

# An efficient method for the oxidation of phenolic compounds using new Co(II) and Fe(II) phthalocyanines

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**Abstract** In this study novel Co(II) and Fe(II) phthalocyanines have been successfully prepared and their structural characterization have been done using with different spectroscopic methods (IR, <sup>1</sup>H-NMR, UV-Vis, mass spectroscopies and elemental analysis). Substituted phenolic compounds as substrate, different kinds of oxidants and novel Co(II) and Fe(II) phthalocyanines as catalyst have been used in all oxidation reactions. Temperature, different oxidants, ox./cat. ratio effects on the catalysis have been determined. Interestingly, Co(II) phthalocyanine exhibits superior catalytic activity and durability in the catalysis over oxidation of p-nitrophenol (4-NP). The present method is simple, environmentally benign and amenable scale up process.

**Keywords** Phthalocyanine · Iron · Cobalt · Phenolic compounds · Oxidation · TBHP

## Introduction

Phenolic compounds are a class of chemical compounds consisting of a hydroxyl functional group (–OH) attached to an aromatic hydrocarbon group, with a ring structure like that of benzene [1]. Especially p-nitrophenols is a toxic and bio-refractory pollutant which can cause considerable

damage to the ecosystem and human health. It can damage the central nervous system, liver, kidney and blood of humans and animals. Para nitrophenols are used in production of many synthetic dyes and pesticides, insecticides, herbicides [2, 3].

Phthalocyanines (Pcs) are highly stable man-made macrocycles. They are typically blue-green in colour and for many decades have been used as commercial dyes and pigments [4]. Metallophthalocyanines (MPcs) have received a great deal of attention due to their interesting electrical, optical and structural properties, followed by numerous application for example chemical sensors [5], photoconductors [6], electrochromic display [7], catalysis [8], liquid crystal [9], nanotechnology [10] and photosensitizers for photodynamic cancer therapy (PDT) [11].

In this study, we use (2E)-1-(4-hydroxyphenyl)-3-pyridine-4-ylprop-2-en-1-one, the chalcone compound, as the starting compound. The chalcones belong to the flavonoid family and consists of open chain flavonoids in which the two aromatic rings are joined by a three-carbon atom  $\alpha,\beta$ -unsaturated carbonyl system. This natural product is being consumed daily through fruits and vegetables, has attracted our attention to explore hybrid structures with them for antidyslipidemic activity as chalcones also exhibits antioxidant activity [12]. Firstly, we have synthesized and characterized Co(II) and Fe(II) phthalocyanines using with spectral data (IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, UV-Vis, mass spectroscopies and elemental analysis). In this report, oxidation of different substituted phenolic compounds (p-nitrophenol, o-chlorophenol, 2,3-dichlorophenol, p-methoxyphenol) have been chosen as the model reaction to study the catalytic activity of the synthesized Co(II) and Fe(II) phthalocyanines; cobalt and iron have been used because they are bioactive metals. Especially the new prepared cobalt(II) (4) phthalocyanine

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has been determined as higher active catalyst than the other phthalocyanine (**5**) during the catalysis. Temperature, different oxidants, ox./cat. ratio effects on the catalysis have also been determined.

## Experimental

### Materials

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

### Synthesis

#### *Synthesis of {4-[(2E)-3-Pyridin-4-ylprop-2-en-1-yl]phenoxy}phthalonitrile (3)*

Compound **3** was synthesized according to the literature [13]. Yield: 2.36 g (74 %). mp: 115–116 °C. IR (KBr pellet),  $\nu_{\max}/\text{cm}^{-1}$ : 3076, 3041 (Ar–H), 2988, 2933, 2827 (Aliph. C–H), 2233 (C≡N), 1678 (C=O), 1603–1587 (C–O), 1528, 1484, 1418, 1357, 1309, 1278, 1247, 1213, 1167, 1093, 1012, 968, 926, 905, 849, 756, 720.  $^1\text{H-NMR}$ . ( $\text{CDCl}_3$ ), ( $\delta$ :ppm): 8.50 (d, 2H, Ar–H), 8.10 (d, 2H, Ar–H), 7.90 (d, 2H, Ar–H), 7.85 (d, 2H, Ar–H), 7.56 (d, 1H, Ar–H), 7.36 (d, 1H, Ar–H), 7.09 (d, 1H, Ar–H) 6.80 (d, 1H, CH=C), 6.20 (d, 1H, –CHCO).  $^{13}\text{C-NMR}$ . ( $\text{CDCl}_3$ ), ( $\delta$ :ppm): 187.37 (C=O), 163.56 (C–O), 158.04 (C–O), 143.51 (Ar–C), 140.78 (Ar–C), 138.51 (Ar–C), 135 (C=C), 131.22 (Ar–C), 128.69 (Ar–C), 127.01 (Ar–C), 125.45 (Ar–C), 123.37 (Ar–C), 121.33 (Ar–C), 115.27 (C<sub>7</sub>≡N), 115.78 (C<sub>8</sub>≡N), 110.70 (Ar–C), 109.88 (Ar–C), 108.72 (Ar–C), 106.45 (Ar–C). MALDI-TOF-MS ( $m/z$ ): Calculated: 361.36; Found: 361.54  $[\text{M}]^+$ .  $\text{C}_{22}\text{H}_{13}\text{N}_3\text{O}$ : calcd. C 75.20; H 3.73; N 11.96 %; found: C 75.01; H 3.65; N 11.21.

#### *Synthesis of {4-[(2E)-3-Pyridin-4-ylprop-2-en-1-yl]phenoxy}phthalocyaninato cobalt (II) (4)*

Compound **4** was synthesized according to the literature [13]. Yield: 382 mg (49 %). Mp > 300 °C. FT-IR  $\nu_{\max}/\text{cm}^{-1}$  (KBr pellet): 3081, 3033 (Ar–H), 2976, 2945, 2856 (Aliph. C–H), 1691 (C=O), 1606–1593 (C–O), 1531, 1495, 1467, 1432, 1388, 1361, 1285, 1263, 1227, 1201, 1197, 1086, 1043, 987, 955, 915, 886, 765, 693. UV-Vis ( $\text{CHCl}_3$ ):  $\lambda_{\max}$ , nm (log  $\epsilon$ ): 678 (4.78), 608 (4.52), 324 (4.72). MALDI-TOF-MS ( $m/z$ ): Calculated: 1504.52; Found: 1506.70  $[\text{M} + 2\text{H}]^+$ .  $\text{C}_{88}\text{H}_{52}\text{N}_{12}\text{O}_4\text{Co}$ : calcd. C 70.25; H: 3.48; N: 11.17 %; found: C 70.33; H 3.61; N 11.07.

#### *Synthesis of {4-[(2E)-3-Pyridin-4-ylprop-2-en-1-yl]phenoxy}phthalocyaninato iron (II) (5)*

Compound **5** was synthesized according to the literature [13]. Yield: 351 mg (45 %). FT-IR  $\nu_{\max}/\text{cm}^{-1}$  (KBr pellet): 3078, 3056 (Ar–H), 2986, 2851 (Aliph. C–H), 1695 (C=O), 1597–1588 (C–O), 1529, 1487, 1448, 1422, 1356, 1341, 1277, 1258, 1234, 1205, 1187, 1091, 1055, 993, 972, 945, 898, 861, 725.  $^1\text{H-NMR}$ . ( $\text{CDCl}_3$ ) ( $\delta$ :ppm): 8.25 (d, 8H, Ar–H), 7.96 (d, 8H, Ar–H), 7.88 (d, 8H, Ar–H), 7.72 (d, 8H, Ar–H), 7.58 (d, 4H, Ar–H), 7.42 (d, 4H, Ar–H), 7.16 (d, 4H, Ar–H) 6.58 (d, 4H, CH=C), 6.34 (d, 4H, –CHCO). UV-Vis ( $\text{CHCl}_3$ ):  $\lambda_{\max}$ , nm (log  $\epsilon$ ): 694 (4.98), 623 (4.28), 332 (4.48). MALDI-TOF-MS ( $m/z$ ): Calculated: 1501.43; Found: 1503.51  $[\text{M} + 2\text{H}]^+$ .  $\text{C}_{88}\text{H}_{52}\text{N}_{12}\text{O}_3\text{Fe}$ : calcd. C 70.39; H 3.49; N 11.19 %; found: C 70.64; H 3.22; N 11.25.

## Results and discussion

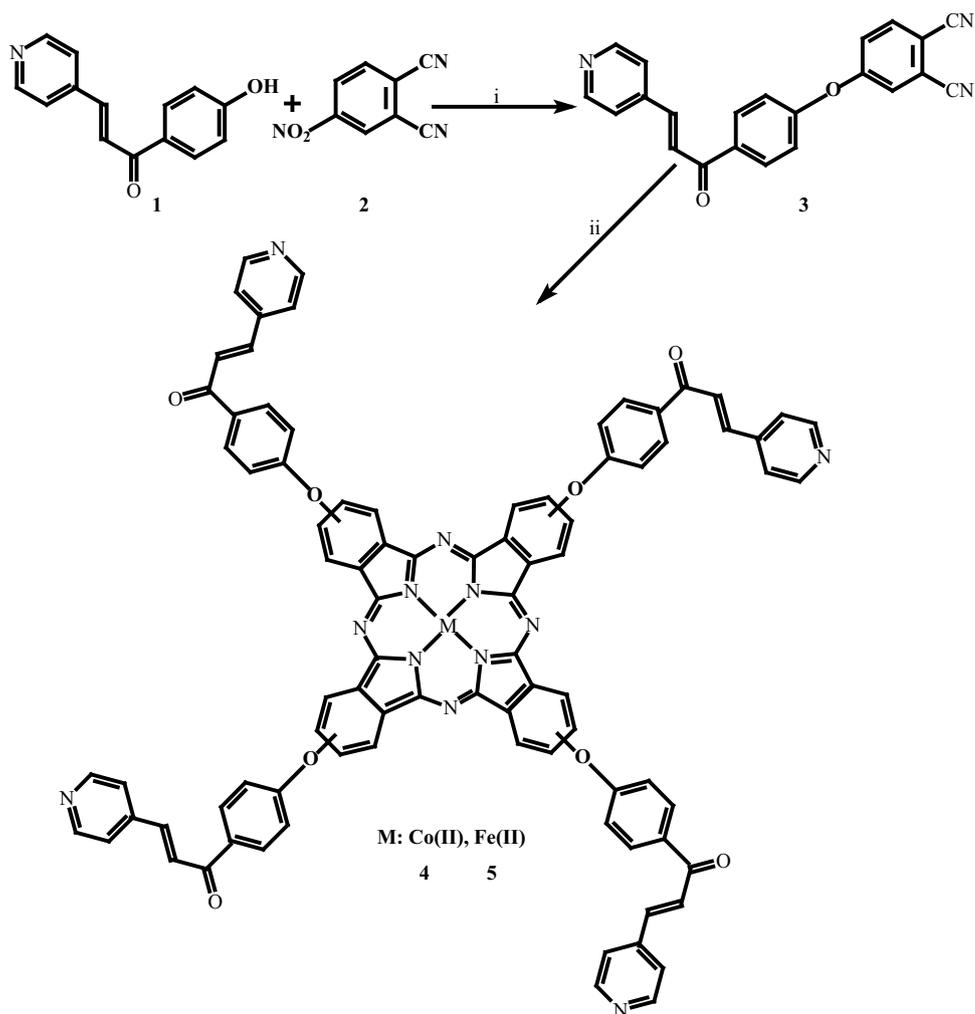
### Synthesis and characterization

Template cyclotetramerization of dinitrile derivative **3** in the presence of anhydrous metal salts ( $\text{CoCl}_2$  and  $\text{Fe}(\text{CH}_3\text{COO})_2$ ) gave the tetrasubstituted phthalocyanine derivatives as shown in Fig. 1. While the cobalt and iron phthalocyanines (**4** and **5**) were isolated by column chromatography on silica gel using chloroform:methanol (9:1). The synthesis of phthalonitrile derivative (**3**) was accomplished in 74 % yield through base-catalyzed aromatic displacement of 4-nitrophthalonitrile with (2E)-1-(4-hydroxyphenyl)-3-pyridine-4-ylprop-2-en-1-one using  $\text{K}_2\text{CO}_3$  as the base in dry DMF (Fig. 1). UV-Vis, IR,  $^1\text{H-NMR}$ , MS and elemental data for the newly synthesized compounds were consistent with the assigned formulation as shown in the experimental section.

The IR spectra clearly indicated the formation of compound **3** with the appearance of absorption band at  $2233\text{ cm}^{-1}$  (C≡N). The  $^1\text{H-NMR}$  spectrum of **3** exhibited aromatic protons at 8.50, 8.10, 7.90, 7.85, 7.56, 7.36, 7.09 ppm as doublet, and olefinic (CH=C, –CHCO) protons at 6.80 and 6.20 ppm as doublet. In the mass spectra of compound **3** the presence of molecular ion peak at  $m/z = 361.54\text{ [M]}^+$  and elemental analysis data confirmed the proposed structures.

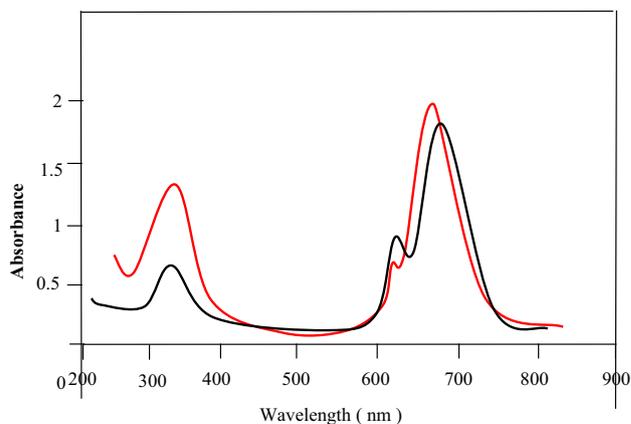
Cyclotetramerization of the dinitrile derivative **3** to the cobalt(II) and iron(II) phthalocyanines **4** and **5** were confirmed by the disappearance of the sharp C≡N vibration of  $2233\text{ cm}^{-1}$ . The  $^1\text{H NMR}$  spectrum of cobalt phthalocyanine **4** could not be taken due to the paramagnetic cobalt(II) centers [14]. The  $^1\text{H-NMR}$  spectrum of peripherally tetra-substituted iron(II) phthalocyanine **5** was as expected.

**Fig. 1** The synthesis of iron and cobalt phthalocyanines. Reagents and conditions: (i) dry DMF,  $K_2CO_3$ , 60 °C; (ii) n-pentanol, DBU, 160 °C,  $CoCl_2$ ,  $Fe(CH_3COO)_2$



The  $^1H$ -NMR spectrum of iron(II) phthalocyanine **5** indicated the aromatic protons at 8.25, 7.96, 7.88, 7.72, 7.58, 7.42, 7.16 ppm and olefinic protons at 6.58, 6.34 ppm. In the mass spectrum of cobalt and iron phthalocyanines **4** and **5**, the presence of molecular ion peaks at  $m/z$  1506.70  $[M + 2H]^+$  and 1503.51  $[M + 2H]^+$  respectively, confirmed the proposed structures.

UV/Vis spectra of the phthalocyanine complexes **4–5** exhibited characteristic absorptions in the Q-band region at around 650–700 nm, attributed to the  $\pi-\pi^*$  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  $\pi-\pi^*$  transitions [15–28]. The Q-band absorptions of  $\pi-\pi^*$  transition for all phthalocyanines **4–5** in  $CHCl_3$  were observed as a single band of high intensity at 678 nm for **4**, 684 nm for **5**. There was also a shoulder at the slightly higher energy side of the Q band for each



**Fig. 2** UV-Vis Spectrum of complex **4** and **5**

phthalocyanine. B band absorptions of the metallophthalocyanines **4–5** were observed at 324, 332 nm respectively (Fig. 2).

**Table 1** Homogeneous oxidation of functional phenols catalyzed by complex **4** and **5**

Substrate	Cat./subs./ox.ratio	Total conversion (%)		Selectivity of complex <b>4</b> (%)		TON	TOF (h <sup>-1</sup> )
		Complex <b>4</b>	Complex <b>5</b>	Quinone <sup>b</sup>	Aldehyde <sup>a</sup>		
p-nitrophenol	1/400/500	93	90	100	–	372	124
	1/400/900	57	45	95	–	228	76
	1/400/1200	33	29	89	–	132	44
o-chlorophenol	1/400/500	63	55	57	43	252	84
	1/400/900	42	38	50	50	168	56
	1/400/1200	35	29	48.5	51.5	140	46.7
2,3-dichlorophenol	1/400/500	41	35	46	53.6	164	54.7
	1/400/900	26	17	57.7	42.3	104	34.7
	1/400/1200	15	11	46.6	53.4	60	20
p-methoxyphenol	1/400/500	22	24	55	45	88	29
	1/400/900	14	9	54	46	56	18.7
	1/400/1200	–	–	–	–	–	–
p-nitrophenol	Without catalyst	–	–	–	–	–	–

<sup>a</sup> Functionalized quinone compound<sup>b</sup> Functionalized aldehyde compound<sup>c</sup> TON = mole of product/mole of catalyst<sup>d</sup> TOF = mole of product/mole of catalyst × time

Conversion was determined by GC

Cat/oxidant ratio = 1/500, Reaction time = 3 h

**Table 2** Different oxidant effect and temperature effect of p-nitrophenol oxidation with complex **4** and **5**

Catalyst	Oxidant	Temperature (°C)	Quinone <sup>a</sup>	Aldehyde <sup>b</sup>	Selectivity of quinone <sup>a</sup>	Total conversion (%)	TON <sup>c</sup>	TOF <sup>d</sup> (h <sup>-1</sup> )
<b>4</b>	TBHP	90	93	–	100	93	372	124
<b>5</b>			90	–	94.7	95	380	126.8
<b>4</b>	H <sub>2</sub> O <sub>2</sub>	90	29	19	60.4	48	192	64
<b>5</b>			21	23	47.7	44	176	58.7
<b>4</b>	m-CPBA	70	15	14	51.7	29	116	38.7
<b>5</b>			17	16	51.5	33	132	44
<b>4</b>	Oxone	90	11	8	57.9	19	76	25.4
<b>5</b>			9	–	100	9	36	12
<b>4</b>	Air	90	–	–	–	–	–	–
<b>5</b>	Oxygen		–	–	–	–	–	–
<b>4</b>	TBHP	70	51	25	67	76	304	101
<b>5</b>			47	21	69	68	272	90.8
<b>4</b>	TBHP	50	38	19	66.6	57	226	75.5
<b>5</b>			36	12	75	48	192	64
<b>4</b>	TBHP	25	15	12	55.5	27	107	35.8
<b>5</b>			15	8	65.2	23	108	36.5
<b>4</b>	Without oxidant	–	–	–	–	–	–	–
<b>5</b>								

<sup>a</sup> Functionalized quinone compound<sup>b</sup> Functionalized aldehyde compound<sup>c</sup> TON = mole of product/mole of catalyst<sup>d</sup> TOF = mole of product/mole of catalyst × time

Conversion was determined by GC

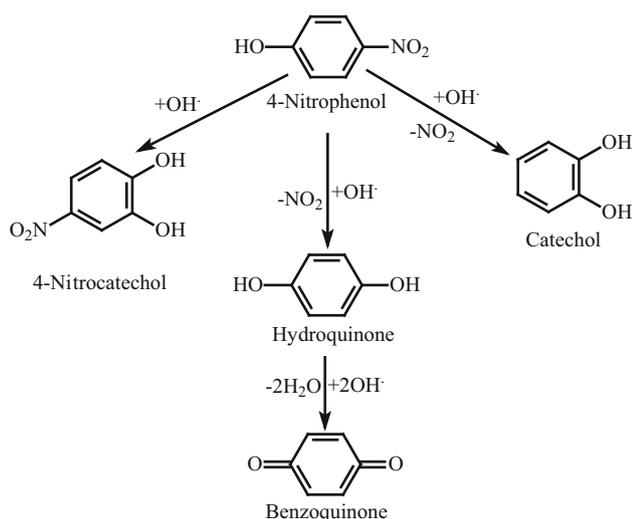
Cat/oxidant ratio = 1/500, Reaction Time = 3 h

## Catalytic studies

### Oxidation of phenolic compounds with **4** and **5**

The catalytic activity of the complexes **4** and **5** were explored for the oxidation of substituted phenolic compounds (p-nitrophenol, o-chlorophenol, 2,3-dichlorophenol and p-methoxyphenol). All the oxidation reactions data were given in Tables 1 and 2. Blank tests without catalyst were performed repeatedly throughout the study to confirm that the any species thereon were not catalytically active. Oxidation conditions were the same for all the tests; however, the total conversion values for the each catalyst are different. In all the oxidation reactions of phenolic compounds gave only two type of product as quinones as main product and benzaldehydes as minor products (Fig. 3). Initially, the complexes were tested for the catalytic oxidation of phenolic compounds in DMF. It was seen that all the catalysts have dissolved pretty well and have showed the best performance in DMF. Conversion of phenolic compounds for all catalysts was determined the end of 3 h in DMF.

As the results are seen in Table 1, the homogeneous oxidation of substituted phenolic compounds catalyzed by complex **4** and **5** with TBHP. By using complex **4**, the higher product conversion and selectivity (93 and 100 %) was obtained then the other complex **5** in p-nitrophenol oxidation with high TON and TOF value the end of 3 h. The reaction rate and conversion with increasing the ratio(cat/subs) up to 1 mol% affording to full conversion of phenolic compounds within 3 h and 93 %. Nevertheless, an increasing in this ratio up to 5 mmol% did not improve the conversion rate [29]. Additionally, ox./cat. ratio raising

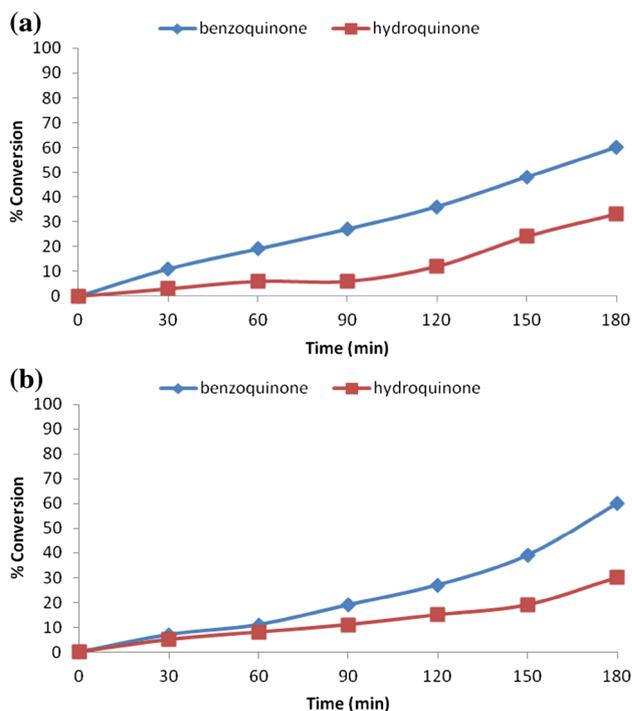


**Fig. 3** Product formed through 4-nitrophenol oxidation by an oxidant in the presence of catalysts **4** and **5**

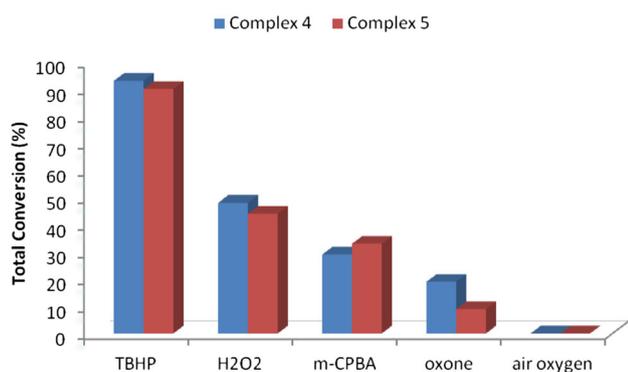
from 500 to 1200 the product decreases for all product species (Table 1). Co(II) phthalocyanine **4** was not able to served due to easily degradation of its ring when the ratio up to 1200.

Figure 4a, b indicate product conversion of both complexes on the oxidation process. Although the conversion of hydroquinone and benzoquinone increased during 3 h, never increasing of product was observed after 3 h.

In Table 2 various types of oxidants were used the oxidation with catalyst **4** and **5**. H<sub>2</sub>O<sub>2</sub> and m-CPBA can serve as an oxidant but low conversion for both complexes due to their degradation. Oxone was used as an oxidant with the lowest conversion but the highest quinone selectivity on the oxidation processes was obtained with complex **5**. On the contrast, TBHP is the best oxidant in this system for both complexes with high conversion and quinone selectivity. Adding TBHP in the reaction media, the reaction color changed from dark blue to light blue, green and then yellow. At the end of the reaction, the reaction color turned to light yellow. The reaction results in the open air, there is no sufficient oxygen in the air for oxidation was observed. Figure 5 was summarized the effect of oxygen source on the reaction rate p-nitrophenol oxidation with complex **4** and **5**.



**Fig. 4** Time-dependent conversion of p-nitrophenol oxidation **a** for catalyst **4**, **b** for catalyst **5**. [Reaction conditions: p-nitrophenol ( $1.33 \times 10^{-3}$  mol), complex **4** ( $3.32 \times 10^{-6}$  mol), complexes **5** ( $3.33 \times 10^{-6}$  mol), TBHP ( $1.66 \times 10^{-3}$  mol), DMF (0.01 L), 3 h and 90 °C]



**Fig. 5** The oxidant effect on p-nitrophenol oxidation [Reaction conditions: p-nitrophenol ( $1.33 \times 10^{-3}$  mol), complex 4 ( $3.32 \times 10^{-6}$  mol), complex 5 ( $3.33 \times 10^{-6}$  mol), TBHP ( $1.66 \times 10^{-3}$  mol), DMF (0.01 L), 3 h and 90 °C]

Temperature effect was investigated with complex 4 and 5 in Table 2. Conversion of p-nitrophenol increased from 27 to 93 % for complex 4 and 23 to 90 % for complex 5 as the temperature increased. There was no

remarkable difference in the percentage of the results show that high temperature tends to increase the conversion and selectivity of products. Therefore, 90 °C was taken to be an optimum temperature in this study to achieve highest conversion.

Previous studies related to phthalocyanines as catalyst in the phenolic compounds oxidation were summarized in Table 3. Sulfonate substituted metallophthalocyanines were investigated on different groups substituted phenolic compounds oxidation [30–34] Different groups substituted metallophthalocyanines were also investigated on 2,6-di-tert-butylphenol, 2,4,6-trichlorophenol and p-nitrophenol oxidation [35–39]. In our previous work, tetrasubstituted Co(II) and Fe(II) phthalocyanine complexes were studied as catalyst in the oxidation of phenolic compounds [40]. The results of our previous work research were valuable because of the high conversion and selectivity of Co(II) phthalocyanine (97 and 87 %). But in this research we achieve to reach the highest quinone selectivity with Co(II) phthalocyanine (100 %).

**Table 3** Catalytic activities towards the homogeneous oxidation of phenolic compounds of some previously reported catalyst

Catalyst	Substrate	Rxn Time (h)	Rxn Temp. (°C)	Oxidant	Conv. (%)	References
CoPcTs <sup>a</sup>	DTBP	24	70	O <sub>2</sub>	66	[31]
CoPcTs <sup>a</sup>	DTBP	2	75	TBHP	61	[32]
FePcTs <sup>b</sup>					39	
CuPcTs <sup>c</sup>					05	
CoPc <sup>d</sup>	DTBP	3	30	TBHP	93	[33]
FePc <sup>e</sup>					–	
MnPc <sup>f</sup>					97	
CuPc <sup>g</sup>					–	
FePcTs <sup>b</sup>	TCP	24	25	H <sub>2</sub> O <sub>2</sub>	24	[34, 35]
FePc <sup>e</sup>	TCP	24	nr <sup>j</sup>	KHSO <sub>5</sub>	85	[36]
CoPc <sup>d</sup>						
CoPcTs <sup>a</sup>	2,4,5-TCP	24	75	H <sub>2</sub> O <sub>2</sub>	67	[37]
FePcOC <sup>h</sup>	TCP	10 min	25	H <sub>2</sub> O <sub>2</sub>	6	[38]
FePcTs <sup>b</sup>	TMP	2	nr <sup>j</sup>	O <sub>2</sub>	77	[39]
CoPc <sup>i</sup>	p-nitrophenol	3	90	TBHP	97	[40]
FePc <sup>i</sup>					75	
CoPc <sup>d</sup>	p-nitrophenol	3	90	TBHP	96	[45]

<sup>a</sup> CoPcTs = Tetrasulphonated cobalt phthalocyanine

<sup>b</sup> FePcTs = Tetrasulphonated iron phthalocyanine

<sup>c</sup> CuPcTs = Tetrasulphonated copper phthalocyanine

<sup>d</sup> CoPc = Substituted cobalt phthalocyanine

<sup>e</sup> FePc = Substituted iron phthalocyanine

<sup>f</sup> MnPc = Substituted manganese phthalocyanine

<sup>g</sup> CuPc<sup>g</sup> = Substituted copper phthalocyanine

<sup>h</sup> FePcOC = Octa cationic iron phthalocyanine

<sup>i</sup> CoPc = Substituted cobalt phthalocyanine

<sup>j</sup> FePc = Substituted iron phthalocyanine

<sup>j</sup> nr = not reported

Based on this catalytic study, the activity of metallophthalocyanine is depend on the nature of the introduced transition metals. The activity of metallophthalocyanines in oxidation reaction follows the order CoPc > FePc. It is known that the catalytic performance of transition metal species depends on the outer d-electron density.

4-NP oxidation proceeds by initial aromatic hydroxyl oxidative attack (similar to phenol oxidation) followed by oxidative fragmentation, with release of nitrates, as confirmed by the identification of 4-nitrocatechol, hydroquinone, benzoquinone and catechol. In this works, p-nitrocatechol and catechol were found as trace amounts (lower 8 %). It is well known that the reaction mechanism of HO· radicals with aromatic compounds proceeds mainly through an electrophilic addition to the aromatic ring [41–44]. The phenolic–OH group is electron-donating for the electrophilic aromatic substitution, thus increasing the electron density both in the ortho and in the para positions [41]. On the other hand, the –NO<sub>2</sub> group is electron-withdrawing, thus being meta directing [41]. In the particular case of p-nitrophenol (i.e., in the presence of both substituents), the electrophilic attack will occur at the ortho position in respect to the –OH group, leading to the formation of p-nitrocatechol an aromatic substitution of the –NO<sub>2</sub> group may occur due to an attack of the radical HO· at the para position in respect to the –OH group, hydroquinone being obtained [42, 43]. Furthermore, an aromatic substitution of the –NO<sub>2</sub> group may occur due to an attack of the radical HO· at the para position in respect to the –OH group, hydroquinone being obtained [42, 43]. Hydroquinone is known to be very easily oxidized into benzoquinone [43]. Thus, benzoquinone formation would be expected from the reaction of hydroquinone with highly oxidizing species such as HO· radicals. Trace amounts of catechol were also detected, probably resulting from the –NO<sub>2</sub> group cleavage and subsequent electrophilic attack of the HO· radical at the ortho position [44].

## Conclusion

In summary, the structure of Fe(II) and Co(II) phthalocyanines were confirmed by IR, <sup>1</sup>H-NMR, UV–Vis, mass spectroscopies and elemental analysis. The optimal conditions of catalysis were found changing the parameters (temperature, different oxidants, subst./cat. ratio). Co(II) phthalocyanine exhibits superior catalytic activity and durability in the catalysis over oxidation of p-nitrophenol (4-NP). The results presented here is vital to both exploration of growth catalysis process and constructing novel morphologies of Co(II) phthalocyanine not only in this paper but also possibly for other systems. The present

method in this work is simple, environmentally benign and amenable scale up process.

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