE_p = 144 mV), R_2 at −1.59 V (ΔE_p = 127 mV) during the cathodic potential scans and one irreversible oxidation reaction O_1 at 0.72 V (ΔE_p = 196 mV), one quasi-reversible oxidation reaction O_2 at 1.30 V (ΔE_p = 130 mV), during the anodic potential scans.

3.2 | Catalytic Studies

Cobalt (II) and copper (II) phthalocyanine **6** and **7** have been tested as homogeneous catalyst precursor for the oxidation of different phenolic compounds. The catalytic reactions were performed under mild conditions (50 °C) in DMF and using different types of oxidant (H_2O_2, m-CPBA, TBHP and air oxygen). Experimental results

TABLE 1 Voltammetric data of the phthalocyanines. All voltammetric data were given versus SCE

Phthalocyanines	Redox processes	$^aE_{1/2}$	$^b\Delta E_p$ (mV)	$^c\Delta E_{1/2}$
CoPc	$\mathbf{R_1}$→$[Co^{II}Pc^{2-}]$ / $[Co^{I}Pc^{2-}]^-$	−0.41	98	1.12
	$\mathbf{O_1}$→$[Co^{II}Pc^{2-}]$ / $[Co^{II}Pc^{-}]^+$	0.71	115	
	$\mathbf{O_2}$→$[Co^{II}Pc^{-}]^+$/ $[Co^{II}Pc]^{2+}$	1.31	130	
CuPc	$\mathbf{R_1}$→$[Cu^{II}Pc^{2-}]$ / $[Cu^{II}Pc^{3-}]^-$	−0.86	144	1.58
	$\mathbf{R_2}$→$[Cu^{II}Pc^{3-}]^-$ / $[Cu^{II}Pc^{4-}]^{2-}$	−1.59	127	
	$\mathbf{O_1}$→$[Cu^{II}Pc^{2-}]$ / $[Cu^{II}Pc^{-}]^+$	0.72	196	
	$\mathbf{O_2}$→$[Cu^{II}Pc^{-}]^+$/ $[Cu^{II}Pc]^{2+}$	1.30	138	

[a]: $E_{1/2}$ values ((E_{pa} + E_{pc})/2) were given versus SCE at 0.100 Vs^{-1} scan rate. [b]: ΔE_p = E_{pa}-E_{pc}. [c]: $\Delta E_{1/2}$ = $E_{1/2}$ (first oxidation)- $E_{1/2}$ (first reduction).

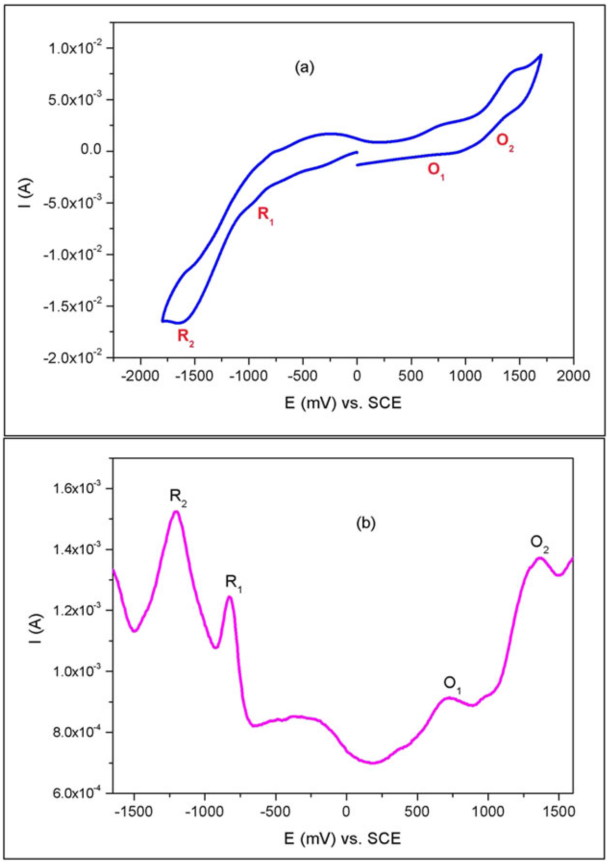
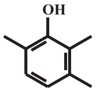
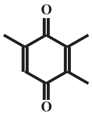
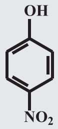
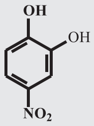
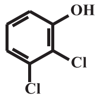
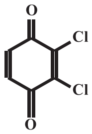
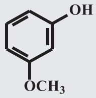
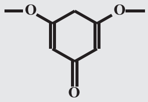


FIGURE 4 (**a**) CV of CuPc. (**b**) SWV of CuPc

illustrated that complexes are effective catalyst for the oxidation of phenols. Among the studied substituted phenols (Table 2), both complexes are more active in 2,3,6-trimethyl phenol than the other phenolic compounds. Entries 1, 2, 3 and 4 illustrate that all phenolic compounds, major products and TON and TOF ratio. The major product as 2,3,6-Trimethyl-1,4-benzoquinone, the key intermediate in the synthesis of vitamin E), the side product as 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenyldiol (BP) were determined in the oxidation of 2,3,6 trimethyphenol oxidation reaction (Figure 5).

In particular, electron-rich aromatic compound, 2,3,6-trimethylphenol, converts relatively faster than the other studied aromatic compounds to related products for both compounds (for compound **6** and **7**). Co (II) phthalocyanine showed the highest activity in the oxidation of 2,3,6-trimethyl phenol (78% in 1 h) in DMF with a high conversion value (97% in 3 h). In this reaction 2,3,6-trimethyl phenol is 97% after 3 h and product selectivity is 95% (Table 2, entry 1). It should be emphasized that in this oxidation, an cobalt (III) Pc complex attacks to the carbon atom para position to the phenoxide oxygen, resulting in the formation of intermediate I. Then 2,3,6-trimethyl-1,4-benzoquinone is formed by proton-mediated elimination of intermediate I (Figure 6) in first 1 h. After 2 h reaction, benzoquinone formation increased to 21%, while 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenyldiol (BP) was at 3%.

TABLE 2 Oxidation of Substituted Phenols Catalyzed by Complex 6 and 7

Entry	Substrate	Major Product	Total Conversion (%)		TON/TOF (h^{-1})	
			6	7	6	7
1			97	80	483/161	398/132.6
2			77	70	383/128	348/116
3			74	76	368/123	378/126
4			57	36	283/94	179/59.8

TON = mole of product/mole of catalyst

TOF = mole of product/mole of catalyst x time

Conversion was determined by GC.

Catalyst/substrate/oxidant ratio = 1/500/800, Reaction Time = 3 hours.

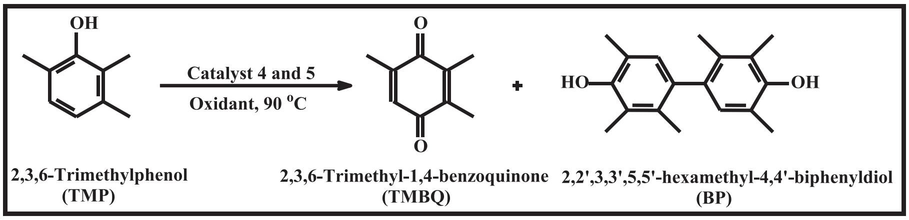


FIGURE 5 The oxidation products of 2,3,6-trimethylphenol

Table 3 shows the effect of the amount of substrate on the conversion of 2,3,6-trimethylphenol. Results of the reactions carried out varying oxidant and substrate amounts are given in Table 3. Firstly, we investigated the effect of the substrate/catalyst molar ratio (500–1500) (Table 3) as the other parameters were kept constant. It is predicted that the reaction rate increased with decreasing of the substrate/catalyst molar ratio. It was decided that the optimal 2,3,6-trimethylphenol conversion was obtained when Substrate/catalyst mole ratio was 500 with good TON value and selectivity (483 for **6,** 398 for **7** and 161 for **6**, 132.6 for **7**). Secondly, oxygen source effect is determined by using with H_2O_2, m-CPBA, TBHP and air oxygen as oxidant. Oxygen was not effective under studied conditions probably the cause of the low-temperature reaction. The results in Table 3 show that H_2O_2 is the best oxidant for 2,3,6-trimethylphenoloxidation in the presence of complex **6** and **7**.

Additionally, TBHP and m-CPBA can serve as an oxidant but low conversion for both complexes. Adding TBHP or m-CPBA in the reaction media, the reaction color changed from green to light brown. It is also known that the soret band of phthalocyanine shifts in the UV–visible spectrum according to type of transition metals in phthalocyanine metal complexes. It was thought that the transition metal in the complex was not hydrolyzed, since it was observed that only the intensity of the soret band of phthalocyanine decreased and no shift was observed around 400–450 nm where is the soret band of the metal-free phthalocyanine during the oxidation.[41] This clue explains that complex **4** and **5** was degraded immediately with TBHP or m-CPBA.[42] The results of studies for complex **4** and **5** using with air oxygen show that there is no formation of products during the oxidation process. Thirdly, the another important parameter is oxidant/catalyst ratio to find the optimal conditions of 2,3,6-trimethylphenol oxidation. When the increasing oxidant/catalyst ratio from 300/1 to 800/1, the rate of the reaction increased. In contrast, while the catalytic oxidation was processing from 800/1 to 1200/1, the conversion inclined to decrasing. At this stage, it is possible that the coordination around the cobalt and copper ion can change and produce inactive intermediate species.[43] This situation is also effects catalytic activity of copper phthalocyanine. Additionally, there were no product detectable in the blank reactions without catalysts. It is proved that presence of the catalyst are essential for the oxidation (Table 3).

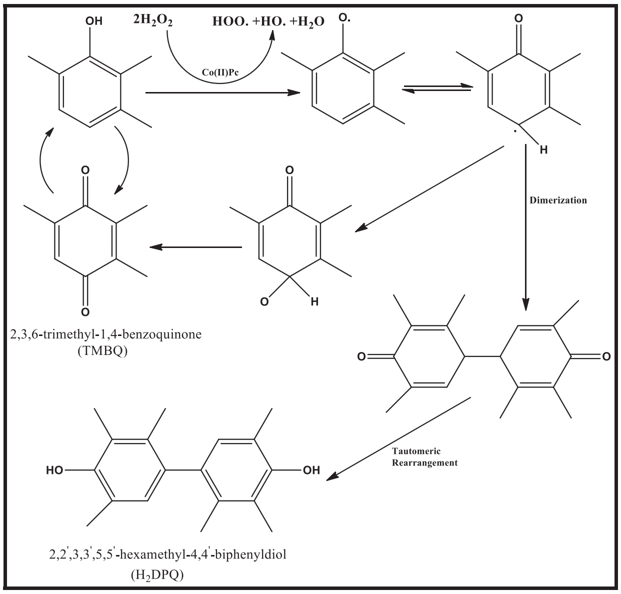


FIGURE 6 Proposed mechanism of 2,3,6-trimethylphenol oxidation

The proposed mechanism for the oxidation of 2,3,6-trimethylphenol catalyzed by catalysts **6** and **7** is shown in Figure 6. When H_2O_2 is the oxidant, it is believed that interaction of catalyst and oxidant creates peroxide and hydroxide radicals then these radicals react with 2,3,6-trimethylphenol and herewith 2,3,6-timethylphenoxide radicals are formed.[44] According to Türk and Cimen, an cobalt (III) Pc complex attacks to the carbon atom para position to the phenoxide oxygen, resulting in the formation of intermediate I in Figure 6. Then 2,3,6-trimethyl-1,4-benzoquinone is formed by proton-mediated elimination of intermediate I.[45] In the formation of 2,2′,3,3′,5,5′-hexamethyl-4,4′-biphenyldiol, C-C coupling occurs between the resonance forms of 2,3,6-timethylphenoxide radicals with unpaired electron at para position. The resulting unstable coupling product rearranges itself into more stable tautomeric form (Figure 6).[46–48] We also foresee that a similar mechanism is contained in the oxidation of 2,3,6-trimethylphenol by the Cu (II)Pc/H_2O_2 system.

TABLE 3 Selective oxidation of 2,3,6-trimethylphenol with catalysts 6 and 7 using different oxidant and temperature

		Temperature (°C)	Conversion (%)		Selectivity^a (%)		TON		TOF (h^{-1})	
Subs./Ox./Cat	**Oxidant**		**6**	**7**	**6**	**7**	**6**	**7**	**6**	**7**
500/300/1	H_2O_2	50	30	29	45	40	149	144	49.8	48.1
500/500/1	H_2O_2	50	52	33	50	49	259	164	86.3	54.8
800/500/1	H_2O_2	50	63	49	53	61	502	390	167.4	130
1200/500/1	H_2O_2	50	70	60	61	61	837	717	279	239
1500/500/1	H_2O_2	50	83	61	70	69	1240	911	413	303.9
500/800/1	H_2O_2	50	97	80	95	89	483	398	161	132.6
500/1000/1	H_2O_2	50	81	48	78	45	403	239	134	79.7
500/1200/1	H_2O_2	50	68	40	60	45	388	199	112.9	66.4
500/800/1	m-CPBA	50	56	66	51	63	279	328	93	109.6
500/800/1	TBHP	50	83	55	78	80	413	274	137.8	91.3
500/800/1	Air oxygen	50	-	-	-	-	-	-	-	-
500/800/1	H_2O_2	75	90	69	80	78	448	343	149.4	114.5
500/800/1	H_2O_2	90	90	68	78	70	448	338	149.4	112.9
500/800/1	H_2O_2	25	49	22	46	35	244	109	81.3	36.5
300/500/free cat.	H_2O_2	50	8	9	-	-	-	-	-	-

TON = mole of product/mole of catalyst

TOF = mole of product/mole of catalyst x time

Conversion was determined by GC.

Reaction Conditions: 500/800/1: 1.41×10^{-3} mol)/ 2.26×10^{-3} mol/2.83×10^{-6} mol

[a]=Selectivity of TMBQ Reaction time = 3 hours.

4 | CONCLUSION

In conclusion, Co (II) and Cu (II) phthalocyanine complexes with 4-((anthracen-9-ylmethylene)amino) phenoxy groups have been synthesized, and characterized with spectroscopic methods. The Co (II) phthalocyanine compound behaves as a homogeneous catalyst precursor for the oxidation of various phenolic compounds with good yield under mild reaction conditions (50 °C) with different oxidants. 2,3,6-Trimethylphenol oxidation reactions are catalyzed by both catalysts with high conversion and selectivity among the all substrates. Converting from environmentally harmfull phenolic compounds into less harmfull oxidation products by Co (II) and Cu (II) phthalocyanines makes this study attractive. Electrochemistry of CoPc, CuPc are studied in solution with voltammetric measurements. Electrochemical analysis of the complexes support the proposed structure of the complexes. While CuPc shows Pc ring based redox processes, CoPc gives metal based electron transfer reactions in addition to the Pc based redox reactions, which enrich the possible usage of the phthaocyanines in various electrochemical technologies.

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