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Novel aqueous soluble cobalt phthalocyanine: synthesis and catalytic activity on oxidation of 2-mercaptoethanol

Yong Pan[a,*], Wenxing Chen[b], Sufang Lu[b], Yifeng Zhang[a]

[a] *Institute of Polymer Science, Zhejiang University, Hangzhou 310027, PR China*
[b] *College of Materials and textiles, Zhejiang Institute of Science and Technology, Hangzhou 310033, PR China*

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Abstract

A new aqueous soluble phthalocyanine, cobalt tetra(*N*-carbonylacrylic)aminephthalocyanine, was synthesized by modification of cobalt tetraaminophthalocyanine with maleic anhydride. The product was characterized by elemental analysis, FT-IR, and TGA. It is soluble in dilute sodium hydroxide solution. Its catalytic efficiency in the oxidation of 2-mercaptoethanol (MEA) was also evaluated in DMF and aqueous solution. Compared with cobalt tetraaminophthalocyanine and cobalt tetracarboxylphthalocyanine, cobalt tetra(*N*-carbonylacrylic)aminephthalocyanine had greater catalytic activity and solubility in aqueous solution. The UV–VIS spectra showed that the aggregation of the phthalocyanine molecular was restrained due to the bulky peripheral substitutions on the cobalt phthalocyanine rings, which leads to the increase of catalytic activity in the oxidation of MEA.

Keywords: Cobalt tetra(*N*-carbonylacrylic)aminephthalocyanine; Catalytic oxidation; Cobalt tetraaminophthalocyanine; 2-Mercaptoethanol; Cobalt tetracarboxylphthalocyanine; UV–VIS spectra

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1. Introduction

Metal phthalocyanines (MtPc) have attracted considerable interest because of their structural similarity to metalloporphyrin complexes found at the active sites of metalloenzymes [1]. These phthalocyanine complexes are potential functional materials for use as sensitizers [2], gas sensors [3], catalysts [4–6] and electrocatalysts [7] because of their high electron transfer abilities. However, they can only be utilized in some fields due to their lower solubility in water and common organic solvents. It has been found that suitable functional groups in the peripheral benzene rings of the phthalocyanine structure can improve the solubility of phthalocyanine in solution, especially in water. Several aqueous soluble cobalt phthalcyanines, such as Co(II)-terasulfophthalocyanine, Co(II)-octacarboxyphthalocyanine, Co(II)-tetracarboxyphthalocyanine and others, have been prepared successfully [8–10].

Cobalt phthalocyanine derivatives (CoPc) are effective catalysts for oxidation of sulfur-containing substrates by dioxygen [1]. The redox process is catalyzed by the ground electronic state of the CoPc and is the result of electron transfer from the sulfur-containing compound to the dioxygen coordinated to the central Co(II) metal atom. Accordingly, the end product will be disulfide, sulfur and thiosulfates for the sulfur-containing substrates (thiols, hydrosulfide and alkali sulfides) [11]. They have been applied effectively in the catalytic oxidation of mercaptans in oil fractions and for removing alkali sulfides from industrial waste water [12,13]. However, one limitation of these catalysts is the formation of inactive dimers of the phthalocyanine complexes in solution, which significantly affects their

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* Corresponding author. Fax: +86 0571 88495083.
E-mail address: panpy@zju.edu.cn (Y. Pan).

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catalytic properties [14]. An efficient strategy is to develop the disaggregation of metal phthalocyanine clusters by the mutual electrostatic force of repulsion of some ionic groups on the phthalocyanine molecules [15].

In this paper, a novel aqueous soluble phthalocyanine, cobalt tetra(*N*-carbonylacrylic)aminephthalocyanine, was synthesized. Elemental analysis, FT-IR and TGA were applied to characterize its structure and thermostability. This work also dealt with the effect of different substituted groups on the phthalocyanine rings upon the oxidation of MEA by O_2 and demonstrated by UV–VIS spectra. Significantly, the unsaturated double bonds of cobalt tetra(*N*-carbonylacrylic)aminephthalocyanine can copolymerize easily with some monomers. Such enzyme mimics give a potential lead for investigating the catalytic mechanism of biological enzymes. This work is still under research.

2. Experimental

2.1. Materials

4-Nitrophthalic acid was obtained from Taixing Sunmy Fine Chemical Co., Ltd. (Jiangshu, China). Maleic anhydride was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Trimellitic anhydride was obtained from Merck & Co., Inc. Ammonium molybdate was purchased from Shanghai Pharmaceutical Co., Ltd. (Shanghai, China). The other chemicals were of reagent grade.

2.2. Synthesis of cobalt phthalocyanine

A phenylanhydride-urea route was adopted in the synthesis of three cobalt phthalocyanines and the structures of complexes are shown in Scheme 1.

2.2.1. Cobalt tetraaminophthalocyanine (1) [16]

4-Nitrophthalic acid (12.66 g, 0.06 mol), 30 g (0.5mol) urea, 4.27 g (0.0152 mmol) $CoCl_2 \cdot 6H_2O$, and 0.15 g ammonium molybdate (catalyst) were finely ground and placed in a 500 ml beaker covered with a glass-surface vessel. The temperature of the reaction mixture was heated slowly to 190 °C and maintained for 5 h. Then the solid product was treated with hydrochloric acid (1.0 M) and sodium hydroxide solution (1.0 M), respectively. After filtration, the product was washed to neutralization with water and dried in vacuo; the yield was 82.1%.

Finely ground cobalt(II) (9.193 g), 4,9,16,23-tetranitrophthalocyanin and 33.73 g of sodium sulfide were dissolved in 180 ml DMF. The solution was kept at 60 °C for 1 h. Then it was poured into 1000 ml water and the dark green product was precipitated and collected by centrifugation. The product was repeatedly rinsed with water and dried in vacuo over P_2O_5, and the pure cobalt complex was obtained with a yield of 89.0%. Anal.: Calc. for $C_{32}H_{20}N_{12}Co \cdot 2H_2O$: C 57.57, H 3.60, N 25.19. Found: C 57.43, H 3.33, N 25.27%.

2.2.2. Cobalt tetra(N-carbonylacrylic) aminephthalocyanine (2)

Product **1** (3.0g) was dissolved in 150 ml DMF. Maleic anhydride (1.32 g) was added and the reaction was kept at 50 °C for 3 h. Then the solution was poured into 1000 ml H_2O and a blue flocculent solid was obtained. The mixture was centrifuged and the precipitate collected. The product was soluble in H_2O at $pH > 6$. The product was then dissolved in sodium hydroxide solution (0.1 M) and filtrated through a glass funnel. The filtrate was acidified to about pH 2. This procedure was repeated three times. The resulting mixture was centrifuged and the precipitate collected. After washing with water, ethanol and ether, the product was dried at reduced pressure over phosphoric anhydride for 24 h. The yield was 89.4%. Anal.: Calc. for $C_{48}H_{28}N_{12}O_{12}Co \cdot 2H_2O$: C 54.39, H 3.02, N 15.86. Found: C 54.31, H 3.06, N 16.25%.

2.2.3. Cobalt tetracarboxylphthalocyanine (3)

This was prepared from trimellitic anhydride and purified according to the method described in the literature [9]. The yield was 52.1%. Anal.: Calc. for $C_{36}H_{16}N_8O_8Co \cdot 2H_2O$: C 55.17, H 2.57, N 14.30. Found: C 55.45, H 2.72, N 14.53%.

2.3. Sample measurement

Chemical structures of phthalocyanine products were characterized with a spectrophotometer (Brucker vector 22) using KBr pellets.

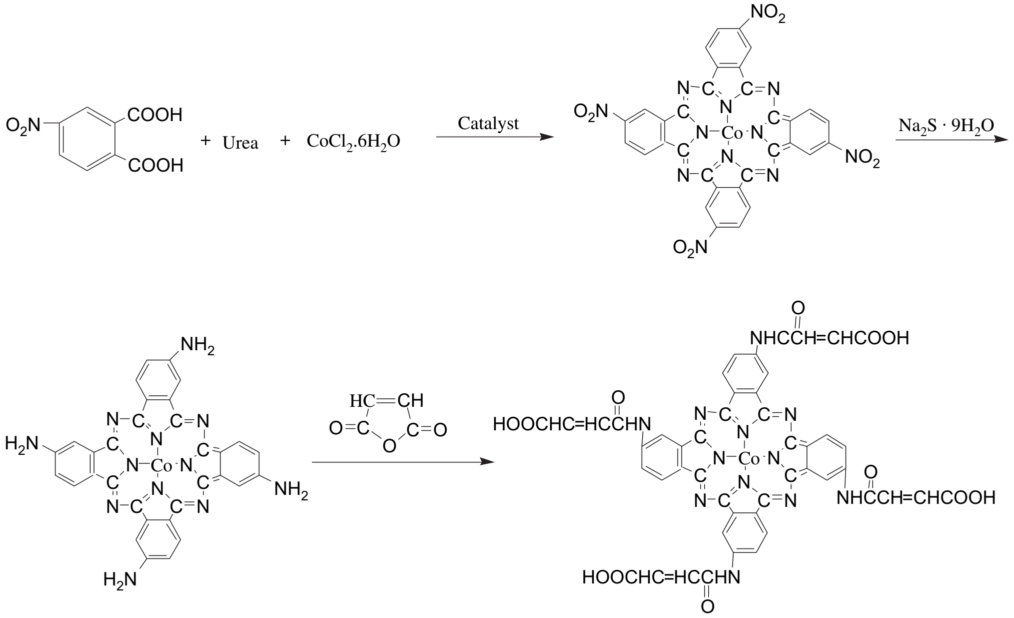
Elemental analysis was carried out with a Carlo Erba1106.

TGA studies were carried out using a Perkin Elemer (GA). The TGA data were obtained with the following conditions: sample size 10 mg, temperature range ambient to 800 °C, heating rate 10 °C/min and nitrogen atmosphere with flow rate 100 ml/min.

UV–VIS spectra of the phthalocyanine complexes were obtained on a Hitachi U-3010 spectrophotometer.

Solubility tests were carried out as follows. An ounce of cobalt phthalocyanines (such as 0.01 g) was placed into 50 ml of solvent (THF, acetone, ethanol, toluene, DMF, H_2O and $CHCl_3$) and vibrated at 25 °C for 24 h in a thermostatic vibrator. The solution was filtered and the insoluble substrate was collected, dried and weighed.

The reaction rates of the oxidation of MEA in the presence of the catalyst were measured by determining the oxygen consumption in the reaction mixture with a gas burette [17]. The system was equipped with a water jacket and the reaction solution agitated by a magnetic



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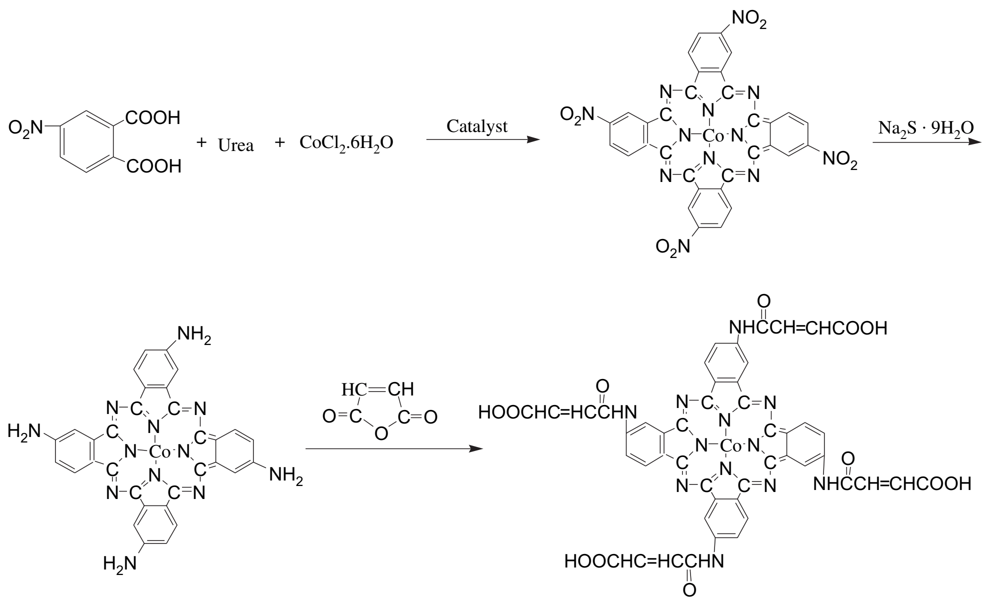

1

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Scheme 1.

stirrer at a speed of 600 rpm. The oxygen burette, the reactor, and the connection pipe were thermostated and the temperature of system regulated by controlling the temperature of the water jacket.

3. Results and discussion

In Scheme 1, product **2** was synthesized under ambient conditions (50 °C and DMF as solvent) and can reach higher yield and purity through a simple dissolving-precipitation method, while the strong alkaline conditions in the hydrolysis always lead to the destruction of phthalocyanine rings and the reduction of yield for product **3**. Fig. 1 shows the FT-IR spectra of phthalocyanine products **1**, **2** and **3**. For product **2**, the absorption peaks at 1133 cm^{-1}, 1100 cm^{-1}, 1064 cm^{-1}, 848 cm^{-1} and 752 cm^{-1} are assigned to phthalocyanine skeleton [18]. Peaks around 1709 cm^{-1} indicate the presence of C=O group, and the band at 3000–3500 cm^{-1} corresponds to OH of the COOH group, respectively; And for product **1**, the absorption peaks at

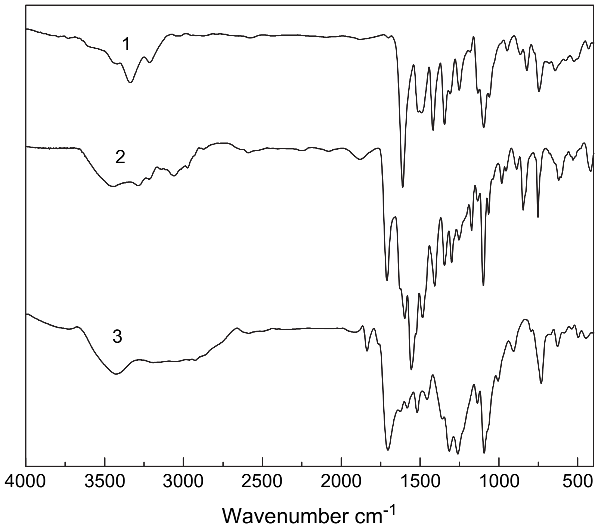

Fig. 1. FTIR spectra of **1**, **2** and **3**.

1136 cm^{-1}, 1095 cm^{-1}, 1059 cm^{-1}, 822 cm^{-1} and 751 cm^{-1} are also assigned to phthalocyanine skeleton. The strong absorption bands around 3300 cm^{-1} are due to the NH_2 group on the ring of phthalocyanine. It could be concluded that some nucleophilic reaction has taken place between product **1** and maleic anhydride.

The thermal stability of phthalocyanine complexes was verified by thermogravimetric analysis. Fig. 2 presents the recorded curves of weight loss for three phthalocyanines and their thermal stabilities follow the order: product **1** > product **3** > product **2** in nitrogen atmosphere. The first weight loss (11.2%) of product **2** takes place between 190 °C and 350 °C corresponding to the decomposition of side chains of cobalt phthalocyanine, while the second weight loss, which starts to destroy the phthalocyanine rings, starts from 484 °C. When heated to 800 °C, most of product **2** had been decomposed.

Table 1
Solubility test of cobalt phthalocyanine derivatives

Sample	THF	$CHCl_3$	Toluene	Ethanol	DMF	H_2O (pH > 7)	Acetone
1	−	−	−	−	+	−	−
2	+−	−	−	−	+	+	−
3	−	−	−	−	+	+	−

+, soluble; −, insoluble; +−, soluble partially.

The solubility of cobalt phthalocyanines was investigated and the result shown in Table 1. In contrast with product **1**, which is only soluble in aprotic solvents like DMF, products **2** and **3** can also be dissolved in dilute sodium hydroxide because the dissociated carboxyl groups on the phthalocyanine rings increase the repulsion force and reduce the aggregation of phthalocyanine molecules, so improving the solubility of complexes. Moreover, product **2** is partially soluble in THF, which is thought due to substituting of the functional groups on the phthalocyanine ring to enhance the solubility of cobalt phthalocyanine derivatives.

The UV/VIS absorption spectra of the phthalocyanine system exhibit characteristic Q and B bands. Many researchers have found that the dimerization of sulfonated copper phthalocyanine causes the Q band to shift to 630 nm. Changes in solvents and differences in the central metal atom do not dramatically change the absorption spectra [19]. Because of the insolubility of product **1** in aqueous solution, three cobalt phthalocyanines were dissolved in DMF and their electronic spectra evaluated in Fig. 3. All of them showed typical electronic spectra with two strong absorption regions,

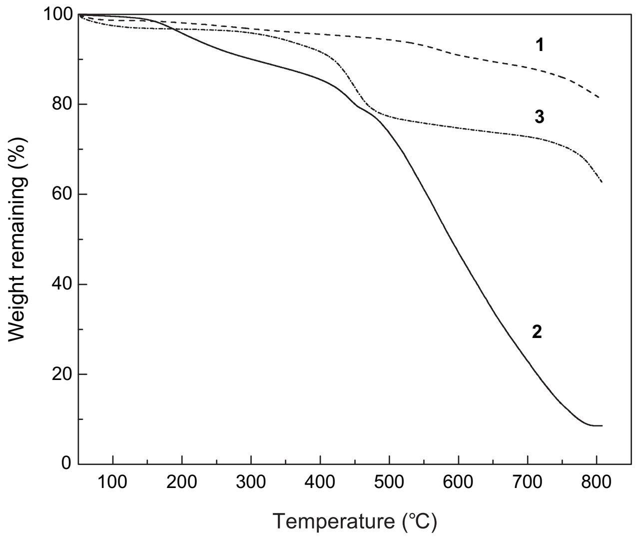

Fig. 2. Dynamic thermogravimetric analytical curves of **1**, **2** and **3**.

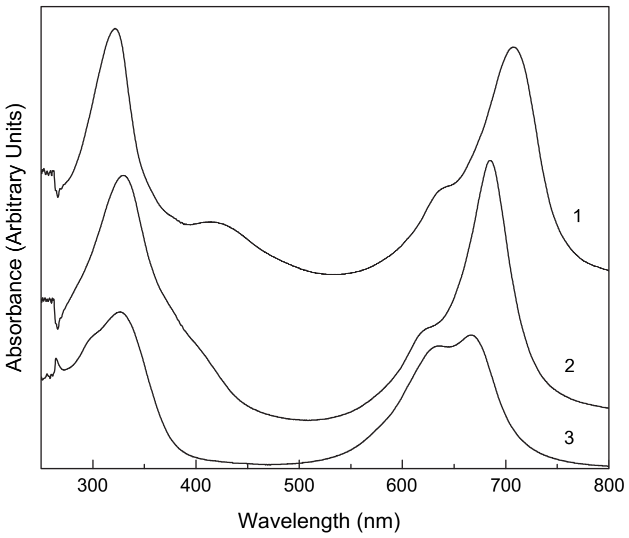

Fig. 3. Visible spectra of **1**, **2** and **3** in DMF solution at 25 °C.

$$HSCH_2CH_2OH + OH^- \longrightarrow {}^-SCH_2CH_2OH + H_2O$$

$$4\,{}^-SCH_2CH_2OH + O_2 + 2H_2O \longrightarrow 2HOCH_2CH_2SSCH_2CH_2OH + 4OH^-$$

Scheme 2.

one in UV region at about 330 nm (B band) and the other in the visible region at 670–720 nm(Q band) with a weaker satellite band around 600–635 nm [20]. From product **1**–**3**, Q bands of three phthalocyanines shift from 708 nm^{-1} to 660 nm^{-1}. This is because the electron-donating ability of amino group weakens after the conjugation effect takes place between the lone electron pair of nitrogen atom and unsaturated double bonds of side chains of product **2**. Additionally, for product **3**, the electronic density of phthalocyanine ring declines most, solely due to the carboxyl group acting as an electron-acceptor group. Significant absorption for product **1** can be observed at 420 nm^{-1} corresponding to the electron-donor capacity of amino group, but the absorption at the same position for product **2** is smaller, while the absorption does not appear at this position for product **3** [21].

It is known that the homogeneous or heterogeneous catalytic oxidation of MEA by oxygen in the presence of cobalt phthalocyanine complexes results in the formation of disulfides, according to the reaction shown in Scheme 2.

The redox process and reaction mechanism have been thoroughly studied [22]. Ionised thiol group ($^-SCH_2CH_2OH$) and an oxygen molecule coordinate reversely with the central metal of phthalocyanine and form a ternary complex. After the ligand exchange process, the pathway involves the single-electron transfer from $^-SCH_2CH_2OH$ to O_2 through the central metal atom, forming the radical $RS^\bullet$ and $O_2^{\bullet-}$. The single-electron transfer process is the rate-determining step in the oxidation reaction. Following the rate-determining step, the succeeding steps are rapid: $O_2^{\bullet-}$ reacts with the other $^-SCH_2CH_2OH$, forming $HOCH_2CH_2SSCH_2$-CH_2OH and O_2^{2-}. The O_2^{2-} ion then reacts with H^+, giving H_2O_2, which is finally decomposed by a catalase-like reaction to O_2 and H_2O.

The linear time dependence of oxygen consumption in MEA homogeneous oxidation allows direct comparison between the estimated rates. The initial reaction rate may be deduced from the slope of the oxygen consumption curve [15], as shown in Scheme 3. Fig. 4 presents rates of MEA oxidation by three phthalocyanines in a homogeneous DMF solution for the insolubility of product **1** in aqueous solution. Compared with product **3**, the oxidation of MEA proceeds at a much higher rate under the catalysis of product **2**, while product **1** has the highest catalytic activity (Table 2). The difference of catalyst effectiveness is attributed to the formation in solution of inactive dimers of the phthalocyanine complexes, which significantly affects their catalytic properties. This aggregation phenomenon is usually depicted as a coplanar association of the aromatic rings driven by enhanced Van der Waals' forces and dimer formation through μ-oxo bridges and was normally determined by two factors: the electron-donating ability and the size of substituted group on the phthalocyanine rings [23]. With the increase of electron-donating ability and size of substituted groups, the aggregation of phthalocyanine will decrease gradually. In Fig. 4, it is observed that the blue shift of the absorption maximum at higher wavelength (around 660–710 nm) and the reduction of intensity along with the enhancement of absorption intensity at lower wavelength (around 620–635 nm). Therefore it can be concluded that most of product **1** and product **2** exist as monomer due to strong electron-donating group (NH_2, product **1**) and bulky substituted group (product **2**), while obvious aggregation takes place in the solution of product **3**. When the dimer of phthalocyanine formats in the solution, it will hinder the coordination of $^-SCH_2CH_2OH$ and O_2 molecule with the cobalt atom. Consequentially, the catalyst effectiveness is substantially reduced. In this case, the aggregation of product **3** is most obvious, so its catalytic activity on MEA is the lowest in DMF solution.

$$Ro = \left.\frac{-d[O_2]}{dt}\right|_{t=0}$$

Scheme 3.

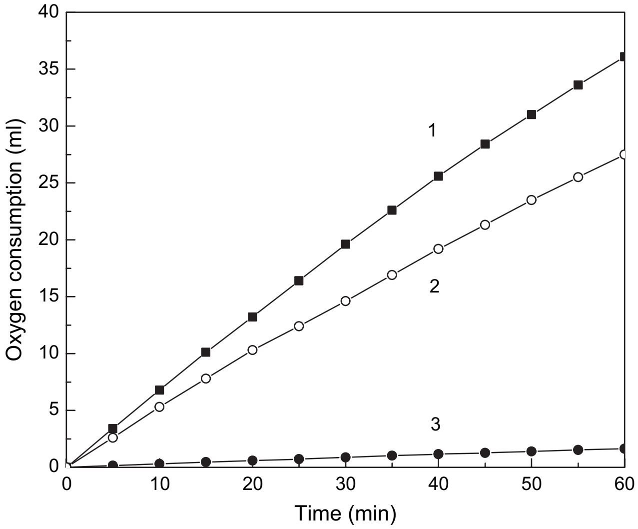

Fig. 4. Oxidation of MEA catalysed by **1**, **2** and **3** in DMF solution ([CoPc], 1×10^{-5} mol/l; $[MEA]_0$, 0.1 mol/l; 25 °C).

The catalytic properties of product **2** and product **3** on the oxidation of MEA were also evaluated in aqueous solution. Fig. 5 illustrates the rate of oxygen consumption during the oxidation of MEA at 25 °C

Table 2
Oxidation of MEA (0.1 mol/l) catalyzed by cobalt phthalocyanines (1.0×10^{-5} mol/l)

No.	Sample	Solvent	Temperature (°C)	R_o[a] (10^{-4} mol l^{-1} min^{-1})	Turnover of MEA after 60 min
1	–	H_2O (pH = 11)	25.0	0.059	2.23
2	–	DMF	25.0	–	–
3	1	DMF	25.0	0.06	1.46
4	2	DMF	25.0	1.10	24.6
5	3	DMF	25.0	1.45	32.2
6	2	H_2O (pH = 11)	25.0	2.13	45.5
7	3	H_2O (pH = 11)	25.0	1.25	28.1
8	2	H_2O (pH = 11)	37.0	3.37	66.3
9	2	H_2O (pH = 11)	50.0	4.95	86.0

[a] $R_o = -d[O_2]/dt$, $t = 0$ min.

and pH 11.0. It is concluded that product **2** is a more effective catalyst than product **3** in this reaction. After 180 min, almost 95.3% of MEA has been eliminated for product **2**, only 71.8% under the catalysis of product **3**.

The dependence of R_o on the pH of the reaction is shown in Fig. 6. It is clear that the oxygen consumption (and thus R_o) increases as pH rises from 6 to 11 and then rapidly decreases. This is attributable to the dissociation of MEA which produces $^{-}SCH_2CH_2OH$ afterward (Scheme 2). In addition, when the pH of the solution is above 11, the excess hydroxyl will hinder the combination between $^{-}SCH_2CH_2OH$ and the phthalocyanine rings, and then lead to a fall in catalytic activity. Meanwhile, the catalytic activity of product **2** was studied at different temperatures (25, 35, 50 °C) and the R_o of catalyst and turnover of MEA after 60 min are presented in Table 2. With the reaction temperature rising, the increment of catalytic activity states that the oxidation of MEA is an endothermic reaction in the presence of product **2** in aqueous solution.

4. Conclusions

A novel aqueous soluble cobalt phthalocyanine was synthesized through modification of cobalt-tetraaminophthalocyanine. Compared with some other phthalocyanine, such as product **1** and product **3**, it has some great advantages:

- It can be synthesized through modification of product **1** under ambient conditions and can give high yield and quality through a simple dissolving-precipitation method.
- Good catalytic activity was achieved on the oxidation of MEA in DMF or aqueous solution.
- With unsaturated double bonds in the side chains of product **2**, it offers an opportunity to copolymerize this product with other monomers. The copolymers are expected to mimic natural enzymes containing an active center and protein matrix. The study on such biopolymers is helpful for us to understand exactly the catalytic mechanism of enzyme.

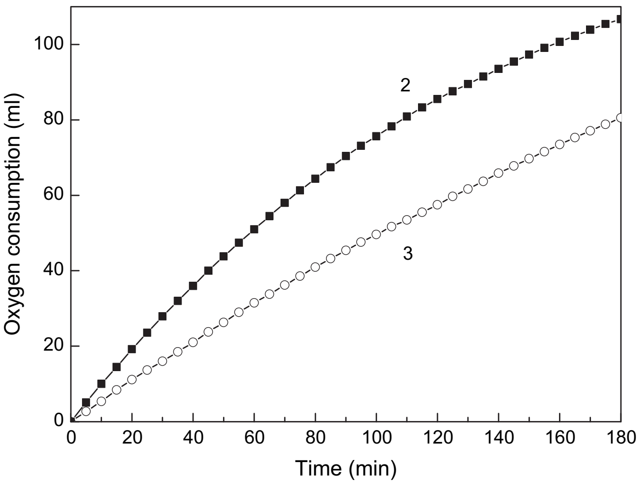

Fig. 5. Oxidation of MEA catalysed by **2** and **3** in aqueous solution ([CoPc], 1×10^{-5} mol/l; $[MEA]_0$, 0.1 mol/l; pH 11; 25 °C).

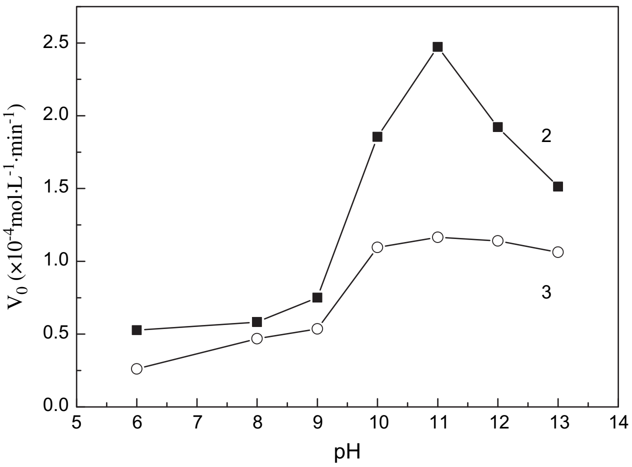

Fig. 6. Effect of pH on the rate of oxidation of MEA catalysed by **2** and **3** in aqueous solution ([CoPc], 1×10^{-5} mol/l; $[MEA]_0$, 0.1 mol/l; 25 °C).

Acknowledgments

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