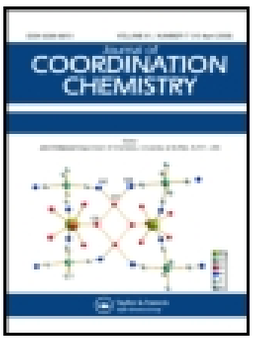

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New peripherally tetra-[*trans*-3,7-dimethyl-2,6-octadien-1-ol] substituted metallophthalocyanines: Synthesis, characterization and catalytic activity studies on the oxidation of phenolic compounds

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In this paper, we elucidated the synthesis, characterization, and investigation of catalytic activity studies of new metallophthalocyanines **4** and **5** as the catalyst for phenolic compounds oxidation by trying different types of oxygen sources. The structural characterization of the products was made by a combination of elemental analysis, FT-IR, LC-MS/MS (for phthalonitrile derivative **3**), MALDI-TOF mass spectral data (for metallophthalocyanines **4**-**7**), UV-vis spectroscopy (for metallophthalocyanines **4**-**7**), ^{1}H NMR and ^{13}C NMR spectroscopies (for compounds **3** and **6**). The synthetic routes for the (*trans*-3,7-dimethyl-2,6-octadien-1-ol) substituted phthalonitrile derivative **3** and corresponding metallophthalocyanines **4**-**7** are outlined in scheme 1. The MPc complexes **4**-**7** were synthesized via cyclotetramerization of compound **3** in the presence of the corresponding anhydrous metal salts ($CoCl_2$ for **4**, $CuCl_2$ for **5**, $Zn(CH_3COO)_2$ for **6** and $MnCl_2$ for **7**) in dry *n*-pentanol as solvent and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as strong base at reflux temperature under nitrogen gas. Phthalocyanines and their metal complexes, in general, display poor solubility in most of the organic solvents, however, the synthesized metallophthalocyanine complexes **4**-**7** were highly soluble in common organic solvents because of the introduction of the methyl groups on alkyl chains of peripheral arms. The catalytic activity of compounds **4** and **5** was evaluated for the oxidation of phenolic compounds such as 4-nitrophenol, *o*-chlorophenol, 2,3-dichlorophenol and *p*-methoxyphenol. CoPc **4** displayed good catalytic performance with a full oxidation of

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4-nitrophenol into the corresponding benzoquinone and hydroquinone with the highest TON and TOF values within 3 h.

Keywords: Synthesis; 4-Nitrophenol oxidation; Manganese(III) chloride phthalocyanine; Catalyst; Cobalt; Phenolic compounds

1. Introduction

Phthalocyanines (Pcs) are well established, versatile and stable macrocyclic compounds [1, 2]. A Pc molecule is composed of four isoindole units connected by azomethine bridges to form an 18-π aromatic macrocycle [3, 4]. The term "phthalocyanine" was used for the first time by Linstead in 1933 to describe the new class of organic compounds [5], after their accidental discovery by Braun and Tcherniac in 1907 [6, 7]. Since then, many scientific types of research have been carried out and devoted to the exploration of their synthesis and properties [8, 9]. Pcs and their metal complexes (MPcs) have found extensive applications in biomedical and industrial fields [1] depending upon their chemical, physical, and optical properties which vary with the central metal ion, its axial coordination or peripheral functionalities [2, 10-12]. These tunable options, 18 π-electronic structure, high thermal and optical properties make Pcs and MPcs promising materials in important scientific areas such as sensors [7, 13, 14], semiconductors [15], dye based solar cells and molecular electronics [16, 17], liquid crystals [11], laser dyes [4], electrochromic systems [2], non-linear optical materials [18], photosensitizers for photodynamic therapy of cancer [19-21], organic field effect transistors [22] and catalysts [23-25].

As it is known, phenolic compounds show high toxicity even at low concentrations. Phenolic compounds are generally found in the effluents of industrial wastewater from assorted activities in diverse industrial sectors such as pesticide productions, resin manufacturing, pharmaceuticals, textile, coking operations, wood products, electrolytic strip tin coating, oil refining, explosive, plastics, coffee, paint, ceramic, paper and pulp [26-30]. Practically, two kinds of technological methods (*i.e.* conventional and advanced methods) are utilized in order to remove phenolic compounds and their effluents from the environment and industrial wastewater. Steam distillation, liquid-liquid extraction, adsorption, catalytic wet air oxidation, ion exchange, solid-phase extraction, wet air oxidation, and biodegradation processes are classified as conventional methods [26]. Advanced technologies for removal of phenols contain

electrochemical oxidation, photo-oxidation, ozonation, UV/H_2O_2, Fenton and Fenton-like treatment, membrane processes (membrane distillation; hollow fiber membranes and extractive membrane bioreactors; photocatalytic membrane reactors; high-pressure membrane processes such as reverse osmosis, pervaporation and nanofiltration) [26, 30-32] and biological treatment (phenol-degrading microorganisms are used to transform phenolic solutions into simple end products [33]; enzymatic treatment that uses an enzyme and a biocatalyst to transform phenolic compounds into harmless or less harmful products from wastewater [34]).

Due to the extensive usage of the precursor for the production of 4-aminophenol as intermediate in the hair-dyeing agent [34], antipyretic drugs [36], photographic developers [37], the catalytic reduction of 4-nitrophenol to 4-aminophenol [38, 39], dyes [40], pesticides [40] and anticorrosion-lubricant [41], 4-nitrophenol (4-NP) is one of the most common pollutant and toxic chemical intermediate that is extensively found in wastewater at the end of the manufacturing processes of agricultural and industrial products [42, 43]. Recently, 4-NP and its derivatives pose some important threat to human health and the ecosystem by causing damage to the central nervous system, kidney, liver, and blood of animals and human beings [44, 45]. According to the United States Environmental Protection Agency (USEPA), nitrophenols are listed as one of the top-114 organic pollutants among various nitroaromatic compounds which remarkably threaten human health and ecological environment owing to bioaccumulation, high toxicity, difficulty in biochemical degradation of carcinogenesis, mutagenesis, and teratogenesis [46, 47].

Geraniol (GE) is a kind of acyclic monoterpene alcohol and largely abundant in some essential oils such as lemon, ginger, orange, rose and lavender. Since it has a pleasant fragrance, GE is substantially employed in a range of flavoring agents in many foods and beverages, cosmetics, perfumes [48, 49] and cleansing materials [48]. Some papers revealed that GE demonstrates anti-tumor activity against various cancer cells [50], insecticidal, antimicrobial, anti-inflammatory properties [48, 51] and remarkable antioxidant effect in various metabolic disorders [52-54].

To the best of our knowledge, numerous reports exist with respect to the antioxidant, anti-inflammatory and anti-tumor studies of GE [55-57], but there is no scientific article related with the catalytic oxidation of phenolic compounds by means of peripherally tetra-substituted GE metallophthalocyanine derivatives. The main purpose of this study is to explore the catalytic activity of the novel synthesized compounds bearing GE units **4** and **5** and to provide the

possibility for these metal complexes as the catalyst. In this context, we have synthesized new tetra-substituted Co(II)Pc, Cu(II)Pc, Zn(II)Pc and Mn(III)C1Pc fused *trans*-3,7-dimethyl-2,6-octadien-1-ol at peripheral positions and investigated the catalytic activity studies of products **4** and **5** as the catalyst on different phenolic compounds oxidation to prevent toxic and harmful effects to the ecosystem and human health. Under the framework of this study, it has been announced the successful application of CoPc and CuPc as being oxidation catalysts for oxidation of 4-nitrophenol, 2-chlorophenol, 2,3-dichlorophenol and 4-methoxyphenol using different oxygen sources.

2. Experimental

2.1. *Materials*

All reactions were carried out under dry nitrogen atmosphere and compounds **4**-**7** were synthesized by using standard Schlenk techniques. 4-Nitrophthalonitrile **2** was synthesized as described by literature procedure [58]. All chemicals and reagents were of reagent grade quality and used as purchased from commercial sources. DMF and *n*-pentanol were dried and purified in accordance with methods in the reported procedure [59]. Column chromatography was carried out on aluminum oxide 90 active basic alumina columns with the indicated eluents. All reactions were monitored by thin layer chromatography (TLC) using 0.25 mm silica gel plates with UV indicator (60 F_{254}).

2.2. *Equipment*

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ascend 400 NMR spectrometer with $CDCl_3$ (deuterated chloroform) as the NMR solvent and chemical shifts were reported (δ) relative to Me_4Si (tetramethylsilane) as the internal standard. Mass spectra were recorded on Bruker Microflex LT MALDI-TOF-MS and Micromass Quattro LC-MS/MS spectrometers. All mass analyses were conducted in positive ion mode using chloroform as the solvent for the mass analyses. FT-IR spectrum was recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer (ATR sampling accessory). The electronic absorption spectrum (Ultraviolet-Visible spectroscopy) was obtained on a Perkin-Elmer Lambda 25 UV/Vis spectrophotometer using a 1 cm path length cuvette at room temperature. Melting points were determined by an electrothermal apparatus. GC Agilent Technologies 7820A equipment (30m×0.32mm×0.50μm

DB Wax capillary column, FID detector) was used for gas chromatography (GC) measurements.

2.3. *Electrochemical measurements*

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

2.4. *General procedure for the oxidation of phenolic compounds*

Experiments were performed in a thermostated Schlenk vessel equipped with a condenser and stirrer. The solution of phenolic compounds and catalyst in the solvent was purified by bubbling nitrogen gas to remove the oxygen. At room temperature, a mixture of phenolic compounds (2.12×10^{-3} mol), catalyst (4.23×10^{-6} mol) and solvent (0.01 L) was stirred in a Schlenk vessel for few minutes. Afterwards, the oxidant *tert*-butyl hydroperoxide (TBHP) (3.38×10^{-3} mol) was added and the reaction mixture was stirred for the desired time. The samples (0.0005 L) were taken at certain time intervals. Each sample was injected at least twice in the gas chromatography (GC), 1 μL each time. The formation of the oxidative products and the consumption of substrates were monitored by gas chromatography. Each run was repeated three or four times. The structure of the oxidation reaction products was verified with ^{1}H NMR spectroscopy.

Temperature program for Analysis of Phenolic Compounds oxidation:

Temperature of Injection Unit: 200 °C

Temperature of Detector Unit: 250 °C

Temperature program:

$$60^{o}C \xrightarrow{1\ s} 60^{o}C \xrightarrow{20^{o}C/\ s} 120^{o}C \xrightarrow{1\ s} 120^{o}C \xrightarrow{40^{o}C/\ s} 280^{o}C \xrightarrow{1\ s} 280^{o}C$$

Carrier Gas: Helium

Flow of carrier gas: 1.5 mL/dk

Sample volume: 1 μL

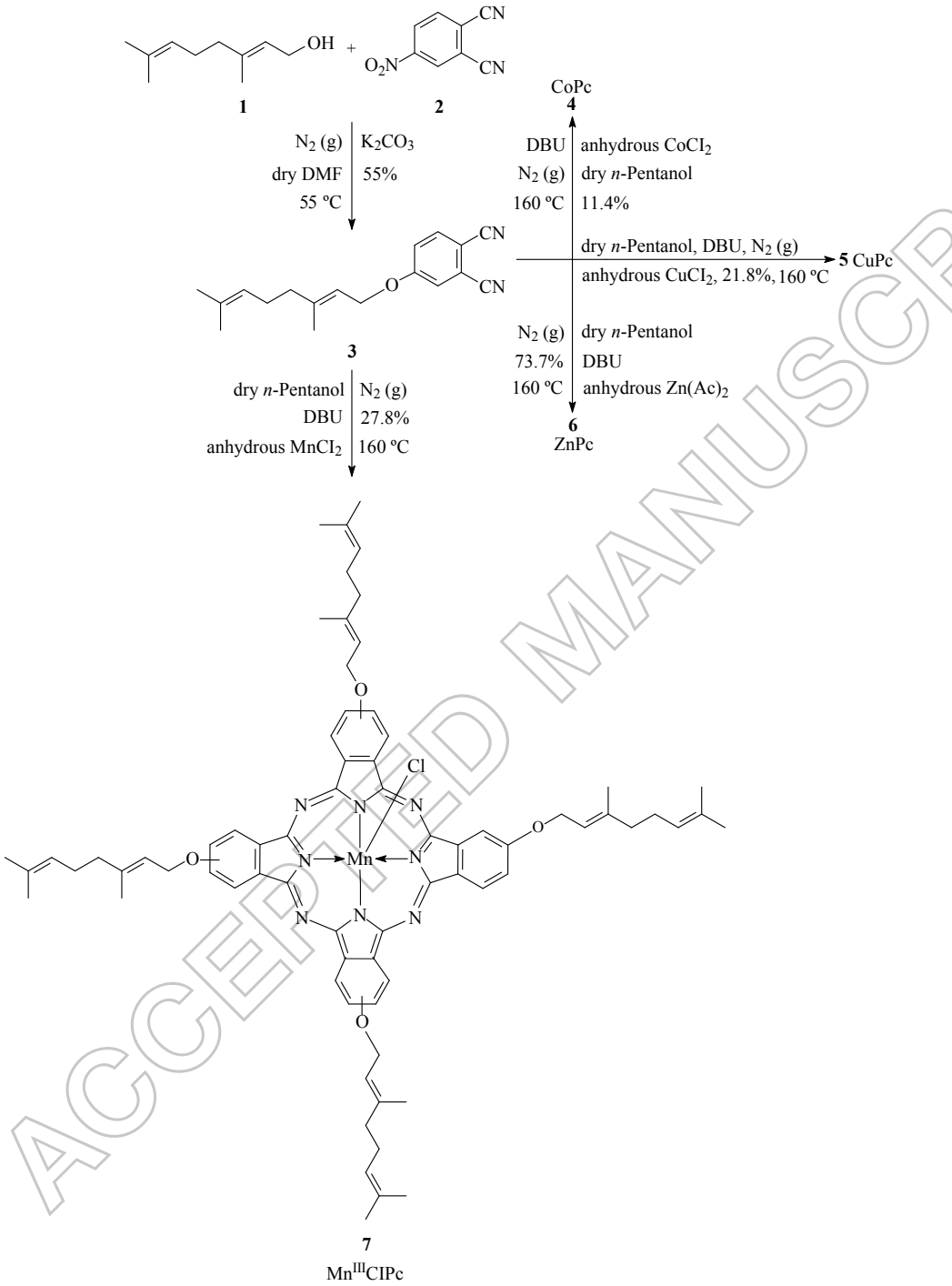
Split ratio: 1/20

2.5. *Synthesis*

2.5.1. (E)-4-((3,7-dimethylocta-2,6-dien-1-yl)oxy)phthalonitrile (3). 4-Nitrophthalonitrile **2** (1.122 g, 6.48 mmol) was added to a solution of geraniol **1** (1.0 g, 6.48 mmol) in dry DMF (10 mL) and the mixture was heated to 55 °C. After stirring for 15 min at the same temperature, finely ground anhydrous K_2CO_3 (3.13 g, 22.65 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 6 days. Afterwards, the mixture was poured into 200 g of a 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: 1.0 g (55%), m.p. 40-44 °C. Elemental analysis: Calc. (%) for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19; N, 9.99, Found (%) C, 76.43; H, 7.32; N, 9.62. FT–IR, ν_{max} (cm^{-1}): 3131/3105/3077 (C-H aromatic), 2973/2928/2863 (CH_2, CH_3), 2228 (C≡N), 1599 (C=C), 1561, 1488, 1472, 1383, 1343, 1290/1252/1092 (C-O-C), 983, 826, 637. ^{1}H NMR in $CDCl_3$, δ(ppm): 7.73-7.70 (d, 1H, Ar-H), 7.28-7.26 (s, 1H, Ar-H), 7.21-7.18 (d, 1H, Ar-H), 5.48-5.43 (t, 1H, CH_3-C=C*H*-CH_2-O), 5.07 (t, 1H, [$(CH_3)_2$-C=C*H*-CH_2]), 4.66-4.64 (d, 2H, Ar-O-C*H*$_2$), 2.13 (s, 4H, C*H*$_2$), 1.84-1.77 (s, 3H, CH_3), 1.69-1.62 (s, 6H, CH_3). ^{13}C NMR in $CDCl_3$, δ(ppm): 161.98, 143.72, 136.14, 132.17, 123.62, 123.39, 119.79, 118.38, 117.36, 115.79 (*C*≡N), 115.37 (*C*≡N), 107.00, 65.92, 39.47 (*C*H_2), 26.15 (*C*H_2), 25.71 (*C*H_3), 17.74 (*C*H_3), 16.93 (*C*H_3). LC-MS/MS (ES^+) *m/z*: Calculated: 280.36, Found: 198.00 $[M\text{-}C_6H_{10}]^+$, 321.00 $[M+K+2H]^+$.

2.5.2. General procedure for the syntheses of MPcs (4-7). The phthalonitrile derivative **3** (0.1 g, 0.357 mmol) was dissolved in 3 mL of dry *n*-pentanol under a blanket of nitrogen gas in a well-stopped Schlenk tube. Catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and anhydrous metal salts (0.178 mmol) [$CoCl_2$, 23.0 mg; $CuCl_2$, 24.0 mg; $Zn(CH_3COO)_2$, 33.0 mg; $MnCl_2$, 22.0 mg] were subsequently added into the solution and the reaction mixture was refluxed at 160 °C for 4 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 H_2O separately and dried *in vacuo*. The crude products were purified by column chromatography on aluminum oxide 90 active basic alumina. Scheme 1

displays the synthetic route for MPcs **4**-**7**.



Scheme 1. Synthesis of precursor phthalonitrile compound **3** and MPcs **4**-**7**.

2.5.2.1. 2(3),9(10),16(17),23(24)-Tetrakis-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-phthalocyaninato cobalt(II) (**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 (100:1) as eluent. The extract was evaporated to dryness and dried under vacuum to give blue solid product **4**. Yield: 12.0 mg (11.4%), m.p. >300 °C. Elemental analysis: Calc. (%) for $C_{72}H_{80}N_8O_4Co$: C, 73.26; H, 6.83; N, 9.49, Found (%) C, 72.44; H, 6.12; N, 9.73. FT-IR, ν_{max} (cm^{-1}): 3183/3066 (C-H aromatic), 2963/2915/2850 (CH_2, CH_3), 1639 (C=N), 1609 (C=C), 1523, 1487, 1472, 1380, 1364, 1230-1097-1056 (C-O-C), 997, 820, 749 (Pc skeleton). UV-vis (chloroform), λ_{max} (in nm) (logε): 326 (4.24), 381 (4.24), 613 (3.88), 675 (4.30). MALDI-TOF-MS *m/z*: Calculated: 1180.39, Found: 1180.20 $[M]^+$.

2.5.2.2. 2(3),9(10),16(17),23(24)-Tetrakis-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-phthalocyaninato copper(II) (**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 as eluent. The extract was evaporated to dryness and dried under vacuum to give blue solid **5**. Yield: 23.0 mg (21.8%), m.p. >300 °C. Elemental analysis: Calc. (%) for $C_{72}H_{80}N_8O_4Cu$: C, 72.98; H, 6.80; N, 9.46, Found (%) C, 71.47; H, 6.62; N, 9.69. FT-IR, ν_{max} (cm^{-1}): 2956/2916/2849 (CH_2, CH_3), 1641 (C=N), 1608 (C=C), 1507, 1483, 1462, 1379, 1343, 1235/1118/1096/1053 (C-O-C), 997, 820, 746 (Pc skeleton). UV-vis (chloroform), λ_{max} (in nm) (logε): 338 (4.07), 384 (3.76), 617 (3.85), 683 (4.31). MALDI-TOF-MS *m/z*: Calculated: 1185.00, Found: 1185.13 $[M]^+$.

2.5.2.3. 2(3),9(10),16(17),23(24)-Tetrakis-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-phthalocyaninato zinc(II) (**6**). MPc **6** was synthesized by following the aforementioned general procedure for MPcs. The crude green product was purified by column chromatography on basic alumina using chloroform as eluent. The extract was evaporated to dryness and dried under vacuum to give green compound **6**. Yield: 78.0 mg (73.7%), m.p. >300 °C. Elemental analysis: Calc. (%) for $C_{72}H_{80}N_8O_4Zn$: C, 72.86; H, 6.79; N, 9.44, Found (%) C, 71.32; H, 6.82; N, 9.60. FT-IR, ν_{max} (cm^{-1}): 2923/2854 (CH_2, CH_3), 1638 (C=N), 1603 (C=C), 1507, 1485, 1445, 1377, 1317, 1221/1085/1044 (C-O-C), 991, 825, 748 (Pc skeleton). ^1H NMR in $CDCl_3$, δ(ppm): 7.80 (s, 4H, Ar-H), 7.38-7.34 (d, 8H, Ar-H), 5.20 (s, 4H, CH_3-C=C*H*-CH_2-O), 5.07-4.91 (s, br, 4H,

[$(CH_3)_2$-C=C*H*-CH_2]), 4.70 (s, 8H, Ar-O-C*H*$_2$), 2.10-2.07 (s, 16H, C*H*$_2$), 1.85-1.60 (s, br, 12H, CH_3), 1.43-1.40 (s, 12H, CH_3), 1.36-1.28 (s, 12H, CH_3). ^{13}C NMR in $CDCl_3$, δ(ppm): 161.37, 144.19, 137.19, 131.97, 123.91, 119.52, 118.97, 117.71, 106.37, 65.92, 65.77, 62.94, 42.84, 39.80, 39.57, 37.20, 36.63, 26.48, 25.76, 17.02, 16.80, 15.31, 14.11. UV-vis (chloroform), λ_{max}, nm (logε): 357 (4.06), 617 (3.67) and 685 (4.29). MALDI-TOF-MS *m/z*: Calculated: 1186.84, Found: 1186.57 $[M]^+$.

2.5.2.4. 2(3),9(10),16(17),23(24)-Tetrakis-((3,7-dimethylocta-2,6-dien-1-yl)oxy)-phthalocyaninato manganese(III) chloride (**7**). Phthalocyaninato manganese(III) chloride **7** was synthesized by following the aforementioned general procedure for MPcs. The crude product was purified by column chromatography on basic alumina using chloroform:ethanol (100:1) as eluent. The extract was evaporated to dryness and dried under vacuum to give dark brown-reddish product **7**. Yield: 30.0 mg (27.8%), m.p. >300 °C. Elemental analysis: Calc. (%) for $C_{72}H_{80}N_8O_4MnCl$: C, 71.36; H, 6.65; N, 9.25, Found (%) C, 70.37; H, 6.43; N, 8.98. FT-IR, v_{max} (cm^{-1}): 3056 (C-H aromatic), 2958/2914-2850 (CH_2, CH_3), 1641 (C=N), 1603 (C=C), 1505, 1483, 1456, 1381, 1341, 1225/1118/1071 (C-O-C), 983, 822, 744 (Pc skeleton). UV-vis (chloroform), λ_{max} (in nm) (logε): 376 (4.85), 527 (4.54), 675 (4.65), 736 (4.99). UV-vis (DMF), λ_{max}, nm (logε): 370 (4.95), 497 (4.59), 659 (4.60) and 731 (5.09). MALDI-TOF-MS *m/z*: Calculated: 1211.84, Found: 1175.97 $[M\text{-}Cl]^+$.

3. Results and discussion

3.1. *Synthesis and characterization*

The synthetic pathways for geraniol-substituted phthalonitrile derivative **3** and corresponding metallophthalocyanines **4**-**7** are demonstrated in scheme 1. Herein, we notified the synthesis, characterization, and investigation of catalytic activity of new metallophthalocyanines **4** and **5** as the catalysts for the oxidation of phenolic compounds by using different types of oxidants. The synthesized new compounds **3**-**7** were verified using UV-vis (for metallophthalocyanines **4**-**7**), ^{1}H NMR and ^{13}C NMR spectroscopies (for compounds **3** and **6**), LC-MS/MS (for phthalonitrile derivative **3**), MALDI-TOF-MS data (for metallophthalocyanines **4**-**7**) and FT-IR, as well as elemental analysis. All results with reference to compounds **3**-**7** were consistent with the assigned formulations in scheme 1.

The new precursor dicyano derivative **3**, (E)-4-((3,7-dimethylocta-2,6-dien-1-yl)oxy)phthalonitrile, was synthesized with 55% yield through reaction of *trans*-3,7-dimethyl-2,6-octadien-1-ol **1** with 4-nitrophthalonitrile **2** in the presence of K_2CO_3 in dry DMF at 55 °C under a nitrogen stream for 6 days through base-catalyzed nucleophilic aromatic displacement reaction of nitro-group for 4-nitrophthalonitrile. MPc complexes **4**-**7** were synthesized via cyclotetramerization of compound **3** in the presence of the corresponding anhydrous metal salts ($CoCl_2$ for **4**, $CuCl_2$ for **5**, $Zn(CH_3COO)_2$ for **6** and $MnCl_2$ for **7**) 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. These newly prepared products **4**-**7** were purified by column chromatography on basic alumina as the column material. The synthesized metallophthalocyanine complexes **4**-**7** were highly soluble in most of common organic solvents such as THF, ethyl acetate, CH_2Cl_2, $CHCl_3$, DMF, diethyl ether, ethyl alcohol, DMSO and acetonitrile due to the methyl groups on alkyl chains of peripheral arms.

3.2. *Spectroscopic characterization*

The synthesis of compound **3** was achieved in 55% yield through base-catalyzed aromatic nitro displacement reaction of 4-nitrophthalonitrile **2** with (E)-3,7-dimethyl-2,6-octadien-1-ol **1** in dry DMF by using anhydrous K_2CO_3 as the base. After synthesis of precursor phthalonitrile product **3**, the peak in the vibrational spectra of compound **1** for the ν(O-H) vibration at 3655 cm^{-1} disappeared and a new vibration was observed at 2228 cm^{-1} belonging to the C≡N functionality, indicative of the formation of targeted molecule **3**. Other characteristic vibrations corresponding to $\nu(C\text{-}H)_{aromatic}$ at 3131/3105/3077 cm^{-1}, $\nu(C\text{-}H)_{aliphatic}$ at 2973/2928/2863 cm^{-1} and $\nu(C\text{-}O\text{-}C)_{ether}$ at 1290/1252/1092 cm^{-1} are consistent with the assigned formulation. In the ^1H NMR spectrum of **3**, the signal associated with the O-H group disappeared and new signals of the aromatic ring protons at δ = 7.73-7.70, 7.28-7.26 and 7.21-7.18 ppm were observed for compound **3**. Other ^1H NMR signals are almost identical with compound **1**. Besides, the presence of signals at δ = 115.79-115.37 ppm (C≡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^+) and obtained with some reasonable parent ion peaks at *m/z*: 198.00 $[M\text{-}C_6H_{10}]^+$ and 321.00 $[M+K+2H]^+$.

The disappearance of the ν(C≡N) vibration at 2228 cm^{-1} approved the cyclotetramerization reactions of phthalonitrile **3** into metallophthalocyanines **4**-**7**. Another

notable difference was the presence of ν(C=N) vibrations of the inner core of metallophthalocyanine molecules **4-7** appearing at 1639 cm^{-1} for **4**, 1638 cm^{-1} for **6** and 1641 cm^{-1} for both **5** and **7**. The characteristic ν(C-O-C) of ether group were seen at 1230/1097/1056 cm^{-1} for **4**, 1235/1118/1096/1053 cm^{-1} for **5**, 1221/1085/1044 cm^{-1} for **6** and 1225/1118/1071 cm^{-1} for **7**. Owing to the paramagnetic nature of the central transition metal ions (Co^{+2}, Cu^{+2} and Mn^{+3}), ^{1}H and ^{13}C NMR measurements of the cobalt(II) **4**, copper(II) **5** and manganese(III) chloride **7** phthalocyanine derivatives were precluded. Aromatic ring protons of product **6** were measured at δ = 7.80 and 7.38-7.34 ppm as singlet and doublet peaks, respectively. Other ^{1}H NMR chemical shift values of zinc(II) phthalocyanine **6** were almost identical with precursor compound **3** except some little changes. In addition to the elemental analyses data, the mass spectral results for the newly synthesized phthalocyanine complexes **4-7** were consistent with the assigned formulations. The mass spectra of **4-7** were measured with MALDI-TOF-MS and were in a good accordance with the proposed structures. The molecular ion peaks were observed at *m/z* = 1180.20 $[M]^{+}$ for **4**, 1185.13 $[M]^{+}$ for **5**, 1186.57 $[M]^{+}$ for **6** and 1175.97 $[M\text{-}Cl]^{+}$ for **7** (figure 1), respectively.

The electronic spectra of phthalocyanine compounds **4-7** displayed the best indications concerning the characteristic B and Q bands of typical MPcs. The electronic absorption spectra of **4-6** were measured in chloroform and demonstrated in figure 2(a). Metallophthalocyanine derivatives **4-6** showed B bands at 326 nm (logε = 4.24) and 381 nm (logε = 3.86) for **4**, 338 nm (logε = 4.07) and 384 nm (logε = 3.76) for **5** and 357 nm (logε = 4.06) for **6**, and intense single Q bands with lower wavelength shoulders at 613 nm (logε = 3.88) and 675 nm (logε = 4.30) for **4**, 617 nm (logε = 3.85) and 683 nm (logε = 4.31) for **5** and 617 nm (logε = 3.67) and 685 nm (logε = 4.29) for **6**. These results are in accordance with the relating MPcs in the literature.

The UV-vis spectra of compound **7** were measured in chloroform and in DMF (figure 2(b)). MnPc complex **7** exhibited B band at 376 nm (logε = 4.85) and Q band at 736 nm (logε = 4.99) with a shoulder at 675 nm (logε = 4.65) in chloroform, and B band at 370 nm (logε = 4.95) and Q band at 731 nm (logε = 5.09) with a shoulder at 659 nm (logε = 4.60) in DMF. The Q-band absorption of product **7** in chloroform (at 736 nm) and in DMF (at 731 nm) was red-shifted with respect to those of complexes **4-6** in the electronic absorption spectra (figure 2(a) and 2(b)). This result is typical of manganese phthalocyanine complexes [60]. It has been suggested [61, 62] that several equilibria exist between MnPc species in air and in DMF

according to Eqs. (1)-(5):

$$PcMn^{II} + O_2 \rightleftharpoons PcMn^{III}(O_2) \quad (1)$$

$$PcMn^{III}(O_2) + PcMn^{II} \rightleftharpoons PcMn^{III}\text{-}O_2\text{-}Mn^{III}Pc \quad (2)$$

$$PcMn^{III}\text{-}O_2\text{-}Mn^{III}Pc \rightleftharpoons 2PcMn^{IV}O \quad (3)$$

$$2PcMn^{IV}O + 2PcMn^{II} \rightleftharpoons 2PcMn^{III}\text{-}O\text{-}Mn^{III}Pc \quad (4)$$

$$4PcMn^{II} + O_2 \longrightarrow 2PcMn^{III}\text{-}O\text{-}Mn^{III}Pc \quad \text{(Net equation) (5)}$$

Although manganese(II) chloride was employed for the synthesis of the MnPc, the negative redox potential of the Mn^{III}/Mn^{II} species makes it air-sensitive and facilitates the formation of $Mn^{III}Pc$ species during the synthesis and purification (taking place in aerobic conditions) [63]. Multiple Q bands might be observed because of the presence of μ-oxo MnPc, $Mn^{II}Pc$ and $Mn^{III}Pc$ species in DMF under air in the ground state electronic absorption spectrum of MnPc complexes. In the UV-vis spectrum of MnPc complexes in DMF, μ-oxo MnPc, $Mn^{II}Pc$ and $Mn^{III}Pc$ species are generally seen at around 620-630 nm, 680-690 nm and near 750 nm, respectively [64-66]. The electronic absorption spectrum of manganese phthalocyanine complex **7** indicated the presence of $Mn^{III}Pc$ and $Mn^{II}Pc$ species by taking into account the positions of the Q-bands in chloroform and DMF. Compound **7** exists mainly as the $Mn^{III}Pc$ complex in chloroform and DMF. On the other hand, we performed a cyclic voltammetry (CV) study to explain different oxidation states of compound **7**. Basic electrochemical parameters, the assignments of the redox couples and estimated electrochemical parameters including the half-wave potentials ($E_{1/2}$), peak-to-peak potential separations (ΔE_p), and difference between the first oxidation and reduction processes ($\Delta E_{1/2}$), were derived from the analyses of complex **7** and these data are tabulated in table 1. In figure 3, CV responses of $Mn^{III}ClPc$ **7** in DCM/TBAP is displayed. $Mn^{III}ClPc$ gave two quasi-reversible reduction processes at -0.29 V $\mathbf{R_1}$ (ΔE_p = 165 mV) and -1.15 V $\mathbf{R_2}$ (ΔE_p = 125 mV), respectively. Also, during the cathodic scan, $Mn^{III}ClPc$ gave one quasi-reversible oxidation $\mathbf{O_1}$ at 1.04 V within the potential window of DCM/TBAP electrolyte system (ΔE_p = 170 mV). $\mathbf{R_1}$ and $\mathbf{R_2}$ reduction processes and oxidation process $\mathbf{O_1}$ were quasi-reversible characters with respect to ΔE_p values. Depending upon the positions of the redox processes, two redox couples ($\mathbf{R_1}$ at -0.29 V and $\mathbf{R_2}$ at -1.15 V) were proposed to the reduction of Mn^{III} to Mn^{II} and then Mn^{II} to Mn^{I} oxidation states. Quasi-reversible

oxidation $\mathbf{O_1}$ at 1.04 V was proposed to Pc based process. These assignments are in agreement with the MnPcs in the literature [67-70]. We also observed absorption bands between 500 and 600 nm in the UV-vis spectrum of complex **7** at 527 nm (logε = 4.54) in chloroform and at 497 nm (logε = 4.59) in DMF. These bands are generally associated with charge transfer in MnPc complexes owing to partially-filled d orbitals in MnPc complexes [64, 70-74]. Q bands of **7** were observed at 736 and 675 nm in chloroform and were red-shifted compared to the spectrum in DMF (at 731 and 659 nm) (figure 2(b)). Positions of Q bands of the spectra of **7** are closely related to the refractive indices of the solvents used for the measurement of the UV-vis spectra. The higher the refractive index of the solvent, the more red-shifted the Q band of the MPc complex concerned. $CHCl_3$ has a refractive index of 1.438, compared to 1.430 for DMF, justifying the red-shift in Q band of the manganese phthalocyanine complexes in $CHCl_3$, relative to that in DMF [64, 75].

3.3. *Catalytic studies*

The main product was determined as benzoquinone and the side product was determined as hydroquinone in the oxidation of 4-nitrophenol oxidation reaction (figure 4). 4-Nitrophenol oxidation proceeds by initial aromatic hydroxyl oxidative attack (similar to phenol oxidation) followed by oxidative fragmentation, with the release of nitrates, as confirmed by the identification of *p*-nitrocatechol, hydroquinone, benzoquinone, and catechol. 4-Nitrocatechol and catechol were found as trace amounts (lower 8%) in this work. It is well known that the reaction mechanism of HO• radicals with aromatic compounds proceeds mainly through an electrophilic addition to the aromatic ring [76-79]. 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 [76]. Furthermore, the -NO_2 group is electron-withdrawing, thus being *meta*-directing [76]. In the particular case of 4-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_2 group may occur due to an attack of the radical HO• at the *para*-position in respect to the -OH group, hydroquinone being obtained [77, 78]. These preliminary results exhibited that only one complex (CoPc **4**) could facilitate the oxidation of 4-nitrophenol and serve as an efficient and selective catalyst. Unfortunately, when Cu(II) phthalocyanine **5** was used as the catalyst, no conversion was

observed. All substrate, catalysts and obtained results within the oxidation processes are demonstrated in table 2. According to the results of this table, Co(II) phthalocyanine **4** demonstrated the highest activity producing benzoquinone as the major product in the 4-nitrophenol oxidation reaction.

Subsequently, optimization of the reaction conditions was performed by selectively evaluating effects of different 4-nitrophenol:catalysts molar ratios, oxidant:catalysts molar ratios, the oxidant and temperature used. In addition, in the blank reactions (without catalysts or oxidants) there were no products detectable. It is proved that presence of the catalyst and oxidant is essential for the oxidation (table 3). As the other parameters were kept constant, the molar ratio was carried out from 300-1000 to determine the influence of substrate on metal ions. The reaction rate increased with decreasing of the substrate:catalyst molar ratio (table 3) as expected. Substrate:catalyst ratio of the oxidation course gave the same main product with TON and TOF values (496 and 165 for Co complex **4**).

To determine oxygen source effect, H_2O_2, *tert*-butyl hydroperoxide (TBHP), *m*-chloroperoxybenzoic acid (*m*-CPBA) and air oxygen were used as the oxidant. The results in table 3 showed that H_2O_2 was the best oxidant for 4-nitrophenol oxidation in the presence of CoPc **4**. Moreover, TBHP and *m*-CPBA can serve as an oxidant but the low conversion was observed for both CoPc **4** and CuPc **5**. The reaction color changed from blue to brown when we added H_2O_2 or *m*-CPBA in the reaction media. This clue explains that complex **4** was degraded immediately with H_2O_2 or *m*-CPBA [80]. The results of catalytic activity study for CoPc **4** and CuPc **5** using air oxygen displayed that there was no formation of products during the oxidation process (figure 5). Another important parameter is oxidant:catalyst ratio to find the optimal conditions of 4-nitrophenol oxidation. When the oxidant/catalyst ratio was increased from 500:1 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 (benzoquinone:hydroquinone ratio) inclined to decrease. At this stage, it is possible that the coordination around the cobalt ion can change and produce inactive intermediate species [81].

The results in table 3 showed that as the reaction temperature was upgraded from 50 °C to 90 °C, the catalytic activity of CoPc **4** did not change. When the temperature was fixed to 50 °C, the maximum total conversion was obtained (99%) with cobalt(II) phthalocyanine **4**. Therefore, 50 °C is the optimum temperature of 4-nitrophenol oxidation for product **4** with H_2O_2

in 3 h. We focused on these catalytic studies and the nature of the introduced transition metals. Although 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 the 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 [25, 82].

Table 4 indicates catalytic activity studies to the homogeneous oxidation of phenolic compounds of some previously reported catalyst. Different peripherally units substituted cobalt(II), iron(II), manganese(III), copper(II) phthalocyanines were investigated on 2,6-di-tert-butylphenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,6-trimethylphenol and 4-nitrophenol oxidation [76, 83-92]. By comparing the catalysts in the literature, it is inferred that compound **4** will be interesting catalyst in 4-nitrophenol, *o*-chlorophenol, 2,3-dichlorophenol and *p*-methoxyphenol oxidation. In the literature, tetrasubstituted Co(II) and Fe(II) phthalocyanine complexes were studied as the catalyst for the oxidation of phenolic compounds [88-90]. The results of our previous papers [91, 92] were valuable because of the high conversion and selectivity of Co(II) phthalocyanine. But in this research, we achieved to reach the highest product conversion and selectivity with Co(II) phthalocyanine at lower temperature (50 °C).

4. Conclusion

Four new transition metal ion inserted tetra-substituted phthalocyanine complexes **4**-**7** bearing geraniol units were designed and synthesized. In order to verify these novel products **3**-**7**, a combination of spectral techniques such as MALDI-TOF-MS data, UV-vis, FT-IR, ^{1}H NMR and ^{13}C NMR was used. Because of the Mn^{III} metal ion center, manganese phthalocyanine complex **7** demonstrated red-shifted Q band relative to those of the other analogs **4**-**6**. It is well known that most of the metal-free and metallophthalocyanine derivatives exhibit low solubility in most common organic solvents. This main disadvantage leads to limitations of their applications in various scientific, technological and industrial fields. Therefore, it is very significant to obtain organo-soluble phthalocyanines (both Pcs and MPcs) that are potentially useful materials for assorted applications. MPcs **4**-**7** are highly soluble in most of the organic solvents and these new

organo-soluble products **4**-**7** are favorable for further scientific studies as well. Co(II) phthalocyanines are readily available oxidation catalysts and found to transfer oxygen from various oxygen-donors to alkanes, alkenes, phenols, and thiols in numerous studies [23, 93, 94]. The catalytic activity of CoPc **4** was examined for the oxidation of 4-nitrophenol using different oxygen sources. The results indicated that the catalyst exhibited satisfactory activity for the oxidation of 4-nitrophenol to the corresponding benzoquinone in 3 h at 50 °C. The optimal conditions were also determined in 4-nitrophenol oxidation with CoPc **4**. All the results indicate that CoPc **4** is an efficient and cleaning technology with cost-efficient, easy-applicable and energy-saving for the toxic and refractory industrial wastewater. Converting from environmentally harmful phenolic compounds into less harmful oxidation products by new CoPc **4** derivative makes this study attractive and useful. On the other hand, newly synthesized CoPc **4** would be a beneficial catalyst for oxidation of thiols, alkenes, and alkanes as well.

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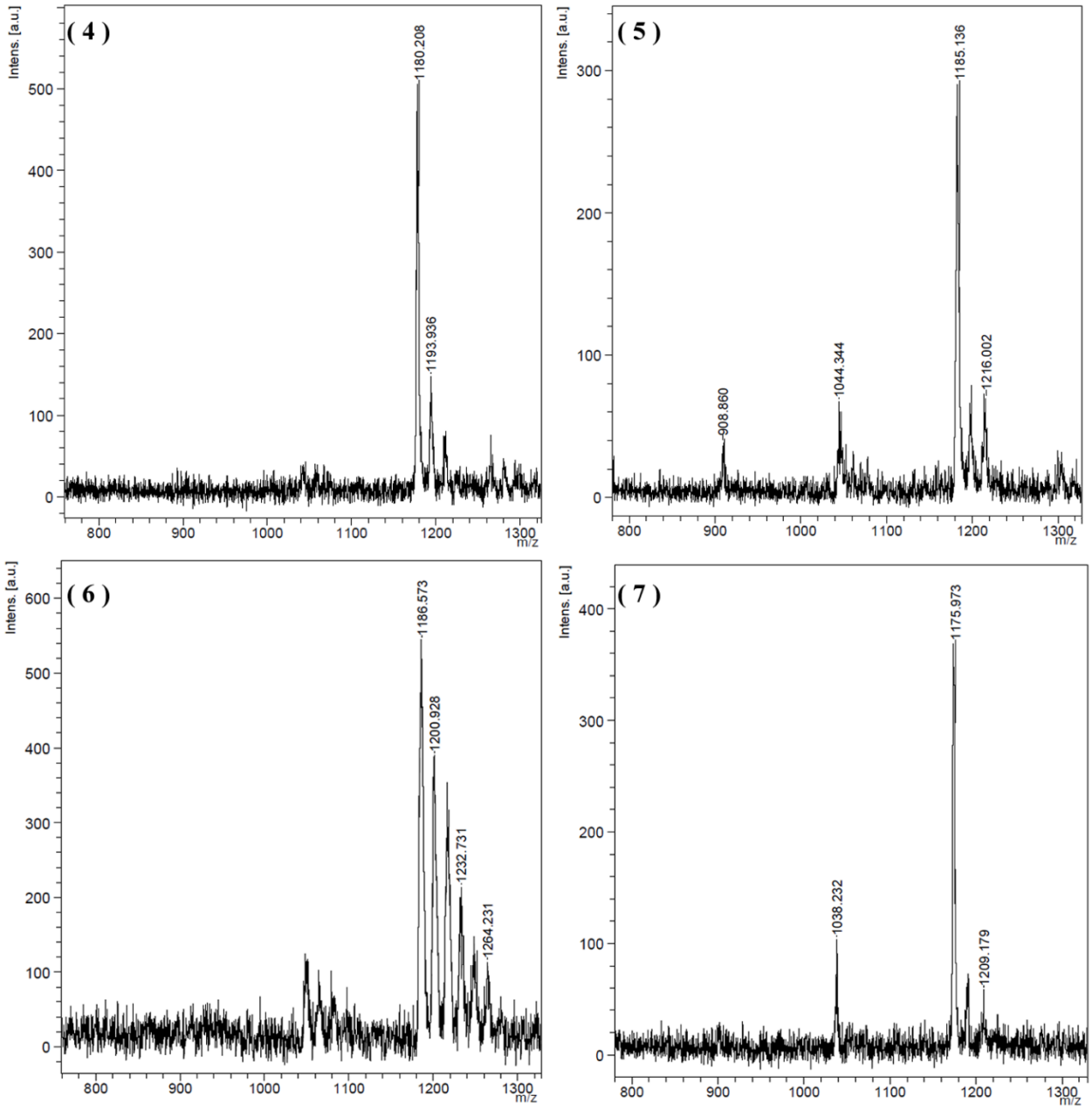


Figure 1. MALDI-TOF mass spectral data of compounds **4**-**7**.

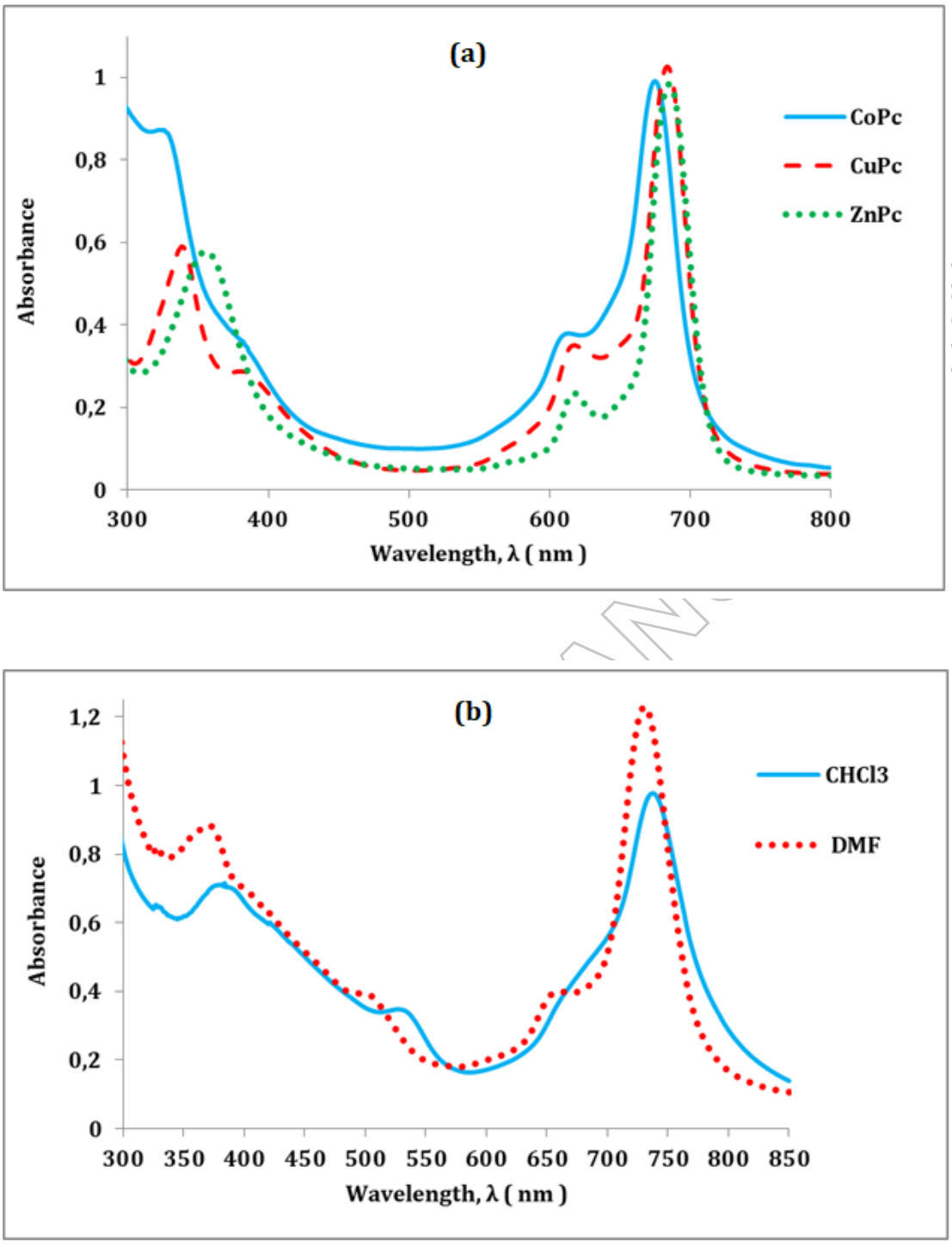


Figure 2. UV-vis spectra of 1.00×10^{-5} M of complexes. (a) Co(II)Pc (blue solid), Cu(II)Pc (red dashed) and Zn(II)Pc (green dotted) in $CHC1_3$. (b) Mn(III)C1Pc in $CHC1_3$ (blue solid) and DMF (red dotted).

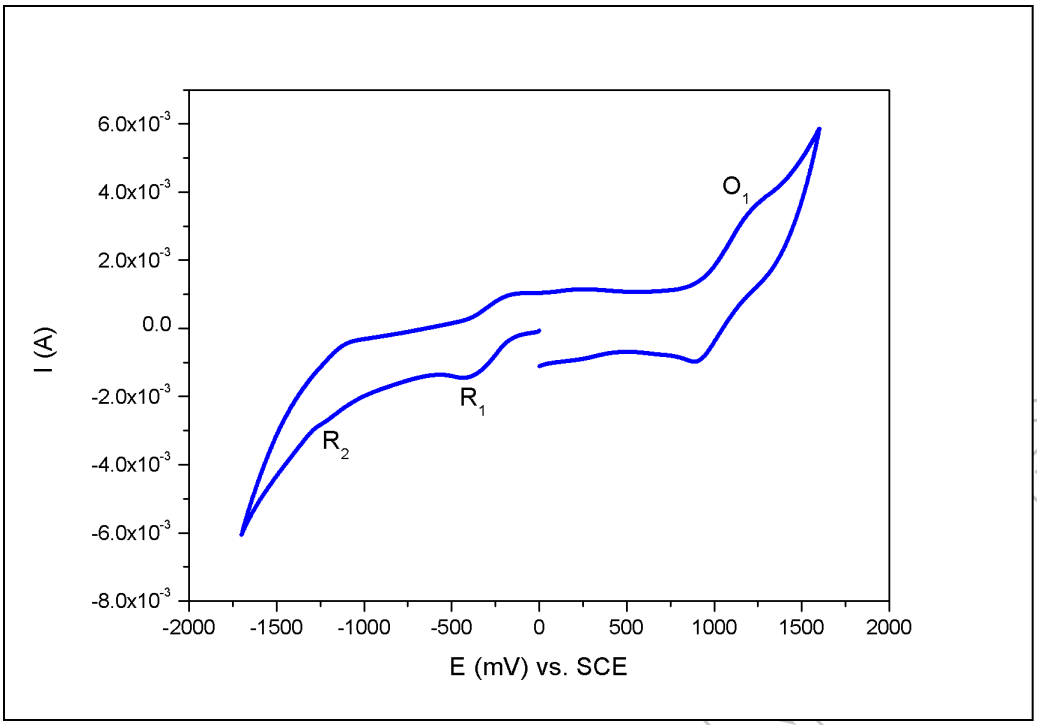


Figure 3. CV of MnC1Pc (**7**) at 100 mV·s^{-1} scan rate on a Pt working electrode in dichloromethane (DCM)/tetrabutylammonium perchlorate (TBAP) electrolyte system.

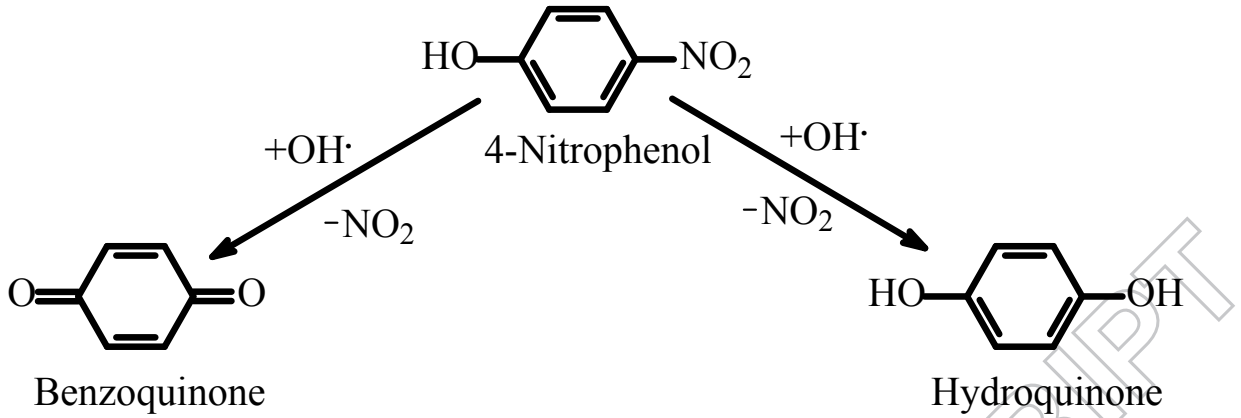


Figure 4. The oxidation products of 4-nitrophenol.

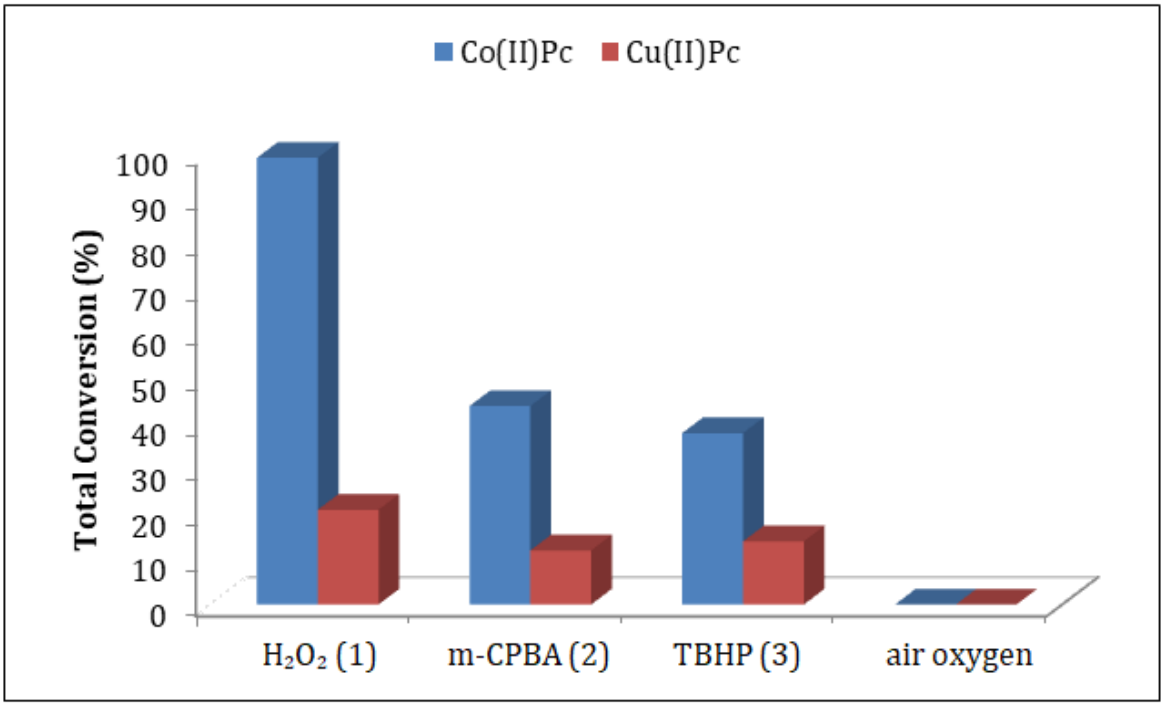


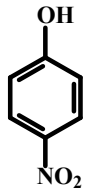
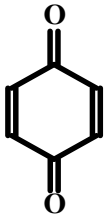
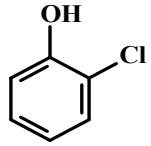
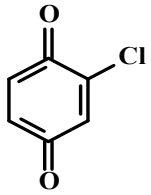
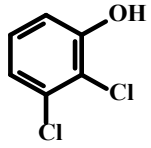
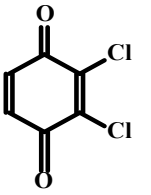
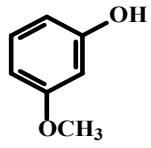
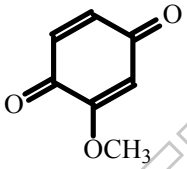
Figure 5. The oxidant effect on 4-nitrophenol oxidation [reaction conditions: 4-nitrophenol (2.12×10^{-3} mol), Co(II)Pc and Cu(II)Pc (4.23×10^{-6} mol), oxidant (3.38×10^{-3} mol), DMF (0.01 L), 3 h and 50 °C].

Table 1. Cyclic voltammetry data of MnC1Pc (**7**). All voltammetric data are given *versus* SCE.

Complex	Redox processes	[a] $E_{1/2}$	[b] ΔE_p (mV)	[c] $\Delta E_{1/2}$
MnClPc	$\mathbf{R_1}\rightarrow$[Cl-$Mn^{III}Pc^{-2}$] / [Cl-$Mn^{II}Pc^{-2}$]$^{-1}$	-0.29	165	1.33
	$\mathbf{R_2}\rightarrow$[$Mn^{II}Pc^{-2}$] / [$Mn^{I}Pc^{-2}$]$^{-1}$	-1.15	125	
	$\mathbf{O_1}\rightarrow$[Cl-$Mn^{III}Pc^{-2}$] / [Cl-$Mn^{III}Pc^{-1}$]$^{+1}$	1.04	170	

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

Table 2. Oxidation of substituted phenols catalyzed by complexes **4** and **5**.

Substrate	Major product	Total conversion (%)		Product selectivity (%)		TON		TOF (h^{-1})	
		4	**5**	**4**	**5**	**4**	**5**	**4**	**5**
		99	21	99	42	496	105	165	35
		70	18	87	60	350	90	116	30
		51	12	74	40	60	349	85	20
		37	20	74	50	185	100	61	33

TON = mole of product/mole of catalyst. TOF = mole of product/mole of catalyst × time. The conversion was determined by gas chromatography (GC). Catalyst/substrate/oxidant ratio = 1/500/800; reaction time = 3 h.

Table 3. Selective oxidation of 4-nitrophenol with catalysts **4** and **5** using different oxidant and temperature.

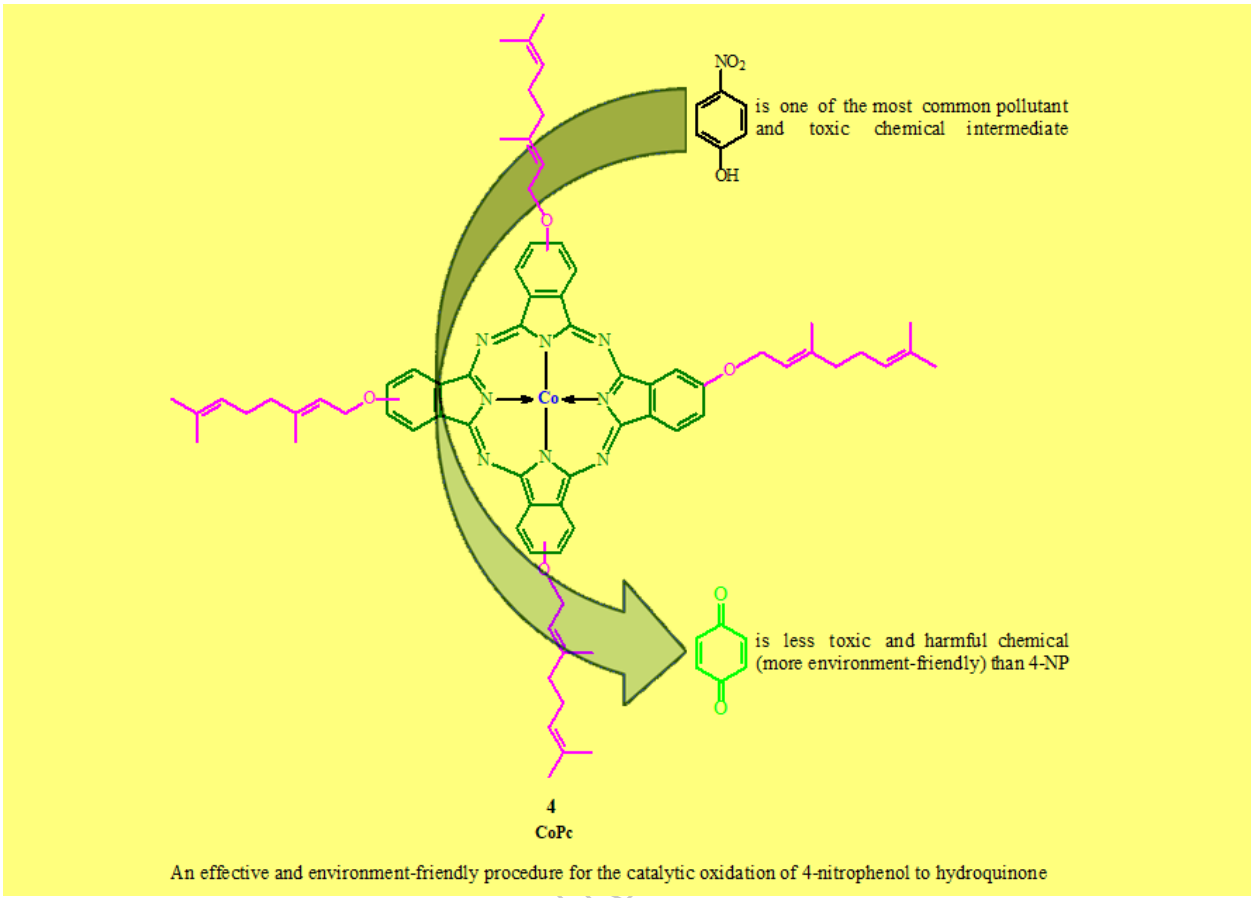
Subs./Ox./Cat	Oxidant	Temperature (°C)	Conversion (%)		Selectivity[a] (%)		TON		TOF (h^{-1})	
			4	**5**	**4**	**5**	**4**	**5**	**4**	**5**
300/800/1	H_2O_2	50	54	12	77	50	162	36	54	12
500/800/1	H_2O_2	50	99	21	99	42	496	105	165	35
800/800/1	H_2O_2	50	68	15	85	37	545	50	181	16
1000/800/1	H_2O_2	50	60	15	85	37	601	150	299	50
500/500/1	H_2O_2	50	45	12	75	34	225	60	75	20
500/1000/1	H_2O_2	50	80	18	94	45	400	90	133	30
500/1200/1	H_2O_2	50	49	16	81	40	245	80	81	26
500/800/1	*m*-CPBA	50	44	12	73	30	220	60	73	20
500/800/1	TBHP	50	38	14	76	35	190	70	63	23
500/800/1	Air oxygen	50	-	-	-	-	-	-	-	-
500/800/1	H_2O_2	75	99	20	99	50	496	100	165	33
500/800/1	H_2O_2	90	99	18	99	45	496	90	165	30
500/800/1	H_2O_2	25	75	17	88	42	496	85	165	28
500/800/free cat.	H_2O_2	50	-	-	-	-	-	-	-	-
500/free ox./1	H_2O_2	50	-	-	-	-	-	-	-	-

TON = mole of product/mole of catalyst. TOF = mole of product/mole of catalyst × time. The conversion was determined by gas chromatography (GC). Reaction conditions: 500/800/1: 2.12×10^{-3} mol)/3.38×10^{-3} mol/4.23×10^{-6} mol. [a] Selectivity of TMHQ. Reaction time = 3 h. *m*-CPBA = *m*-chloroperoxybenzoic acid. TBHP = *tert*-butyl hydroperoxide.

Table 4. Catalytic activities towards the homogeneous oxidation of phenolic compounds of some previously reported catalysts.

Catalyst	Substrate	Rxn Time (h)	Rxn temp. (°C)	Oxidant	Conv. (%)	Ref.
CoPcTs[a]	DTBP	24	70	O_2	66	[83]
FePc[e]	TCP	24	nr[i]	$KHSO_5$	85	[84, 85]
CoPc[d]						
CoPcTs[a]	2,4,5-TCP	24	75	H_2O_2	67	[87]
FePcTs[b]	TMP	2	nr[j]	O_2	77	[87]
CoPc[d]	4-Nitrophenol	3	90	TBHP	96	[88]
CoPcTs[a]	DTBP	2	75	TBHP	61	[89]
FePcTs[b]					39	
CuPcTs[c]					05	
CoPc[d]	DTBP	3	30	TBHP	93	[90]
FePc[e]					-	
MnPc[f]					97	
CuPc[g]					-	
FePcTs[b]	TCP	24	25	H_2O_2	24	[91]
FePcOC[h]	TCP	10 min	25	H_2O_2	6	[76]
CoPc[i]	4-Nitrophenol	3	90	TBHP	97	[92]
FePc[i]					75	

[a] CoPcTs = Tetrasulphonated cobalt phthalocyanine. [b] FePcTs = Tetrasulphonated iron phthalocyanine. [c] CuPcTs = Tetrasulphonated 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. DTBP = Di-*tert*-butyl peroxide. TCP = 2,4,6-Trichlorophenol. 2,4,5-TCP = 2,4,5-Trichlorophenol. TMP = 2,3,6-Trimethylphenol.



4
CoPc

An effective and environment-friendly procedure for the catalytic oxidation of 4-nitrophenol to hydroquinone