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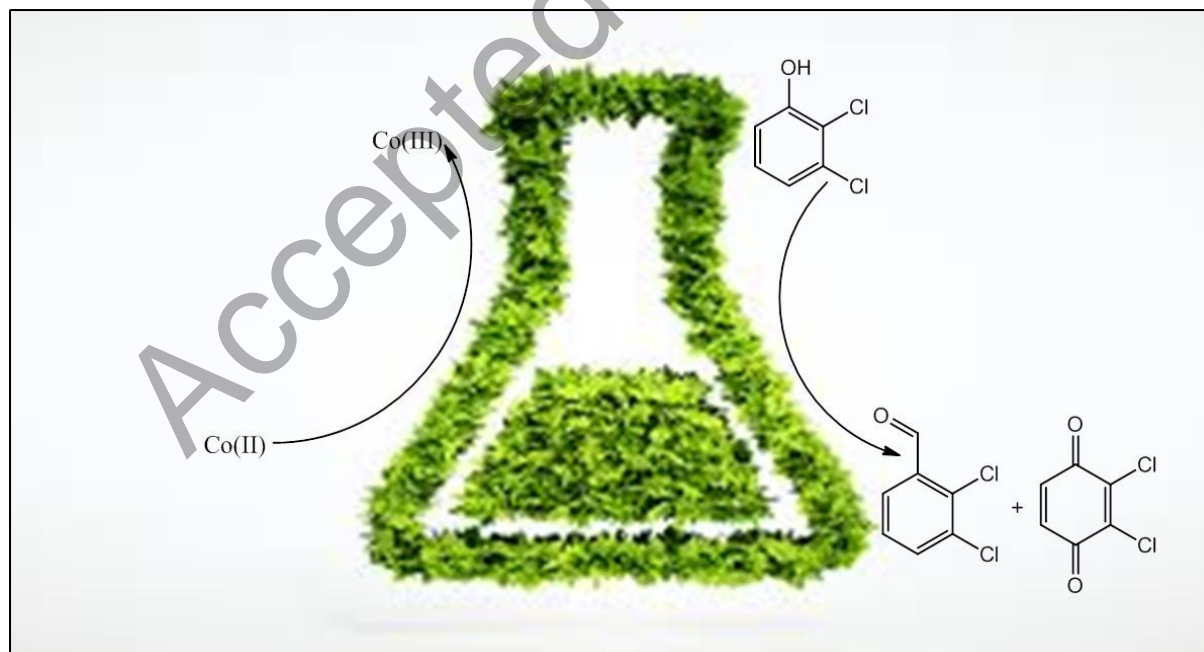
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Degradation of substituted phenols with different oxygen sources catalyzed by Co(II) and Cu(II) phthalocyanine complexes

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Research on substituted phenol degradations has received substantial attention. In this work, effective Co(II) and Cu(II) phthalocyanine complexes as catalysts were studied in order to degrade toxic phenols to harmless products. The effect of various process parameters such as initial concentration of phenol, catalyst, oxygen sources and temperature on the degradation reaction was investigated to achieve maximum degradation efficiency. The catalytic activities of Co(II) and Cu(II) phthalocyanines were evaluated for oxidation of phenolic compounds such as *p*-nitrophenol, *o*-chlorophenol, 2,3-dichlorophenol and *m*-methoxyphenol. Co(II) phthalocyanine displayed good catalytic performance in degradation of 2,3-dichlorophenol to 2,3-dichlorobenzaldehyde and 2,3-dichloro-1,4-benzoquinone with the highest TON and TOF values within 3 h at 50 °C. The fate of catalyst during the degradation process was followed by UV-Vis spectroscopy.

Graphical Abstract



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Keywords: Degradation; Substituted phenols; Catalyst; Phthalocyanine

1. Introduction

Phenolic compounds derived from pesticides, coal conversion, petroleum and petrochemical industries are considered by the Environmental Protection Agency (EPA) as toxic water pollutants, based on their carcinogenic effects and high chemical stability [1] even in concentrations less than 1 ppb. They have negative effects on marine life and aquatic environments when discharged into streams [2]. Phenol from wastewater can be removed by conventional technologies like adsorption, coagulation, and enzyme oxidation [3-5]. However, these conventional technologies do not completely degrade the organic pollutants and can produce secondary pollutants [6].

Progress has been made in the catalytic degradation of organic pollutants using different metal catalysts [7, 8]. Phthalocyanine metal complexes (MPcs) are structurally analogous to porphyrin complexes [9]. Due to the structural similarity with porphyrin metal complexes, phthalocyanine complexes show bioinspired chemistry associated with porphyrin complexes [10]. Recently phthalocyanines have been utilized as catalysts for different synthetic reactions [11-15]. The catalytic properties of metallophthalocyanines depend on the metal and structure of the phthalocyanine moiety. Different metals inserted in the core of the phthalocyanine ring are active in specific reactions.

A few classes of metal complexes were developed to overcome the oxidation/selectivity problem, particularly using bio-inspired systems [16, 17]. Some natural enzymes are able to cleave C-H bonds at ambient conditions utilizing high-valent metal-oxo (HVMO) intermediates [18]. Some complexes of transition metals where coordination environments stabilize such species can mimic selective biological C-H activation pathways (such as the radical rebound mechanism of P450) [19]. The ability of phthalocyanines and porphyrins to stabilize HVMO species is remarkable, and complexes with porphyrin ligands have been extensively investigated as catalysts for C-H activation [20]. In contrast to porphyrins, phthalocyanines have not been as studied in such reactions due to their more complicated syntheses. Phthalocyanines form HVMO species upon reaction with peroxides, *e.g.*, H₂O₂, TBHP and *m*-chloroperbenzoic acid (mCPBA) [21-23]. The *m*-CPBA oxidant stands apart from other peroxides due to the complex reaction

mechanism and tendency to oxidize stereoselectively even under metal-free conditions although low yields and conversion [24].

We have synthesized and characterized (E)-4-((2-morpholinoethyl)imino)methylphenoxy substituted Co(II) and Cu(II) phthalocyanine complexes. Because the solubility of phthalocyanines increases in organic solvents by using substituents such as alkyl, alkoxy, aryloxy, and alkylthio chains and bulky groups, E-4-((2-morpholinoethyl)imino)methylphenoxy groups have been used as substituents. Catalytic activities of Co(II) and Cu(II) phthalocyanine complexes have been investigated for phenolic oxidation with different oxygen sources.

2. Experimental

The equipment, materials, general procedure and method for oxidation of phenolic compounds are given as supplementary materials.

2.1. Synthesis

2.1.1. (E)-4-((2-morpholinoethyl)imino)methylphenoxyphthalonitrile (3).
4-Nitrophthalonitrile **2** (0.74 g, 4.27 mmol) and (E)-4-((2-morpholinoethyl)imino)methylphenol **1** (1.0 g, 4.27 mmol) in dry DMF (10 mL) were heated to 55 °C. After stirring for 15 min at 55 °C, finely ground anhydrous K₂CO₃ (1.767 g, 12.81 mmol) was added in small portions over 2 h with efficient stirring and degassed several times. The mixture was stirred at 55 °C under a nitrogen stream for 3 days. Afterwards, the mixture was poured into 200 g of crushed ice-water mixture and stirred for 2 h. The resulting brown solid was collected by filtration and washed with ethyl alcohol and water in turn, and subsequently dried *in vacuo*. Yield: 1.09 g (71%), m.p. 72–75 °C. FT-IR: ν_{max} (cm⁻¹) = 3236–3112–3089 (C–H aromatic), 2969–2924–2862 (CH₂, CH₃), 2232 (C≡N), 1660 (C=N), 1484, 1454, 1387, 1347, 1306, 1276, 1248, 1114, 1089, 951, 914, 878, 771, 661. ¹H NMR (ppm, CDCl₃): δ = 8.28 (d, 1H, CH=N), 7.98–7.63 (m, 3H, Ar–H), 7.29–7.10 (m, 3H, Ar–H), 3.89 (t, 2H, CH₂-N=CH), 3.72 (m, 4H, CH₂-O), 2.60 (t, 2H, CH₂-N), 2.35 (m, 4H, CH₂-N). ¹³C NMR (ppm, CDCl₃): δ = 160.02 (C₁₄), 156.46 (C₁₃), 154.93 (C₇), 136.16 (C₁₈), 135.74 (C₁₆), 132.16 (C₈), 127.48 (C₁₀), 125.64 (C₁₇), 124.56 (C₁₅), 123.46 (C₉), 122.90 (C₁₂), 122.14 (C₁₁), 116.93 (C₂₀), 115.63 (C₂₁), 106.85 (C₁₉), 66.25 (C₁,C₃), 60.18 (C₆), 57.35 (C₅), 56.73 (C₂,C₄). LC-MS/MS (ES⁺) *m/z*: Calculated: 360.41 Found: 399.52 [M+K]⁺.

2.1.2. General procedure for the syntheses of MPcs (4 and 5). The phthalonitrile derivative **3** (0.25 g, 0.693 mmol) was dissolved in 3 mL of dry *n*-pentanol under a blanket of nitrogen in a well-stoppered Schlenk tube. Catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and anhydrous metal salts (0.173 mmol) [CoCl₂, 22.45 mg; 23.3 mg; CuCl₂] were subsequently added into the solution and the reaction mixture was refluxed at 160 °C for 8 h. After cooling to room temperature, the reaction mixture was diluted and the product was precipitated by adding 10 mL of ethanol. The resulting precipitate was filtered off, washed with EtOH and H₂O separately and dried *in vacuo*. The crude products were purified by column chromatography on aluminium oxide 90 active basic alumina. Figure 1 displays the synthetic route for the MPcs **4** and **5**.

2.1.2.1. Cobalt(II) phthalocyanine (4). MPc **4** was synthesized by following the aforementioned general procedure for MPcs. The crude blue product was purified by column chromatography on basic alumina using chloroform:ethanol (98:2) as eluent. The extract was evaporated to dryness and dried under vacuum to give blue **4**. Yield: 124 mg (48%), m.p. >300 °C. FT-IR: ν_{max} (cm⁻¹) = 3161–3046 (C–H aromatic), 2963–2915–2850 (CH₂, CH₃), 1635 (C=N), 1605 (C=C), 1532, 1455, 1432, 1366, 1314, 1228, 1093, 1049, 957, 863, 755. UV-Vis (chloroform), λ_{max} , nm (log ϵ): 328 (4.32), 384 (3.55), 614 (3.92) and 676 (4.32). MALDI-TOF-MS m/z : Calculated: 1500.52, Found: 1518.53 [M+H₂O]⁺.

2.1.2.2. Copper(II) phthalocyanine (5). Phthalocyaninato copper(II) derivative **5** was synthesized by following the aforementioned general procedure for MPcs. The crude blue product was purified by column chromatography on basic alumina using chloroform:ethanol (96:4) as eluent. The extract was evaporated to dryness and dried under vacuum to give blue solid **5**. Yield: 110 mg (42%), m.p. >300 °C. FT-IR: ν_{max} (cm⁻¹) = 3025, 3011 (C–H aromatic), 2973, 2816, 2809 (C–H aliphatic), 1643 (C=N), 1609 (C=C), 1575, 1503, 1482, 1432, 1383, 1239–1122–1098–1050 957, 865, 732. UV-Vis (chloroform), λ_{max} , nm (log ϵ): 336 (3.88), 386 (4.10), 620 (3.50) and 680 (4.42). MALDI-TOF-MS m/z : Calculated: 1505.18, Found: 1523.17 [M+H₂O]⁺.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic pathways for (E)-4-((2-morpholinoethyl)imino)methyl)phenoxy substituted phthalonitrile derivative **3** and corresponding metallophthalocyanines **4** and **5** are demonstrated in figure 1. The synthesized new compounds **3-5** were characterized by using UV-Vis (for **4** and **5**), ^1H NMR and ^{13}C NMR spectroscopies (for **3**), LC-MS/MS (for **3**), MALDI-TOF mass spectral data (for **4** and **5**) and FT-IR. The MPc complexes **4** and **5** were synthesized via cyclotetramerization of **3** in the presence of the corresponding anhydrous metal salts (CoCl_2 for **4**; CuCl_2 for **5**) in dry *n*-pentanol as solvent and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as strong base at 160 °C under nitrogen atmosphere. **4** and **5** were purified through column chromatography on basic alumina. **4** and **5** were soluble in most common organic solvents such as THF, CH_2Cl_2 , CHCl_3 , DMF and DMSO due to the substituted groups.

The synthesis of **3** was achieved in 71% yield through base-catalyzed aromatic nitro displacement of 4-nitrophthalonitrile **2** with (E)-4-((2-morpholinoethyl)imino)methyl)phenol **1** in dry DMF by using anhydrous K_2CO_3 as the base. After synthesis of **3**, the peak in the vibrational spectra of **1** for the O-H vibrations at 3650 cm^{-1} disappeared and a new vibration was observed at 2232 cm^{-1} belonging to the $\text{C}\equiv\text{N}$ functionality, indicative of the formation of **3**. Other characteristic vibrations corresponding to aromatic CH stretchings at $3236\text{--}3112\text{--}3089\text{ cm}^{-1}$; aliphatic CH stretches at $2969\text{--}2862\text{ cm}^{-1}$ are consistent with the assigned formulation. In the ^1H NMR spectrum of **3**, the signal associated with the O-H disappeared and new signals of the aromatic ring protons at $\delta = 8.28, 7.98\text{--}7.63$ and $7.29\text{--}7.10$ ppm were observed for **3**. Other ^1H NMR signals are almost identical with **1**. The presence of signals at $\delta = 115.82\text{--}115.45$ ppm ($\text{C}\equiv\text{N}$) in the ^{13}C NMR spectrum of **3** proved the proposed structure. The mass spectrum of **3** was measured with electrospray ionization technique (ES^+) showing the parent ion peak at m/z : $399.52 [\text{M}+\text{K}]^+$.

The disappearance of the $\text{C}\equiv\text{N}$ vibration at 2232 cm^{-1} indicated the cyclotetramerization of **3** into the metallophthalocyanines **4** and **5**. Also shown was the presence of $\text{C}=\text{N}$ vibrations of the inner core of **4** and **5** at 1635 cm^{-1} for **4** and 1641 cm^{-1} for **5**. Owing to the paramagnetic nature of Co^{+2} and Cu^{+2} , ^1H and ^{13}C NMR measurements of **4** and **5** cannot be taken [25]. The mass spectra of **4** and **5** were measured with MALDI-TOF-MS and were in a good accord with

the proposed structures. Molecular ion peaks were observed at $m/z = 1518.53$ $[M+H_2O]^+$ for **4** and 1523.17 $[M+H_2O]^+$ for **5**.

The electronic spectra of **4** and **5** displayed the best indications concerning the characteristic B and Q bands of typical MPcs. The electronic absorption spectra of **4** and **5** were measured in chloroform (figure 2). Metallophthalocyanine derivatives **4** and **5** showed B bands at 328 nm ($\log\epsilon = 4.32$) and 384 nm ($\log\epsilon = 3.55$) for **4**, 336 nm ($\log\epsilon = 3.88$) and 386 nm ($\log\epsilon = 4.10$) for **5** and intense single Q bands with lower wavelength shoulders at 614 nm ($\log\epsilon = 3.92$) and 676 nm ($\log\epsilon = 4.32$) for **4** and 620 nm ($\log\epsilon = 3.56$) and 680 nm ($\log\epsilon = 4.42$) for **5**. These results are in accord with MPcs in the literature.

3.2. Catalytic studies

The catalytic activities of Co(II) and Cu(II) phthalocyanine complexes were explored for oxidation of substituted phenolic compounds. All the oxidation reaction data are given in tables 1 and 2. In experiments for 3 h oxidant and auxiliary chemicals on the conversion and yields were investigated. Phenolic compounds can be turned into various organic compounds in oxidation reactions. In this work, two fragments were determined due to attack by catalytically active species. In blank reactions (using no catalysts or oxidants) no product was detectable (table 3), showing that catalyst and oxidant are essential for the oxidation. The main product was determined as 2,3-dichloro-1,4-benzoquinone and the side product was determined as 2,3-dichlorobenzaldehyde in the oxidation of 2,3-dichlorophenol (figure 3). Influence of substrate, catalysts and results for oxidation processes are demonstrated in table 1. According to the results of this table, **4** demonstrated the highest activity and selectivity producing 2,3-dichloro-1,4-benzoquinone as major product in 2,3-dichlorobenzaldehyde oxidation. The results of the catalytic oxidation of phenolic compounds by H_2O_2 in the presence of **4** are shown in figure 4. This figure shows that 2,3-dichlorophenol oxidation has higher total conversion than the other substrates with catalyst **4**.

As the other parameters were kept constant, the molar ratio was increased from 300–1000 to determine the influence on substrate to metal ion ratio. The reaction rate increased with decreasing of the substrate/catalyst molar ratio (table 2) as expected. Substrate/catalyst ratio on the oxidation gave the same main product with TON and TOF values (313 and 104.5 with **4**).

To determine oxygen source effect, H₂O₂, TBHP, *m*-CPBA and air were used as oxidants. The results in table 2 show that H₂O₂ was the best oxidant for 2,3-dichlorophenol oxidation in the presence of **4**. Moreover, TBHP and *m*-CPBA can serve as oxidants but low conversions were observed for **4** and **5**. The reaction color changed from light blue to brown when we added TBHP or *m*-CPBA, suggesting that **4** was degraded immediately with TBHP or *m*-CPBA [26, 27]. The catalytic activity studies for **4** and **5** using air displayed no formation of products during the oxidation process (figure 5). To find the optimal reaction conditions, oxidant/catalyst ratio was tested in 2,3-dichlorophenol oxidation. When the oxidant/catalyst ratio was increased 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 decreased. At this stage, it is possible that the coordination around the cobalt ion can change and produce inactive species [28-30].

Oxygen activation in oxidation reactions is a challenging problem. Co(II) complexes are involved in one-electron reduction of oxygen to form superoxo (Co(III)-) or peroxy derivatives (Co(III)-O-O-Co(III)) [31, 32]. V.N. Shishkin *et al.* reported that the cobalt complex with 4-octasulfophenyltetrapyrizinoporphyrazine (a ligand with pronounced electron-withdrawing properties) catalyzes the reactions of thiourea and N,N'-dimethylthiourea with oxygen [33, 34]. The reaction occurs under mild conditions to form the corresponding urea and sulfur in high yield. In our work, we studied the catalytic oxidation reactions of phenolic compounds with different oxygen sources and activated oxygen.

Temperature was also tested, changing from 50 °C to 90 °C, the catalytic activity of **4** change little. When the temperature was fixed to 50 °C, the maximum total conversion was obtained (87%) with **4**. Therefore, 50 °C is the optimum temperature of 2,3-dichlorophenol oxidation for **4** with TBHP in 3 h. We are interested in the transition metals that are used in catalytic work. Despite metallophthalocyanines are flat, π -conjugated carbon systems, their electronic properties are determined to a large extent by the central metal. The electronic configuration of central metal can change the catalytic activity of the phthalocyanine complex. The activity of metallophthalocyanines in oxidation follows the order CoPc>CuPc. It is known that the catalytic performance of transition metal species depends on the outer d-electron density [35].

Changes in the catalysts were monitored by UV–vis spectroscopy during the oxidation reaction. Decomposition of Co(II) phthalocyanines frequently occurs with addition of an oxidant [26-30, 35, 36]. Co(II) phthalocyanine in chloroform has distinctive sharp vibronic Q band due to the monomer in the absence of oxygen source [37]. Before adding oxidant, characteristic sharp Q band of Co(II) phthalocyanine is seen at 668 nm (figure 6). As the oxidation reaction proceeds, this Q band shifts to 673 nm, broadens and disappears at the end of the reaction. Shifting from 668 to 673 nm attested to oxidation of Co(II)-Pc to Co(III)-Pc [38-40]. After 3 h, this oxidized intermediate decomposed and there was no further conversion to products. As shown in figure 6, as the reaction progresses, widening and disappearing of Q band are interpreted as in Co(II) phthalocyanine [38-40].

Some previously reported catalysts are summarized in table 3. Different peripheral groups substituting cobalt(II), iron(II), manganese(III) and copper(II) phthalocyanines were investigated with 2,6-di-tert-butylphenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,6-trimethylphenol and *p*-nitrophenol oxidation [41-48]. In table 3, tetrasulfonated iron phthalocyanine was used in trichlorophenol oxidation with H₂O₂. In the same work, 24% reaction conversion was obtained in 24 h at 25 °C. According to table 3, two oxidations with H₂O₂ were carried out for tetrasulfonated cobalt phthalocyanine and octacationic iron phthalocyanine catalyst. The former employed 2,4,5-trichlorophenol oxidation for 24 h at 75 °C with 67% conversion and the latter was trichlorophenol oxidation for 10 min at 25 °C with 6% conversion. By comparing the catalyst in these reports, it is inferred that **4** will be an interesting catalyst in 2,3-dichlorophenol oxidation. In our previous work, tetrasubstituted Co(II) and Fe(II) phthalocyanine complexes were studied as catalysts in oxidation of phenolic compounds [26-30, 35, 36] with high conversion and selectivity of Co(II) phthalocyanine. But in this research we are able to reach the highest product conversion and selectivity for Co(II) phthalocyanine with lower temperature (50 °C) for 2,3-dichlorophenol oxidation.

4. Conclusion

Tetra substituted phthalocyanine complexes **4** and **5** bearing (E)-4-((2-morpholinoethyl)imino)methyl)phenoxy units were synthesized. In order to verify **3-5**, a combination of spectral techniques such as MALDI–TOF mass spectral data, UV–Vis, FT–IR, ¹H NMR and ¹³C NMR was used. MPcs **4** and **5** are soluble in most organic solvents and the

catalytic activity of CoPc **4** was examined for oxidation of 2,3-dichlorophenol using different oxygen sources. CuPc **5** shows catalytic activity with 75% and 72% product selectivity for 2,3-dichlorophenol and m-methoxyphenol oxidation. The results indicate that **4** showed activity for oxidation of 2,3-dichlorophenol to the corresponding 2,3-dichloro-1,4-benzoquinone as major product in 3 h at 50 °C. The optimal conditions were also determined in 2,3-dichlorophenol oxidation with **4**. All the results indicated that **4** with catalytic oxidation was an efficient technology for industrial waste application. Converting from environmentally harmful phenolic compounds into less harmful oxidation products by CoPc **4** derivative makes this study intriguing.

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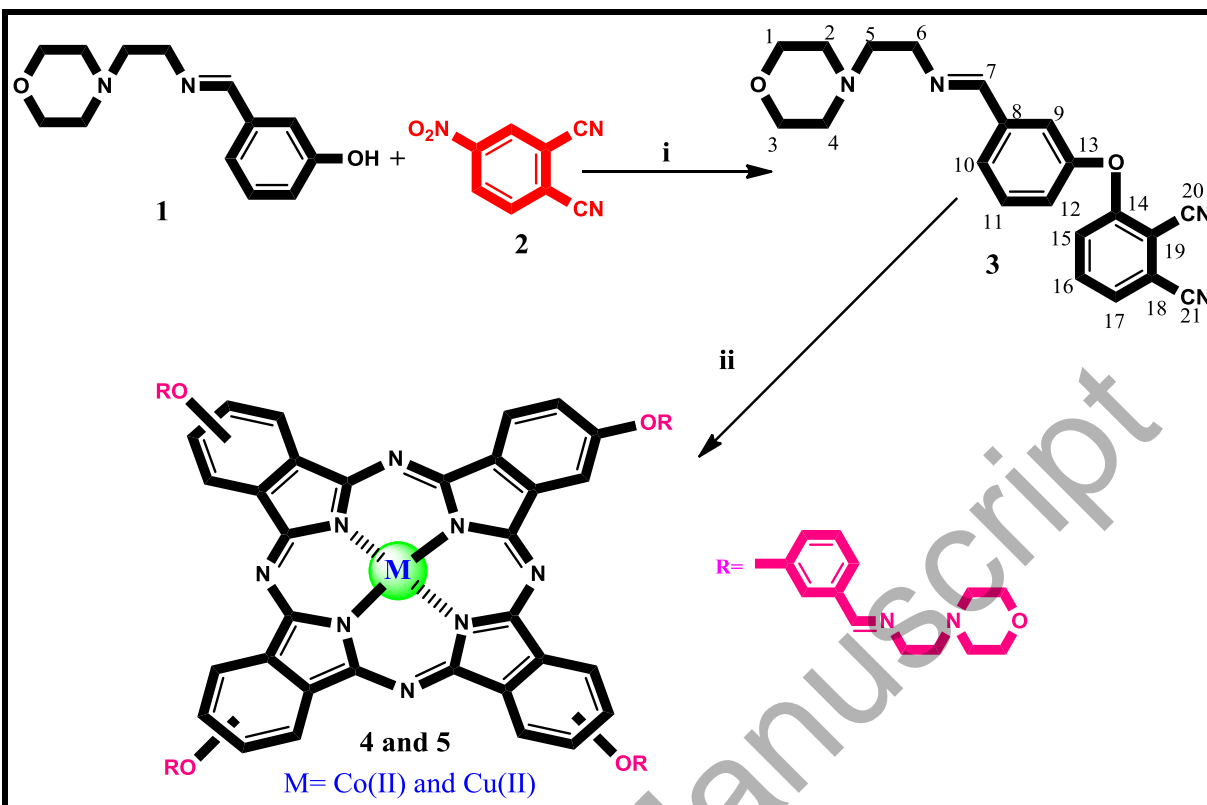


Figure 1. Synthesis of precursor phthalonitrile compound **3** and MPcs **4** and **5**. Reagents and conditions: (i) dry DMF, K_2CO_3 , 60 °C, 96 h; (ii) *n*-pentanol, DBU, 160 °C, $CoCl_2$, $CuCl_2$.

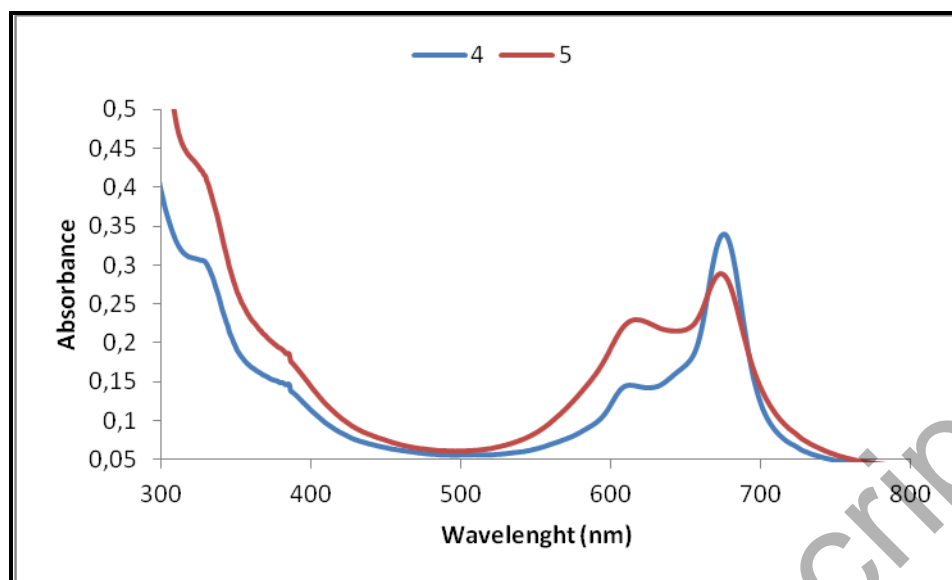


Figure 2. UV-Vis spectra of 1.00×10^{-5} M of complexes. Co(II)Pc, Cu(II)Pc in CHCl₃.

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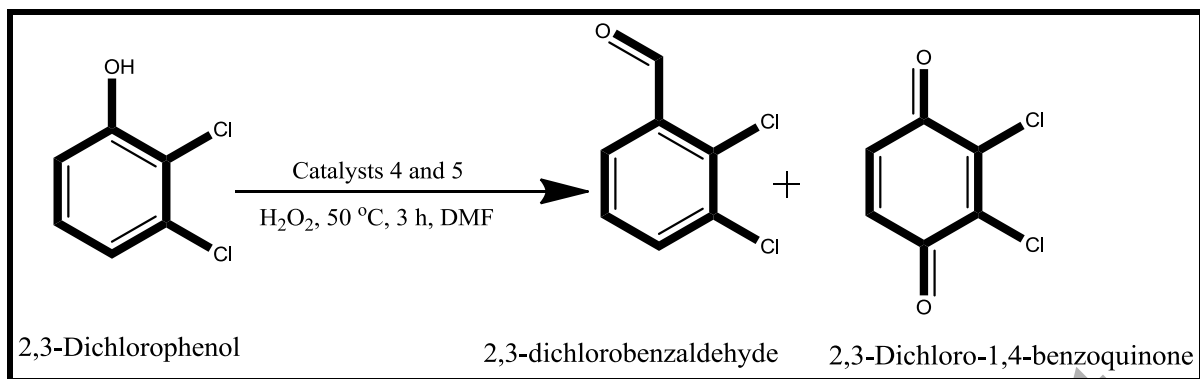


Figure 3. The oxidation products of 2,3-dichlorophenol.

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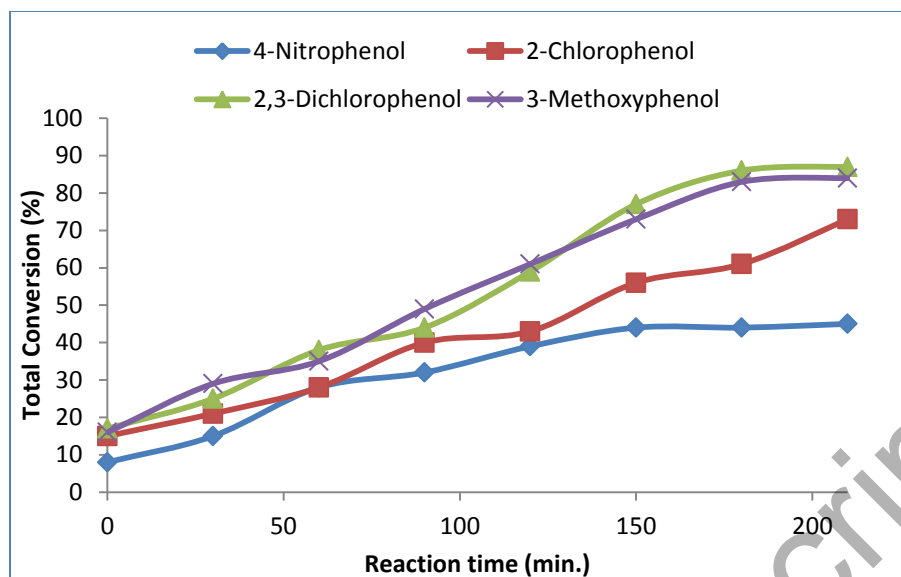


Figure 4. Time-dependent conversion of phenolic compounds oxidation with H_2O_2 as an oxidant for **4**.

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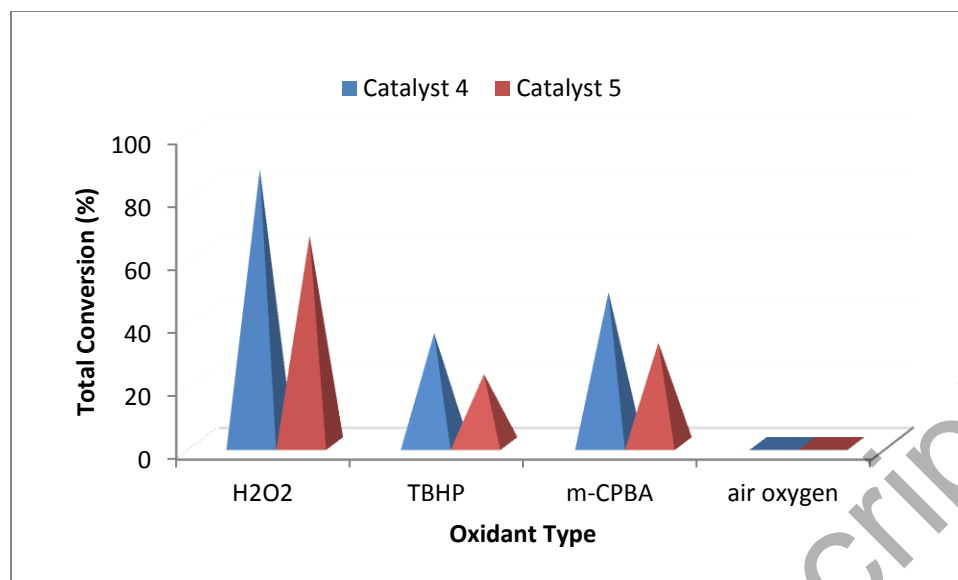


Figure 5. The oxidant effect on 2,3-dichlorophenol oxidation [reaction conditions: 2,3-dichlorophenol (1.20×10^{-3} mol), Co(II)Pc and Cu(II)Pc (3.33×10^{-6} mol), oxidant (2.66×10^{-3} mol), DMF (0.01 L), 3 h and 50 °C].

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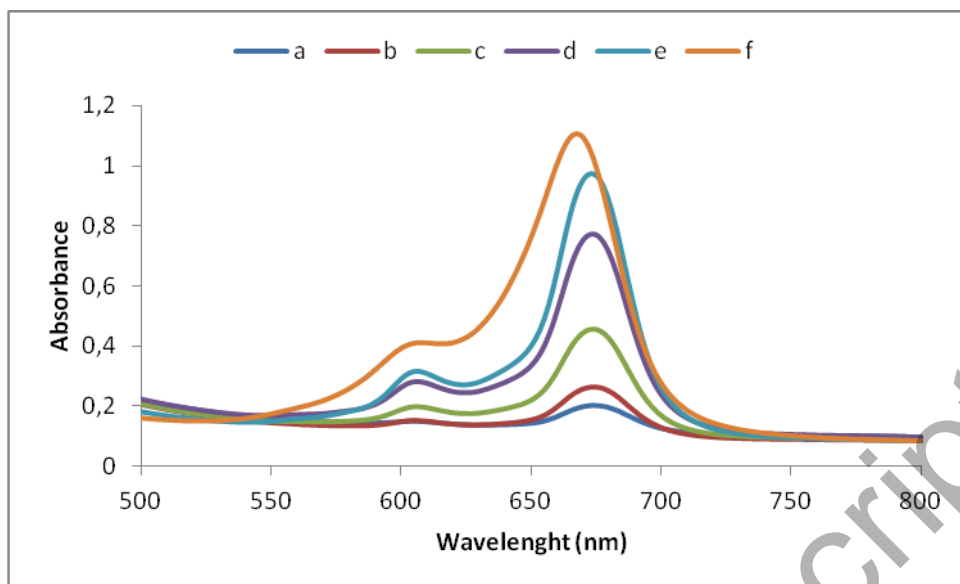
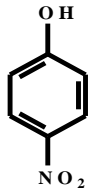
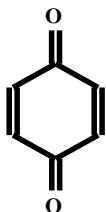
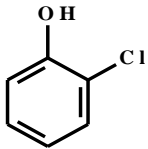
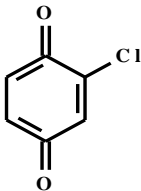
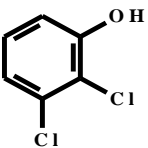
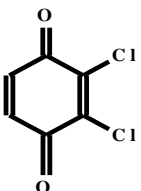
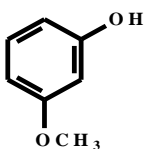
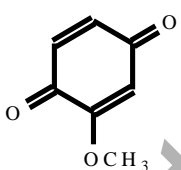


Figure 6. Time-dependent changes in the visible spectrum of the oxidized complex **4** observed on addition of TBHP (2.66×10^{-3} mol) to a reaction mixture containing 1.20×10^{-3} mol 2,3-dichlorophenol and 3.33×10^{-6} mol complex **4** catalyst in 10 ml: (e) 36 min; (d) 72 min; (c) 108 min; (b) 144 min; (a) 180 min after addition of TBHP. All spectra for the oxidized complex **4** were taken after sixfold dilution with acetonitrile. (f) Visible spectrum of (non-oxidized) complex **4** in DMF.

Table 1. Oxidation of substituted phenols catalyzed by **4** and **5**.

Substrate	Major product	Total conversion (%)		Product selectivity (%)		TON		TOF (h ⁻¹)	
		4	5	4	5	4	5	4	5
		45	47	27	21	162	169	54	56
		73	65	76	63	263	234	87.6	78
		87	66	92	72	313	237	104.5	79.2
		84	48	79	75	302	173	100.9	57.6

TON = mole of product / mole of catalyst

TOF = mole of product / mole of catalyst × time

Conversion was determined by GC.

Catalyst/substrate/oxidant ratio = 1/600/800, Reaction time = 3 h.

Table 2. Selective oxidation of 2,3-dichlorophenol with **4** and **5** using different oxidant and temperature.

Subs./Ox./Cat	Oxidant	Temperature (°C)	Conversion (%)		Selectivity ^a (%)		TON		TOF (h ⁻¹)	
			4	5	4	5	4	5	4	5
300/800/1	H ₂ O ₂	50	63	40	56	48	113	72	37.6	24
600/800/1	H ₂ O ₂	50	87	66	92	72	313	237	104.5	79.2
900/800/1	H ₂ O ₂	50	77	68	80	59	416	367	138	122
1200/800/1	H ₂ O ₂	50	75	58	83	48	540	418	180	139
600/300/1	H ₂ O ₂	50	51	37	63	68	183	133	61	44.4
600/500/1	H ₂ O ₂	50	69	55	79	65	248	180	82.8	60
600/1200/1	H ₂ O ₂	50	53	48	65	45	190	172	63.6	57
600/800/1	<i>m</i> -CPBA	50	48	32	55	40	173	115	57.6	38
600/800/1	TBHP	50	35	22	58	43	126	79	42	26
600/800/1	Air oxygen	50	-	-	-	-	-	-	-	-
600/800/1	H ₂ O ₂	75	87.3	44	91	65	313	158	104.5	53
600/800/1	H ₂ O ₂	90	86	40	90	52	309	144	103	48
600/800/1	H ₂ O ₂	25	43	25	55	31	155	90	52	30
600/800/free cat.	H ₂ O ₂	50	-	-	-	-	-	-	-	-
600/free ox./1	H ₂ O ₂	50	-	-	-	-	-	-	-	-

TON = mole of product / mole of catalyst

TOF = mole of product / mole of catalyst × time

Conversion was determined by GC.

Reaction conditions: 600/800/1: 1.20×10⁻³ mol / 3.33×10⁻³ mol / 2.66×10⁻⁶ mol

^aSelectivity of TMHQ, Reaction time = 3 h

Table 3. Catalytic activities towards the homogeneous oxidation of phenolic compounds of some previously reported catalysts.

Catalyst	Substrate	Reaction time (h)	Reaction temp. (°C)	Oxidant	Conv. (%)	Ref.
CoPcTs ^a	DTBP	24	70	O ₂	66	[37]
FePc ^e CoPc ^d	TCP	24	nr ^j	KHSO ₅	85	[38, 39]
CoPcTs ^a	2,4,5-TCP	24	75	H ₂ O ₂	67	[40]
FePcTs ^b	TMP	2	nr ^j	O ₂	77	[40]
CoPc ^d	<i>p</i> -nitrophenol	3	90	TBHP	96	[41]
CoPcTs ^a FePcTs ^b CuPcTs ^c	DTBP	2	75	TBHP	61 39 05	[42]
CoPc ^d FePc ^e MnPc ^f CuPc ^g	DTBP	3	30	TBHP	93 - 97 -	[43]
FePcTs ^b	TCP	24	25	H ₂ O ₂	24	[29]
FePcOC ^h	TCP	10 min	25	H ₂ O ₂	6	[44]
CoPc ⁱ FePc ⁱ	<i>p</i> -nitrophenol	3	90	TBHP	97 75	[31]

^a CoPcTs = tetrasulfonated cobalt phthalocyanine

^b FePcTs = tetrasulfonated iron phthalocyanine

^c CuPcTs = tetrasulfonated copper phthalocyanine

^d CoPc = substituted cobalt phthalocyanine

^e FePc = substituted iron phthalocyanine

^f MnPc = substituted manganese phthalocyanine

^g CuPc^g = substituted copper phthalocyanine

^h FePcOC = octa cationic iron phthalocyanine

^j nr = not reported