ORIGINAL ARTICLE



Preparation, characterization of new Co(II) and Cu(II) phthalocyanines and their catalytic performances in aerobic oxidation of substituted phenols

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Abstract

Substituted phenol pollutants are produced as by products of many industrial processes. Aerobic oxidations for their degradation in the context of effluent treatment or environmental remediation often lack selectivity. In this work Co(II) and Cu(II) phthalocyanines-catalyzed approach is described that converts substituted phenols into less harmfull products. New cobalt(II) and copper(II) phthalocyanine complexes are used as catalyst for degradation of substituted phenols with different oxidants. The oxidation process exhibits remarkable selectivity and conversion owing to the fact that Co(II) and Cu(II) phthalocyanines work with high performance.

Keywords Phthalocyanine · Cobalt · Copper · Substituted phenols · Aerobic oxidation

Introduction

Substituted phenols are found to be one of the most prevalent contaminants of wastewater streams from petrochemical, polymeric resins, pharmaceuticals, coal conversion plants and chemical industries [1, 2]. Due to their high aqueous solubility and weak adsorption to soils, phenolic compounds are common pollutants in natural waters [3]. Considering their negative impact to the environment in general, phenols are recognized by both U.S. EPA [4] and European Commission [5], as priority pollutants, while the World Health Organization recommended the permissible concentration of phenolic contents in potable waters to be ≤ 1 g L⁻¹ [6, 7]. They are characterized by low biodegradability making them difficult to remove from the environment by natural occurring processes. Thus, there is a need to develop energy efficient and economical method for degradation of phenolic compounds with high selective catalysts.

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In the last decade, increased interest has developed on new catalsyst systems of metal centered tetrapyrrole macrocyclics. As an analogue to porphyrin, phthalocyanine compounds are a kind of N₄-macrocycles with high stability, diverse coordination properties, excellent spectroscopic characteristics and reversible redox chemistry [8, 9]. Due to the facile preparation, good thermal stability, high catalytic activity and low toxicity, metallophthalocyanine-based catalysts have attracted considerable attention for their environmental applications [10] especially in the treatment of dye pollutants, which are a serious source of environment contamination in many countries [11, 12]. Because of the redox properties of metal, cobalt phthalocyanines are widely used in many catalytic processes [13-16]. At this point, low solubility of phthalocyanines appears as a disadvantage in catalytic processes. It can be improved by attaching sulfo [17] or quaternary ammonium groups [18], crown ethers [19], long substituted alkyl [20], alkoxy [21], alkylthio [22], macrocyclic groups [23] peripherally or non-peripherally position on the phthalocyanine ring. Thanks to the 4-(9-anthryl(methyl)) amino substituent groups, Co(II) and Cu(II) phthalocyanine complexes 4 and 5 can readily dissolve in common organic solvents [24]. When environmentally friendly oxygen was used as oxidant, substituted metallophthalocyanines acted as homogeneous catalysts in oxidation of toluene, benzyl alcohol, olefins, phenols [16, 25-28]. However, these conventional reactions usually required high temperature and

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pressure, and faced difficult to separate catalysts. In this paper, 4-(9-anthryl(methyl))amino substituted cobalt(II) **4** and copper(II) **5** phthalocyanine have been synthesized and reported that the successfull application of Co(II) and Cu(II) phthalocyanines as oxidation catalysts for oxidation of 2,3-dichlorophenol, 4-methoxyphenol, 4-nitrophenol, 2,3,6-trimethylphenol under mild conditions.

Experimental

Materials

The used materials, equipments and catalysis procedure were supplied as supplementary information.

Synthesis

Synthesis of 4-[9-anthryl(methyl)amino] phthalonitrile (3)

4-Nitrophthalonitrile (2) (2.00 g, 11.55 mmol) was dissolved in 10 mL dry DMF under N2 atmosphere, and of 9-(methylaminomethyl)anthracene (1) (2.55 g, 11.55 mmol) added to mixture. After stirring for 30 min at 55 °C, finely ground anhydrous K₂CO₃ (4.781 g, 34.65 mmol) was added portion wise within 2 h. The reaction mixture was stirred under N2 at 60 °C for 3 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 P2O5 for 4 h and recystallized from ethanol to give red crystalline powder. Yield: 3.28 g (85%). mp: 85–87 °C. Anal.calc. for $C_{23}H_{15}N_3$ IR (KBr pellet), $\nu_{max}/$ cm⁻¹: 3091, 3067 (Ar–H), 2945, 2933, 2876 (Aliph. C–H), 2229 (C≡N), 1510-1486 (C-N), 1436, 1413, 1398, 1375, 1325, 1277, 1260, 1215, 1172, 1136, 1085, 978, 955, 911, 886, 869, 833, 782, 753. ¹H-NMR. (CDCl₃), (δ:ppm): 7.86 (m, 4H, Ar-H), 7.68 (s, 1H, Ar-H), 7.55 (m, 4H, Ar-H), 7.34 (d, 1H, Ar-H), 7.25 (d, 1H, Ar-H), 7.07 (s, 1H, Ar–H), 3.12 (s, 3H, N–CH₃). ¹³C-NMR. (CDCl₃), (δ:ppm): $162.68(C_{16}), 136.92(C_3-C_8), 136.50(C_{14}), 136.70(C_{20}),$ 126.66 (C_1-C_{10}) , 126.14 (C_7) , 125.16 (C_9-C_2) , 124.48 (C_4-C_{13}) , 123.23 $(C_{11}-C_6)$, 119.56 $(C_{12}-C_5)$, 118.45 (C_{17}) , 117.34(C₂₁), 115.88 (C₂₂ \equiv N), 115.45(C₂₃ \equiv N), 104.85(C₁₉), 102.90 (C18), 36.55(C15). MALDI-TOF-MS, (m/z): Calculated: 333.38; Found: 351.37 $[M + H_2O]^+ C_{23}H_{15}N_3$: calcd. C 82.86; H 4.54; N 12.60%; found: C 81.74; H 4.50; N 12.41.

General procedure of metal phthalocyanines 4-5

To give the metal phthalocyanies, the mixture of phthalonitrile compound 3 (0.8 g, 2.39 mmol), the related anhydrous metal salt ($CoCl_2$) (77.47 mg, 0.598 mmol) for compound **4**, CuCl_2 (80.46 mg, 0.598 mmol) for compound **5** and two drops of DBU was heated at 160 °C in dry n-pentanol (3 mL) in a sealead tube, and stirred for 24 h. At the end of the reaction, green product was precipitated by addition of ethanol (20 mL) and filtered off. Along 2 h, the green solid product was refluxed with ethanol (30 mL), filtered off again and washed with hot ethanol, distilled water and diethyl ether. After drying under vacuum, the product was purified on basic alumina column with chloroform–methanol (94:6) for compound **4**, (92:8) for compound **5** solvent system as eluent.

Synthesis of cobalt(II) phthalocyanine (4) Yield: 350 mg (42%). Mp > 300 °C. Anal.calc. for $C_{92}H_{60}N_{12}$ Co FT-IR ν_{max}/cm^{-1} (KBr pellet): 3088, 3012 (Ar–H), 2991, 2983, 2856 (Aliph. C–H), 1620, 1590, 1555, 1483, 1433, 1402, 1390, 1357, 1277, 1245, 1186, 1135, 1094, 1044, 916, 871, 751, 732. UV–Vis (CHCI₃): λ_{max} , nm (log ε): 674 (4.88), 610 (4.46), 327(4.80). MALDI-TOF-MS, (m/z): calculated: 1392.47; found:1393.38 [M+H]⁺ $C_{92}H_{60}N_{12}$ Co: calcd. C 79.35; H 4.34; N 12.07%; found: C 78.85; H 4.27; N 12.18.

Synthesis of copper(II) phthalocyanine (5) Yield: 400 mg (45%). Mp > 300 °C. Anal.calc. for C₉₂H₆₀N₁₂Cu FT-IR ν_{max} /cm⁻¹ (KBr pellet): 3090, 3056 (Ar–H), 2990, 2933, 2870 (Aliph. C–H), 1603, 1582, 1540, 1482, 1467, 1413, 1365, 1327, 1293, 1256, 1191, 1062, 990, 945, 830, 756, 704. UV–Vis (CHCI₃): λ_{max} , nm (log ε): 672 (4.94), 617 (4.44), 325 (4.58). MALDI-TOF-MS, (m/z): Calculated:1397.08; Found:1398.12 [M+H]⁺ C₉₂H₆₀N₁₂Cu: calcd. C 79.09; H 6.33; N 12.04%; found: C 78.92; H 6.38; N 12.12.

Results and discussion

Synthesis and characterization

We synthesized new symmetrical 4-(9-anthryl(methyl)) amino substituted Co(II) and Cu(II) phthalocyanines. The synthetic strategy for the synthesis of the target compounds 4 and 5 is shown in Fig. 1. Compound 1 was reacted with 4-nitrophthalonitrile with K_2CO_3 in DMF to form compound 3 with 85% yield. Then, compound 3 was converted into phthalocyanines through the usual cyclotetramerization reactions in the presence of DBU and a metal salt CoCl₂ and CuCl₂ in 1-pentanol with good yields. These compounds were eventually fully characterized by a combination of elemental analysis and spectroscopic data (UV–Vis, FT-IR, MALDI-TOF mass). The spectral investigations of all of the novel products were consistent with the given structures. Co(II) and Cu(II) phthalocyanines 4 and 5 were purified by column chromatography on basic alumina using



Fig. 1 The synthetic route of the phthalonitrile, cobalt phthalocyanine and copper phthalocyanine. Reagents and conditions: (i) dry DMF, K_2CO_3 , 60 °C, 96 h; (ii) n-pentanol, DBU, 160 °C, CoCl₂, CuCl₂

[(CHCl₃:CH₃OH, 94:6) or (CHCl₃:CH₃OH, 92:8)] solvent mixtures as eluents, respectively.

In the IR spectrum, sharp characteristic peak of the C \equiv N stretching vibration of the phthalonitrile was obtained at 2229 cm⁻¹. In the ¹H NMR spectrum of compound **3**, the aromatic protons were obtained at 7.86–7.07 ppm and aliphatic protons were obtained at 3.12 ppm. The ¹³C-NMR spectra of compound **3** indicated carbon atoms between at 162.68–36.55 ppm. The nitrile carbon atoms for compound **3** were also observed at 115.88 and 115.45 ppm. In the mass spectum of compound **3**, the presence of molecular ion peak at $m/z = 351.37 [M + H_2O]^+$ confirmed the proposed structures. The results of the elemental analysis also confirmed the structure of compound **3**.

Here, by comparing the IR spectrum absorption bands between the phthalonitrile 3 and metal-phthalocyanines,

the sharp peak characteristic of the C=N stretching vibration of the phthalonitrile at 2229 cm⁻¹ disappeared in all phthalocyanines, indicative of phthalocyanine formation. All metal-phthalocyanine compounds display almost similar IR absorption bands. The NMR spectra of peripherally tetra-substituted Co(II) and Cu(II) phthalocyanines 4 and 5 were not be able to take into precluded owing to their paramagnetic nature [29]. The mass spectra of compounds 4 and 5, which showed peaks at $m/z = 1393.38 [M+H]^+$ and 1398.12 [M+H]⁺ respectively support the proposed formula for these compounds. The results of the elemental analysis also confirmed the structure of complexes 4 and 5.

Co(II) and Cu(II) phthalocyanines were soluble in most of organic solvents such as, tetrahydrofuran (THF), dichloromethane, chloroform, DMF, DMSO and pyridine. For compounds 4 and 5 in CHCl3, the Q bands caused by π - π * transitions were observed at 674 and 672 nm respectively (Fig. 2). The shoulders of compounds 4 and 5 were observed at: 610 for 4, 617 for 5. Q band regions of compounds 4 and 5, the longer wavelength absorptions are due to the monomeric species and shorter wavelength absorptions are due to the aggregated species [30–32]. So, in CHCl₃ at 1×10^{-5} mol dm⁻³ concentration, monomeric behaviour of MPcs was proved by the dominance of the longer wavelength absorptions. B bands arising from deeper π levels to LUMO were observed at: 327 and 325 for compounds 4 and 5, respectively (Fig. 2). In contrast to MPcs, the Q-band absorptions of metal-free Pcs split to Qx and Qy, and there were two strong absorption bands in the visible region.

Catalytic studies

The oxidation of substituted phenols with different oxygen source (TBHP, m-CPBA, H_2O_2 and air oxygen) catalyzed by Co(II) and Cu(II) phthalocyanines **4** and **5** has been investigated. The reactions were carried out in a 10 mL DMF at different temperature. The oxidations were monitored by GC analysis quantitatively. Among the substituted phenol oxidation process, 2,3,6 trimethylphenol oxidation gave the highest product conversion and selectivity (Table 1). 2,3,6-Trimethyl-1,4-benzoquinone (TMBQ) determined as major product and 2,2',3,3',5,5'-hexamethyl-4,4'-biphenyldiol (BP) as side product were determined (Fig. 3).

Oxidation of substituted phenols did not proceed in the absence of either oxidant or catalysts **4** and **5**. Dioxygen in air under the reactions were carried out was not acted as an oxidant for the reactions in the absence of oxidant. It is proved that presence of the catalyst and oxidant are essential for the oxidation. All substrate, major products, catalysts within the oxidation processes are summarized in Table 1.

We also investigated how the concentrations of the oxidant, substrate and temperature affect the oxidation of 2,3,6-trimethylphenol. Results of the reactions carried out varying oxidant, substrate and catalyst amounts are given in Table 2. Firstly, we investigated the effect of the substrate/



Fig. 2 UV-Vis spectrum of complex 4 and 5 in chloroform

catalyst molar ratio (500-1500) (Table 2) as the other parameters were kept constant. It is predicted that the reaction rate increased with decreasing of the substrate/catalyst molar ratio. Substrate/catalyst ratio (500) on the oxidation course gave same main product (TMBQ) with good TON value and selectivity. (475 for 4, 360 for 5 and 80 for 4, 85 for 5). Secondly, oxygen source effect is determined by using with H_2O_2 , m-CPBA, TBHP and air oxygen as oxidant. The results in Table 2 show that TBHP is the best oxidant for 2.3.6-trimethylphenoloxidation in the presence of complex 4 and 5. Additionally, H₂O₂ and m-CPBA can serve as an oxidant but low conversion for both complexes. Adding H₂O₂ or m-CPBA in the reaction media, the reaction color changed from green to light brown. This clue explains that complex 4 and 5 was degraded immediately with H_2O_2 or m-CPBA [33]. The results of studies for complex 4 and 5 using with air oxygen show that there is no formation of products during the oxidation process.

Thirdly, the another important parameter is oxidant/catalyst ratio to find the optimal conditions of 2,3,6-trimethylphenol oxidation. When the increasing oxidant/catalyst ratio from 300/1 to 800/1, the rate of the reaction increased. In contrast, while the catalytic oxidation was processing from 800/1 to 1200/1, the conversion inclined to decrasing. At this stage, it is possible that the coordination around the cobalt and copper ion can change and produce inactive intermediate species [34].

According to the results in Table 2, when the temperature was increased from 25 to 50 °C, the total conversion was changed from 95 to 44% for complex 4 and 72–50% for complex 5. It is not observed any product conversion beyond 50 °C. Therefore 50 °C is the optimum temperature of 2,3,6-trimethylphenol oxidation with TBHP in 3 h.

Table 3 indicates catalytic activities towards the homogeneously oxidation of phenolic compounds of some previously reported catalyst. Different groups substituted cobalt(II), iron(II), manganese(III), copper(II) phthalocyanines were investigated on 2,6-di-tert-buthylphenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,6-trimethylphenol oxidation and 4-nitrophenol oxidation [33, 35–45]. Comparing the catalysts in these literatures, it is infered that complex **4** will be interesting catalysts in 2,3-dichlorophenol, 4-methoxyphenol, 4-nitrophenol, 2,3,6-trimethylphenol oxidation.

The proposed mechanism for the oxidation of 2,3,6-trimethylphenol catalyzed by catalysts **4** and **5** is shown in Fig. 4. When TBHP is the oxidant, it is believed that interaction of catalyst and oxidant creates ter-butoxide and ter-perbutoxide radicals then these radicals react with 2,3,6-trimethylphenol and herewith 2,3,6-timethylphenoxide radicals are formed [27]. According to Türk and Cimen, an cobalt(III)Pc complex attacks to the carbon atom para position to the phenoxide oxygen, resulting in the formation of intermediate I Table 1Oxidation ofsubstituted phenols catalyzed bycomplex 4 and 5



TON = mole of product/mole of catalyst

 $TOF = mole of product/mole of catalyst \times time$

Conversion was determined by GC

Catalyst/substrate/oxidant ratio = 1/500/800, reaction time = 3 h



Fig. 3 The oxidation products of 2,3,6-trimethylphenol

in Fig. 4. Then 2,3,6-trimethyl-1,4-benzoquinone is formed by proton-mediated elimination of intermediate I. In the formation of 2,2',3,3',5,5'-hexamethyl-4,4'-biphenyldiol, C-C coupling occurs between the resonance forms of 2,3,6-timethylphenoxide radicals with unpaired electron at para position. The resulting unstable coupling product rearranges itself into more stable tautomeric form. (Fig. 4) [46, 47] We also foresee that a similar mechanism is contained in

Table 2Selective oxidationof 2,3,6-trimethylphenol withcatalysts 4 and 5 using differentoxidant and temperature

Subs./Ox./Cat	Oxidant	Temperature (°C)	re Conversion (%)		Selectivity ^a (%)		TON		$TOF(h^{-1})$	
			4	5	4	5	4	5	4	5
500/300/1	TBHP	50	66	63	72	68	330	315	110	105
500/500/1	TBHP	50	64	66	65	66	320	330	106.7	110
800/500/1	TBHP	50	36	56	50	70	288	448	96	149.3
1200/500/1	TBHP	50	29	53	78	74	348	636	116	212
1500/500/1	TBHP	50	19	39	62	58	285	585	95	195
500/800/1	TBHP	50	95	72	80	85	475	360	158.3	120
500/1000/1	TBHP	50	70	49	56	67	350	245	116.7	81.7
500/1200/1	TBHP	50	46	43	49	57	230	215	76.7	71.7
500/800/1	m-CPBA	50	50	55	65	59	250	275	83.3	91.7
500/800/1	H_2O_2	50	64	58	77	69	320	290	106.7	96.7
500/800/1	Air oxygen	50	-	-	-	-	-	-	-	-
500/800/1	TBHP	75	90	72	82	79	450	360	150	120
500/800/1	TBHP	90	93	70	61	63	465	350	155	116.7
500/800/1	TBHP	25	44	50	49	39	220	250	73.3	83.3
300/500/free cat.	TBHP	50	9	8	-	-	-	-	-	-
300/free ox./1	TBHP	50	_	_	_	_	_	-	-	-

TON = mole of product/mole of catalyst

TOF = mole of product/mole of catalyst × time

Conversion was determined by GC

Reaction conditions: 500/800/1: $1.79 \times 10^{-3} \text{ mol}/2.87 \times 10^{-3} \text{ mol}/3.58 \times 10^{-6} \text{ mol}$

^aSelectivity of TMBQ reaction time = 3 h

Table 3Catalytic activitiestowards the homogeneousoxidation of phenoliccompounds of some previouslyreported catalyst

Catalyst	Substrate	Rxn time (h)	Rxn temp. (°C)	Oxidant	Conv. (%)	Ref.
CoPc ¹	4-Nitrophenol	3	90	TBHP	97	[33]
FePc ¹					75	
CoPcTs ^a	DTBP	24	70	O ₂	66	[35]
FePc ^e CoPc ^d	ТСР	24	60 °C	KHSO ₅	85	[36, 37]
CoPcTs ^a	2,4,5-TCP	24	75	H_2O_2	67	[38]
FePcTs ^b	TMP	2	nr ⁱ	O ₂	77	[39]
CoPc ^d	p-nitrophenol	3	90	TBHP	96	[40]
CoPcTs ^a	DTBP	2	75	TBHP	61	[41]
FePcTs ^b					39	
CuPcTs ^c					05	
CoPc ^d	DTBP	3	30	TBHP	93	[42]
FePc ^e					_	
MnPc ^f					97	
CuPc ^g					_	
FePcTs ^b	TCP	24	25	H_2O_2	24	[43]
FePcOC ^h	ТСР	10 min	25	H_2O_2	6	[44]

 a CoPcTs = Tetrasulponated cobalt phthalocyanine

^bFePcTs = Tetrasulponated iron phthalocyanine

^cCuPcTs = Tetrasulponated copper phthalocyanine

 d CoPc = Substituted cobalt phthalocyanine

^eFePc = Substituted iron phthalocyanine

 $^{\rm f}$ MnPc = Substituted manganese phthalocyanine

^gCuPc^g = Substituted copper phthalocyanine

^hFePcOC = Octa cationic iron phthalocyanine

ⁱnr=Not reported



Fig. 4 Proposed mechanism of 2,3,6-trimethylphenol oxidation

the oxidation of 2,3,6-trimethylphenol by the Cu(II)Pc/TBHP system.

Conclusion

In this work, we report on the synthesis of Co(II) and Cu(II) phthalocyanines **4** and **5** which were characterised using IR, UV–Vis, MALDI-TOF mass spectroscopies and elemental analyses. The optimal conditions are deteremined in 2,3,6-trimethylphenol oxidation with catalyst **4** and **5**. Results show that Co(II)phthalocyanine enables high catalytic performance for 2,3,6-trimethylphenol oxidation under the optimal conditions. Additionally, toxic phenolic compounds, are durable in nature, tun into less harmful products with the use of complex **4** and **5**. The most convenient oxidation conditions are determined with TON, TOF and selectivity for this practicable, time and energy-saving method.

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