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Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

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To cite this article: Ece Tuğba Saka, Gülbinar Sarki & Halit Kantekin (2015) Facile synthesis of highly active Co(II) and Fe(II) phthalocyanine catalysts for aerobic oxidation of phenolic compounds, Journal of Coordination Chemistry, 68:7, 1132-1141, DOI: 10.1080/00958972.2015.1015529

To link to this article: http://dx.doi.org/10.1080/00958972.2015.1015529

Journal of Coordination Chemistry, 2015
Vol. 68, No. 7, 1132–1141, http://dx.doi.org/10.1080/00958972.2015.1015529

Facile synthesis of highly active Co(II) and Fe(II) phthalocyanine catalysts for aerobic oxidation of phenolic compounds

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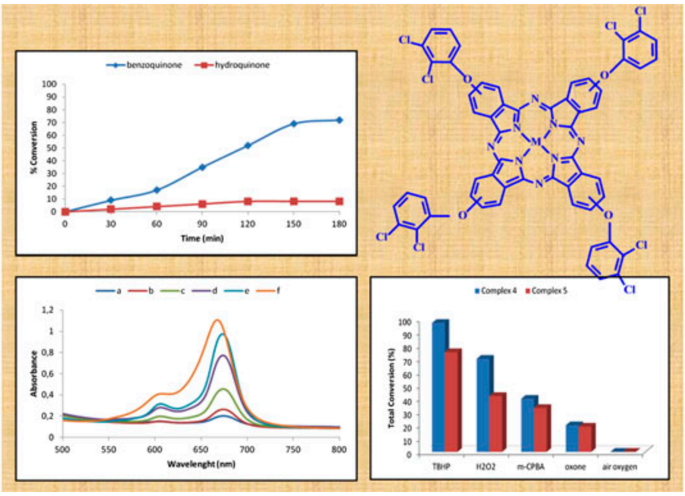
(*Received 6 November 2014; accepted 15 January 2015*)



In this work, 2,3-dichlorophenoxy substituted cobalt and iron phthalocyanines have been synthesized and used as efficient catalysts for aerobic oxidation of nitrophenols. Co(II) and Fe(II) phthalocyanines have been characterized by IR, ^{1}H NMR, ^{13}C NMR, UV–vis, and mass spectroscopies. *tert*-butyl hydroperoxide (TBHP), *m*-chloroperoxybenzoic acid, hydrogen peroxide, and air oxygen have been used as oxygen source. These catalysts offered the highest activity on 4-nitrophenol oxidation in 3 h. In order to achieve the best reaction conditions, oxidant ratio, temperature, and oxidant type have been investigated with different nitrophenols in 3 h.

Keywords: Phthalocyanine; Iron; Cobalt; Nitrophenols; Aerobic oxidation; TBHP

1. Introduction

Phenolic compounds are often needed in making plastic and explosive materials, production of detergents, making insect repellents, and weed killers. They are also used in petroleum

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*Corresponding author. Email: ece_t_saka@hotmail.com industry and forestry industry [1]. Phenolic compounds are environmental pollutants (especially water pollutants) so their oxidation reactions have environmental importance. Phenolic compound residues in industrial wastes that can reach potable water and green plants. According to European Environment Agency registrations of 2010, the amount of the phenolic compounds has spread in the environment of Europe and are now at 2000 tons per year. The oxidation of phenols means that these molecules can be easily removed by micro-organisms and destruction in soil, water, and green plants from phenol compounds has been prevented [2, 3].

There are many studies in the literature on oxidation [4–12]. Phthalocyanines containing cobalt(II) and iron(II) can oxidize different phenolic compounds to quinones and aldehydes. Selective oxidation of phenol to quinones is the key step in preparation of many vitamins and valuble synthetic precursors. Quinones are powerful intermediates in organic synthesis and show biological activity, since quinone fragments often occur within the molecular frameworks of natural products [13].

In this work, we have synthesized 2,3-dichlorophenoxy substituted cobalt(II) **4** and iron(II) **5** phthalocyanine. Aggregation behavior of phthalocyanines influences their solubility, since many phthalocyanine complexes are poorly soluble in organic solvents [14–21]. With 2,3-dichlorophenoxy substituent, Co(II) and Fe(II) phthalocyanine complexes **4** and **5** can readily dissolve in organic solvents [22]. Phthalocyanines bearing halogens (–F, –Cl, and –Br) were used as catalysts in several works. Introducing electron-withdrawing groups to peripheral sites of the phthalocyanines generally shifts the redox processes of the complexes to positive potentials [23, 24]. Herein, we report the application of Co(II) and Fe(II) phthalocyanines as catalysts for oxidation of phenolic compounds in a homogeneous catalytic system.

2. Experimental

The used materials, equipment, and general procedure for the oxidation of phenols are supplied as supplementary information.

2.1. *Synthesis*

2.1.1. Synthesis of 4-(2,3-dichlorophenoxy)phthalonitrile 3. 4-Nitrophthalonitrile **1** (2.11 g, 12.2 mM) was dissolved in 20 mL dry DMF under N_2 and 2,3-dichlorophenol **2** (2 g, 12.2 mM) was added to the mixture. After stirring for 30 min at 60 °C, finely grounded anhydrous K_2CO_3 (5.05 g, 36.6 mM) was added portion wise within 2 h. The reaction mixture was stirred under N_2 at 60 °C for 5 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 light-brown crystalline powder. Yield: 2.57 g (78%). M.p.: 125–126 °C. Anal. Calcd for $C_{14}H_6Cl_2N_2O$: IR (KBr pellet), ν_{max}/cm^{-1}: 3093, 3076, 3042 (Ar–H), 2974, 2232 (C≡N), 1602–1565 (C–O), 1479, 1442, 1425, 1285, 1272, 1247, 1159, 1189, 1053, 1100, 960, 878, 836, 797, 719, 701. ^{1}H NMR. ($CDCl_3$), (δ: ppm): 7.98 (d, H, Ar–H), 7.78 (d, H, Ar–H), 7.51 (d, 1H, Ar–H), 7.20 (d, H, Ar–H), 7.11 (d, H, Ar–H), 6.81 (d, H, Ar–H). ^{13}C NMR. ($CDCl_3$), (δ: ppm): 160.76, 153.12, 135.64, 135.35, 127.58, 125.65, 125.35, 124.03, 123.20, 117.54, 115.52(C≡N), 115.27(C≡N), 112.77, 107.25. MALDI-TOF-MS, (m/z): Calculated: 289.11; Found: 290 $[M + 1]^+$.

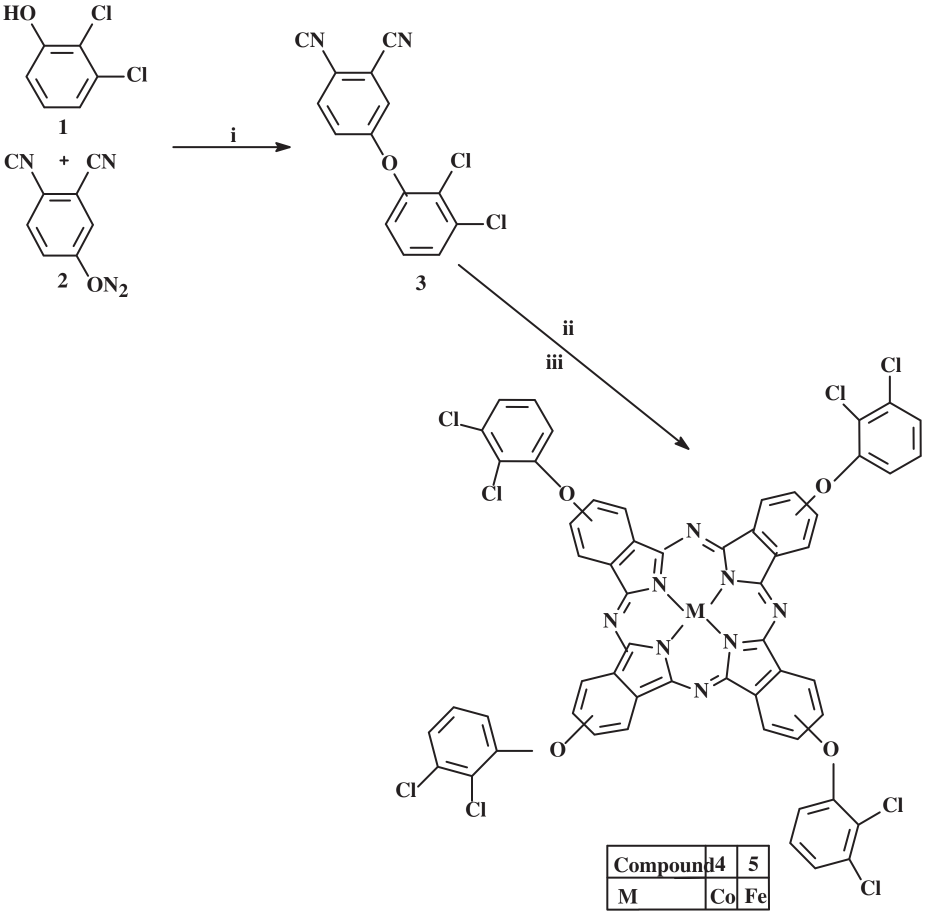
2.1.2. Synthesis of cobalt(II) phthalocyanine 4. A mixture of phthalonitrile **3** (0.5 g, 1.722 mM), anhydrous $CoCl_2$ (112.5 mg, 0.862 mM) and dry DMAE (5 mL) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature, the reaction mixture was precipitated by the addition of ethanol and green precipitate was refluxed in EtOH (40 mL) for 3 h. After then the obtained dark-green product was filtered off, washed with hot EtOH and then dried in vacuo over P_2O_5. Finally, green product was purified through an alumina column using $CHCl_3:MeOH$ (5 : 2) as eluting solvent system. Yield: 90 mg (42%). Anal. Calcd for $C_{56}H_{24}Cl_8N_8O_4Co$: IR (KBr tablet) ν_{max}/cm^{-1}: 3065 (Ar–H), 2960, 2920, 2850, (Aliph. C–H), 1716, 1610, 1573, 1523, 1472, 1407, 1426, 1444, 1330, 1216, 1117, 1053, 1089, 975, 924, 911, 822, 768, 734. UV–vis ($CHCl_3$): λ_{max}, nm (log ε): 670 (5.03), 614 (4.63), 331 (5.00), 316 (4.98). MALDI-TOF-MS, (*m/z*): Calculated: 1215.05; Found:1214 $[M-H]^+$.

2.1.3. Synthesis of iron(II) phthalocyanine 5. A mixture of phthalonitrile **3** (0.5 g, 1.722 mM), anhydrous $Fe(CH_3COO)_2$ (150 mg, 0.862 mM), and dry DMAE (5 mL) was heated and stirred at 160 °C in a sealed glass tube for 24 h under N_2. After cooling to room temperature the green crude product was precipitated with ethanol, filtered and washed first with ethanol then diethyl ether and then dried in vacuo. Purification of the product was accomplished by column chromatography with silica gel using $CHCl_3:CH_3OH$ (5 : 1) as solvent system. Yield: 93 mg (45%). Anal. Calcd for $C_{56}H_{24}Cl_8N_8O_4Fe$: IR (KBr tablet) ν_{max}/cm^{-1}: 3071, (Ar–C–H), 2918, 2849 (Aliph. C–H) 1611, 1573, 1472, 1427, 1445, 1332, 1251, 1186, 1116, 1080, 1051, 951, 923, 908, 789, 769, and 747. ^{1}H NMR. ($CDCl_3$), (δ: ppm): 8.50 (8H, Ar–H), 8.23 (8H, Ar–H), 7.83 (4H, Ar–H), 7.77 (7H, Ar–H), 6.63 (12H, Ar–H). ^{13}C NMR. ($CDCl_3$), (δ: ppm): 160.80, 155.72, 148.56, 144.68, 141.07, 137.55, 132.09, 129.80, 125.46, 124.21, 120.98, 114.89, 108.86, and 106.18. UV–vis ($CHCl_3$): λ_{max}, nm (log ε): 692 (4.94), 345 (4.93). MALDI-TOF-MS, (*m/z*): Calculated:1213.64; Found:1212.79 $[M-H]^+$.

3. Results and discussion

3.1. *Synthesis and characterization*

Cobalt(II) and iron(II) phthalocyanines **4** and **5** with four 2,3-dichlorophenoxy groups were synthesized as reported [25]. All compounds were identified through various spectroscopic techniques such as ^{1}H NMR, FT-IR, UV–vis and MALDI-TOF. The synthetic route as outlined in scheme 1 started with the synthesis of 2,3-dichlorophenoxy phthalonitrile, **3**. In conversion of **3** into the iron and cobalt phthalocyanines, the sharp peak for the C≡N vibration disappeared in IR spectra. NMR spectrum of **4** could not be taken because of the paramagnetic cobalt(II) centers [26]. The ^{1}H NMR spectrum of **5** was as expected, showing aromatic protons as multiplets at 8.50 (8H, Ar–H), 8.23 (8H, Ar–H), 7.83 (4H, Ar–H), 7.77 (7H, Ar–H), and 6.63 (12H, Ar–H) ppm. ^{13}C NMR spectrum of **5** showed typical chemical shifts for aliphatic carbon signals at 160.80, 155.72, 148.56, 144.68, 141.07, 137.55, 132.09, 129.80, 125.46, 124.21, 120.98, 114.89, 108.86, and 106.18. The MALDI-TOF mass spectrum showed 1214 $[M-H]^+$ peak for **4**, 1212.79 $[M-H]^+$ peak for **5**, respectively.



Scheme 1. The synthesis of iron and cobalt phthalocyanines. Reagents and conditions: (i) dry DMF, K_2CO_3, 60 °C; (ii) $CoCl_2$, 175 °C, 350 W for 8 min; (iii) n-pentanol, DBU, 160 °C, $Fe(CH_3COO)_2$.

The UV/Vis spectra of cobalt(II) and iron(II) phthalocyanines **4** and **5** in DMF at room temperature are shown in figure 1. *Q*-bands were observed at 666 nm for **4**, 687 nm for **5** with the shoulders at 604 nm for **4**, 602 nm for **5**, and the B bands were observed between 360 and 329 nm.

3.2. *Catalytic studies*

3.2.1. Oxidation of phenolic compounds with 4 and **5**. Phenolic compounds (1.64×10^{-3} M), catalyst (4.11×10^{-6} M), and oxidant (2.05×10^{-3} M) in DMF (0.01 L) were used at 90 °C with 900 rpm. Slowly progressive reactions in the absence of **4** and **5** under these conditions demonstrate that catalysts have a role in this oxidation process. Tables 1–3 show catalytic studies of **4** and **5** for oxidation of some phenolic compounds. Quinones as main product and benzaldehydes as minor products are determined for the

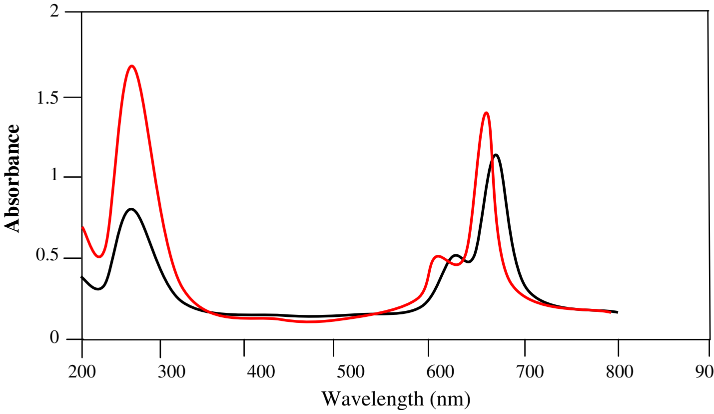


Figure 1. UV–vis spectrum in DMF for **4** (red) and **5** (black) (see http://dx.doi.org/10.1080/00958972.2015.1015529 for color version).

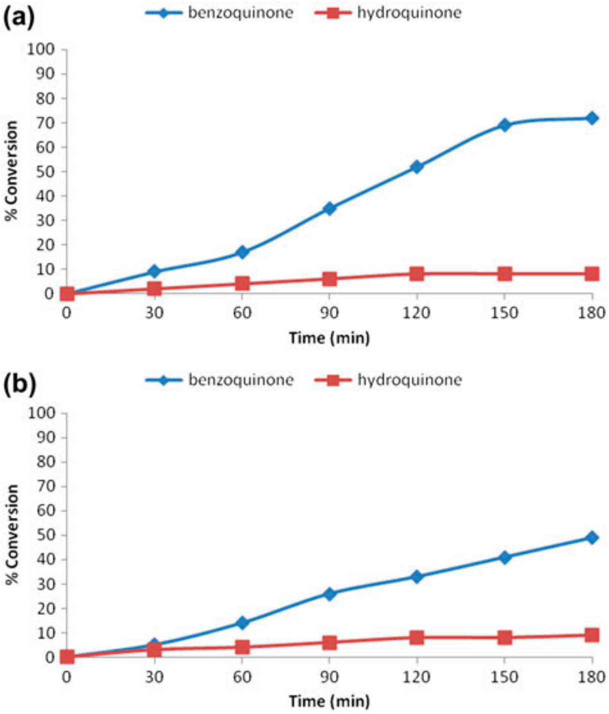


Figure 2. Time-dependent conversion of 4-nitrophenol oxidation (a) for **4**, (b) for **5**. [Reaction conditions: 4-nitrophenol (1.64 × 10^{-3} M), **4** (4.11 × 10^{-6} M), **5** (4.10 × 10^{-6} M), TBHP (2.05 × 10^{-3} M), DMF (0.01 L), 3 h, and 90 °C].

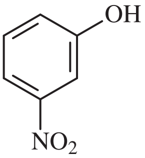
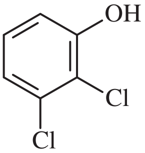
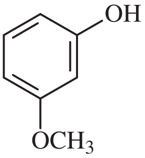
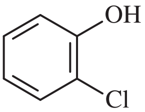
oxidation processes [figure 2(a) and (b)]. In the experiments without catalyst, conversion was not observed. Various parameters on the percentage conversion and selectivity of products were examined (tables 1–3).

Table 1 shows the homogeneous oxidation of functionalized phenols catalyzed by **4** and **5** with TBHP. By using **4**, the highest product conversion (97%) was obtained in 4-nitrophenol oxidation with high TON and TOF. When **4** was used as catalyst in 400/1 substrate/catalyst ratio, the highest quinone selectivity was determined. While the ratio increases toward 1200, the product conversion decreases [10]. Additionally, 2,3-dichlorophenol and 4-methoxyphenol are catalyzed by **4** with good quinone selectivity (74% and 73%).

The effect of amount of oxidant for oxidation of functionalized phenols with **4** was examined (table 1). With TBHP as oxidant in 3 h **4** catalyzed 4-nitrophenol with 500/1 oxidant/catalyst ratio. At the same ratio, **4** catalyzed 2-chlorophenol, 2,3-dichlorophenol, 4-methoxyphenol and 4-nitrophenol oxidations. Increasing the ratio to 1500, the product conversion decreases for all substrates. Fast degradation of the phthalocyanine ring of **4** was observed when more oxidant was added.

In table 2 different oxidants were used in 4-nitrophenol oxidation with **4** and **5**. Hydrogen peroxide (H_2O_2) and *m*-chloroperoxybenzoic acid (*m*-CPBA) give low conversion for both complexes. Adding H_2O_2 or *m*-CPBA in the reaction media, the reaction color changed from blue to brown, indicating that **4** and **5** were degraded immediately with H_2O_2 or *m*-CPBA. Clearly, 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

Table 1. Homogeneous oxidation of functionalized phenols catalyzed by **4** and **5**.

Substrate	Cat./subs./ox.ratio	Total conversion (%)		Selectivity of complex **4** (%)		TON	TOF (h^{-1})
		Complex **4**	Complex **5**	Quinone[b]	Aldehyde[a]		
	1/400/500 1/800/500 1/1200/500	97 60 39	75 45 21	87 75 51	– – –	388 480 468	129 160 156
	1/400/500 1/800/500 1/1200/500	78 43 21	61 35 18	74 58 57	25 41 41	312 344 252	104 114 84
	1/400/500 1/800/500 1/1200/500	63 28 9	47 21 12	73 50 66	26 50 34	252 224 108	84 74 36
	1/400/500 1/800/500 1/1200/500	29 17 –	25 – –	65 58 –	35 42 –	116 136 –	38 45 –

[a] Functionalized quinone compound.
[b] Functionalized aldehyde compound.
TON = mole of product/mole of catalyst.
TOF = mole of product/mole of catalyst × time.
Conversion was determined by GC.
Substrate/catalyst ratio=300, reaction time = 3 h.

Table 2. Effects of different oxidant and temperature for 4-nitrophenol oxidation with **4** and **5**.

Catalyst	Oxidant	Temperature (°C)	Quinone[a]	Aldehyde[b]	Selectivity of quinone[a]	Total conversion (%)	TON[c]	TOF[d] (h^{-1})
4	TBHP	90	87	–	87	97	389	129
5			65	–	75	75	300	100
4	TBHP	70	58	10	85	68	272	90
5			42	11	79	53	212	70
4	TBHP	50	35	10	77	45	180	60
5			22	9	70	31	124	41
4	TBHP	25	17	9	65	26	104	34
5			9	9	50	18	72	24
4	H_2O_2	90	55	15	78	70	280	93
5			33	9	78	42	168	56
4	*m*-CPBA	90	28	12	70	40	160	53
5			16	7	48	33	131	43
4	Oxone	90	12	8	60	20	80	26
5			10	9	52	19	76	25
4	Air	90	–	–	–	–	–	–
5	oxygen		–	–	–	–	–	–

[a] Functionalized quinone compound.
[b] Functionalized aldehyde compound.
[c] TON = mole of product/mole of catalyst.
[d] TOF = mole of product/mole of catalyst × time.
Conversion was determined by GC.
Cat/oxidant ratio = 1/500, reaction time = 3 h.

changed from blue to green and then brown. At the end of the reaction, the reaction color turned to colorless. In air, there is not sufficient oxygen for oxidation. Figure 3 summarizes the effect of oxygen source on the reaction rates for 4-nitrophenol oxidation with **4** and **5**.

In table 2, the 4-nitrophenol oxidation was carried out with **4** and **5** at different temperatures. As the reaction temperature increased, the catalytic activity of **4** and **5** increased. According to table 2, when the temperature was reduced from 90 to 25 °C, the total conversion changed from 97% to 26% for **4** and 75% to 18% for **5**. At 25 °C, quinone and aldehyde conversion was the lowest; 90 °C is the optimum temperature of 4-nitrophenol oxidation with TBHP in 3 h (TON: 389, TOF: 129 for **4** and TON: 300, TOF: 100 for **5**).

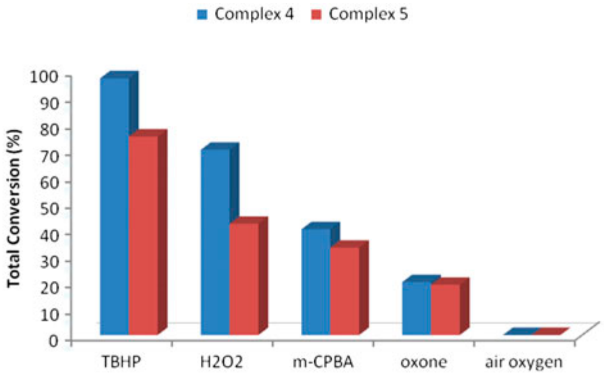


Figure 3. The oxidant effect on 4-nitrophenol oxidation [Reaction conditions: 4-nitrophenol (1.64×10^{-3} M), **4** and **5** (4.11×10^{-6} M), TBHP (2.05×10^{-3} M), DMF (0.01 L), 3 h and 90 °C].

Table 3. Catalytic activities for homogeneous oxidation of phenolic compounds of previously reported catalysts.

Catalyst	Substrate	Rxn time (h)	Rxn temp. (°C)	Oxidant	Conv. (%)	Ref.
CoPcTs[a]	DTBP	3	70	TBHP	70	[27]
CoPcTs[a]	DTBP	2	75	TBHP	61	[28]
FePcTs[b]					39	
CuPcTs[c]					05	
CoPc[d]	DTBP	3	30	TBHP	93	[29]
FePc[e]					–	
MnPc[f]					97	
CuPc[g]					–	
FePcTs[b]	TCP	24	25	H_2O_2	24	[30, 31]
FePc[e]	TCP	24	nr[I]	$KHSO_5$	85	[32]
CoPc[d]						
CoPcTs[a]	2,4,5-TCP	24	75	H_2O_2	67	[33]
FePcOC[h]	TCP	10 min	25	H_2O_2	6	[34]
FePcTs[b]	TMP	2	nr[I]	O_2	77	[35]
CoPc[d]	4-nitrophenol	3	90	TBHP	96	[36]

[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 = Substituted copper phthalocyanine.
[h] FePcOC = Octa cationic iron phthalocyanine.
[I] nr = not reported.

Table 3 compares catalytic activities towards homogeneous oxidation of phenolic compounds of some previously reported catalysts. Tetrasulfonated cobalt, iron, copper, and manganese phthalocyanines were investigated on 2,6-di-tert-butylphenol (DTBP), 2,4,6-trichlorophenol, 2,4,5-trichlorophenol and 2,3,6-trimethylphenol oxidation [27–31]. Türk investigated the oxidation of DTBP with TBHP catalyzed by cobalt(II) phthalocyanine tetrasulfonate ([CoPcTS](4-)) in a 4:1 methanol–water mixture. He found that the conversion of DTBP was 70% in 3 h and 86% in 8 h when the amounts of DTBP, TBHP and [CoPcTS](4-) in millimoles were 0.300, 1.52, and 3.0×10^{-3}, respectively [27]. Kopkallı studied 2,6- and 2,10-ionenes and soluble poly(vinylbenzyl)trimethylammonium chloride polyelectrolytes as catalyst supports for cobalt-, iron- and copper-phthalocyanine tetrasulfonates on the autoxidation of DTBP in water by molecular oxygen [28]. Kothari and Tazuma determined the oxidation of DTBP with $O_{2(g)}$ catalyzed by ([MPc], M = Co^{2+}, Fe^{2+}, Mn^{2+}, Cu^{2+}) in DMF [29]. Substituted cobalt, iron, manganese and copper phthalocyanines were also investigated on 4-nitrophenol oxidation [32–37]. All studies related to oxidation of phenolic compounds and their data are summarized in table 3. Among all of these catalysts, **4** and **5** are interesting catalysts in 2-chlorophenol, 2,3-dichlorophenol, 4-methoxyphenol and 4-nitrophenol oxidation. Especially, **4** shows excellent activity on 4-nitrophenol oxidation.

Degradation of phthalocyanine complexes were followed for the duration of the oxidation process using UV–visible spectroscopy [38, 39]. In figure 4, **4**, chloroform has sharp *Q* band due to the monomeric species in the absence of an oxygen source [40]. Before the oxidation starts, sharp *Q* band of Co(II) phthalocyanine is at 666 nm [figure 4(f)]. After adding TBHP, this *Q* band shifts to 672 nm, broadens and disappears at the end of the reaction. Shifting from 666 to 672 nm indicated oxidation of Co(II)-Pc to Co(III)-Pc [38, 39]. At the end of the oxidation, *Q* band of Co(II) phthalocyanine disappears. The reaction color, from blue to green and then to brown and finally colorless, backs this up. Similar situation occurs for oxidation with **5**. In figure 5 after adding the oxidant, *Q* band of **5** shifts to

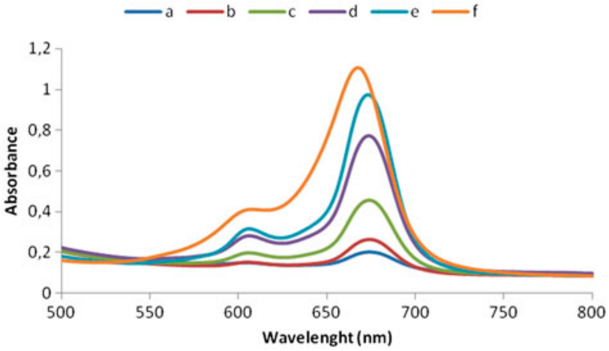


Figure 4. Time-dependent changes in the visible spectrum of the oxidized **4** observed on addition of TBHP (2.05×10^{-3} M) to a reaction mixture containing 1.64×10^{-3} M 4-nitrophenol and 4.11×10^{-6} M **4** in 10 mL: (e) 36 min; (d) 72 min; (c) 108 min; (b) 144 min; (a) 180 min after addition of TBHP. All spectra for oxidized **4** were taken after sixfold dilution with DMF. (f) Visible spectrum of (non-oxidized) **4**.

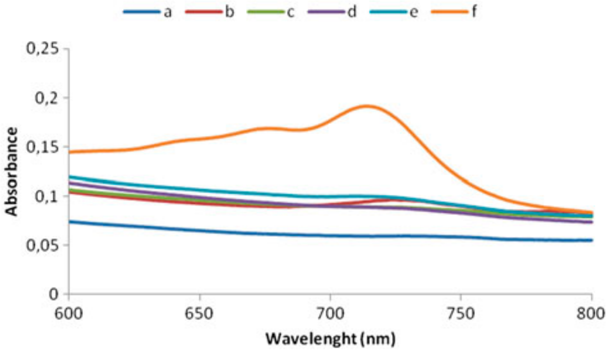


Figure 5. Time-dependent changes in the visible spectrum of the oxidized **5** observed on addition of TBHP (2.05×10^{-3} M) to a reaction mixture containing 1.64×10^{-3} M 4-nitrophenol and 4.10×10^{-6} M **5** in 10 mL: (e) 36 min; (d) 72 min; (c) 108 min; (b) 144 min; (a) 180 min after addition of TBHP. All spectra for oxidized **5** were taken after sixfold dilution with DMF. (f) Visible spectrum of (non-oxidized) **5**.

687 nm and disappears at the end of the reaction. As the event occurs, the color of the reaction solution changed from blue to colorless. The results reflect that **4** is more active than **5** on 4-nitrophenol oxidation with TBHP.

4. Conclusion

Co(II) and Fe(II) phthalocyanines have been characterized by several spectroscopic methods. Catalytic activities of Co(II) and Fe(II) phthalocyanines showed excellent catalytic performance in different phenol oxidations using TBHP as oxidant. Co(II) phthalocyanine shows excellent catalytic activity on 4-nitrophenol oxidation with high yield and selectivity in 3 h. Converting from environmentally harmful phenolic compounds into less harmful oxidation products by Co(II) and Fe(II) phthalocyanines makes this study attractive. These catalytic reactions are feasible, time-saving in terms of procedure and determined the best oxidation conditions with high TON and TOF.

Funding

This study was supported by The Scientific & Technological Research Council of Turkey (TÜBİTAK, project no: 113Z598).

Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2015.1015529].

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