Preparation and characterization of poly-Schiff base cobalt-copper phthalocyanine bimetallic complex

LI XI-LAN, SONG JIA-LONG, GUO XIU-FEN, SUN GUAG-YAN
Zhuhai College of Jilin University, Zhuhai519041
corresponding author’s e-mail: renxiue19@jluzh.edu.cn

Abstract: Schiff bases can undergo coordination reactions with metals to form polymer complexes. The method of synthesizing Schiff base is simple and easy to operate. This article mainly synthesizes mononuclear metal copper phthalocyanine and polymer o-phthalimide salicylaldehyde Schiff base cobalt-copper phthalocyanine bimetallic complex, and the Schiff base complex. It is analyzed and characterized by infrared, ultraviolet and scanning electron microscopy.

1. Preface
Salen Schiff base has been widely studied in the field of simulating cytochrome P-450 catalyzed epoxidation of olefins due to its central structure is very similar to that of metalloporphyrin [1], but it is easy to inactivate and difficult to use after use. Recycling, so polymerization is one of the solutions. Phthalocyanine (H₂Pc) is a synthetic compound with a tetraazatetrabenzoporphyrin structure. The structure is similar to the porphyrin that exists widely in nature, and the molecule has an 18-electron macrocyclic conjugated system. Phthalocyanine has high stability to light, heat and even acid and alkali, and has strong coordination ability. It can react with almost all metal elements to form metal complexes with special colors, commonly known as metal phthalocyanines. Cyanine (metallophthalocyanine, MPc) [2].

Molecular oxygen is an essential element for life activities. This substance has the characteristics of easy availability of raw materials, high oxidation efficiency, and environmental friendliness. Therefore, molecular oxygen is the most ideal oxidant in the field of biomimetic catalytic oxidation and the most promising oxidant for industrial applications [3]. In the long-term research, the author found that metal porphyrins or porphyrin-like compounds are covalently bonded to the polymer chain and exhibit good catalytic activity and selectivity with the participation of molecular oxygen [4, 5, 6, 7]. In this paper, a polymer Schiff base cobalt-copper phthalocyanine bimetallic complex was synthesized by the method of interfacial polycondensation, and its catalytic performance was studied.

2. Experimental part
2.1. Experimental instrument
Infrared spectroscopy (IR): IRAffinity-1 produced by Shimadzu Corporation of Japan
Ultraviolet visible spectrophotometer (UV-Vis): adopts UV-2450 produced by Shimadzu Corporation of Japan
Scanning Electron Microscope (SEM): Japan JEOL UK Oxford Scanning Electron Microscope-Energy Spectrometer, model JSM-5600LV Oxford-Inca
2.2. Experimental reagents
2,4-Dihydroxybenzaldehyde (Analytical grade, Shanghai Reagent No. 1 Factory); Copper chloride (Analytical grade, Tianjin Shuanghuan Chemical Reagent Factory); Cobalt acetate (Analytical grade, Beijing Shuanghuan Chemical Reagent Factory); Formic anhydride (analytical grade, Tianjin No. 1 Chemical Reagent Factory); o-phenylenediadmine (analytical grade, China National Pharmaceutical Group) Shanghai Chemical Reagent Company); n-propanol (analytical grade, Shanghai Jianxin Chemical Co., Ltd. Reagent Factory); Chlorosulfonic acid (analytical grade, Shanghai Jinshanting New Chemical Reagent Factory); Dichloromethane (Analytical grade, Shanghai Jianxin Chemical Co., Ltd. Reagent Factory); Trichloromethane (Analytical grade, Shanghai Jianxin Chemical Co., Ltd. Reagent Factory); Anhydrous ethanol (AR), LaiyangShuangshuang Chemical Reagent Factory, China; Toluene (Analytical Pure, Shanghai Jianxin Chemical Co., Ltd. Reagent Factory); Ammonia (Analytical Pure, Guangzhou Chemical Reagent Factory).

2.3. Preparation of mononuclear metal copper phthalocyanine (PcCu) \(^8\)
Accurately weigh 5.1 g of CuCl\(_2\)-2H\(_2\)O, 26.67 g of phthalic anhydride, 54.1 g of urea and about 2% of the total weight of ammonium molybdate into a mortar, carefully grind into a powder and mix it evenly. The powder was transferred to a beaker, stirred continuously and heated to 165-185°C, until the entire substance became purple-black, and continued to be heated to 200°C for a constant temperature reaction for 2 hours. The product after the reaction was naturally cooled to room temperature, filtered, washed with methanol to remove trichlorobenzene in the filter cake, and then washed with 2% sodium hydroxide solution and hydrochloric acid solution, and finally washed with water until the pH value was medium It can be transferred to an oven at 80°C for drying, and approximately 14.17 g of dark blue copper phthalocyanine can be obtained, with a purity of about 95% and a yield of 82%.

2.4. Preparation of cobalt-copper phthalocyanine bimetallic complexes of high polymer o-phenylenediimide salicylaldehyde Schiff base
Weigh 0.81 g of Co(di-OHSalphen) into 5 mL of 0.8 mol/L NaOH aqueous solution, keep stirring until it is completely dissolved, then add about 5% of PTC, and slowly add 0.97 g of copperphthalein dissolved under stirring 2 mL of ClCH\(_2\)CH\(_2\)Cl solution of cyanine sulfonyl chloride. At this time, you can see the formation of insoluble substances. Continue the reaction for 2 h under stirring. The product is suction filtered, and then washed with 10% NaOH aqueous solution, ethanol and water several times. After vacuum drying, 0.95 g of black flake polymer can be obtained, with a yield of 60%.

3. Results and discussion
3.1. Infrared spectrum
Table 1 shows the attribution of the infrared spectrum absorption peak data of ligands and macromolecular metal complexes. Among them, the vibration absorption peaks of the aromatic ring (Ar-H) of small molecule ligands and polymer metal complexes both appear at about 3070 cm\(^{-1}\). Because the C=N double bond and the benzene ring can form a larger conjugated system, the absorption peak shifts to the low wave number direction, appearing in the range of 1660-1620 cm\(^{-1}\), and the absorption peak part of the (C=C) with the benzene ring overlapping. After the two ligands of CuPcSO\(_2\)Cl and Co(di-OHSalphen) undergo polycondensation reaction to form a polymer Schiff base cobalt-copper phthalocyanine binuclear complex, the characteristic absorption peak of as(SO\(_2\)) moves to the low wavenumber direction, which is 1365 cm\(^{-1}\). The characteristic absorption peak of s(SO\(_2\)) shifts to the high wavenumber azimuth, which is 1193 cm\(^{-1}\). At the same time, the characteristic absorption peaks of Co-N, Co-O and Cu-N bonds also appeared at 460500 cm\(^{-1}\), indicating that the transition metal ions are coordinated with the N and O atoms of the two functional ligands, and finally A metal complex is formed.
Table 1 R data (cm\(^{-1}\)) and attribution of the monomer and its polymer Schiff base cobalt-copper phthalocyanine binuclear complex

| Complexes          | \(v_{(Ar-H)}\) | \(v_{(C=N)}\) | \(v_{(C-O-C)}\) | \(v_{as(S-O)}\) | \(v_{s(S-O)}\) | \(v_{(Co-O)}\) | \(v_{(Co-N)/v_{(Co-N)}}\) |
|--------------------|----------------|---------------|-----------------|----------------|----------------|----------------|---------------------|
| CuPc               | 3051           | 1615          | ----            | ----           | ----           | 428            |                     |
| PSalenCo-PcCu      | 3086           | 1608          | 1265/1179/1089  | 1365           | 1193           | 504            | 463/450             |

3.2. Characterization of UV-Vis Spectra

Metal phthalocyanines have obvious absorption in the ultraviolet and visible regions. Visible light region has stronger absorption and is generally named Q absorption band; while its absorption in ultraviolet region is relatively weak, and is generally called B band or Soret band. The test data of Salen-type Schiff bases, metal phthalocyanines and their high-molecular polymers are shown in Table 2. Different from Schiff bases, the characteristic absorption peaks of phthalocyanine and its derivatives not only absorb in B, but also have obvious absorption in Q band. First, the UV-Vis spectrum of CuPc was tested in a tetrahydrofuran solution with a concentration of 1.5×10\(^{-4}\) mol\(\cdot\)L\(^{-1}\). The B band and Q band showed significant absorption peaks at 310, 560, and 690 nm. Due to the poor solubility of PSalenCo-PcCu, the UV-Vis diffuse reflectance spectrum of the solid sample was tested, and the characteristic peaks appeared at 310, 600 and 730 nm. From a comprehensive point of view of the results, because the ligand and polymer both contain benzene rings, they have stable absorption at 310 nm in the B band in the ultraviolet region, but the absorption range of the Q band in the visible region is larger, but it shows a certain change rule. That is, the absorption position of the absorption peaks of CuPc and PSalenCo-PcCu extends to the high band. The reason for this phenomenon is most likely due to the chromophore action of the ligand, which drives the red shift of the polymeric metal phthalocyanine compound.

Table 2 Ultraviolet-visible electronic absorption spectra of ligands and polymer compounds

| Compounds          | B band \(\lambda\) (nm) | Intensity (Abs) | Q band \(\lambda\) (nm) | Intensity (Abs) |
|--------------------|-------------------------|-----------------|-------------------------|-----------------|
| CuPc               | 310                     | 2.0             | 560, 690                | 2.4, 1.9        |
| PSalenCo-PcCu      | 310                     | 1.7             | 600, 730                | 1.7, 1.5        |

3.3. Polymer Morphology

In order to observe the appearance of small molecule CuPc and high molecular polymer PsalPhenCo-PcCu more intuitively, the author did a scanning electron microscope test on it, and its appearance is shown in Figure 1. It can be seen from the figure that the small molecule CuPc belongs to relatively regular needle-like crystals, while the polymer PsalPhenCo-PcCu shows an obvious flat sheet structure. Therefore, we can infer that CuPc with a small molecule structure is polycondensed in a plane two-dimensional direction; while the polymer PsalPhenCo-PcCu can be regarded as a regular planar macromolecular polymer.
4. Conclusion
In this project, the poly-Schiff base cobalt-copper phthalocyanine bimetallic complex (PSalenCo-PcCu) was prepared for the first time by the method of interfacial polycondensation. The composition and structure of the complex were studied, and the infrared spectra and ultraviolet spectra of the ligand and the complex were measured. Visible spectroscopy, and the structure of the polymer was characterized by scanning electron microscopy. The author found that the overall structure of the poly-Schiff base cobalt-copper phthalocyanine bimetallic complex is flaky, which fully proves that the phthalocyanine and the Schiff base are polymerized in a two-dimensional plane.

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