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Synthesis and Characterization of Meso-Tetra (o-nitro) phenyltetraphenylporphyrin (IV)

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ABSTRACT

Benzoporphyrin is a porphyrin derivative with β-pyrrole ring and benzene ring. It is a macrocyclic aromatic compound with 18π electron structure. Because of the benzene ring, the porphyrin conjugation system is expanded, which enriches the π-electrons with special structure and properties. Therefore, it has a wide range of applications and can be used as a new type of photosensitizing molecules. It shows good application in light functional materials prospect. In this paper, the thermo-coagulation method was used to synthesize the intermediate-tetrakis (o-nitro) n phenyltetraphenylpyridinium zinc (II) (P-phenanthroline) by using potassium phthalimide, o-nitrophenylacetic acid and zinc acetate as raw materials. With hydrochloric acid and glacial acetic acid zinc ions were removed in the ice water bath, resulting in the media-tetra (o-nitro) phenyl tetraphenylporphyrin. Under microwave heating, the median-four (O-nitro) phenyl tetraphenylporphyrin (IV) was prepared by the reaction of o-nitro-phenyl-tetraphenylporphyrin with stannous chloride. These compounds were characterized using UV and infrared spectroscopy.

KEYWORDS: porphyrin; synthesis; spectral characterization

1. Introduction

1.1. Introduction to porphyrins

Porphyrin (s) is a macromolecule heterocyclic compound formed by the interconnection of four α-carbon atoms of the pyrrole subunit through a methine bridge (= CH-). The four nitrogen atoms in the center contain a soliton of metal porphyrins which are capable of generating 18 P electrons in combination with metal ions, and the electron mobility in the ring is very good. Therefore, most of the metal porphyrins have good optical properties. During the formation of metal porphyrins, transition between the electronic energy level occurred, which absorbing or radiating energy.

The parent compound of Porphyrin is porphin (porphin, C20H14N4). Porphin is aromatic, contains 18 π electrons in its closed ring. In general, the 5, 10, 15, 20 positions on the pyrrole ring is called meso, and the four nitrogen atoms occupy position 21, 22, 23 and 24, respectively. The position of the porphyrin ring relative to the β position is also called the β position of porphins. When the hydrogen atoms on the large conjugated ring of the porphine are partially or totally substituted by other groups, the resulting derivative is porphyrin whose nitrogen atoms can be combined with metal ions to produce very stable organic Complexes and metalloporphyrins. There are many natural porphyrins and their metal complexes, such as chlorophyll [1], heme [2], vitamin B12, cytochrome P-450 [3], catalase, and so on. The most prominent chemical activity of the porphyrin system is that it is easy to form a 1: 1 complex with metal ions [4]. Due to the special structure and properties of porphyrin compounds, it has a wide range of uses. Natural porphyrin compounds have many special physiological activities [5], and many of the functions of life processes are related to metalloporphyrins. In addition, there are many broad applications in other fields, such as materials chemistry, pharmacochemistry, electrochemistry, photophysics and photochemistry [6], analytical chemistry, organic chemistry, biomimetic chemistry [7], and photochemistry [9] prospect.

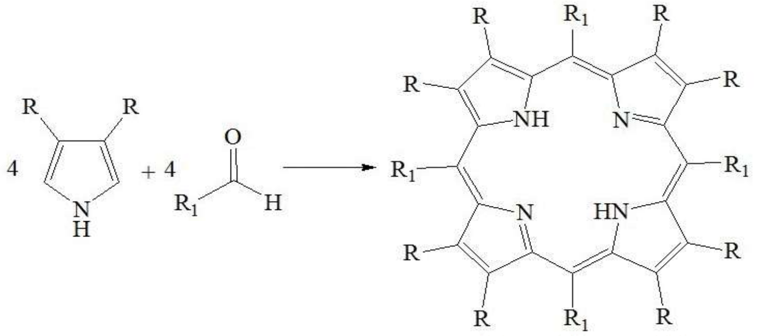
1.2. Synthesis of porphyrins

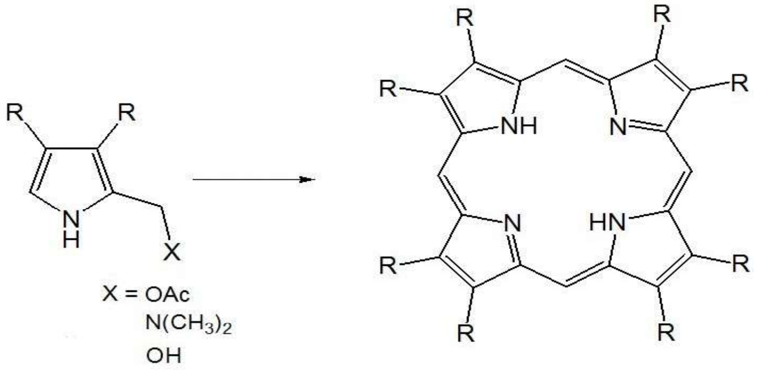
There are many porphyrin synthesis methods, mainly as follows:

1.2.1. The tetramerization of monopyrrole

Alder-Longo method [10], using the reaction between 2,5-unsubstituted pyrrole and aldehyde with the provision of bridged methylene, to obtain a symmetrical porphyrin, which can be used to synthesize meso-substituted porphyrin (Figure 1). By changing the types of substituents R and R1, adjusting the ratio of aldehydes and pyrrole, a variety of symmetric and asymmetric porphyrins can be synthesized.

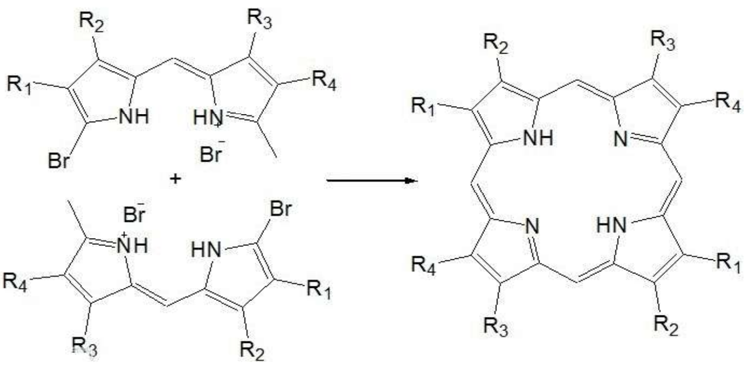
The tetrameric reaction of another monopyrrole is the use of 2-substituted pyrrole as the starting material to obtain a symmetrical (two different substituents in the alternate position) porphyrin, which is also known as the 'head-to-tail' condensation ring [11] (Figure 2).



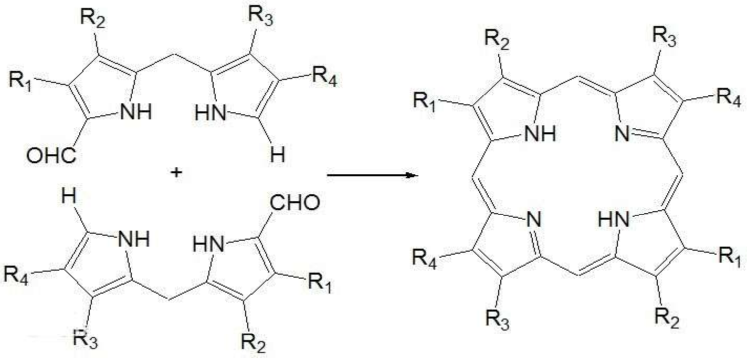


1.2.2. The condensation of dipyrrole intermediates

Fischer method [12]: A higher yield of porphyrins (see Figure 3) is obtained from 1-bromo-9-methyldipyrromethenes at 200 °C of organic acids (usually propionic acid).

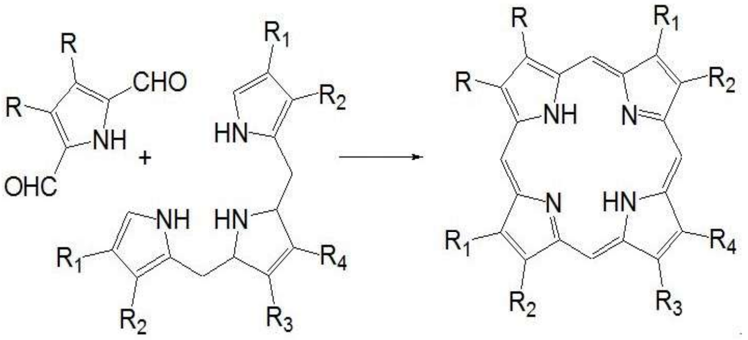


MacDonald Act [13]: 1-unsubstituted-9-formyldipyrromethanes is self-aggregating in an acid catalyst (such as hydroiodic acid or p-toluenesulfonic acid) (Figure 4). This synthesis method is more commonly used as dipyromethane is easier to prepare.



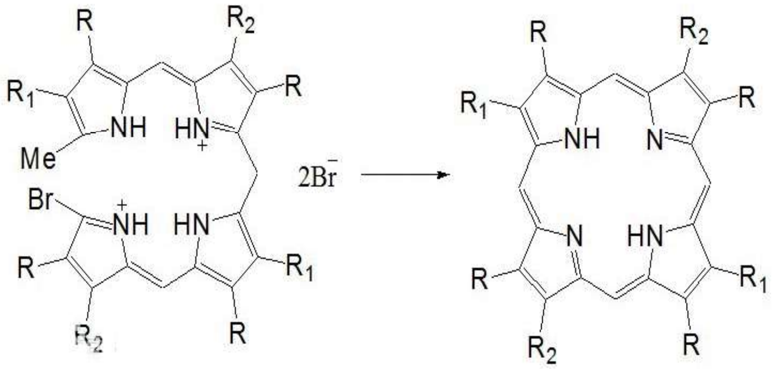
1.2.3. '3 + 1' synthetic method [14]

The tripyrrole compound utilizes the condensation between β-H and the aldehyde group of dicarboxylpyrrole (Figure 5) to obtain the target molecule.



1.2.4. Linear tetrapyrrole cyclization [15]

Direct condensation with 1-bromo-19-methyl-a, c-biladienes as the intermediate cyclization to obtain the target porphyrin compound (Fig. 6).



1.2.5 Solid-phase microwave method [16]

In 1992 the French chemist Petit and its collaborators reported the first use of solid-phase microwave method to synthesis TPP, with the yield of 9.5%. After that, many researchers have also used this method to synthesize porphyrins and the yield can be as high as 36% [17].

Microwave heating method is heating due to the medium within the material in the electric field that causes, this heating method has three characteristics: (1) the presence of a large number of ions accelerates heating; (2) quickly reach the reaction temperature.Microwave heating method is popular as the reaction is simple and rapid, produces high yield of products which are easy for separation and with little pollution or no pollution.

1.3. Application of porphyrins

(1) Porphyrin molecular switch

Molecular switch is an important component of molecular computer. Its main advantage is the combination of high density, fast response and high energy efficiency.

(2) Simulate biological photosynthesis

Porphyrin compounds are the core part of macromolecules that constitute chlorophyll and other organisms, involved in the plant photosynthesis and a series of important processes. From the beginning of the early 80s, many porphyrin supramolecular systems containing carotenoids and quinone have been designed and synthesized to simulate and understand the process of photoelectron and energy transfer in the center of photosynthesis, and have made great progress.

(3) Applications in solar cells

There are two kinds of organic solar cells prepared using porphyrins and their derivatives: the Schottky and the P-N heterojunction type. [The Schottky type is missing here:The structure of the PN-type solar cell is: glass substrate / indium-tin oxide (ITO) / n-type dye / p- Type dye / electrode.

(4) In the application of organic electroluminescence

In recent years, porphyrin-doped luminescent materials have become a new research hotspot for organic electroluminescent materials because of their unique photoelectric properties. The porphyrin compounds have strong fluorescence in the solution, but the fluorescence of the solid is weak and the quantum efficiency is low as the porphyrin molecules are easily aggregated to produce their own fluorescence quenching. Therefore, the use of a single porphyrin material as a light-emitting diode is difficult to achieve. In recent years, the introduction of porphyrins dopping or the introduction of porphyrins in polymer chains has become a research hotspot for organic electroluminescent materials. The porphyrin exists mainly in uncoordinated or coordinated form with metal.

(5) In the optical storage device applications

The use of porphyrin compounds in optical storage involves the use of specific optical properties to design new optical memory devices or to improve and increase the performance of optical storage materials.

(6) In the application of light guide materials

Organic Photoconductor (OPC) is a photographic information function material, which refers to a new organic functional material that can cause the formation and migration of photogenerated carriers under the action of light. The device has been applied to electrostatic copying, holography, laser printing and other information processing equipment. It has become an indispensable pillar in this contemporary information society. The study on the photoconductivity of porphyrin has been paid more and more attention, but most of it has studied the doping effect of porphyrin with other excellent photoconductive materials.

1.4. Select the purpose and meaning

In recent years, the synthesis of metal porphyrin complexes is very active. Previously, the synthesis of porphyrin complexes was carried out by liquid phase heating method, which was easy to produce side reactions, and separation and purification were more difficult. At present, solid phase coordination chemistry has been applied to the synthesis of complexes and solid materials. The solid phase synthesis method has been used to synthesize the complex of porphyrin-tetrakis (4-hydroxyphenyl) porphyrin (THPP) with Cu, Pb. As solid phase synthesis is fast and simple, it avoided the side effects of reflow. Yet, the detection means is not perfect, thus it needs to be further studied. At the same time, it has been found that the method of preparing organic metal porphyrin complexes by microwave heating and refluxing is easy and simple. It can be detected by infrared, ultraviolet and fluorescence spectroscopy. It has a very broad prospect. Porphyrins and metalloporphyrins as intermediates of porphyrin series reagents can improve their yields, make their reaction conditions mild, better synthetic properties, and make it better for people to use.

2. Materials and methods

2.1. Experimental materials

2.1.1 Major instruments

DZF-6051-type vacuum oven (Shanghai Jinghong Experimental Equipment Co., Ltd.);

KQ5200B ultrasonic cleaning device (Kunshan City ultrasound Instrument Co., Ltd.);

SHZ-IIID circulating water vacuum pump (Shanghai Yalong biochemical equipment factory);

EL104 electronic balance (METTLER TOLEDO Instruments (Shanghai) Co., Ltd.);

101-2AB type electric thermostat blast oven (Wuhan Founder Experimental Equipment Co., Ltd.);

Perkin-Elmer Fourier Transform-Infrared Spectrometer (Perkin-Elmer, USA);

VARIAN Cary UV-Vis spectrophotometer (VARIAN);

Three music licensing microwave oven WP650D type microwave oven (Nanjing three music Electric Corporation);

2.1.2 Major reagents

Phthalimide (Sinopharm Chemical Group Co., Ltd., AR);

O - nitrophenylacetic acid (Shanghai Experimental One Chemical Reagent Co., Ltd., AR);

Zn (Ac) 2 · 2H2O (Tianjin Kay Tong Chemical Reagent Co., Ltd., AR);

DMF (Tianjin Kay Tong Chemical Reagent Co., Ltd., AR);

Potassium hydroxide (Shanghai Test Chemical Reagent Co., Ltd., AR);

Glacial acetic acid (Tianjin Beilian Fine Chemicals Development Co., Ltd., AR);

Hydrochloric acid (Kaifeng Dongda Chemical Co., Ltd. reagent factory, AR);

Methanol (Sinopharm Group Chemical Reagent Co., AR);

Stannous chloride (Tianjin Kay Tong Chemical Reagent Co., Ltd., AR);

Aluminum oxide (Tianjin Kay Tong Chemical Reagent Co., Ltd., AR);

Anhydrous ethanol (Xilong Chemical Co., Ltd., AR).

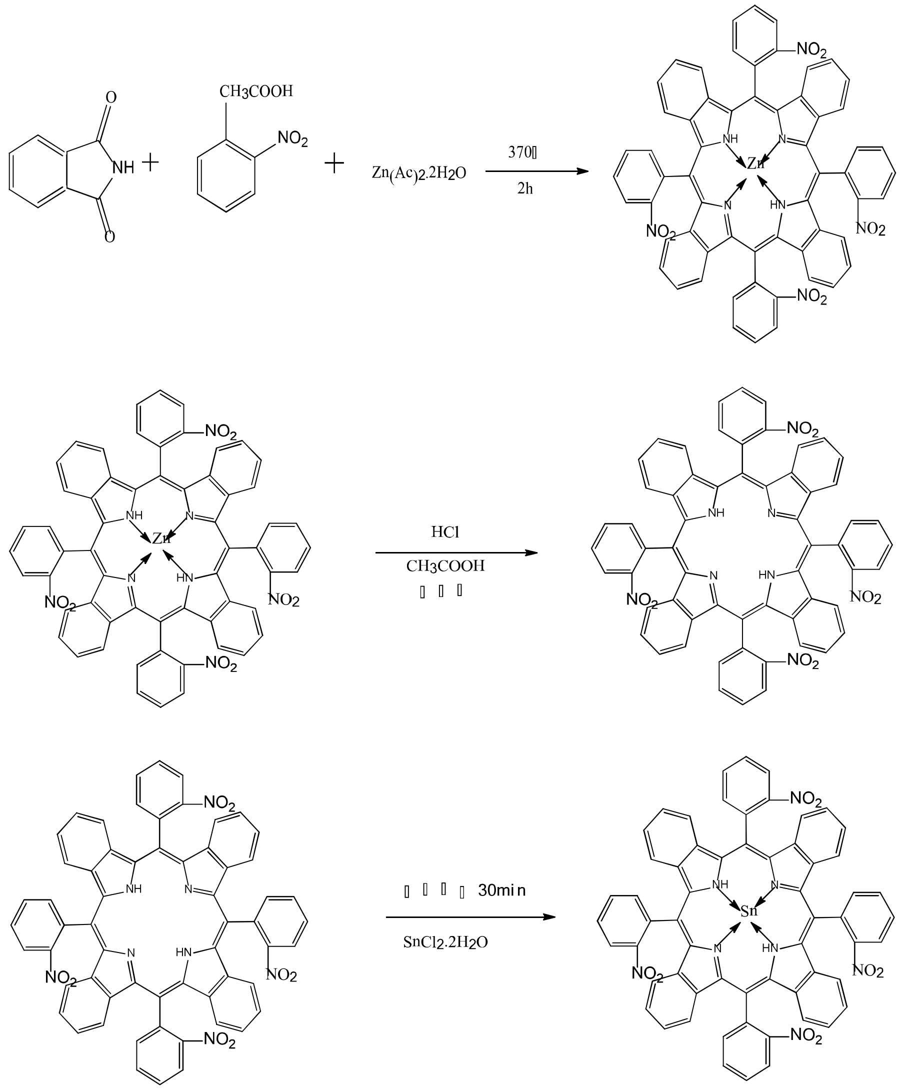
2.2. Synthesis of Benzophenones

2.2.1 Synthesis principle of benzoporphyrin

The use of thermal coagulation method [18] with phthalimide potassium, zinc acetate, o-nitrophenylacetic acid as raw material to synthesis tetraphenyltetraphenylporphyrin zinc is a classic reaction. The mechanism is that the α-C of o-nitrophenylacetic acid reacts with the carbonyl group of potassium phthalimide. The resulting compound is obtained by removing carbon dioxide to form the median carbon of porphyrin and further polymerizing to obtain porphyrin ring.

In this experiment, phthalimide potassium, zinc acetate, o-nitrophenylacetic acid as raw materials. Porphyrin with neutral carbon was obtained by removing a carbon dioxide molecule from the compound formed from the reaction between the α-C of o-nitrophenylacetic acid and the carbonyl of potassium phthalimide.With zinc (19) as the template, the intermediate - tetra (o - nitro) phenyltetraphenylporphyrin zinc (II) was obtained. (II) In the presence of hydrochloric acid and glacial acetic acid, the zinc ions were removed in the ice water bath to obtain free benzoporphyrin, and then the mixture was treated with DMF (II) as the solvent, stannous chloride solid was added, and the intermediate - tetra (o - nitro) phenyltetraphenylporphyrin (IV) was obtained by microwave heating and refluxing.

2.2.2 Synthesis of Benzophenones



2.3. Synthesis of benzoporphyrin

2.3.1 Preparation of phthalimide potassium salt

2.50 g of phthalimide was weighed into a 250 ml round bottom flask and 20 ml of absolute ethanol was added to the flask with a graduated cylinder. In addition, 2.00 g of potassium hydroxide was weighed into a 100 ml small beaker, 12 ml of a methanol solution was added to the small beaker, stirred with a glass rod until the potassium hydroxide solid was completely dissolved. The flask was placed on a magnetic stirrer and stirred at room temperature. The methanol solution of potassium hydroxide was slowly added to the round bottom flask with a dropper. After the solution was added dropwise, the mixture was stirred for about 90 minutes. After the reaction was complete, the product from the flask was removed and the filter was filtered and the solid from the filter paper was dried in an oven and the product was taken as 2.53 g of potassium phthalimide.

2.3.2 Preparation of median - tetra (o - nitro) phenyltetraphenylporphyrin zinc (II)

To a 250 ml round bottom flask was added 0.1493 g (1 mmol) of potassium phthalimide, 0.2563 g (1.4 mmol) of o-nitrophenylacetic acid, 0.1962 g (0.8 mmol) of Zn (Ac) 2 · 2H2O, (O-nitro) phenyltetraphenylporphyrin zinc (II), weighing 0.11g, was obtained by heating for 120 min.

2.3.3 Preparation of median - tetra (o - nitro) phenyltetraphenylporphyrin

0.75g of tetra (o - nitro) phenyltetraphenylporphyrin was wrapped with gauze and putinto the Soxhlet extractor [20], with DMF as a solvent for siphoning. While waiting for the color of the extract to gradually become lighter, heating was stopped, and the device was removed. Until the solution is cooled, part of DMF was collected with rotary evaporator distillation,, dark green viscous liquid is remained in the flask. Part of the green solution was taken into the beaker and placed in the ice bath. Acetic acid and 6mol / L hydrochloric acid were added into the beaker. The reaction was monitored with UV absorption until the absorption peak at 630nm disappeared. Addition of glacial acetic acid and hydrochloric acid was stopped when the absorption peak at 660nm appeared. 15 ml of ice water was added to the solution, placed in ice water bath for 10h. Layers appeared in the solution; black solid material precipitation at the lower layer of, yellow brown transparent liquid at the upper layer of which was filtered and dried to produce the product median - four (o- Nitro) phenyltetraphenylporphyrin 0.10 g.

2.3.4 Preparation of meso-tetra (o-nitro) phenyltetraphenylporphyrin (IV)

20 ml of a median-tetrakis (o-nitro) phenyltetraphenylporphyrin solution dissolved in DMF was added to a 50 ml round bottom flask and 0.02 g of SnCl2 · 2H2O was heated with microwave. The reaction was monitored by ultraviolet absorption spectroscopy until the absorption peak at 660nm completely disappeared and the absorption peak at appeared. After completion of the reaction, the solution was filtered and dried to give 0.05g of a black neutral-tetrakis (o-nitro) phenyltetraphenylporphyrin (IV) product. The intermediate-tetrakis (o-nitro) phenyltetraphenylporphyrin (IV) was dissolved in DMF, subjected to column chromatography with Al2O3 and eluted with DMF as the eluent. The first batch of green solution obtained was collected, poured into ice water for precipitation. Via suctioning and filtering, the median - tetra (o - nitro) phenyl tetraphenyl porphyrin (IV) produced.

2.4. Characterization of porphyrins

(O-nitro) phenyl tetraphenylporphyrins and meso-tetra (o-nitro) phenyltetraphenylporphyrin (IV) were prepared by UV - Spectral analysis.

3. Results and Analysis

3.1. UV-Visible Absorption Spectrometric Determination Results and Analysis

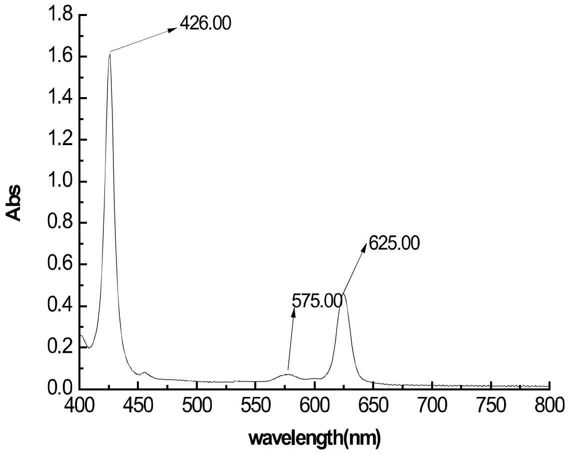


Figure 1. Neutral - tetra - (o - nitro) phenyl tetraphenyl porphyrin zinc (II) UV spectrum

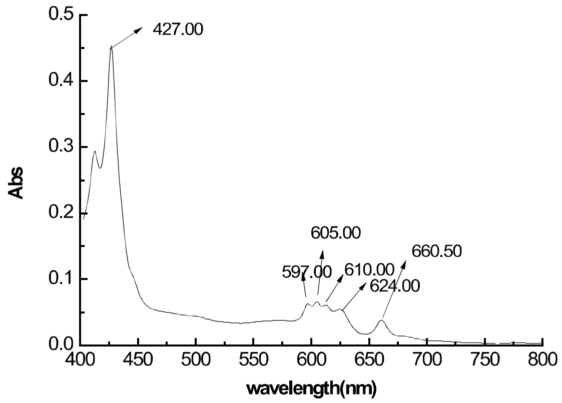


Figure 2. Ultraviolet spectrum of median-tetrakis (o-nitro) phenyl tetraphenylporphyrin

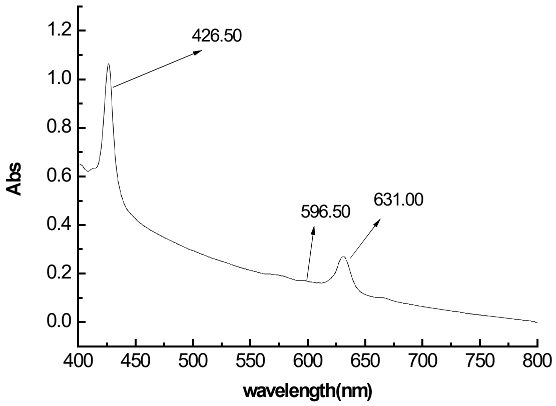


Figure 3. Ultraviolet spectrum of the median-tetra- (o-nitro) phenyltetraphenylporphyrin and tin (IV)

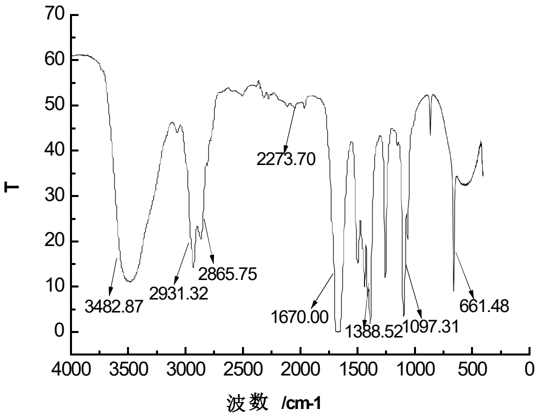


Figure 4. Infrared spectra of mid-tetra- (o-nitro) phenyltetraphenylporphyrin (DMF as solvent)

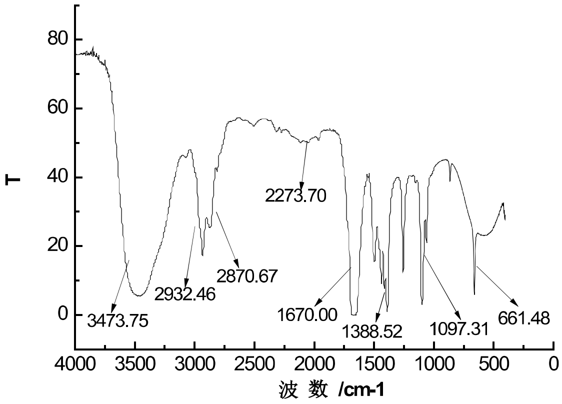


Figure 5. Neutral-tetra- (o-nitro) phenyl tetraphenylporphyrin porphyrin tin (IV) Infrared spectrum (DMF as solvent)

It can be seen from Fig. 5 that there is a strong absorption peak at 1670 cm-1, belonging to υC = N stretching vibration absorption peak,

The absorption peak of the skeleton of the benzene ring was observed at 1560 cm-1, 1542 cm-1, 1498 cm-1, 1435 cm-1, and the bending vibration absorption peak of benzene ring appeared at 661 cm-1. Cm-1, which may be a small amount of NH stretching vibration absorption peak of free benzene porphyrin which does not react with tin ions. The absorption peaks at 2932 cm-1 and 2870 cm-1 are the asymmetric stretching vibration absorption peaks and symmetrical stretching vibration absorption peaks of saturated C-H. In addition, this infrared map, in 3600cm-1 or so there are many clutter absorption peak, the product may be caused by a very small amount of water.

4. Conclusions

(1) This experiment is an improvement to the traditional heating experiment. Traditional experiments to phthalimide potassium, zinc acetate, sodium phenylacetate as raw material, heating also through nitrogen. In this experiment, phthalimide potassium, zinc acetate, o-nitrophenylacetic acid as raw materials, eliminates the o-nitrophenyl acetic acid intoo-nitrophenyl acetic acid sodium step. Due to o-nitrophenylacetic acid as a raw material, a large amount of carbon dioxide gas is generated at a temperature of 370 °C, and the generated carbon dioxide gas can be protected as a protective gas. The reaction system is not oxidized, thus eliminating the important step of passing nitrogen, which greatly simplifies the reaction step.

(2) The median - tetrakis (o-nitro) phenyltetraphenylporphyrin zinc (II) and hydrochloric acid and glacial acetic acid in the ice bath under the conditions of dezincification, the ice bath time should be long enough. If the experimental conditions allowed, you can put it in the refrigerator for a night, and then in the ice bath for 2 to 3h. The longer the incubation time, the more precipitation produced. You will find a black insoluble material precipitation.. The insoluble matter obtained by suctioning the solution was placed in a beaker and dissolved in DMF. The reaction process was measured by UV detection until the absorption peak at 625 nm disappeared and the absorption peak appeared at 610 nm and 660 nm.

(3) (O) -tetra-tetrakis (o-nitro) phenyltetraphenylpyridinium zinc (II), meso-tetrakis (o-nitro) phenyltetraphenylporphyrin and (O-nitro) phenyltetraphenylporphyrin tin (IV), are characterized by UV-visible spectroscopy. (The maximum absorption peak of the three is the corresponding wavelength. The maximum absorption peak of the tetramethylpyrrolidium zinc compound is 625nm, and the wavelength corresponding to the maximum absorption peak of the median - tetra (o - nitro) phenyltetraphenylporphyrin is 610nm, 660nm and (O-nitro) phenyltetraphenylporphyrin tin (IV) corresponding to the maximum absorption peak of the wavelength becomes 631nm. The maximum absorption peak corresponding to the wavelength may be due to porphyrin containing different metal ions. The difference in the electronegativity between zinc ions and tin ions resulting in a slight displacement of the absorption peaks in the UV-absorption spectrum.

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