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(E)-4-(4-(3-(2-fluoro-5-(trifluoromethyl)phenyl)acryloyl)phenoxy) Substituted Co(II) and Cu(II) phthalocyanines and their catalytic activities on the oxidation of phenols

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ABSTRACT

Phenols from various man-made activities pose threats to public health and aquatic ecosystems. A number of technologies (e.g., adsorption, oxidation, and biological methods) have been proposed and tested to remove phenolic compounds from different sources. Among these technologies, oxidation process is considered one of the most efficient tools for abating phenolic compounds because of low cost, easy scalability, and ecofriendly production. In this work, we aim to synthesize and characterize potential catalysts (Co(II) and Cu(II) phthalocyanines **6** and **7**) for phenolic compounds oxidation. Different parameters influenced the oxidation process were determined and phenolic compounds oxidize to the less harmful products with high conversion and yield in the presence of Co(II) and Cu(II) phthalocyanine catalysts.

1. Introduction

Phenolic compounds are widely used in different industries including paints, fertilizers, surfactants, explosives, textiles, rubbers, plastics, curing agents, and antioxidants [1]. The exposure to phenols and its derivatives poses a serious problem to the human being as well as to the environment, due to which they are tagged as hazardous and top priority pollutants. Phenolic wastewater has carcinogenic, teratogenic and mutagenic influences on the growth and reproduction of aquatic organisms and contaminates drinking water sources [2,3]. Phenolic compounds are classified by the US Environmental Protection Agency as priority pollutants and negatively affect the taste and odor of water in concentrations as low as 0.5 mg/L. Additionally, they can be easily absorbed through skin contact, potentially acting as potent endocrine disruptors [4,5].

Metal phthalocyanines (MPcs) are very useful and versatile class of organic chromophores. Both unsubstituted and substituted phthalocyanines of transition metals are widely used as active layers of chemical sensors [6–8]. Introduction of electron donating or withdrawing substituents to phthalocyanine macrocycles has been shown to change the activity of MPcs to various substrates due to modification of both the electronic distribution in the aromatic macrocycle and the molecule energetic levels [9–12]. Electron withdrawing fluorine substituents decrease the electron density of the aromatic macrocycle and increase the oxidation potential of the MPc molecule [9–12]. This makes the fluorosubstituted phthalocyanines more active to the reducing different pheonls [13]. Cobalt phthalocyanine (CoPc), which is constituted by a cobalt atom located in the central cavity of a two-dimensional structure consisting of 18-π electron aromatic macrocycle, has attracted great interests as a catalyst because of its remarkable chemical properties and thermal stability [14–16]. Because of these reasons, we choosed fluorine groups to synthesize Co(II) and Cu(II) phthalocyanines.

Some previously reported catalysts are summarized in Table 1. Different peripherally groups substituted cobalt(II), iron(II), manganese(III), copper(II) phthalocyanines were investigated on 2,6-di-tert-buthylphenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,6-trimethylphenol and *p*-nitrophenol oxidation [17–24]. In Table 3, tetrasulfonated iron phthalocyanine was used in trichlorophenol oxidation reaction with H_2O_2 oxygen source. In the same work, 24% reaction conversion was obtained 24 h at 25 °C. According to Table 3, two oxidation works with H_2O_2 oxygen source were carried out tetrasulfonated cobalt phthalocyanine and octacationic iron phthalocyanine catalyst. The former employees 2,4,5

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Table 1
Catalytic activities towards the homogeneous oxidation of phenolic compounds of some previously reported catalyst.

Catalyst	Substrate	Rxn Time (h)	Rxn Temp. (°C)	Oxidant	Conv. (%)	Ref.
CoPcTs[a]	DTBP	24	70	O_2	66	[35]
FePc[e]	TCP	24	nr[i]	$KHSO_5$	85	[36,37]
CoPc[d]						
CoPcTs[a]	2,4,5-TCP	24	75	H_2O_2	67	[38]
FePcTs[b]	TMP	2	nr[j]	O_2	77	[38]
CoPc[d]	*p*-nitrophenol	3	90	TBHP	96	[39]
CoPcTs[a]	DTBP	2	75	TBHP	61	[40]
FePcTs[b]					39	
CuPcTs[c]					05	
CoPc[d]	DTBP	3	30	TBHP	93	[41]
FePc[e]					–	
MnPc[f]					97	
CuPc[g]					–	
FePcTs[b]	TCP	24	25	H_2O_2	24	[27]
FePcOC[h]	TCP	10 min	25	H_2O_2	6	[42]
CoPc[i]	*p*-nitrophenol	3	90	TBHP	97	[29]
FePc[i]					75	

[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.

trichlorophenol oxidation reaction 24 h at 75 °C with 67% conversion and the latter was used trichlorophenol oxidation reaction 10 min at 25 °C with 6% conversion. By comparing the catalyst in these literatures, it is inferred that the compound **6** will be interesting catalyst in 2,3-dichlorophenol oxidation. In our previous work, tetrasubstituted Co(II) and Fe(II) phthalocyanine complexes were studied as catalyst in the oxidation of phenolic compounds [25–31]. In this work, firstly (2E)-3-[2-fluoro-5-(trifluoromethyl) phenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one **3,** (E)-4-(4-(3-(2-fluoro-5-(trifluoromethyl)phenyl)acryloyl)phenoxy)phthalonitrile **5** and then cobalt(II) **6** and copper(II) **7** phthalocyanines have been synthesized and characterized with spectral data (IR, ^{1}H NMR, ^{13}C NMR, UV–Vis, mass spectroscopies). Secondly, oxidation of different phenolic compounds (4-nitrophenol, 3-chlorophenol, 2,3-dichlorophenol, 3-methoxyphenol) was chosen as the model reaction to study the catalytic activity of the synthesized Co(II) and Cu(II) phthalocyanines.

2. Experimental

The used materials, equipments and the general procedure for the oxidation of phenolic compounds were reported as supplementary information.

2.1. Synthesis

2.1.1. (2E)-3-[2-fluoro-5-(trifluoromethyl)phenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one (3)

Chalcone compound **3** was synthesized via Claisen-Schmidt condensation using NaOH as a catalyst. 4′-hydroxyacetophenone (1.36 g, 10 mmol) and NaOH (0.80 g, 20 mmol) were dissolved in a mixed solvent of H_2O (100 mL)/ethanol (50 mL) in a flask and stirred for half an hour. Then, the ethanol solution of 2-fluoro-5-(trifluoromethyl)benzaldehyde (1.92 g, 10 mmol) was added drop by drop and reaction mixture was stirred for 24 h in room temperature. The reaction was followed and monitored by TLC. After the reaction was completed, 0.1 N HCl was added until the pH value was about 6. The solid product was filtered and washed with cold chloroform and then water. The obtained compound was dried with a freezedryer and the purity was checked with TLC. The yield 2.23 g (72%). M.p.: 144–146 °C. Rf: 0.70 (Ether). FT-IR (cm^{-1}): 3356 (O–H), 3058 (Ar–H), 1655 (C=O), 1569 (HC=CH), 1109 (Arom. C–F), 835 (Aliph. C–F). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): $\delta = 7.8$ (AB, $J = 16.0$ Hz, 1H, H-2); $\delta = 8.2$ (AB, $J = 16.0$ Hz, H-3); $\delta = 8.1$ (d, $J = 8.0$ Hz, 2H, H-2′/6′); $\delta = 6.9$ (d, $J = 8.0$ Hz, 2H, H-3′/5′); $\delta = 7.6$ (d, $J = 8.0$ Hz, 1H, H-3″); $\delta = 7.8$ (m, H-4″); $\delta = 8.6$ (d, $J = 8.0$ Hz, 1H, H-6″); 10.6 (bs, 1H, –OH). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 187.1 (C-1), 126.5 (C-2), 132.4 (C-3), 129.1 (C-1′), 132.0 (C-2'/6′), 115.9 (C-3'/5′), 163.1(C-4′), 126.7 and 126.3 (d, $J_{CF} = 30.0$ Hz, C-1″), 164.2 and 161.7 (d, $J_{CF} = 255.0$ Hz, C-2″), 117.9 and 117.7 (d, $J_{CF} = 23.0$ Hz, C-3″), 129.5 (C-4″), 125.6, 124.2, 124.1 and 122.9 (dd, $J_{CF} = 140/120$, Hz C-5″), 126.8 (C-6″), 129.1 (-CF_3). Poz. LC-MS/MS m/z (%) ($C_{16}H_{10}F_4O_2$: 310.06): 333 (100) $[M+Na]^+$, 311 (85) $[M+1]^+$.

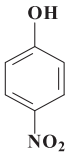
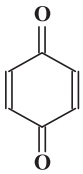
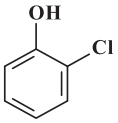
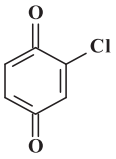
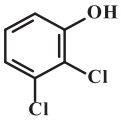
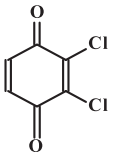
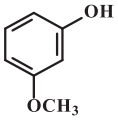
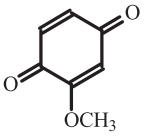
2.1.2. (E)-4-(4-(3-(2-fluoro-5-(trifluoromethyl)phenyl)acryloyl) phenoxy)phthalonitrile (5)

Compound **5** was synthesized according to the literature [32]. Yield: 1.74 g (62%). mp: 202–204 °C. IR (KBr pellet), ν_{max}/cm^{-1}: 3075, 3041 (Ar–H), 2972, 2930, 2866 (Aliph. C–H), 2233 (C≡N), 1588, 1565, 1486, 1412, 1387, 1328, 1268, 1273, 1211, 1165, 1122, 1090, 1074, 982, 951, 834, 787, 740, 660. ^{1}H NMR. ($CDCl_3$), (δ:ppm): 8.20 (d, 1H, Ar–H), 7.88 (m, 4H, Ar–H), 7.62 (d, 2H, Ar–H), 7.45 (m, 3H, Ar–H), 7.26 (s, 1H, Ar–H), 6.80 (d, 1H, Ar–H). ^{13}C NMR. ($CDCl_3$), (δ:ppm): 188.45 (C=O), 163.45 (ArC-F), 156.56 (ArC-O), 154.70 (ArC-O), 139.44 (C=C), 132.11 (ArC), 129.73 (ArC), 128.66 (ArC), 127.88 (C=C), 127.34 (ArC), 124.68 (ArC), 124.48 (ArC), 123.78 (ArC), 123.55 (ArC), 123.11 (ArC), 122.65 (ArC), 121.94 (ArC), 121.60 (ArC), 121.36 (ArC), 120.83 (ArC), 120.48 (ArC), 120.12 (ArC), 116.46 (C≡N), 118.22 (C≡N). MALDI-TOF-MS, (m/z): Calculated: 436.36; Found: 454.38 $[M+H_2O]^+$.

2.1.3. Synthesis of cobalt (II) phthalocyanine (6)

Compound **6** was synthesized according to the literature [32]. Yield: 272 mg (44%). Mp > 300 °C. FT-IR ν_{max}/cm^{-1} (KBr pellet):

Table 2
Oxidation of substituted phenols catalyzed by complex **6** and **7**.

Substrate	Major Product	Total Conversion (%)		Product Selectivity (%)		TON		TOF (h^{-1})	
		6	7	6	7	6	7	6	7
		51	50	32	26	305	299	101.6	99.8
		75	68	80	85	449	407	149.8	135.8
		89	72	90	72	533	431	177.7	143.8
		79	59	75	66	473	353	157.8	117.8

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 = 1/600/800, Reaction Time = 3 h.

Table 3
Selective oxidation of 2,3-dichlorophenol with catalysts **6** and **7** using different oxidant and temperature.

Subs./Ox./Cat	Oxidant	Temperature (°C)	Conversion (%)		Selectivity[a] (%)		TON		TOF (h^{-1})	
			6	7	6	7	6	7	6	7
300/800/1	H_2O_2	50	65	50	54	46	195	150	65	50
600/800/1	H_2O_2	50	89	72	90	72	533	431	177.7	143.8
900/800/1	H_2O_2	50	74	66	78	57	666	594	222	198
1200/800/1	H_2O_2	50	70	54	86	49	840	648	280	216
600/300/1	H_2O_2	50	62	45	65	70	372	270	124	90
600/500/1	H_2O_2	50	70	57	77	63	360	342	120	114
600/1200/1	H_2O_2	50	55	45	59	47	330	270	110	90
600/800/1	*m*-CPBA	50	49	39	50	45	294	234	98	78
600/800/1	TBHP	50	37	28	60	41	222	162	74	54
600/800/1	Air oxygen	50	–	–	–	–	–	–	–	–
600/800/1	H_2O_2	75	89.6	47	90.9	68	537	282	179	94
600/800/1	H_2O_2	90	79	45	88	59	474	270	158	90
600/800/1	H_2O_2	25	61	31	51	39	366	186	122	62
600/800/free cat.	H_2O_2	50	–	–	–	–	–	–	–	–
600/free ox./1	H_2O_2	50	–	–	–	–	–	–	–	–

TON = mole of product/mole of catalyst.
TOF = mole of product/mole of catalyst x time.
Conversion was determined by GC.
Reaction Conditions: 600/800/1: 1.66 × 10-3 mol)/2.22 × 10-3 mol/2.77 × 10-6 mol.
[a] = Selectivity of TMHQ Reaction time = 3 h.

3087, 3054 (Ar–H), 2993, 2940, 2861 (Aliph. C–H), 1556, 1478, 1454, 1430, 1403, 1386, 1361, 1291, 1266, 1245, 1228, 1190, 1087, 1063, 1049, 1020, 990, 972, 894, 867, 780, 689. UV–Vis ($CHCl_3$): λ_{max}, nm (log ε): 689 (4.88), 618 (4.77), 319 (4.48). MALDI-TOF-MS, (*m*/*z*): Calculated: 1804.36; Found:1324.37$[M+H_2O+2H]^+$. $C_{96}H_{48}F_{16}N_8O_4$Cosoluble in $CHCl_3$, CH_2Cl_2, DMF, DMSO.

2.1.4. Synthesis of copper (II)phthalocyanine ***(7)***

Compound **7** was synthesized according to the literature [32]. Yield: 286 mg (44%). FT-IR ν_{max}/cm $^{-1}$ (KBr pellet): 3078, 3057 (Ar–H), 2989, 2862 (Aliph. C–H), 1553, 1490, 1487, 1455, 1427, 1399, 1365, 1297, 1276, 1244, 1223, 1178, 1045, 1021, 986, 943, 893, 852, 827. UV–Vis ($CHCl_3$): λ_{max}, nm (log ε): 692 (4.76), 624 (4.58), 324

(4.75). MALDI-TOF-MS, (*m*/*z*): Calculated: 1808.98; Found: 1829.01 $[M+H_2O+2H]^+$. $C_{96}H_{48}F_{16}N_8O_4Cu$ soluble in $CHCl_3$, CH_2Cl_2, DMF, DMSO.

3. Results and discussion

3.1. Synthesis and characterisation

All synthetic routes for (2E)-3-[2-fluoro-5-(trifluoromethyl) phenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one (3), (E)-4-(4-(3-(2-fluoro-5-(trifluoromethyl)phenyl)acryloyl)phenoxy)phthalonitrile (5) and Co(II) and Cu(II) phthalocyanines (7 and 8) were shown in Fig. 1. At the first step of the work (2*E*)-3-[2-fluoro-5-(trifluoromethyl)phenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one (chalcone) was prepared with the Claisen-Schmidt consendation of 4′-hydroxyacetophenone and 2-fluoro-5-(trifluoromethyl)benzaldehyde in basic condition according to known procedure as given in Fig. 1 [33–35]. The purity of chalcone was checked by TLC and its structure was identified by spectroscopic methods. FT-IR spectra of this compound showed characteristic absorption bands of –OH, C=O and aliphatic C=C groups at 3356 cm-1, 1655 cm^{-1} and 1569 cm^{-1}, respectively. The most prominent feature of the structural characterisation of chalcone compound is the assignment of the proton resonance of its α,β-unsaturated moiety, which was done by a careful analysis of its ^1H and ^2D-COSY NMR. From the values of the vicinal coupling constants ($^3J_{H\alpha-H\beta} = 16.0/16.0$ Hz) it was probable to determine the *trans* configuration of these two protons. ^{13}C NMR (APT) also supported the formation of chalcone with the number of carbon atoms. Moreover in the ^{13}C NMR, the aromatic and aliphatic carbons containing fluoro atoms appeared as doublets and doublet of doublet in the region 117.7–164.2 ppm due to C–F coupling. In LC-MS/MS spectrum showed $[M+Na]^+$ and $[M+1]^+$ fragments as base peaks. Thus, it is seen that all structural analyzes support the structure.

Second step, the nucleophilic aromatic nitro displacement of (2E)-3-[2-fluoro-5-(trifluoromethyl)phenyl]-1-(4-hydroxyphenyl) prop-2-en-1-one with compound 4 was carried out in dry DMF and anhydrous K_2CO_3 as strong base at 60 °C for 72 h. (E)-4-(4-(3-(2-fluoro-5-(trifluoromethyl)phenyl)acryloyl)phenoxy)phthalonitrile was obtained with %62 yield and characterized with NMR, FT-IR, mass spectral data. In the FT-IR spectrum, the formationof(E)-4-(4-(3-(2-fluorotrifluoromethyl)phenyl)acryloyl)phenoxy)phthalonitrile 5 was clearly confirmed by the disappearance of the –OH band at 3356 cm^{-1} and appearance of the sharp peak for the –C≡N vibration at 2233 cm^{-1}. The ^{1}HNMR spectrum of compound 5 was recorded in $CDCl_3$. The chemical shift of –OH proton in precursor compound **3** at 10.6 ppm^{-1} disappeared after the formation of dinitrile compound 5. All aromatic and aliphatic protons of compound 5 were observed at between 8.20 and 6.80 ppm. ^{13}C NMR spectrum of this compound obviously specified the presence of dinitrile carbon atoms with peaks at 116.46 and 118.22 ppm. In the mass spectrum of compound 5, the expected molecular ion peak was observed at *m*/*z*: 454.38 $[M+H_2O]^+$.

Peripherally tetra (E)-4-(4-(3-(2-fluoro-5-(trifluoromethyl) phenyl)acryloyl)phenoxy substituted Co(II) and Cu(II) phthalocyanines **6** and **7** were prepared by cyclotetramerization reaction using phthalonitrile precursor **5**. One of the important evidence that the cyclotetramerization reaction is taking place is the loss of sharp

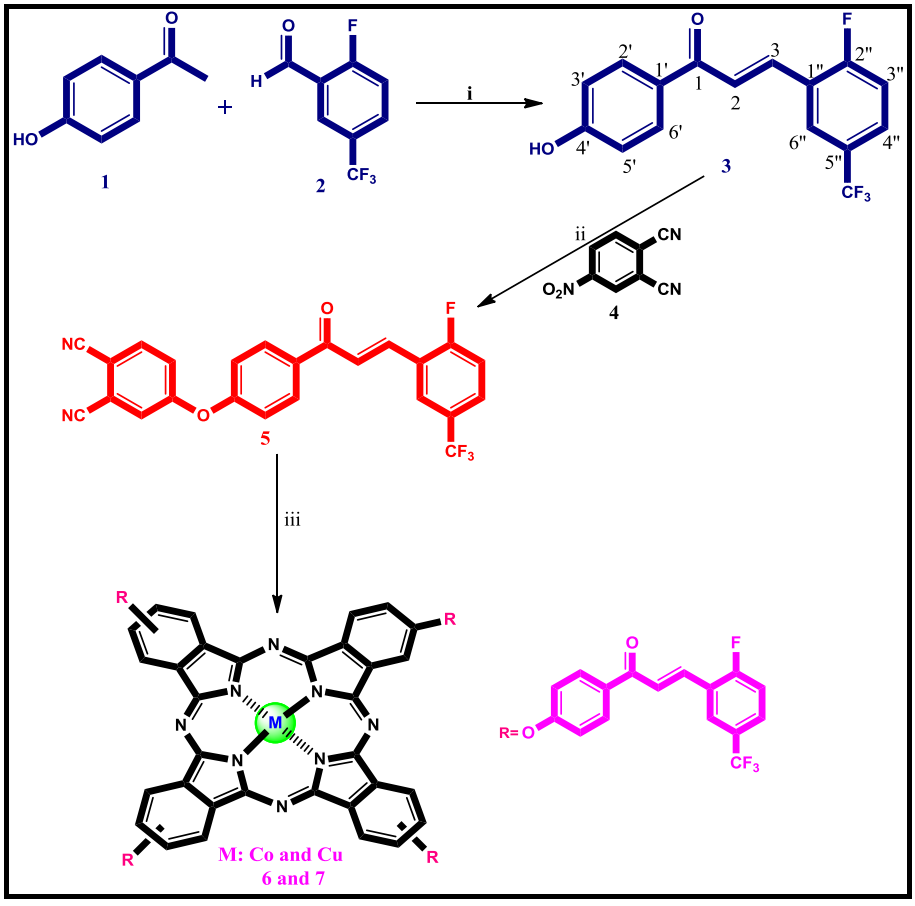


Fig. 1. Synthesis of precursor phthalonitrile compound **3** and MPcs **6 and 7** Reagents and conditions: (i) dry DMF, K_2CO_3, 60 °C, 96 h; (ii) n-pentanol, DBU, 160 °C, $CoCl_2$, $CuCl_2$.

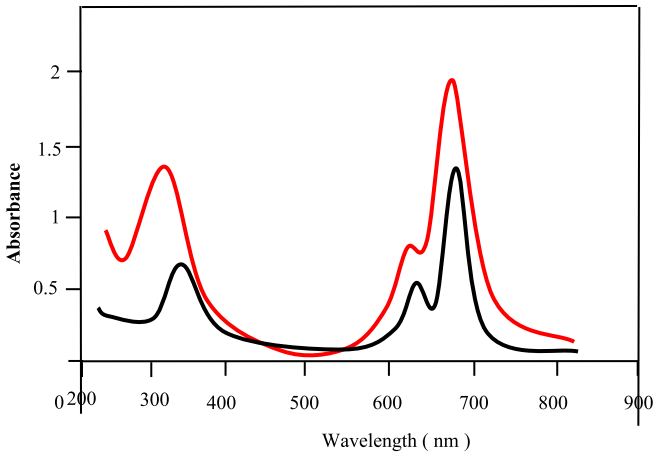


Fig. 2. UV–Vis spectra of 1.00×10^{-5} M of complexes. **(a)** Co(II)Pc, Cu(II)Pc in $CHCl_3$.

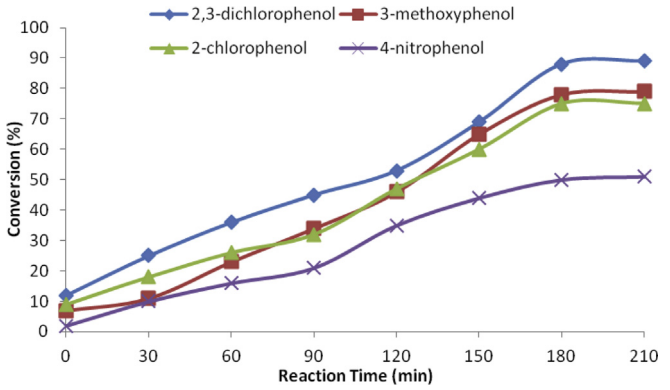


Fig. 4. Time-dependent conversion of phenolic compounds oxidation with H_2O_2 as an oxidant for catalyst **6**.

nitrile peak (at 2233 cm^{-1}) in the infrared spectrum. The ^1H NMR and ^{13}C NMR spectrum of cobalt and copper phthalocyanine **6** and **7** could not be taken due to the paramagnetic metal centers [36]. Metal free and metallophthalocyanines are generally insoluble common organic solvents. However, in this work, thanks to (E)-4-(4-(3-(2-fluoro-5-(trifluoromethyl)phenyl)acryloyl)phenoxy groups Co(II) and Cu(II) phthalocyanine complexes 6 and 7 have good solubility in $CHCl_3$, CH_2Cl_2, THF, DMF.

In the mass spectrum of cobalt and copper phthalocyanines **6** and **7**, the presence of molecular ion peaks at *m/z* 1324.37 $[M+H_2O+2H]^+$ and 1829.01 $[M+H_2O+2H]^+$ respectively, confirmed the proposed structures.

UV/Vis spectra of the phthalocyanine complexes **6** and **7** show characteristic absorptions in the Q-band region at around 650–700 nm, attributed to the π-π^* transition from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) of the Pc^{-2} ring, and in the B band region (UV region) at around 300–400 nm, arising from the deeper π-π^* transitions. The Q-band absorptions of π-π^* transition for all phthalocyanines **6** and **7** in $CHCl_3$ were observed as a single band of high intensity at 689 nm for **4**, 692 nm for **5**. 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** and **7** were observed at 319, 324 nm respectively (Fig. 2).

3.2. Catalytic studies

3.2.1. Oxidation of phenolic compounds with complex *6* and *7*

The catalytic properties of Co(II) and Cu(II) phthalocyanine complexes were investigated for the oxidation of substituted phenolic compounds. All the oxidation reactions results were given in Tables 2 and 3. All experiments maintained 3 h oxidant and auxiliary chemicals on the conversion and yields were investigated. Phenolic compounds can be turned into variety of organic compounds in oxidation reactions. The blank reactions were carried out (using no catalysts or oxidants) and there were no product detectable (Table 3). It is proved that presence of the catalyst and oxidant are essential for the oxidation. The main products was determined as 2,3-dichloro-1,4-benzoquinone and the side product was determined as 2,3-dichlorobenzaldeyde in the oxidation of 2,3-dichlorophenol oxidation reaction (Fig. 3). Influence of all substrate, catalysts and obtaining results within the oxidation processes are demonstrated in Table 2. According to the results of this table, Co(II) phthalocyanine **6** demonstrated the highest activity and selectivity producing 2,3-dichloro-1,4-benzoquinone as major product in 2,3-dichloroquinol oxidation reaction. The results of the catalytic oxidation of phenolic compounds by H_2O_2 in the presence of **6** are shown in Fig. 4. This figure showed that 2,3-dichlorophenol oxidation reaction has higher total conversion than the other substrates with catalyst **6.**

As the other parameters were kept constant, the molar ratio was carried out in the range of 300–1000 to determine the influence on substrate to metal ions. The reaction rate increased with decreasing of the substrate/catalyst molar ratio (Table 3) as expected. Substrate/catalyst ratio on the oxidation course gave same main product with TON and TOF values (533 and 177.7 for Co complex **6**).

Oxygen activation in oxidation reactions is a challenging problem of modern chemistry and biochemistry. Co(II) complexes are involved in the one-electron reduction of oxygen to form the superoxo (Co(III)–) or peroxo derivatives (Co(III)– –Co(III)) [37,38]. V.N. Shishkin et al. reported that the cobalt complex with 4-octasulfophenyltetrapyrazinoporphyrazine (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

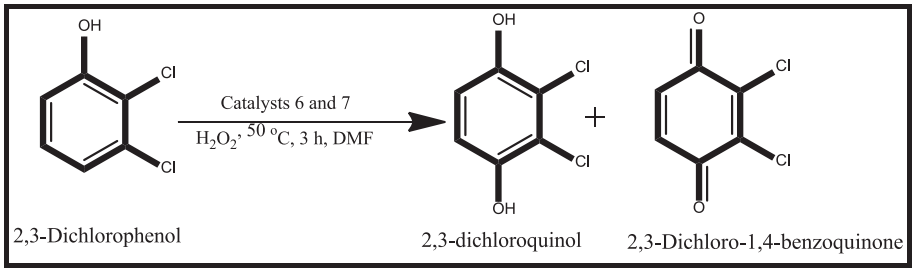


Fig. 3. The oxidation products of 2,3-dichlorophenol.

urea and sulfur in high yield. In this work, we studied the catalytic oxidation reactions of phenolic compounds with different oxygen sources and achieved to activate oxygen.

To determine oxygen source effect, H_2O_2, TBHP, *m*-CPBA and air oxygen were used as oxidant. The results in Table 2 showed that H_2O_2 was the best oxidant for 2,3-dichlorophenol oxidation in the presence of the CoPc **6**. Moreover, TBHP and *m*-CPBA can serve as an oxidant but low conversion was observed for both CoPc **6** and CuPc **7**. The reaction color changed from light blue to brown when we added TBHP or *m*-CPBA in the reaction media. This clue explains that the complex **6** was degraded immediately with TBHP or *m*-CPBA [39,40]. When H_2O_2 was used as an oxygen source, reaction color was bright blue color for 36 min and then changed to yellow and light yellow at the end. This observation proved that phthalocyanine catalyst can be more catalytically active with H_2O_2 as an oxygen source in this catalytical process. The results of catalytic activity studies for CoPc **6** and CuPc **7** using with air oxygen displayed that there was no formation of products during the oxidation process (Fig. 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 inclined to decreasing. At this stage, it is possible that the coordination around the cobalt ion can change and produce inactive intermediate species [41–43].

Temperature effect were also tested as the reaction temperature was upgraded from 50 °C to 90 °C, the catalytic activity of the CoPc **6** change little bit. When the temperature was fixed to 50 °C, the maximum total conversion was obtained (89%) with cobalt(II) phthalocyanine **6.** Therefore, 50 °C is the optimum temperature of 2,3-dichlorophenol oxidation for product **6** with TBHP in 3 h. We are interested in the nature of the introduced transition metals that are used in these catalytic works. Despite metallophthalocyanines are representatives for flat, π-conjugated carbon systems, their electronic properties are determined to a large extent by the central metal atom. The electronic configuration of central metal atom can change the catalytic activity of phthalocyanine. The activity of metallophthalocyanines in oxidation reaction follows the order CoPc>CuPc. It is known that the catalytic performance of transition metal species depends on the outer d-electron density [36].

Changing of the catalyst was monitored by UV–vis spectrophotometer during the oxidation reaction. Decomposition of Co(II) phthalocyanines is a frequent situation in oxidation process with the addition of an oxidant [25–31]. Co(II) phthalocyanine in chloroform has distinctive sharp vibronic Q band due to the monomeric species in the absence of oxygen source [32]. Before adding oxidant, characteristic sharp Q band of Co(II) phthalocyanine is seen at 668 nm (Fig. 6). With the oxidation reaction proceeds, this Q band shifts to 673 nm, broads and disappears at the end of the reaction. Shifting from 668 to 673 nm attested that metal oxidation of Co(II)-Pc to Co(III)-Pc [41–43]. After 3 h, this oxidized intermediate decomposed. Besides, there was no further conversion of any products. Similar statement can be formed for Fig. 6. As the reaction time progresses, widening and disappearing of Q band are interpreted as in Co(II) phthalocyanine [41–43].

Some reports with Co (II) and Cu(II) phthalocyanine can gain highest turnover number and turnover frequency but at 90 °C [27,29,31]. When compared with the other catalysts in the literature, complex **6** and **7** have high TON and TOF value in lower temperature (50 °C). The results of our previous work research were also valuable because of the high conversion and selectivity of Co(II) phthalocyanine. But in this research we are able to reach the highest product conversion and selectivity with Co(II) phthalocyanine in lower temperature (50 °C) for 2,3-dichlorophenol oxidation.

4. Conclusion

In conclusion, tetra substituted phthalocyanine complexes **6** and **7** bearing (E)-4-(4-(3-(2-fluoro-5-(trifluoromethyl)phenyl) acryloyl)phenoxy) units were designed and synthesized. In order to verify these novel products **3**–**5**, a combination of spectral techniques such as MALDI–TOF mass spectral data, UV–Vis, FT–IR, ^{1}H NMR and ^{13}C NMR was used. MPcs **6**–**7** are highly soluble in most of the organic solvents and the catalytic activity of CoPc **6** was examined for the oxidation of 2,3-dichlorophenol using different oxygen sources. CuPc **7** shows feasible catalytic activity with 72% and 85% product selectivity for 2,3-dichlorophenol and m-methoxyphenol oxidation. The results indicated that the catalyst **6** showed convincing activity for the 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 CoPc **6**. All the results indicated that CoPc **6** with catalytic oxidation was an efficient and cleaning technology for industrial waste application. Converting from environmentally harmful phenolic compounds into less harmful oxidation products by CoPc **6** derivative makes this study intriguing.

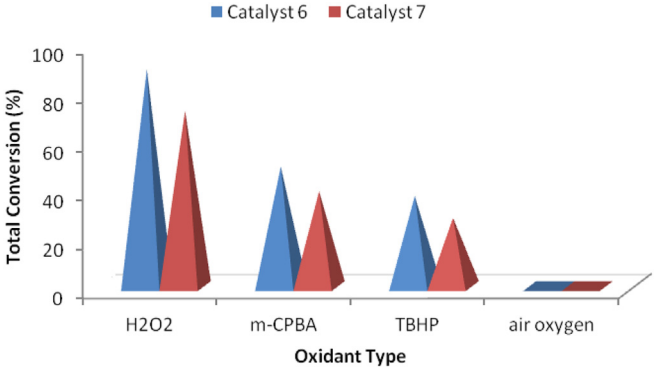


Fig. 5. The oxidant effect on 2,3-dichlorophenol oxidation [Reaction conditions: 2,3-dichlorophenol (1.66×10^{-3} mol), Co(II)Pc and Cu(II)Pc (2.77×10^{-6} mol), oxidant (2.22×10^{-3} mol), DMF (0.01 L), 3 h and 50 °C].

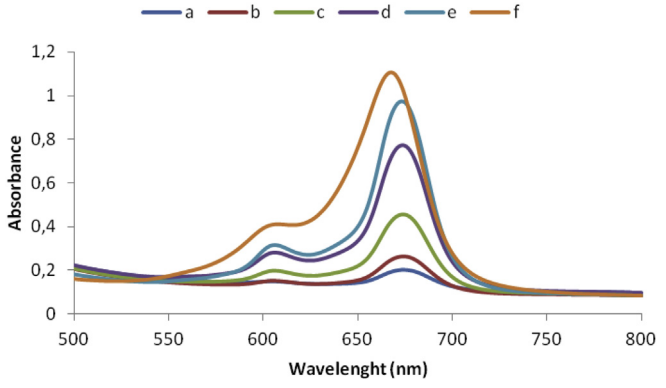


Fig. 6. Time-dependent changes in the visible spectrum of the oxidized complex **6** observed on addition of TBHP (2.22×10^{-3}mol) to a reaction mixture containing 1.66×10^{-3}mol 2,3-dichlorophenol and 2.77×10^{-6}mol complex **6** catalyst in 10 mL: (e) 36 min; (d) 72 min; (c) 108 min; (b) 144 min (a) 180 min after addition of TBHP. All spectra for the oxidized complex **6** were taken after sixfold dilution with acetonitrile. (f) Visible spectrum of (non-oxidized) complex **6** in DMF.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.05.012.

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