

# Synthesis and characterization of 5, 10, 15, 20-Tetrakis (4-Tolyl)Porphyrin and its Tin and Cobalt complexes: investigation of their photodynamic properties in degradation of Methylene blue

Hossein Ghafuri\*, Rahmatollah Rahimi\*, Zahra Movahedinia, Solmaz Zargari, Shirin Rahmani

Department of Chemistry, Iran University of Science and Technology, Tehran 16846-13114, Iran

(E-mail: [rahimi\\_rah@iust.ac.ir](mailto:rahimi_rah@iust.ac.ir), [ghafuri@iust.ac.ir](mailto:ghafuri@iust.ac.ir))

## Abstract

In present work, the synthesis and characterization of 5, 10, 15, 20-tetrakis (4-tolyl) porphyrin [H<sub>2</sub>TTP] and its metal complexes with tin and cobalt were investigated. H<sub>2</sub>TTP complex was characterized by UV-vis, FT-IR and <sup>1</sup>H NMR spectra. The photodynamic degradation activity of these compounds was investigated by destruction of methylene blue under visible light irradiation.

**Keyword:** Synthesis, Porphyrin, Photodynamic degradation, Methylene blue

## 1. Introduction

Colored wastewater from textile industry is one of the largest sources of pollution of the aquatic environment. One of the so used colors in the textile industry is methylene blue. Due to limited efficiency, the biological treatment of pollutants is not satisfying [1]. Photodynamic treatment provides an eco-friendly pathway for degradation of pathogenic microorganisms from wastewater. This technique is considered as a promising and new technology for wastewater treatment [2]. Use of porphyrin absorbents for separating several pollutants including methylene blue has been specially considered.

Porphyrins, the pigments of life, are having a 2D 18  $\pi$ -electron structure, and they play a prospective role in enzymes, catalytic reactions, PDT and conversion of solar energy [3]. The efficiency of the porphyrin photosensitizing effect depends on the presence and nature of complexed metal ions and on the structure of the side chains of the tetrapyrrole core [4]. Metalloporphyrins are an important group of sensitizers with a porphyrin skeleton. Their photosensitizing properties have led to their utilization in photodynamic therapy. The nature

of the central metal ion has significantly affected their photophysical properties [5]. Certain metalloporphyrins such as SnPp are being tested as drugs for the treatment of Neonatal hyperbilirubinemia [6]. This article has been specially considered the use of porphyrin photosensitizer for degradation of several pollutants including methylene blue.

## **2. Experimental**

### **2.1. Synthesis of 5, 10, 15, 20-Tetrakis-(4-Tolyl) Porphyrin (H<sub>2</sub>TTP)**

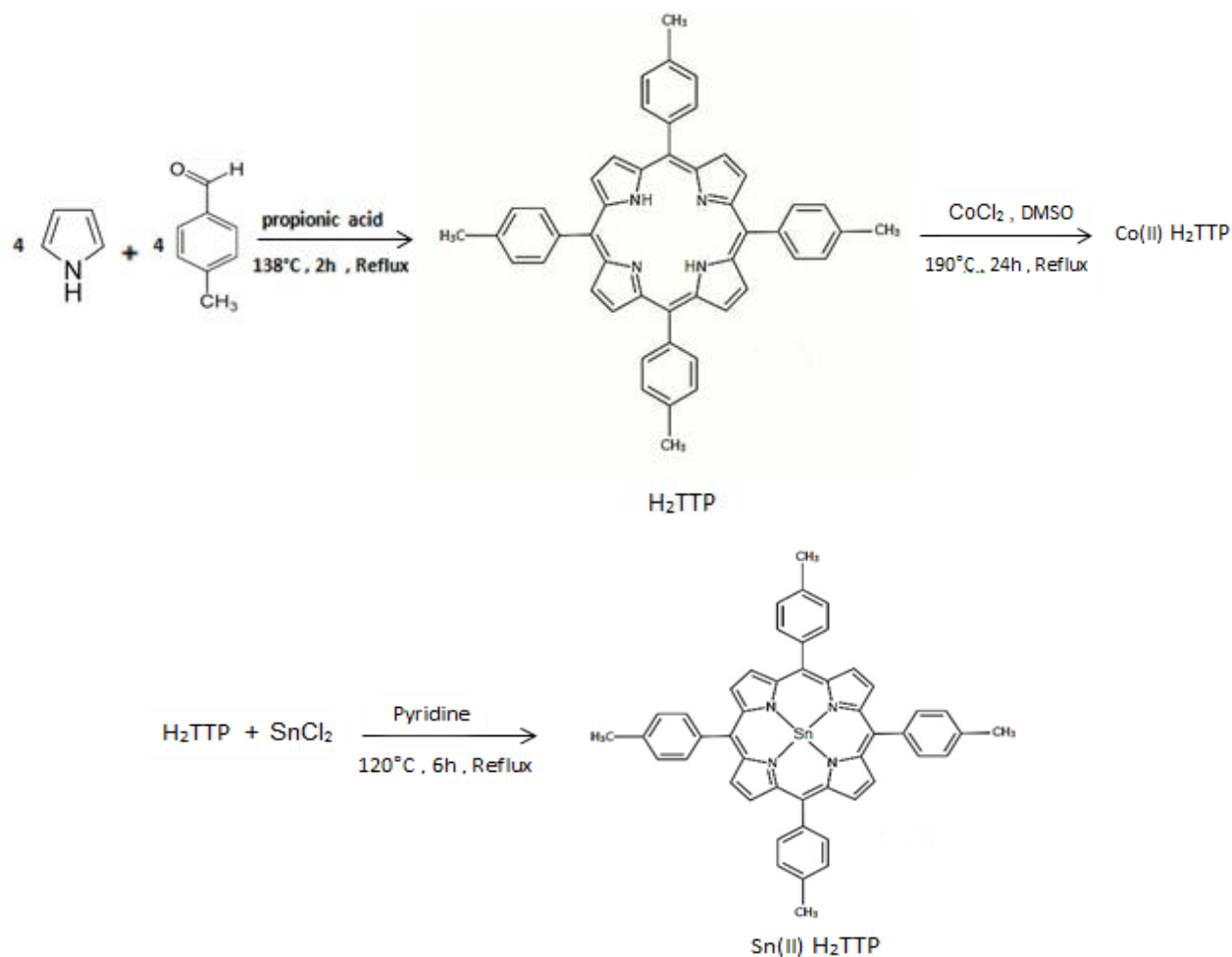
To prepare H<sub>2</sub>TTP, pyrrole and 4-methylbenzaldehyde were refluxed in propionic acid for 2h at 138°C. The product was obtained by filtration and washed with DI.IR (KBr):  $\nu_{\max} = 3448, 3024, 2920, 2852, 1635, 1471, 1350, 1218, 1182, 968, 798, 738, \text{ and } 526 \text{ cm}^{-1}$ .

### **2.2. Synthesis of Sn(II) 5, 10, 15, 20-Tetrakis-(4-Tolyl) Porphyrin**

To prepare tin complex of H<sub>2</sub>TTP, SnCl<sub>2</sub>·2H<sub>2</sub>O and H<sub>2</sub>TTP were refluxed in pyridine for 6h at 120°C. The complex was obtained with filtration.

### **2.3. Synthesis of Co(II) 5, 10, 15, 20-Tetrakis-(4-Tolyl) Porphyrin**

To prepare Cobalt complex of H<sub>2</sub>TTP, CoCl<sub>2</sub>·6H<sub>2</sub>O (0.1 g, 6 mmol), and H<sub>2</sub>TTP (0.1 g, 1 mmol) were refluxed in DMSO (28 mL) for 24 h. Then, 1 M HCl (ca. 80 mL) was added to the solution to cause deposition of the crude product as a purple solid, which was collected by filtration, washed with water, and dried in vacuo. The prepared sample was redissolved in 0.1 M NaOH (ca. 25 mL) followed by addition of 1 M HCl (ca. 40), which caused deposition of the product as a purple solid. The final products was collected by filtration and dried in vacuo [7].

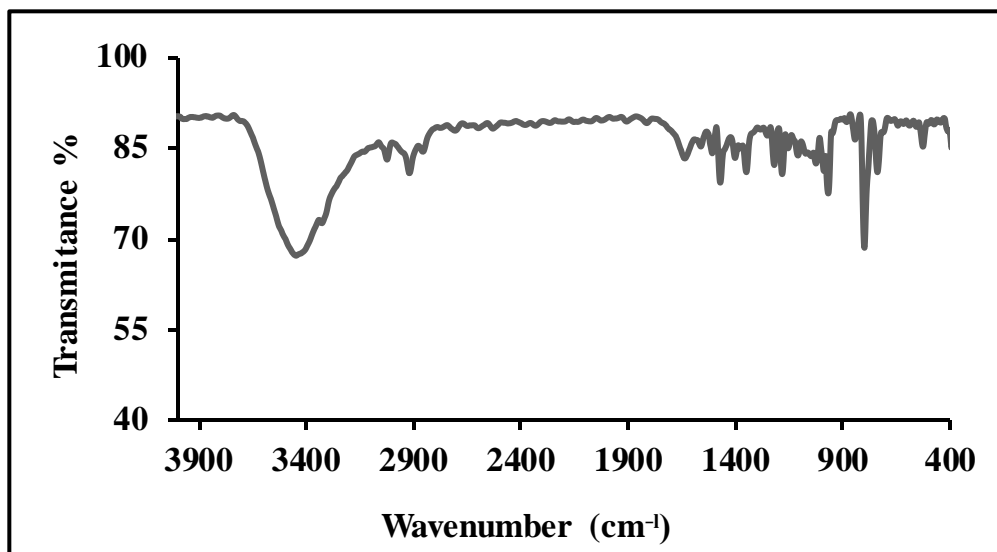


**Scheme 1.** Synthesis of 5, 10, 15, 20-tetrakis (4-tolyl) porphyrin (H<sub>2</sub>TTP), Co(II) H<sub>2</sub>TTP and Sn(II)H<sub>2</sub>TTP

### 3. Results and discussion

#### 3.1. FT-IR spectra analysis

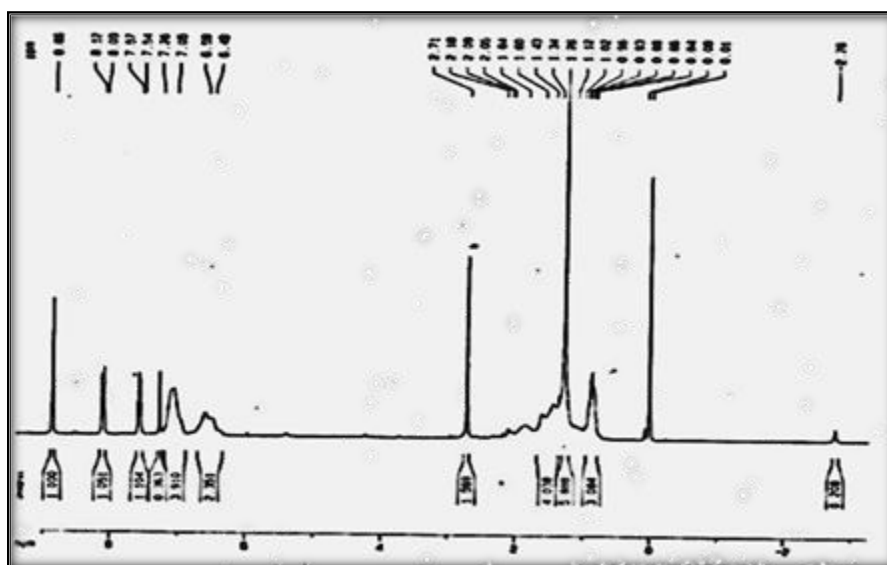
The FT-IR spectra were recorded on a FT-IR spectrometer (4000 - 400 cm<sup>-1</sup>) in KBr pellets. As shown in Fig. 1, FT-IR spectra of compound with the characteristic peak of C-H vibration of toluene in the range of 2920 cm<sup>-1</sup> indicated that the relative schiff base porphyrin were successfully synthesized. Moreover disappearance of N-H vibration around 3448 cm<sup>-1</sup> and emergence of C-H vibration of aromatic around 3024 cm<sup>-1</sup> predicated that the related metalloporphyrin were also quantitatively prepared.



**Fig. 1.** The FT-IR Spectrum of 5, 10, 15, 20-tetrakis (4-tolyl) porphyrin

### 3.2. <sup>1</sup>H NMR Spectra analysis

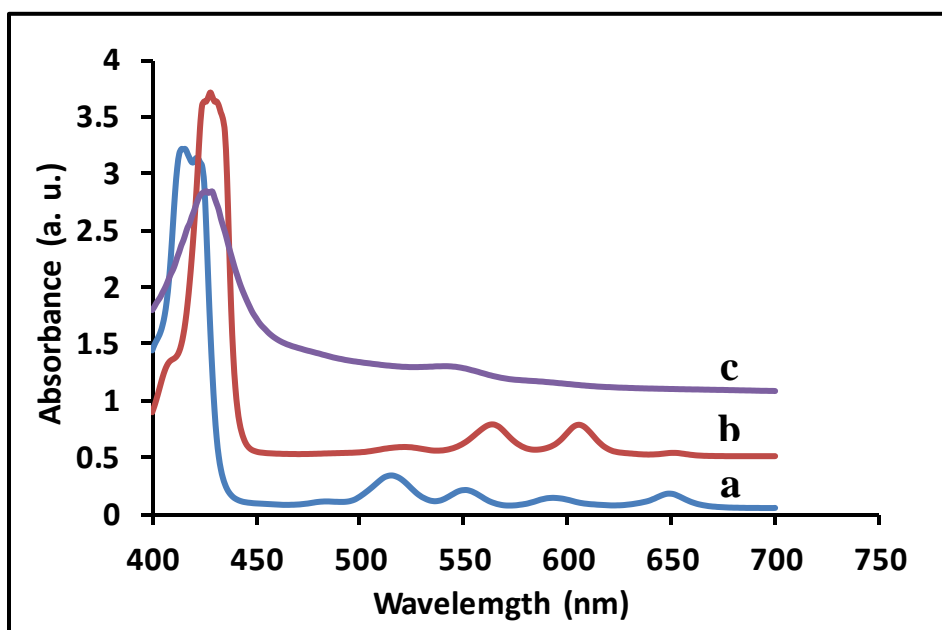
The <sup>1</sup>H NMR spectrum of H<sub>2</sub>TTP was recorded at 400 MHz and in CDCl<sub>3</sub>. Peak appeared in the weakest field can be attributed to the pyrrole hydrogens. Peak in the area of almost 3 ppm can be attributed to the methyl groups of H<sub>2</sub>TTP. As shown in Fig. 2, in stronger fields of H NMR spectrum, in the range of 7 to 8 ppm, two peaks can be seen. These peaks are related to the aromatic hydrogens which attached to the phenyl ring. Because of the differences in the chemical environment of ortho and meta hydrogen, these peaks appear in two different fields.



**Fig. 2.** The H NMR Spectrum of 5, 10, 15, 20-tetrakis(4-tolyl) porphyrin

### 3.2. UV-Vis Spectra Analysis

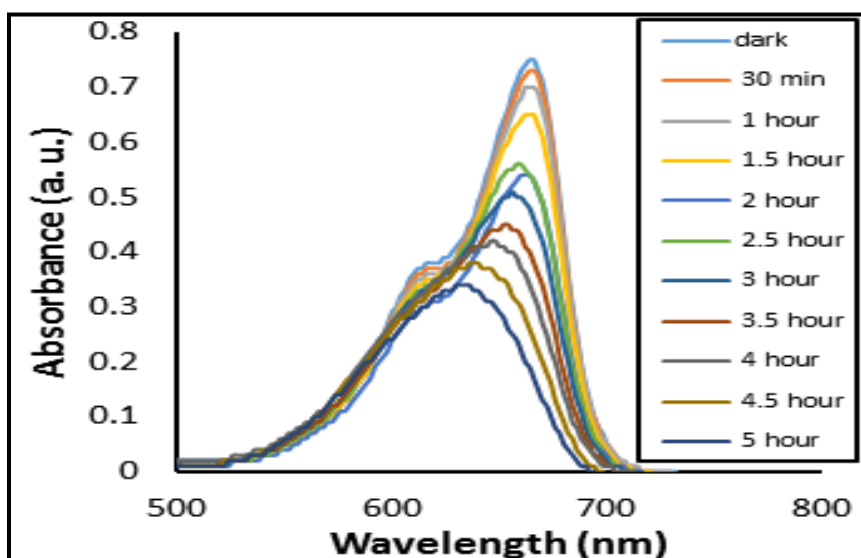
As shown in Fig. 3, the UV-vis spectrum of H<sub>2</sub>TTP showed a band centered at 420 nm (Soret band), and four Q bands absorptions at 515, 550, 590 and 650 nm, respectively. The insertion of Sn(II) and Co(II) into the porphyrin ring caused redshift of 3 nm of the corresponding Soret band as well as a decreasing number of Q bands in UV-vis spectrum. This is because when the hydrogen ions of N-H was replaced by Sn(II) and Co(II), the symmetry of porphyrin ring increases [4].



**Fig. 3.** The UV-Vis spectrum of a) H<sub>2</sub>TTP, b) Sn(II)H<sub>2</sub>TTP and c) Co(II)

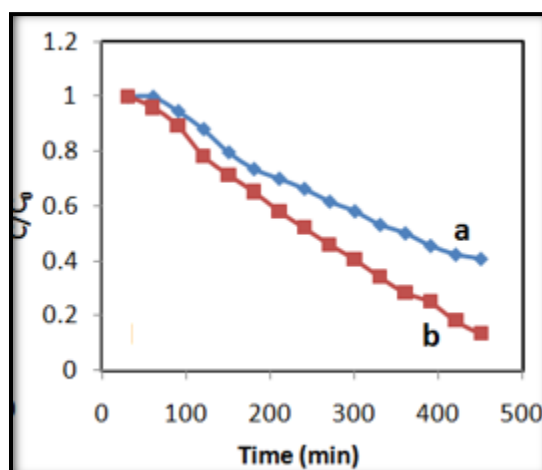
### 3.3. Investigation of the photodynamic degradation of Methylene blue (MB)

Fig. 4 shows the UV-Vis absorption spectrum of the MB solution at different reaction times, in which the absorption spectrum of the original solution shows two characteristic peaks at 610 and 660 nm. It is clear that under the irradiation of the visible light, the MB concentration is gradually decreased as a result of the visible light irradiation.



**Fig. 4.** Absorption spectrum of destruction of MB under vs. irradiation times by Sn(II)H<sub>2</sub>TTP

Fig. 5 displays the plots of time dependence on the unconverted fraction ( $C/C_0$ ) by Sn(II)H<sub>2</sub>TTP complex on MB photodegradation at 25°C. Comparisons of curves show that the photodynamic activity of the Sn(II)H<sub>2</sub>TTP complex is higher than H<sub>2</sub>TTP. With regard to the photodegradation results a proper photodegradation was not showed for Co(II)H<sub>2</sub>TTP under visible light irradiation. This indicates the importance of the effect of the central metal on the photodynamic activity of prepared metalloporphyrin. Therefore, only the metal ion, among the other factors, plays an important role in the photodynamic activity.



**Fig. 5.** Photodegradation of Mb (6 ppm) in the presence of a) only visible light and b) Tin complex of porphyrin

## Conclusions

In this work, we prepared synthesis of 5, 10, 15, 20-Tetrakis-(4-Tolyl) Porphyrin and its tin and cobalt complexes. To investigate the photodynamic activity of the prepared tin and cobalt complexes, the photodegradation of methylene blue was carried out under the visible light irradiation. The results indicate that the photodynamic activity of the Sn(II)H<sub>2</sub>TTP complex is higher than H<sub>2</sub>TTP and Co(II)H<sub>2</sub>TTP. This indicates the importance of the effect of the central metal on the photodynamic activity of prepared metalloporphyrin. Therefore, only the metal ion, among the other factors, plays an important role in the photodynamic activity.

## References

- [1]. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui ,Ch. Guillard , J.M. Herrmann , *Applied Catalysis B: Environmental* 31 (2001) 145–157.
- [2] C. Pablos, R.v. Grieken, J. Marugán, B. Moreno, *Catalysis Today* 161 (2011) 133-139
- [3]. M. K. Panda, K. Ladomenou, A. G. Coutsolelos, *Coordination Chemistry Reviews* 256 (2012) 260– 262.
- [4]. J. Fuchs, S. Weber, R. Kaufmann, *Free Radical Biology & Medicine*, Vol. 28, No. 4, pp. 537–548, 2000.
- [5]. P. Moro, M. P. Donzello, C. Ercolani, F. Monacelli, G. Moretti, *Journal of Photochemistry and Photobiology A: Chemistry* 220 (2011) 77–83.
- [6]. R. Chandra, M. Tiwari, P. Kaur, M. Sharma, R. Jain, S. Dass, *Indian Journal of Clinical Biochemistry* , 2000, 15(SuppL ), 183-199.
- [7]. T. Nakazono,A.R. Parent, K. Sakai, *Chem. Commun.*, 2013,49, 6325-6327.