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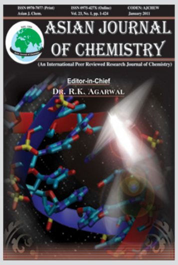

Facile Synthesis of a Water-Soluble Cobalt Phthalocyanine Derivative

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The water-soluble tetra-β-carboxymethyleneaminophthalocyanine cobalt is synthesized, in one step, from tetra-β-aminophthalocyanine cobalt. The synthesized compound, as a catalyst in oxidation of sulfide, behaves enhanced catalytic activity relative to tetra-β-carboxyphthalocyanine cobalt.

Key Words: Phthalocyanine, Synthesis, Solubility, Catalysis.

INTRODUCTION

Phthalocyanine (Pc) molecules possess of special 18-π electron conjugated aromatic systems that endow them with not only high chemical stabilities but also superior electronic transfer abilities[1]. The outstanding properties cause them have significant applications in many areas such as catalysis[2], photochemistry[3], electrochemistry[4], nonlinear optics[5], information storage[6] and photodynamic therapy[7], *etc*. These applications can be reinforced by modifying phthalocyanine compounds, *e.g.*, displacing two hydrogen atoms in the center of phthalocyanine ring with different metals[8] or substituting hydrogen atoms around the periphery of phthalocyanine ring with different substituents[9], to generate new derivatives with enhanced functions. It is well known that some water-soluble metal phthalocyanine derivatives have found special applications as catalysts in industrial desulphurization[10]. As catalysts, the high catalytic efficiency and strongly antitoxic function against cyanide met under industrial circumstance are necessary. The water-soluble cobalt phthalocyanine compounds including carboxylic groups had the two efficacies[11]. But one limitation difficultly shook off for them is the intermolecular congregating action in water, which leads lowly active oligomers to form and accordingly derogates the catalytic activities greatly[12]. An efficient strategy to restrain aggregation is to increase the intermolecular electrostatic repulsion force by linking new ionized groups on periphery of phthalocyanine rings[13]. Based on this idea, a water-soluble cobalt phthalocyanine derivative **2** bearing four carboxymethyleneamino groups around molecular periphery was designed and synthesized from tetra-β-aminophthalocyanine cobalt **1** and characterized by MS, ^{1}H NMR, IR, UV-vis, *etc*. The catalysis of **2** in oxidation of sulfide was studied and compared with tetra-β-carboxyphthalocyanine cobalt **3**. The results showed that **2** behaved lower congregating tendency and higher catalytic activity.

EXPERIMENTAL

Compounds **1** and **3** were synthesized according to the methods described as in the literatures[14,15], respectively. 40 % 2-oxoacetic acid, DMSO and $Na_2S\cdot 9H_2O$ are commercial available and used without further purification.

^{1}H NMR spectra were recorded on a Bruker AV 400 spectrometer. IR spectra were measured on a Magna 560 FT-IR spectrometer. UV-Vis spectra were taken on a Cary 500 UV-vis-NIR spectrophotometer. MS spectra were obtained on a LDI-1700-TOF mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer.

General procedure: Synthesis of **2**: The black green powder of **1** (1.15 g, 1.8 mmol) was added to DMSO (8 mL). The resulting solution was stirred for 10 min and then 40 % 2-oxoacetic acid (2 mL) was added. The solution was stirred at 60 ºC for 24 h and then poured into 0.1 mol/L hydrochloric acid (50 mL). After precipitation and filtration, the crude product was washed thoroughly with the same hydrochloric acid and dried in air to afford blue powder **2** (1.32 g, 86 %); ^{1}H NMR (400 MHz, DMSO): δ 13.18 (s, 4H, broad, 4COOH), 9.24 (s, 4H, 4N=CHC), 9.58 (d, 4H, broad, J = 8Hz, 4ArH), 9.50 (d, 4H, broad, $J = 8$Hz, 4ArH), 8.33 (s, 4H, broad, 4ArH); MS (DMSO): m/z calcd for $[M^+]$: 855.6, found: 856.9 $[M^+ + 1]$; IR (KBr, ν_{max}, cm^{-1}): 3741, 3624, 1691, 1676, 1653, 1577, 1550, 1540, 1516, 674, 650, 418; Anal. calcd. (%) for $C_{40}H_{20}N_{12}O_8Co$ (855.6): C 56.15, H 2.36, N 19.64, found (%): C 56.11, H 4.58, N 19.71.

Catalytic oxidation of sulfide: All experiments for the catalytic oxidation of sulfide were performed at 27.5 ºC. Standard Na_2CO_3-$NaHCO_3$ buffer solution (Na_2CO_3: 0.3 M, $NaHCO_3$: 0.1 M, pH 10) was employed as solvent to dissolve compounds **2** and **3**, *etc*. A reaction instillation[16] was framed like Fig. 1. A 100 mL airtight three-neck flask equipped with a magnetic stirrer and enveloped with rubber plugs was used as the reactor. The middle neck was connected *via* rubber plug, glass tube and latex tube with detecting device, namely, an U-type equipment designed with two 50 mL burettes in-between connected by a section of latex tube. The U-type tube was infused with some water to airproof the reactor to show oxygen consumption during reaction. The consumed oxygen in reaction equals to the volume indicated by uplifted surface in the left burette or depressed surface in the right burette under equal pressures inside and outside the airtight reactor. The equal pressures were maintained by adjusting two burettes up and down to cause water columns in them to be equal height. Before reaction, the reactor was turn upside down. The solutions of catalyst **2** (5 mL, 0.05 mmol/L) and sodium sulfide (5 mL, 100 mmol/L) were injected into the left and right necks of reactor through rubber plugs, respectively. The system was not purged with oxygen and the air in it was directly used as oxidant. After the pressure was tuned to be equilibrium as aforesaid method, the reactor was set rightly and the mixture was stirred. The reaction was monitored by oxygen-consumed volume recorded at regular minutes during the course of reaction. As a control experiment, the kinetics of oxidation of sodium sulfide with compound **3** as catalyst was carried out by the similar protocol.

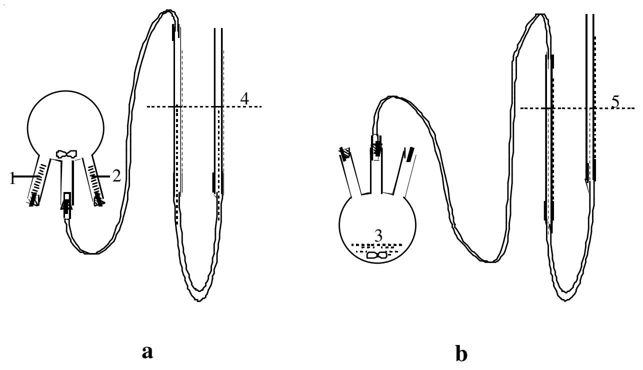
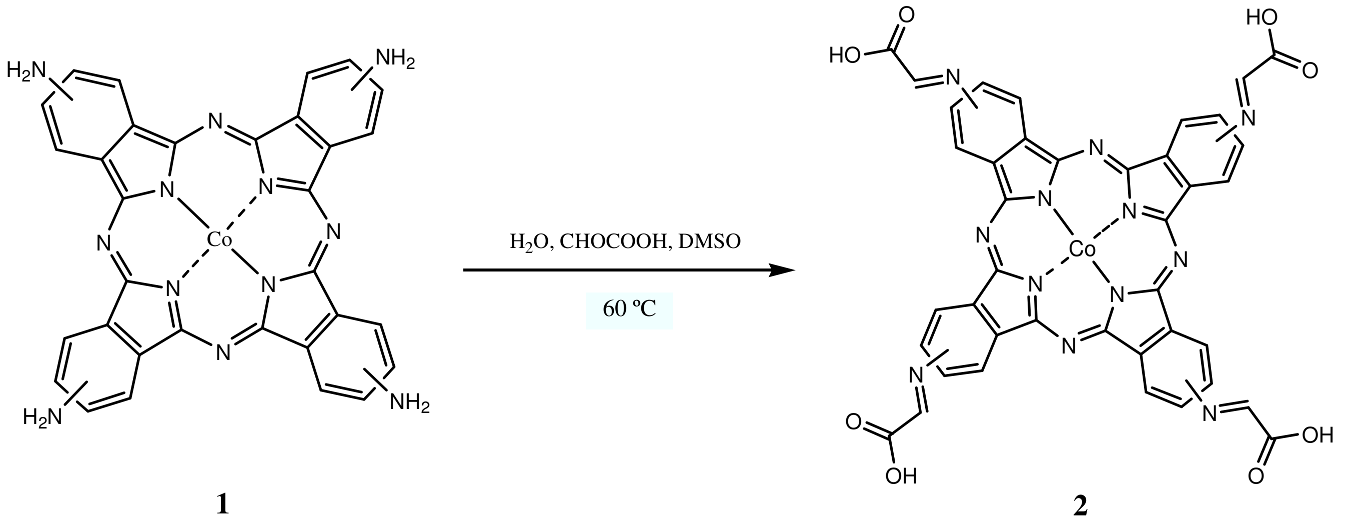


Fig. 1. Simple instillation for catalytic oxidation of sulfide before (a) and during (b) reaction: (1) solution of catalyst **2**; (2) solution of sodium sulfide; (3) reaction mixture; (4) water surface height before reaction; (5) water surface height after catalytic reaction beginning

RESULTS AND DISCUSSION

In general, the substituted metal phthalocyanine compounds were synthesized by cyclotetramerization of resultant phthalonitrile derivatives[17]. The compound **2** was prepared by the common method, it required that 2-oxoacetic acid firstly was taken as an original substrate to synthesize corresponding phthalonitrile, which further was polymerized to be phthalocyanine compound. But 2-oxoacetic acid was unstable under the conventional reaction condition and so the substituted phthalonitrile was difficult to be synthesized. Presuming the targeted phthalonitrile might to be obtained, pure compound **2** was also difficult to be synthesized for that some sub-reactions were likely to occur due to the activity of carboxymethyleneamino group in the phthalonitrile compound. Thus, a novel way is introduced to prepare compound **2**, namely derivation from compound **1** *via* Schiff-base reaction occurred between the amino groups of compound **1** and the carbonyl groups of 2-oxoacetic acid (**Scheme-I**). In the experimental performance, 40 % 2-oxoacetic acid was mixed with DMSO according to 1:4 ratio (v/v), in which 2-oxoacetic acid reacted with compound **1** at 60 ºC. The result showed that compound **1** could be totally transformed into water-soluble product **2** within 2 h. Contrarily when pure 2-oxoacetic acid was treated with compound **1**, could not be completely converted into water-soluble product. The reason might be that the suitable amount of water contained in solution stabilized 2-oxoacetic acid and avoided some sub-reactions of 2-oxoacetic acid occurring at 60 ºC.



Scheme-I: Synthesis of **2** from **1**

Compound **2** can not be dissolved in water in a range of pH ≤ 6, so the purification could be realized by firstly acidifying reaction mixture with 0.1 mol/L hydrochloric acid to precipitate compound **2** and then filtrating by vacuum, washing with the same acid and drying in air. But compound **2** is easily dissolved in aqueous solution in a range of pH ≥ 7 or some polar organic solvents, *e.g.*, THF, DMF and DMSO. The excellent water solubility is attributed to the electrostatic repulsion force among carboxymethyleneamino groups and the affinity between substituent and water. The fine solubility facilitates characterization by MS, ^{1}H NMR, UV-vis, *etc*. The ^{1}H NMR spectrum displayed that all protons in compound **2** are broad bands due to the impact from the center metal in a square planar environment and the oxygen and nitrogen atoms in the substituents. The UV-vis spectra show that the T peak of compound **1**, induced from the electron transfer from amino groups through phthalocyanine ring to center metal[14], has disappeared in the UV-vis spectrum of compound **2** (Fig. 2), which implies that the amino groups have not existed in compound **2** as a result of aforesaid Schiff-base reaction. The Q absorption (640 nm) of compound **2** in aqueous solution offers a broad band and shifts blue 44 nm relative to the Q absorption (684 nm) of compound **2** in DMF (Fig. 2). This phenomenon is common for water-soluble phthalocyanines behaving in water for that some H-type aggregates have formed by face-to-face interaction of phthalocyanine molecules[18]. However, comparing with compound **3**[11], compound **2** gives a correspondingly narrower Q band in water, which means that the aggregation has been effectively restrained in some extent owing to its new molecular structure. This improved dispersion is also testified by TOF-MS, which displays that only monomers and dimers and no oligomers are checked in the aqueous solution of compound **2** (Fig. 3).

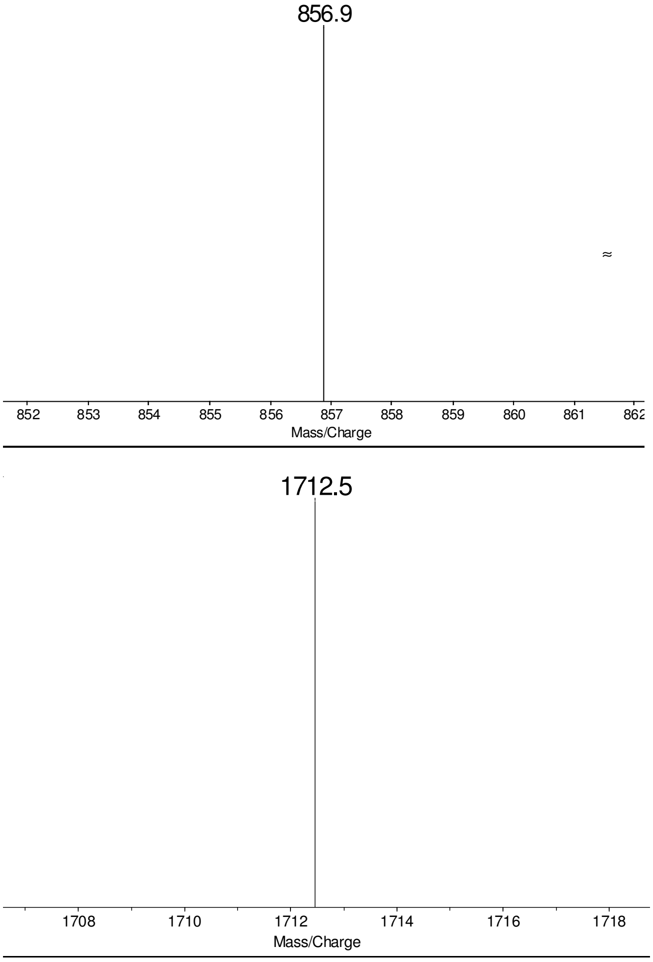


Fig. 3. TOF-MS of **2** in water: m/z, 856.9 (monomer); 1712.5 (dimer)

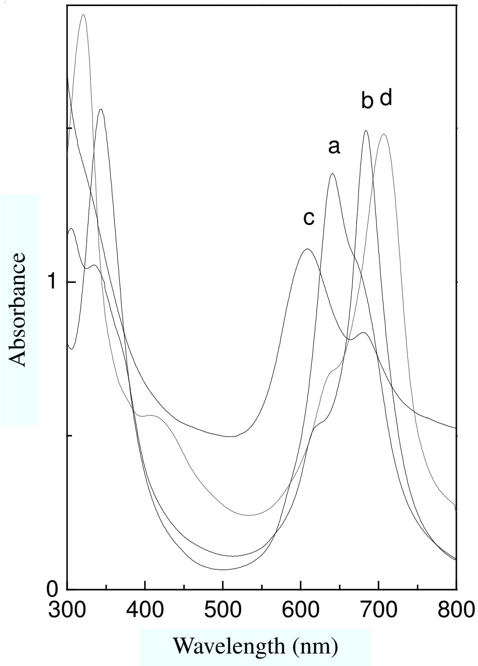


Fig. 2. UV-Vis spectra of **2** in water (a) and DMF (b), **3** in water (c) and **1** in DMF (d) 1.0 × 10^{-5} mol/L

In order to understand the catalytic activity of compound **2**, a catalytic oxidation reaction of sodium sulfide and a control experiment were performed with compounds **2** and **3** as catalysts, respectively. Fig. 4 revealed that the catalytic activity of compound **2**, denoted by the oxygen-consumed rate in the course of oxidation reaction of sodium sulfide at 27.5 ºC and pH 10. After 30 min, the volume of consumed oxygen in the reaction system with compound **2** as catalyst was almost three times of that with compound **3** as catalyst. That was to say that compound **2** was more effective catalyst than compound **3** in this reaction. In terms of the molecular structures of compounds **2** and **3**,

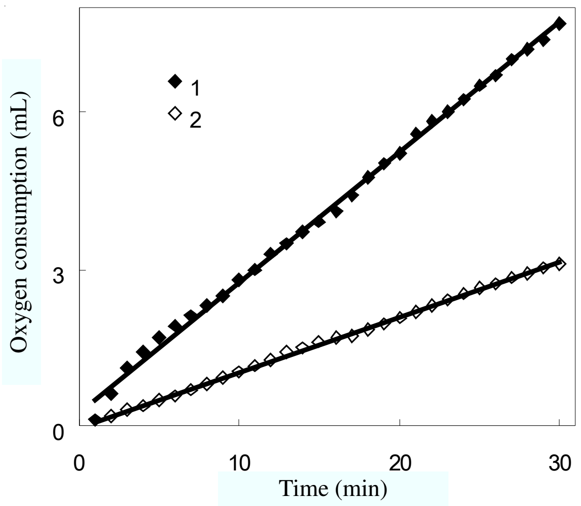


Fig. 4. Kinetics of oxidation of sodium sulfide catalyzed by **2** (1) and **3** (2), respectively

the enhanced catalysis of compound **2** should be derived from the carboxymethyleneamino groups, in which the carboxy groups and the nitrogen atoms all helped to enhance phthalocyanine-intermolecular repulsion force and solvent affinity and then disturbed formation of much aggregates in water. The fine dispersion will favour catalytic activities[12]. So, compound **2** behaved better catalytic activity than compound **3**.

Conclusion

In summary, a new cobalt phthalocyanine derivative **2** with both excellent water-solubility and enhanced catalysis was synthesized by a facile strategy, namely derivation from **1** *via* one step Schiff-base reaction occurring between amino groups of **1** and carbonyl groups of 2-oxoacetic acid. Carboxymethyleneamino groups cause **2** to be easily dissolved in aqueous solutions at pH ≥ 7 and behave enhanced catalysis in oxidation of sulfide. The synthetic protocol is suitable to prepare some structurally special phthalocyanine compounds that might not be synthesized by common cyclotetramerization of resultant phthalonitrile derivatives. It is imaged that a series of water-soluble cobalt phthalocyanine derivatives, bearing functionalized groups to enhance the intermolecular repulsion to restrain molecular aggregates, will be synthesized by the similar way *via* replacing 2-oxoacetic acid with other suitable substrates, from which some desired catalysts should be found.

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