Synthesis and Structural Characterizations of *meso*-Tetraphenyl Porphyrin

TIANXIANG ZHAO[1], JIANBIN ZHANG[1,2,*], XIAOXIA YANG[1], QIUXIA XU[1] and GONGJIA LAN[1]

[1]College of Chemical Engineering, Inner Mongolia University of Technology, Huhhot 010051, P.R. China
[2]Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P.R. China

*Corresponding author: Tel/Fax: +86 471 6575722; E-mail: tadzhang@pku.edu.cn

In this paper, tetraphenyl porphyrin (H_2TPP) was synthesized by using pyrrole and benzaldehyde as raw materials under the catalysis of *p*-nitrobenzoic acid. The prepared tetraphenyl porphyrin was re-crystallized in a mixed system of methanol and methylene chloride (CH_2Cl_2) and the yield of tetraphenyl porphyrin is 34.2 %. Tetraphenyl porphyrin was characterized by using FTIR, UV-visible, ^{1}H NMR and fluorescence spectrophotometer. The effects on the yield of tetraphenyl porphyrin at different volumes of dimethylbenzene as solvent were explored.

Keywords: Tetraphenylporphyrin, Recrystallization, Structural characterization.

INTRODUCTION

Porphyrin is a special kind of macrocyclic conjugated aromatic system, which received widespread attention as a result of having many special physiological activities. One of the most wide spread of all naturally occurring prosthetic group is the class of highly coloured pigments known as porphyrin. These tetrapyrrolic macrocycles play critical roles in a wide range of biological processes, including electron transfer, oxygen transfer and photosynthetic processes and they have a statement of "life pigment"[1-3]. Tetraphenyl porphyrin (H_2TPP) is precursors for the synthesis of many metal-porphyrin compounds and its synthesis and applications have received continuous attention due to their special structures and properties. The synthesis method of tetraphenyl porphyrin was proposed by Zhang[4] and the method was proved to be time-consuming and a low production rate. Previous workers[5-7] proposed that tetraphenyl porphyrin can be synthesized by the method of condensation of pyrrole and benzaldehyde under the protection of N_2, with boron trifluoride and ether complex [$(C_2H_5)_2O·BF_3$] as catalyst; however, due to many steps and harsh reaction conditions, the method was not used. Guo *et al.*[8] proposed a synthetic method using $AlCl_3$ as catalyst; in the process, although the yield could reach 30 %, $AlCl_3$ easily react with water to cause the difficulties of product separation.

In this work, tetraphenyl porphyrin was synthesized by using pyrrole and benzaldehyde as raw materials under the catalysis of *p*-nitrobenzoic acid. The prepared tetraphenyl porphyrin was recrystallized in a mixed system of methanol and methylene chloride. Tetraphenyl porphyrin was characterized by using FTIR, UV-visible, ^{1}H NMR and fluorescence spectrophotometer. Meanwhile, the effect on the yield of tetraphenyl porphyrin at different volumes of solvent of dimethylbenzene was explored.

EXPERIMENTAL

UV-visible spectra were obtained on a Shimadzu 2450 spectrometer in CH_2Cl_2 at room temperature. Infrared spectra (4000-400) cm^{-1} of solid samples were taken as 1 % dispersion between two KBr pellets using a Nexus 670 spectrophotometer. Fluorescence spectra were determined by using an F-4500 fluorescence spectrometer. ^{1}H NMR spectra were acquired by using a Bruker ARX-400 nuclear magnetic resonance spectrometer and $CDCl_3$ was used as a NMR solvent. All solid reagents were weighed using a Sartorius BS224S electric balance. Product obtained after filtration was dried under vacuum dried at 80 °C under the DZF-6053 vacuum drying oven.

Pyrrole (≥ 99 %) was purchased from Shanghai Sinopharm Co., Ltd. Dichloromethane (≥ 99.5 %) was purchased from Tianjin Siyou Co., Ltd. Dimethylbenzene (≥ 99 %) was purchased from Tianjin Fuyu Co., Ltd. All other reagents and solvents were reagent grade and used as received.

General procedure: Tetraphenyl porphyrin was synthesized by using pyrrole and benzaldehyde and the reaction device and experimental mechanism as shown in Fig. 1.

A solution of 0.02 mol pyrrole, 0.02 mol benzaldehyde and 0.01 mol *p*-nitrobenzoic acid as catalyst in 100 mL dimthylbenzene was refluxed for 1.5 h in a 250 mL three-
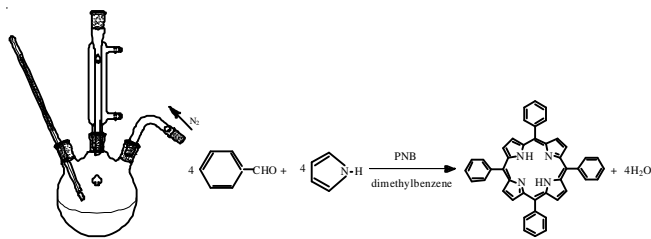
Fig. 1. Reaction equipment and mechanism of tetraphenylporphyrin

necked round-bottom flask at 134 °C. The reaction started with N₂ purge protection and stopped with N₂ until the temperature to stabilize. The colour of reaction system soon changes into dark purple from light yellow. After the reaction, the temperature of the system decreased by 80 °C, adding 100 mL of methanol and standing for 2 h with shaking in a refrigerator at -5 °C. Purple black solid was obtained by air pump filtration and washed several times with methanol. The resulting solid was dissolved in a mixed solvent of CH_2Cl_2 and CH_3OH and recrystallized, then the bright purple product obtained after filtration was dried under vacuum at 80 °C for 5 h. In the process, the weight of product is 1.0512 g with a yield of 34.2 %.

Under the conditions of pyrrole 0.02 mol, benzaldehyde 0.02 mol, *p*-nitrobenzoic acid 0.01 mol and the reaction temperature at 134 °C, the effects on the yield of dimethylbenzene in the different volumes were explored. Yield of tetraphenyl porphyrin synthesized at different volumes of dimethylbenzene as shown in Table-1. When the volume of dimethylbenzene is 100 mL, the yield of tetraphenyl porphyrin can arrive at larger value. Little solvent will result in incomplete reaction or formation of by-products. In contrast, the purification is not conducive to the precipitation of crystals.

TABLE-1
YIELD OF H₂TPP AT DIFFERENT VOLUMES OF DIMETHYLBENZENE

Dimethylbenzene (mL)	H₂TPP (g)	Yield (%)
80	0.6825	22.2
100	1.0512	34.2
120	0.7283	23.7
150	0.5258	17.1

RESULTS AND DISCUSSION

Infrared spectra (4000-400) cm⁻¹ of solid samples were taken as 1 % dispersion between two KBr pellets. As shown in the Fig. 2: 3313 and 959 cm⁻¹ for N-H stretching vibration and in-plane bending vibration on the porphine ring, 3052 cm⁻¹ is =CH- stretching vibration, 1542 cm⁻¹ is C=C skeleton vibration on the pyridine ring, 1459 cm⁻¹ is C=C stretching vibration peak on the aryl ring, 1342 cm⁻¹ for the C=N stretching vibration, 795 cm⁻¹ is skeleton vibration peak on the benzene ring, 841 cm⁻¹ is C-N stretching vibration peak. The results are consistent with the literatures[9-13].

UV spectra were determined by using CH_2Cl_2 as reference, the results shown in Fig. 3. The UV spectral results showed that the Soret absorption band of synthetic products appeared a strong absorption peak of 418 nm[9-13], which is consistent with the ultraviolet absorption peak of tetraphenyl porphyrin at Soret absorption band. Product of the absorption band in Q
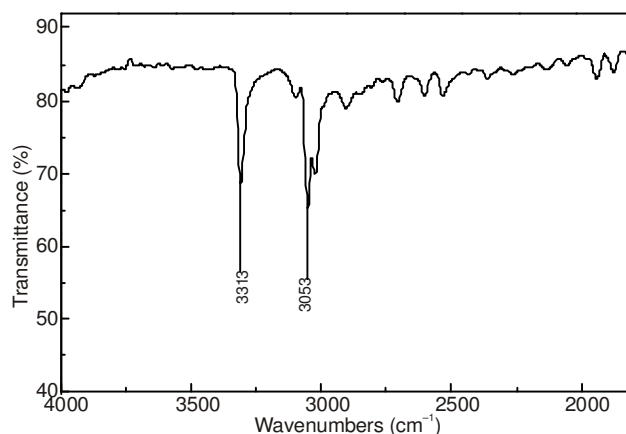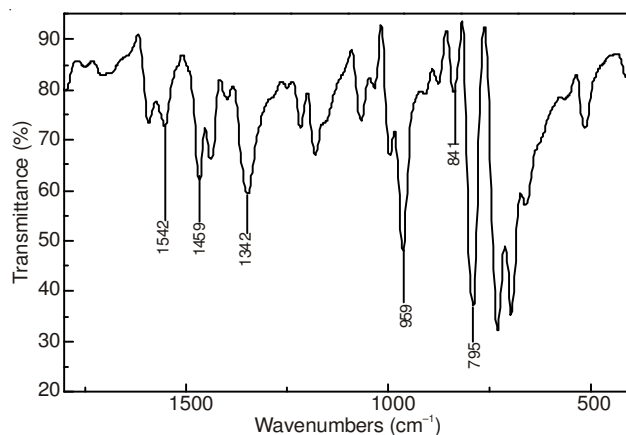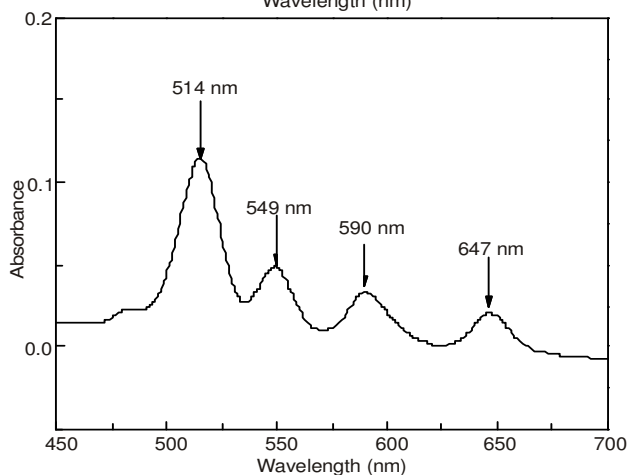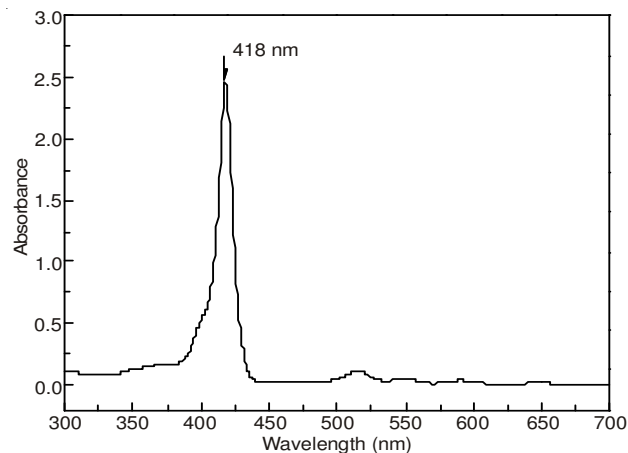

Fig. 2. FTIR spectra of product

Fig. 3. UV-visible spectra of product

had 4 absorption peaks as follows: 515 nm, 549 nm, 590 nm and 646 nm, which is consistent with the features of tetraphenyl porphyrin in this absorption band[9-13].

Fluorescence spectra of product CH_2Cl_2 solution were determined under a concentration of 1.952×10^{-5} mol/L, when the excitation wavelength was set at 515 nm with the slit for 5 nm. Under this condition, the intensity of emission spectrum was strong, as shown in Fig. 4. The maximum length of excitation synthetic of product can be determined to be 515 nm, which confirmed that the product was tetraphenyl porphyrin[9].
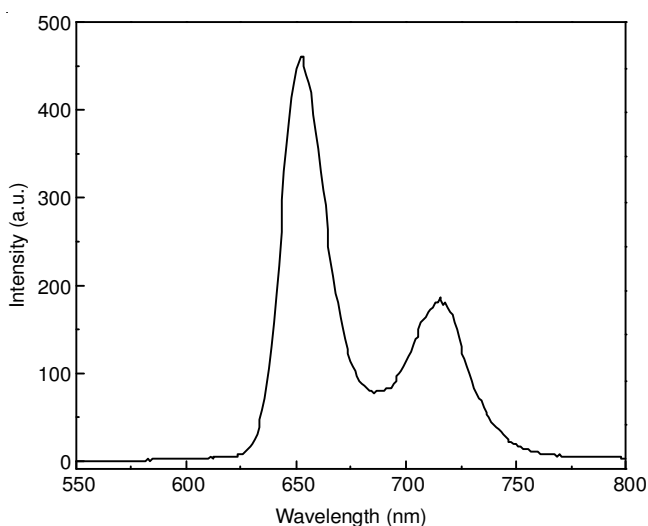

Fig. 4. Fluorescence spectrum of product

In ^{1}H NMR spectrum, it is notable that tetraphenyl porphyrin are aromatic compounds and the ring current in magnetic fields caused the N-H protons appear upfield about -2.76 ppm and the protons of porphyrin cycle appear downfield at (8.60-8.83) ppm. Resonances due to the *meso*-phenyl protons consist of two doublets, one for ortho (7.99-8.22) ppm and another for meta hydrogens (7.25-7.78) ppm[14-15], which is consistent with the features of tetraphenyl porphyrin in this absorption band.

Conclusion

Experiments show that tetraphenyl porphyrin (H_2TPP) can synthesize in 100 mL of dimethylbenzene when *p*-nitrobenzoic acid was used as catalyst at 134 °C for 1.5 h. Tetraphenyl porphyrin was characterized by using FTIR, UV-visible, ^{1}H NMR and fluorescence spectrophotometer. When the volume of dimethylbenzene is 100 mL and pyrrole and benzaldehyde is at 0.2 mol/L, the yield arrived at 34.2 %.

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