



Substituted Co(II) and Cu(II) metallophthalocyanines from new Schiff base containing pyrrole units: Synthesis, characterization and investigation of photocatalytic activity on 2,3-dichlorophenol oxidation

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Abstract

In this article, novel Schiff base compound **1** bearing pyrrole moiety has been synthesized from the reaction of 1-hydroxybenzaldehyde with 1,2-aminophenylpyrrole for the first time. The cobalt phthalocyanine and copper phthalocyanine (**3–4**) were prepared by the cyclotetramerization of the novel phthalonitrile compound **2** and the corresponding metal salts. The new phthalonitrile compound **2** was synthesized by the reaction between 4-((E)-{[2-(1H-pyrro-1-yl)phenyl]imino}methyl)phenol **1** and 4-nitrophthalonitrile in DMF. The all new compounds (**1–4**) have been characterized by FT-IR spectroscopy, ¹H-NMR/¹³C-NMR, mass, UV–Vis spectroscopy techniques and elemental analysis (for metallophthalocyanines). Chlorine-bearing phenols are of a class of pollutants. They have been regarded as a potential risk to environment and human health. It is important to advanced effective techniques to remove chlorinated phenols in wastewater. For this purpose, we investigated that different parameters influenced the photooxidation process were determined and 2,3-dichlorophenol oxidize to the less harmful products with high conversion and yield in the presence of Cu(II) and Co(II) phthalocyanine catalysts.

Keywords Metallophthalocyanine · Schiff base · Pyrrole · 2,3-Dichlorophenol · Photocatalysis

Introduction

Phthalocyanines compounds (Pcs) have been considered to be promising nominee due to their unique physical, electronic and optical properties. Except for their use as dyes, Pcs have been broadly studied because they have been applied to many scientific field applications such as

chemical sensors, catalysis, oxidation, electrochromic agents, semiconductors, photosensitizers for photodynamic cancer therapy (PDT), liquid crystals, nonlinear optics and solar energy conversion [1–5]. The chemical properties of the substituent groups attached to the peripheral positions of phthalocyanine significantly affect the properties of Pcs, such as their solubility, aggregation, electronic absorption and photocatalysis properties [6].

Pyrrole itself is not naturally occurring. A lot of bioactive natural products (such as vitamin B₁₂, bilirubin, porphyrins and chlorophyll) and synthetic drugs contain a pyrrole moiety as their skeleton [7, 8]. They were found to possess a wide variety of biological activities such as anticancer, antifungal, antibacterial, anti-inflammatory and antioxidants [9–16]. Schiff bases derived bearing pyrrole moiety are effective many areas. Also, Schiff bases are known great interest due to their biological properties [17]. The mentioned facts about pyrrole group encouraged us to synthesize of new Schiff base bearing pyrrole moiety and its metallophthalocyanines.

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Water contamination with chlorinated organic compounds have been informed as an environmental threat [18]. Chlorophenols have been used in wood preservers, fungicides, dyes, herbicides and drugs [19]. Excessive chlorophenol consumption of the industry leads to large amounts of water pollution. Most of chlorophenols are extremely mutagenic, carcinogenic, toxic and they are high persistence and bioaccumulation in the environment [19, 20]. Therefore, chlorophenols have been listed as the important priority contaminants in many countries. They have great potential risks to human health [21, 22]. The conventional treatment processes such as flocculation, adsorption, photocatalysts, membrane filtration and biodegradation are not very effective in decreasing the risk of chlorophenols in the environment because of the stable molecular structure and biotoxicity of chlorophenols, [23, 24]. Hence, researchers are still working to develop more effective technology for chlorophenols treatment.

In this work, the synthesis, characterization and structural examination of Schiff base bearing pyrrole group **1**, phthalonitrile **2** and Co(II) and Cu(II) Pcs (**3–4**) containing 4-((E)-{[2-(1H-pyrro-1-yl)phenyl]imino}methyl)phenol groups were described. Furthermore, photocatalytic activity on 2,3-Dichlorophenol oxidation of the phthalocyanines were investigated.

Experimental

Materials

The used materials and equipments were supplied as supplementary information.

Synthesis

Synthesis of 4-((E)-{[2-(1H-pyrro-1-yl)phenyl]imino}methyl)phenol (1)

1-Hydroxybenzaldehyde (0.77 g, 0.63 mmol) was dissolved 50 mL of alcohol under nitrogen gas. 1,2-Aminophenylpyrrole (1 g, 0.63 mmol) was added this solution with stirring for 30 min and 6 drops of CH_3COOH were added in this mixture. The reaction mixture was refluxed under nitrogen for 24 h. After the mixture was cooled, the solvent was removed under vacuum and recrystallized from methanol to light pink product. Yield: 0.58 g (35.72%). IR (ATR), $\nu_{\text{max}}/\text{cm}^{-1}$: 3343 (Aliph-OH), 3056 (Ar-H), 1608–1592 (C=N), 1512 (C=C), 1474, 1336, 1284, 1247, 1160, 1111, 832, 754, 695. $^1\text{H-NMR}$. (CDCl_3), (δ :ppm): 9.91 (s, 1H, Ph-OH), 8.51–8.50 (m, 1H, HC=N), 8.30–8.27 (m, 1H, Ar-H), 7.91–7.88 (m, 4H, Ar-H), 7.59–7.46 (m, 2H, Ar-H), 7.05–6.94 (m, 5H, Ar-H). $^{13}\text{C-NMR}$. (CDCl_3), (δ :ppm): 159.30, 153.47,

135.77, 130.49, 129.48, 129.32, 129.12, 128.06, 126.87, 126.02, 124.53, 116.63, 116.38, 115.74, 114.89, 114.85, 109.22. MS (ESI), (m/z): Calculated: 262.30; Found: 261.26 $[\text{M} - \text{H}]^+$.

Synthesis of 4-4-((E)-{[2-(1H-pyrro-1-yl)phenyl]imino}methyl)phenoxy] phthalonitrile (2)

Compound **1** (0.6 g, 2.29 mmol) and 4-nitrophthalonitrile (0.4 g, 2.29 mmol) were dissolved in dry DMF (10 mL) and the solution was stirred at 60 °C. Then, powdered dry K_2CO_3 (0.95 g, 6.87 mmol) was added to the system in eight equal portions over 2 h. The mixture was stirred under N_2 at 60 °C for 5 days. After five days, the reaction mixture was poured into ice-water and stirred at room temperature to yield a product. The mixture was filtered and washed with water then dried in vacuum and recrystallized from ethanol to pink product. Yield: 0.4 g (45%). IR (ATR), $\nu_{\text{max}}/\text{cm}^{-1}$: 3095 (Ar-H), 2232 (C \equiv N), 1592–1561 (C=N), 1486–1475 (C=C), 1425, 1375, 1280, 1252, 1208, 1098, 1043, 933, 837, 750, 716. $^1\text{H-NMR}$. (CDCl_3), (δ :ppm): 8.58 (s, 1H, HC=N), 8.35 (d, 1H, Ar-H), 8.17–8.13 (t, 4H, Ar-H), 7.96–7.94 (m, 2H, Ar-H), 7.65–7.61 (m, 4H, Ar-H), 7.40–7.38 (d, 2H, Ar-H), 7.10–7.01 (m, 2H, Ar-H). $^{13}\text{C-NMR}$. (CDCl_3), (δ :ppm): 161.01, 155.79, 152.53, 136.87, 135.89, 135.52, 131.26, 129.99, 128.47, 127.16, 126.04, 124.52, 123.75, 123.18, 120.60, 117.30, 117.15, 116.36, 115.86, 115.23, 114.84, 109.20, 108.93. MS (ESI), (m/z): Calculated: 388.42; Found: 387.19 $[\text{M} - \text{H}]^+$.

General procedure for synthesis of metallophthalocyanines (3, 4)

Substituted phthalonitrile **2** (0.1 gr, 0.26 mmol) and for metallophthalocyanines corresponding anhydrous metal salts [CoCl_2 (17 mg, 0.13 mmol); CuCl_2 (17.40 mg, 0.13 mmol)] were dissolved in 1.5 mL of DMAE. Then the temperature was raised to 160 °C and stirred for 24 h under nitrogen atmosphere. Methanol was added to the medium and the green raw products were filtrated and washed with hot ethanol, methanol and diethyl ether. The green product was purified on alumina column with chloroform:methanol (10:1) for compound **3**, (10:1) for compound **4** solvent system as eluent. Spectral data of these products were given below.

Cobalt(II) phthalocyanine (3) Yield: 25 mg (11%). mp: > 300 °C. IR (ATR) $\nu_{\text{max}}/\text{cm}^{-1}$: 3063 (Ar-CH), 1597–1504 (C=N), 1472–1462 (C=C), 1365, 1227, 1160, 1095, 929, 832, 750, 712. UV-Vis (THF): λ_{max} , nm (log ϵ): 663 (5.06), 601 (4.55), 330 (4.23). MALDI-TOF-MS m/z: Calculated: 1610.93; Found: 1611.07 $[\text{M} + \text{H}]^+$. Elemental Analysis, Anal, calc. for $\text{C}_{100}\text{H}_{64}\text{N}_{16}\text{O}_4\text{Co}$: C, 74.49; H, 3.97; N, 13.91; Found: C, 72.40; H, 2.96; N, 12.00%.

Copper(II) phthalocyanine (4) Yield: 35 mg (17%). mp: > 300 °C. IR (ATR) $\nu_{\max}/\text{cm}^{-1}$: 3056 (Ar–CH), 1597–1504 (C=N), 1474–1423 (C=C), 1320, 1229, 1161, 1097, 929, 835, 753, 715. UV–Vis (THF): λ_{\max} , nm (log ϵ): 676 (4.98), 608 (4.64), 340 (4.97). MALDI-TOF–MS m/z : Calculated: 1615.55; Found: 1616.32 [M+H]⁺. Elemental Analysis, Anal, calc. for C₁₀₀H₆₄N₁₆O₄Cu: C, 74.29; H, 3.96; N, 13.87; Found: C, 70.36; H, 4.35; N, 12.82.

General procedure for the photooxidation of substituted phenols

Experiments were carried out in a photocatalytic reactor equipped with stirrer and 18 pieces 8 W UV lamp. The solution of 2,3-dichlorophenol and catalyst in solvent was degassed. A mixture of 2,3-dichlorophenol (3.72×10^{-3} mol), catalyst (3.10×10^{-6} mol), oxidant (2.48×10^{-3} mol) and solvent (0.01 L) was stirred in a reaction vessel for 1 h at room temperature. The samples (0.5 mL) were taken at certain time intervals. Each sample was injected at least twice in the GC, 1 μL each time. Formation of products and consumption of substrates were monitored by GC. The structure of the reaction products was confirmed by ¹H-NMR spectroscopy.

Results and discussion

Synthesis and characterization

The general synthetic pathway for the synthesis of schiff base compound **1**, phthalonitrile derivative **2** and its cobalt(II) **3**, copper(II) **4** phthalocyanine complexes were given in Fig. 1. All novel compounds (**1–4**) were fully characterized by IR, ¹H-NMR/¹³C-NMR (for compounds **1–2**), UV–Vis (for compounds **3–4**), MS spectral data and elemental analysis for metallophthalocyanines. 4-((E)-{[2-(1H-pyrro-1-yl)phenyl]imino}methyl)phenol **1** was prepared through acid catalyzed reaction of 1-hydroxybenzaldehyde with 1,2-aminophenylpyrrole in alcohol. The formation of compound **1** was confirmed by the combination of spectroscopic data. The main feature characterizing its IR spectra is the presence of OH band at 3343 cm^{-1} , the disappearance of the band corresponding to NH₂ and C=O groups and the detection of a strong C=N stretching band at 1608–1592 cm^{-1} evidenced the formation of the schiff base **1**. In the ¹H NMR of the compound **1** revealed a singlet at $\delta=9.91$ ppm to the phenolic OH group, another signal characterized at the ¹H-NMR spectrum at $\delta=8.51$ corresponding to the imine (–N=CH) group (Fig. 2). The characteristic ¹³C-NMR signal of at δ : 159.30 ppm (C-imine) and the other signals (Ar–C)

supported the structure. The mass spectra of compound **1** confirmed the structure proposed, with the molecular ion at 261.26 [M–H]⁺.

The synthesis of 4-{4-((E)-{[2-(1H-pyrro-1-yl)phenyl]imino}methyl)phenoxy} phthalonitrile **2** was obtained through base-catalyzed aromatic displacement of 4-nitrophthalonitrile with schiff base compound **1** using K₂CO₃ as the base in dry DMF. In the IR spectrum of phthalonitrile compound **2** was clearly verified with the disappearance of the OH group of **1** and the presence of C≡N group by the sharp stretching bands at 2232 cm^{-1} . In the ¹H-NMR spectrum of compound **2** at $\delta=9.91$ ppm (Ph-OH signal) was disappeared (Fig. 3). In the ¹³C-NMR spectrum of compound **2** indicated the presence of nitrile carbon atom (C≡N) at $\delta=115.86$ – 115.23 ppm. In the mass spectra of phthalonitrile compound **2**, the molecular ion peak was observed at m/z : 387.19 [M–H]⁺, confirmed the proposed chemical structure.

Cyclotetramerization of compound **2** to the peripherally tetra-substituted metallophthalocyanines (**3–4**) were accomplished in the presence of metal salts (CoCl₂ and CuCl₂) at 160 °C in DMAE in 24 h under inert atmosphere. In the IR spectra, the formation of metallophthalocyanines (**3–4**) was clearly confirmed by the disappearance of the C≡N band. The ¹H-NMR spectra of CoPc and CuPc could not be determined owing to the paramagnetic nature [25]. The molecular ion peaks are identified at $m/z=1611.07$ [M+H]⁺ for CoPc **3** (Fig. 4) and 1616.32 [M+H]⁺ for CuPc **4**.

Phthalocyanine complexes have two strong characteristic region in the UV–Vis spectrum; B band is at 300–500 nm and the more energetic absorption, known as the Q band, near 600–700 nm [25]. The UV–Vis absorption spectrum of synthesized cobalt and copper phthalocyanines (**3** and **4**) in THF at 12×10^{-6} M concentration was shown Fig. 5. In the UV–Vis absorption spectra of **3** and **4** Q band absorptions were observed at 663/601 (corresponds to degenerate D_{4h} symmetry) and 676/608 nm, respectively. Also in the B band absorptions were observed at 330 and 340 nm, respectively.

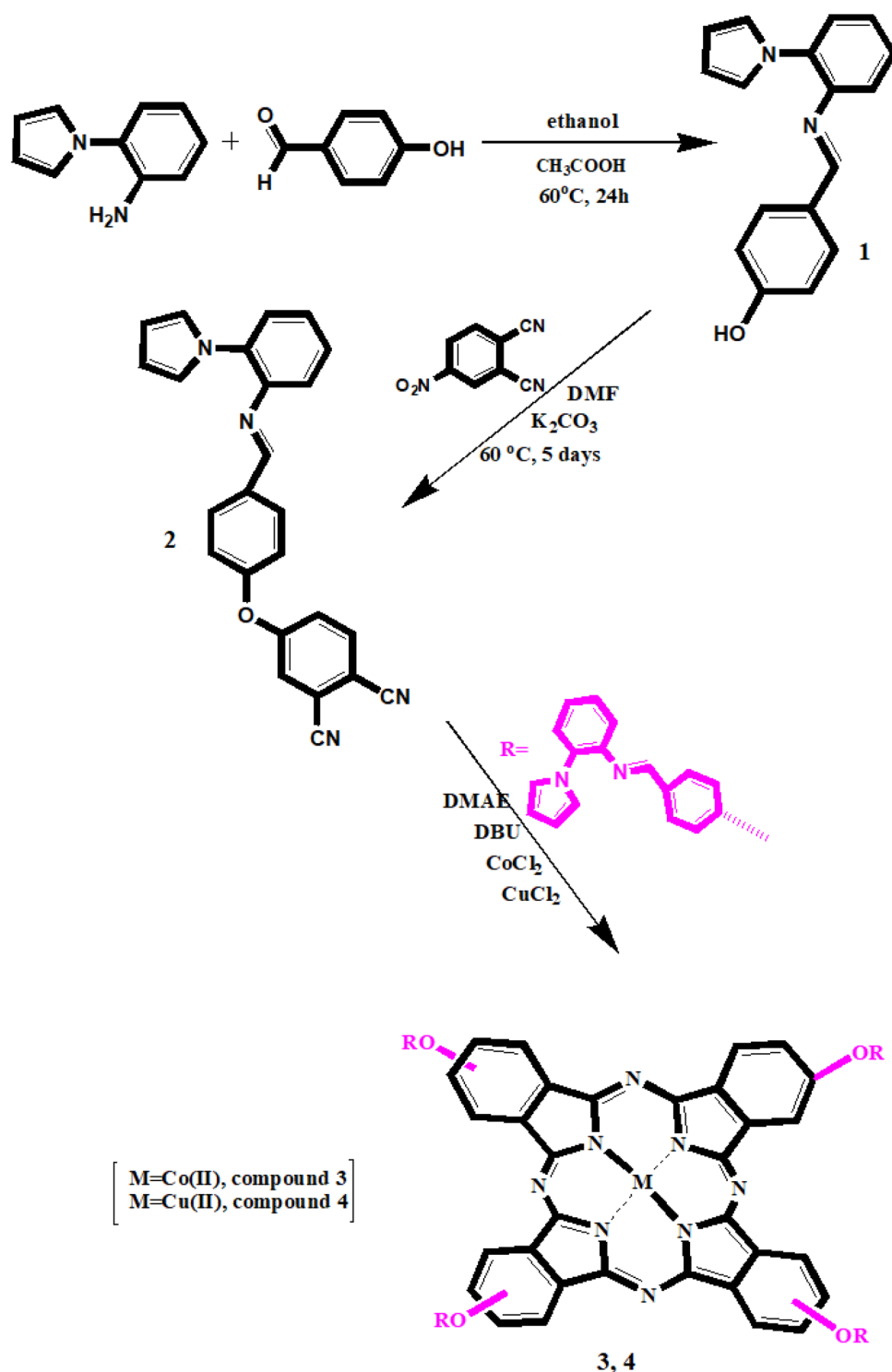
The metallophthalocyanines **3** and **4** have the same peripherally but they have different metal ions in core. The CuPc **4** showed red-shifted Q band comparison to the CoPc **3** phthalocyanine complex. The Q band intense of phthalocyanines **3** and **4** were observed in CoPc > CuPc (Fig. 5).

Catalytic studies

Oxidation of phenolic compounds with complex **3** and **4**

The catalytic properties of Co(II) and Cu(II) phthalocyanine complexes were investigated for the photooxidation of 2,3-dichlorophenol. The oxidation reaction results were given in Table 1. All experiments maintained 1 h oxidant and auxiliary chemicals on the conversion and yields were

Fig. 1 The synthesis route of compounds 1–4



investigated. The blank reactions were carried out (using no catalysts or oxidants) and there were no product detectable (Table 1). It is proved that presence of the catalyst and oxidant are essential for the oxidation. The main products was determined as 2,3-dihydroxy-1,4-benzoquinone and the side product was determined as 2,3-dichloroquinol in the oxidation of 2,3-dichlorophenol photooxidation reaction (Fig. 6).

After the photocatalytic studies, the photodegradation amount of 2,3-dichlorophenol was calculated with the equation below [26].

$$X_{(t)} = C_0 - C_{(t)}/C_0$$

In the equation above, $X(t)$ is the molar fraction of 2,3-dichlorophenol, C_0 is the first concentration and $C(t)$ is

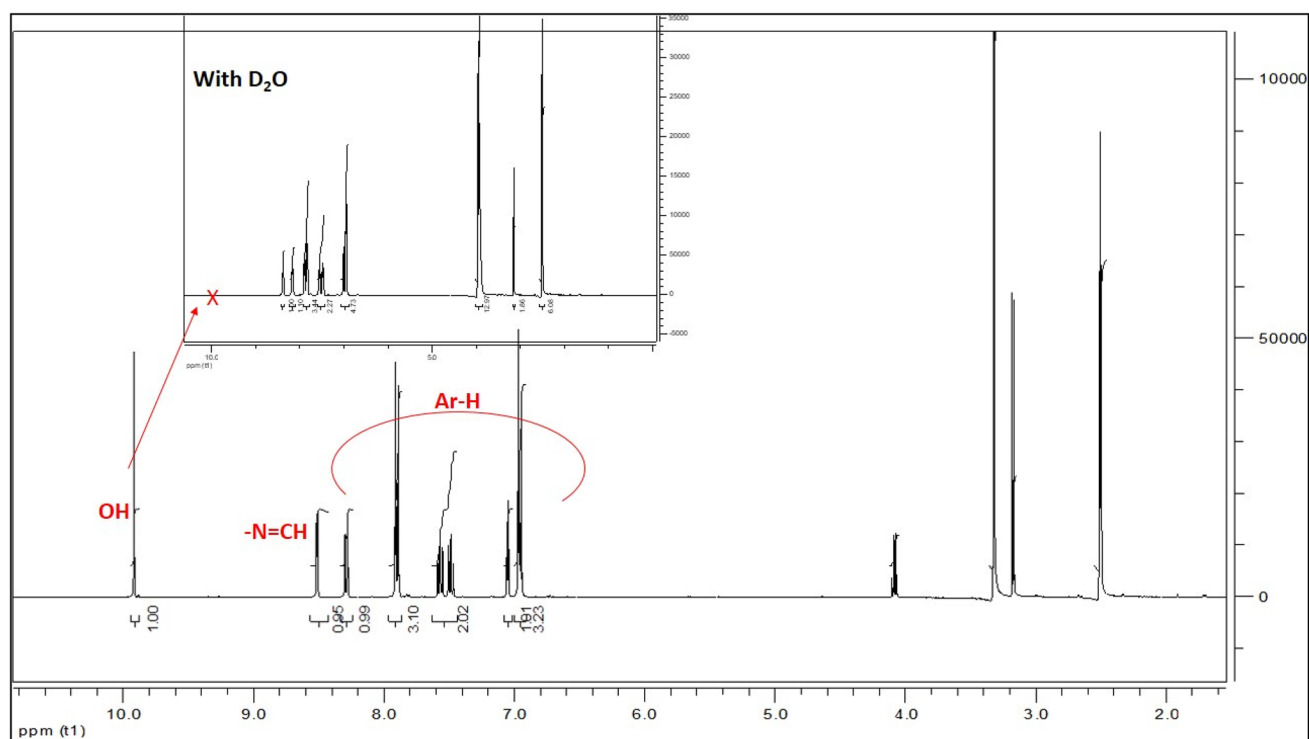


Fig. 2 ^1H -NMR spectrum of compound 1

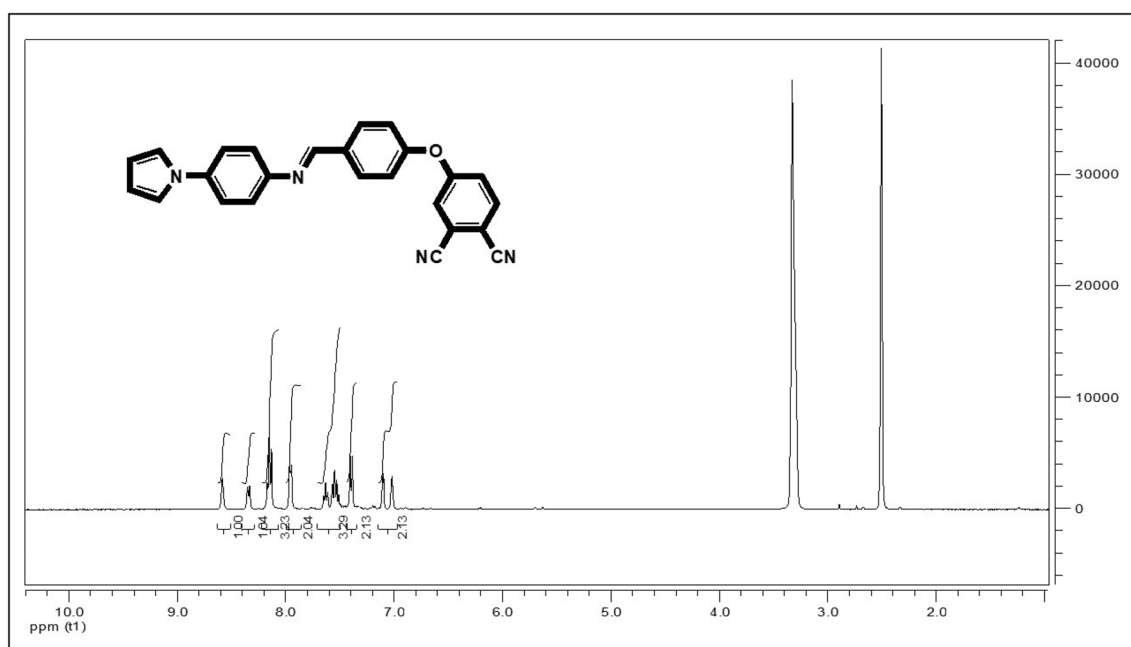


Fig. 3 ^1H NMR spectrum of phthalonitrile compound 2

the concentration of 2,3-dichlorophenol as a function of illumination time. This equation shows a similar profile with the photocatalytic degradation of the other dyestuffs [26–28]. For this purpose, 100 mL of 0.025 M 2,3-dichlorophenol

solution and 5 mg of solid catalyst and oxidant (H_2O_2) were reacted in a photoreactor for 1 h under visible light. During the photocatalytic reaction, all samples from taking reaction medium were diluted with dichloromethane

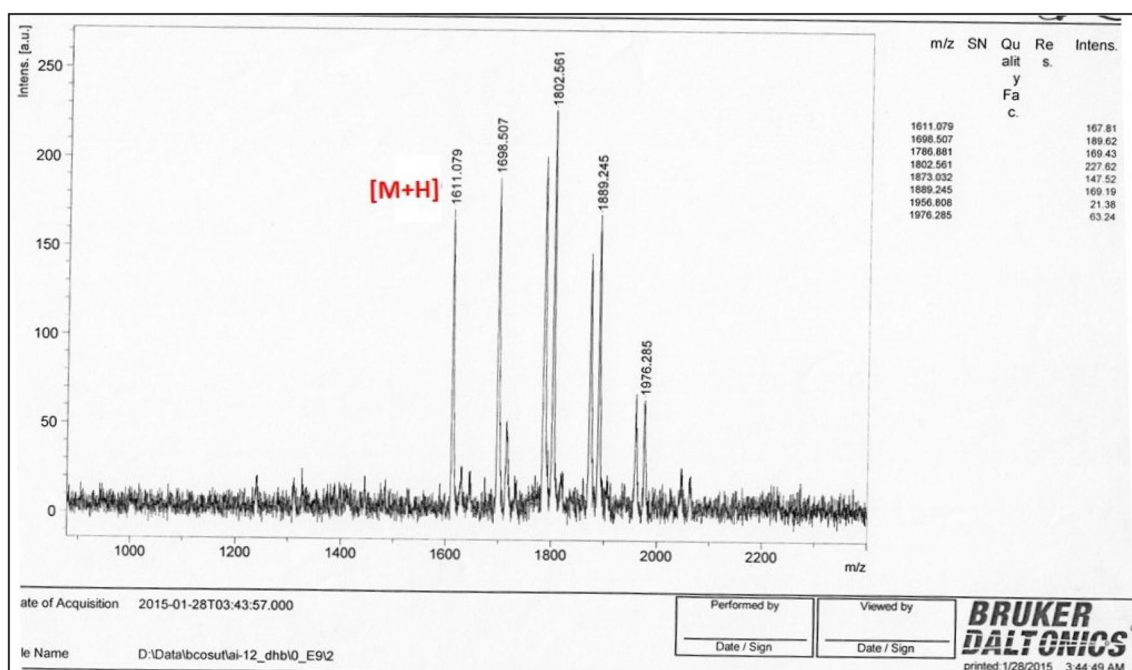


Fig. 4 MALDI TOF MS spectrum of CoPc 3

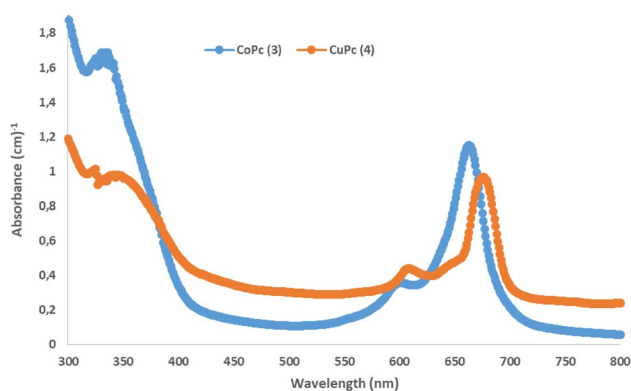


Fig. 5 UV-vis absorption spectra changes of CoPc and CuPc in THF

and injected into the injection port of a GC apparatus, with phenol being the internal reference in this case. As a result, we have observed that a great portion of 2,3-dichlorophenol has been degraded and after 60 min, the degradation rate has been fixed. Data about photocatalytic oxidation of 2,3-dichlorophenol that was sensitized with complex **3** under visible light were presented in Fig. 7.

Oxygen activation in oxidation reactions is a challenging problem of modern chemistry and biochemistry. Co(II) complexes are involved in the one-electron reduction of oxygen to form the superoxo (Co(III)⁻) or peroxy derivatives (Co(III)⁻ -Co(III)) [29, 30]. V.N. Shishkin et al. reported that the cobalt complex with 4-octasulfophenyltetrapyrrolineporphyrin (a ligand with pronounced

electron-withdrawing properties) catalyzes the reactions of thiourea and *N,N'*-dimethylthiourea with oxygen [31, 32]. The reaction occurs under mild conditions to form the corresponding urea and sulfur in high yield. In this work, we studied the catalytic oxidation reactions of 2,3-dichlorophenol with different oxygen sources and achieved to activate oxygen.

To determine oxygen source effect, TBHP, H₂O₂, *m*-CPBA were used as oxidant. The results in Table 1 showed that H₂O₂ was the best oxidant for 2,3-dichlorophenol oxidation in the presence of cobalt phthalocyanine **3**. Also, TBHP and *m*-CPBA can serve as an oxidant. But low conversion was observed for both CoPc **3** and CuPc **4**. The reaction color changed from light blue to brown when we added TBHP or *m*-CPBA in the reaction media. This clue expresses that the complex **3** was degraded immediately with TBHP or *m*-CPBA [33, 34]. When H₂O₂ was used as an oxygen source, reaction color was bright blue color for 30 min and then changed to yellow and light yellow at the end. This observation proved that phthalocyanine catalyst can be more photocatalytically active with H₂O₂ as an oxygen source in this catalytic process. Figure 8 shows the relationship between oxidant type and the total conversion.

To find the optimal reaction conditions, oxidant/catalyst ratio was tested in 2,3-dichlorophenol oxidation. When the oxidant/catalyst ratio was increased from 400/1 to 1200/1, the rate of the reaction increased. In contrast, while the catalytic oxidation was processing from 1200/1 to 1800/1, the conversion inclined to decreasing. At this stage, it is possible

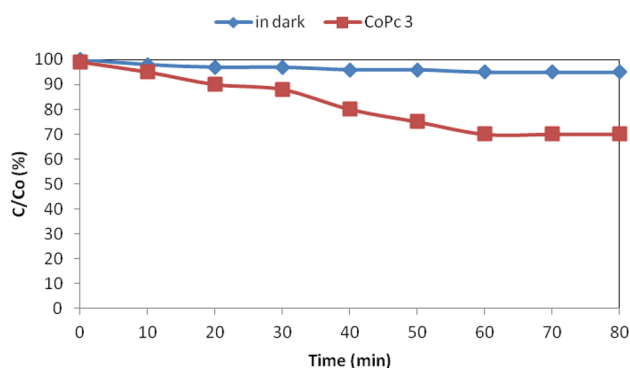
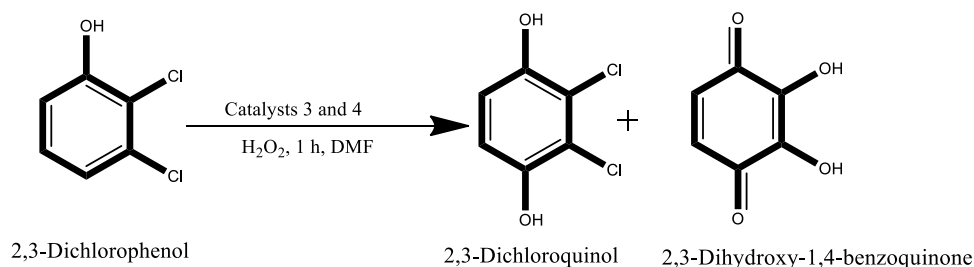
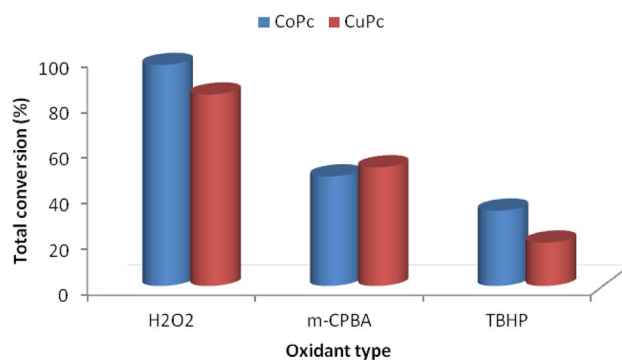
Table 1 Selective oxidation of 2,3-dichlorophenol with catalysts **3** and **4** using different oxidant and temperature

Subs./Ox./Cat	Oxidant	Conversion (%)		Selectivity ^a (%)		TON		TOF (h ⁻¹)	
		3	4	3	4	3	4	3	4
400/800/1	H ₂ O ₂	49	28	51	43	196	112	196	112
800/800/1	H ₂ O ₂	65	49	88	68	520	392	520	392
1200/800/1	H ₂ O ₂	97	83	90	90	1164	996	1164	996
1600/800/1	H ₂ O ₂	90	78	88	80	1440	1248	1440	1248
1800/800/1	H ₂ O ₂	75	56	66	63	1350	1008	1350	1008
1200/800/1	<i>m</i> -CPBA	48	51	61	58	576	612	576	612
1200/800/1	TBHP	33	18	49	41	396	227	396	227
600/800/free cat.	H ₂ O ₂	–	–	–	–	–	–	–	–
600/free ox./1	H ₂ O ₂	–	–	–	–	–	–	–	–

TON = mole of product/mole of catalyst

TOF = mole of product/mole of catalyst x time

Conversion was determined by GC

Reaction conditions: 1200/800/1: 3.72×10^{-3} mol/ 2.48×10^{-3} mol/ 3.10×10^{-6} mol^aSelectivity of 2,3-dihydroxy-1,4-benzoquinone Reaction time = 1 h**Fig. 6** The oxidation products of 2,3-dichlorophenol**Fig. 7** The photocatalytic oxidation of 2,3-dichlorophenol with near visible light irradiation CoPc **3** and in dark**Fig. 8** The oxidant effect on 2,3-dichlorophenol oxidation [Reaction conditions: 2,3-dichlorophenol (3.72×10^{-3} mol), Co(II)Pc and Cu(II)Pc (3.10×10^{-6} mol), oxidant (2.48×10^{-3} mol), DMF (0.01 L), 1 h at room temperature]

that the coordination around the cobalt ion can change and produce inactive intermediate species [35].

We are interested in the nature of the introduced transition metals that are used in these catalytic works. Considering metallophthalocyanines are representatives for flat, π -conjugated carbon systems, their electronic properties are determined to a large extent by the central metal atom. The

electronic configuration of central metal atom can change the catalytic activity of phthalocyanine. The activity of metallophthalocyanines in oxidation reaction follows the order $\text{CoPc} > \text{CuPc}$. It is known that the catalytic performance of transition metal species depends on the outer d-electron density [34].

In general, the OH groups in the chlorophenol ring are ortho and para directing with activation, whereas Cl substituents are ortho and para directing with deactivation. When the OH radical, an electrophilic reagent, is attacking 2,3-dichlorophenol, it is expected to attack the electron rich positions and cause to generate major para or ortho substituted intermediates (2,3-dichloroquinol). The route in Fig. 9 shows that the detected intermediates are all rationalized as being formed by hydrogen abstraction, followed by para or ortho hydroxylation of the ring. Hydroxyl radical attack preferentially the aromatic moiety due to their electrophilic character to form the hydroxylated compound. The product are then followed to dechlorinate through the OH attack and finally oxidized to quinone [36].

Some previously reported catalysts are summarized in Table 2. Different groups substituted cobalt(II), iron(II), aluminium(III), copper(II) and metal free phthalocyanines were investigated on photooxidation of different pollutants [37–43]. In the literature, there are quite a few studies about photocatalytic applications of phthalocyanine on the environmental pollutants degradation. Some of them are focused on get high singlet oxygen quantum yield and efficiency without any measurements of product conversion, selectivity, turnover number and turnover frequency. In our previous work, tetrasubstituted Co(II), Fe(II) and Cu phthalocyanine complexes were also studied as catalyst in the oxidation of phenolic compounds [44–51]. By comparing the catalyst

in these literatures and our works, it is inferred that the compound **3** will be interesting catalyst in 2,3-dichlorophenol photooxidation. The results of previous our works were also valuable because of the high conversion and selectivity of phthalocyanine. But in this research it is the first time to investigate the photocatalytic activity of newly synthesized Co(II) **3** and Cu(II) **4** phthalocyanines on 2,3-dichlorophenol oxidation with high product conversion and selectivity.

Conclusion

In this paper, novel CoPc and CuPc (**3–4**) which are substituted with pyrrole carrying four Schiff bases on the peripheral positions were synthesized. Firstly, the Schiff base ligand **1** was prepared and then novel phthalonitrile compound **2**, starting compound of phthalocyanines, was synthesized via S_N2Ar type substitution reaction. The synthesized compounds have been characterized IR, NMR, UV–Vis and MS spectroscopies techniques and elemental analysis. The MPcs **3–4** are highly soluble in most of the organic solvents and the catalytic activity of **3** and **4** were examined for the oxidation of 2,3-dichlorophenol using different oxygen sources. The CuPc **4** showed feasible catalytic activity with 83% and 90% product conversion and selectivity for 2,3-dichlorophenol photooxidation. The results indicated that the catalyst **3** showed convincing activity for the

Fig. 9 The proposed mechanism of 2,3-dichlorophenol

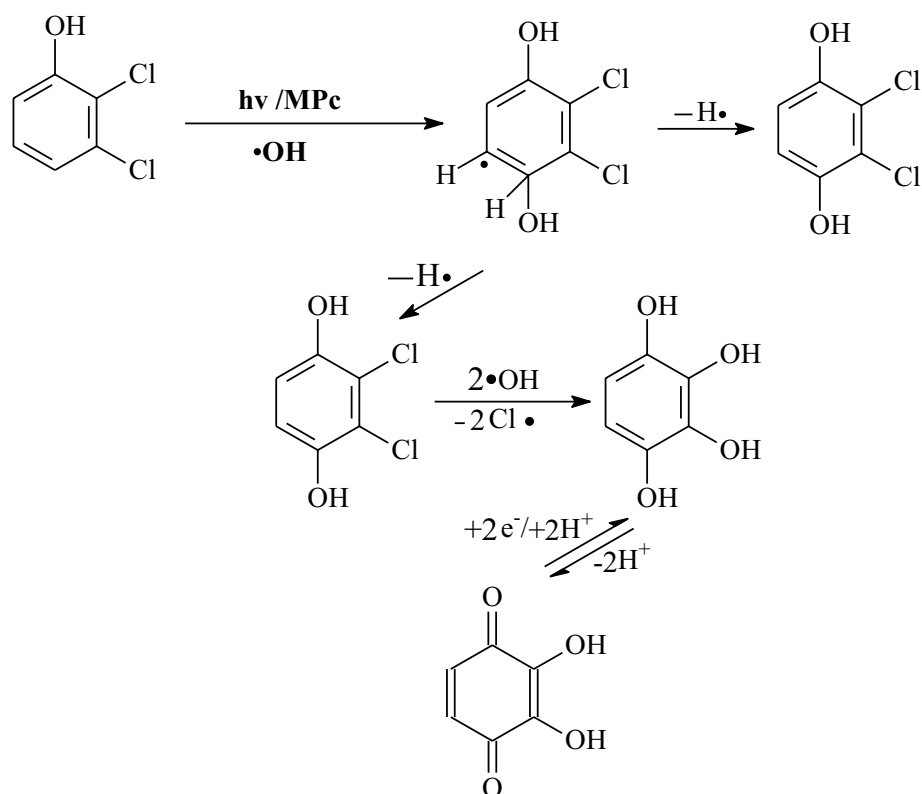


Table 2 Catalytic activities of phthalocyanines towards the photooxidation of different organic compounds in some previously reported catalyst

Catalyst	Substrate	Rxn Time (h)	Rxn Temp. (°C)	Oxidant	Conv. (%)	References
ZnTsPc ^a	Methyl orange-Orange G	10 min	nr	O ₂	nr	[36]
FePc ^b	Ethyl benzene	9 h	rt	O ₂	> 99	[37]
CoTNPc ^c	Malachite green	30 min	nr	–	99.2	[38]
CoPc ^d	2-Mercaptoethanol	2	rt	–	nr ^e	[39]
Metal free Pc ^f	Sulfide ion	1	rt	O ₂	70	[40]
CuPc ^g	4-Nitrophenol	5	27	–	nr ^h	[41]
CoPc ⁱ	4-Chlorophenol	3	rt	O ₂	99.99	[42]
ZnPc ^j					97.05	

^aZnTs-CoFerrite = 2-[5-(phenoxy)-isophthalic acid] 9(10), 16(17), 23(24)-tris (tertbutyl) phthalocyaninato Zn(II)

^bFePc-POF = four-branched tetra-amine FePc-porous organic framework

^cCoTNPc/SnIn₄S₈ = Tetranitrocobalt phthalocyanine/ternary chalcogenide

^dCoPc = Cobaltphthalocyanine/C₆₀

^enr = Turnover number is given as 8.4

^fMetal free Pc = Metal free phthalocyanine/TiO₂

^gCuPc = Copper phthalocyanine/TiO₂

^hnr = Quantum yield is given as 1.9

ⁱCoPc = 2,9,16,23-tetrakis-(4-carboxyphenylsulphonyl) phthalocyaninato cobalt(II)/TiO₂

^jZnPc = 2,9,16,23-tetrakis-(4-carboxyphenylsulphonyl) phthalocyaninato zinc(II)/TiO₂

nr not reported

photooxidation of 2,3-dichlorophenol to the corresponding 2,3-dihydroxy-1,4-benzoquinone as major product in 1 h at room temperature with the highest conversion, selectivity and TON (respectively; 97%, 90% and 1164). The optimal conditions were also determined in 2,3-dichlorophenol oxidation with CoPc **3**. All the results indicated that CoPc **3** with catalytic oxidation were efficient and cleaning technology for industrial waste application. Transformation environmentally harmful phenolic compounds into less harmful oxidation products by CoPc **3** derivative makes this study intriguing.

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