



## Microwave Assisted Synthesis of *meso*-Tetraphenylporphyrin and Its Application for Trace Metal Spectrophotometric Determination

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(Received: 7 July 2012;

Accepted: 29 April 2013)

AJC-13411

The synthesis of *meso*-tetraphenylporphyrin with quantitative yield in presence of *p*-toluene sulfonic acid as new catalyst under microwave irradiation was accomplished. The *meso*-tetraphenylporphyrin was characterized by means of elemental analysis, UV-visible spectra, <sup>1</sup>H NMR spectra, infrared spectra and was used as chelating agent for direct determination of zinc ions by UV-visible spectroscopy.

**Key Words:** Microwave, *Meso*-tetraphenylporphyrin, Zinc, UV-visible spectroscopy.

### INTRODUCTION

The porphyrins comprise an important class of macrocyclic compounds that serve nature in a variety of ways. The metalloporphyrin rings play an important role in important biological systems. They have also been verified as efficient sensitizers and catalyst in a number of chemical processes<sup>1,2</sup>.

Traditionally, porphyrins and metalloporphyrins syntheses have been carried out in acidic conditions such as propanoic acid or in a halogenated solvent<sup>3-5</sup>. In most cases, toxic oxidizing reagents are used to convert the initial porphyrinogen product to porphyrin. The porphyrin nucleus is a tetradentate ligand in with the space available for a coordinated metal has maximum diameter of approximately 3.7 Å. The porphyrin ring system and the porphyrin complexes with transition metal ions are very stable<sup>6</sup>.

The application and importance of porphyrins and metalloporphyrins have gained increasing interest in last decades in analytical chemistry, significantly. The porphyrins are one class of superior colourimetric compounds that became useful as the reagents in spectrophotometric methods for the determination of metal ions. Application of porphyrins as spectrophotometric reagents have two problems, the first one is that the absorption spectra of the reagent often overlaps with metal chelates and the second one is that the rate of reaction is lower than with the common reagent<sup>7</sup>.

In this paper *meso*-tetraphenylporphyrin has been synthesized promptly, by combination of pyrrole and benzaldehyde under microwave irradiation<sup>8</sup>. Moreover, it has been characterized with UV-visible spectra, H NMR spectra, infrared spectra. The complex of zinc *meso*-tetraphenylporphyrin was formed in room temperature and was used for direct determination of zinc ions.

### EXPERIMENTAL

All of materials were prepared in the quartz vessel. The microwave oven used for synthesis of tetraphenylporphyrin was LG, intellowave, 1000 W. UV-VIS spectra were measured by Cary100 Cone UV-VIS system. H NMR Spectra and FT-IR spectra were recorded by Bruker, 300 MHz, 7T, FT-H NMR system and thermo Nicolet FT-IR system, respectively. All experimental procedures were performed at room temperature.

All the reagents were used without more purification and were of analytical grade. Glacial acetic acid was prepared by adding 20 mL acetic anhydride to 1 liter glacial acetic acid.

**Synthesis of *meso*-tetraphenylporphyrin:** The *meso*-tetraphenylporphyrin was synthesized by reaction of pyrrole (0.4 mL) with benzaldehyde (0.53 mL) and 0.05 g of *p*-toluene sulfonic acid in a Pyrex bottle under microwave irradiation at 2 min intervals for 10 min. Catalyst was removed by filtration and washed thoroughly with ultrapure water. A chromatographic column for separation of product mixture was prepared by applying the silica gel (100-200 mesh size) and hexane eluting with 7:1 (v/v) hexane-ethyl acetate solution.

Accordingly, the *meso*-tetraphenylporphyrin was prepared and characterized by UV-visible, H NMR and FT-IR spectroscopy. UV-VIS spectroscopy showed the characteristic Soret band at 418 nm and Q band at 511, 544, 594 and 653 nm in toluene. The IR spectrum of H<sub>2</sub>TPP in KBr exhibited at 3430, 3314, 3140, 3054, 3021, 2920, 2856, 2603, 2529, 2352, 2257, 1886, 1469, 1399, 990, 962, 955, 798, 646 and 556 cm<sup>-1</sup>. Furthermore, H NMR spectrum and chemical shifts as shown in Table-1 indicates the *meso*-substituted porphyrin structure.

TABLE-1  
HNMR CHEMICAL SHIFTS ( $\Delta$ [P.P.M.] FROM TMS) OF  
*meso*-TETRAPHENYLPORPHYRIN

Parent compound	<i>meso</i> Substituent (Position)	NH	Substituent-H	Pyrrole-H	Solvent
Porphyrin	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	3.6 0	8.08	7.27	CDCl <sub>3</sub>
			8.59	7.76	
			8.86	7.78	
				7.97	

**Preparation of solution:** Glacial acetic acid was prepared by adding 20 mL of acetic anhydride to 1 L glacial acetic acid. At least 12 h before used the *meso*-tetraphenylporphyrin solution was prepared by refluxing 0.269 g of *meso*-tetraphenylporphyrin in 250 mL glacial acetic acid for 7 h. Zinc acetate solution was prepared by dissolving reagent grade metal acetates in glacial acetic acid. The acid was kept hot and water added slowly in 0.5 mL.

## RESULTS AND DISCUSSION

**Microwave assisted procedure:** Microwave irradiation has recently been a fast procedure for chemical synthesis<sup>9-12</sup>. In this paper, the procedure for preparation of *meso*-tetraphenylporphyrin, take only 10 min. However, the classical methods present some experimental limitations likes, long reaction times and sometimes low yields. These limitations are not associated with microwave irradiation<sup>13,14</sup>. No solvent is necessary in the reactions described in this study and the reaction condition is moderate. The synthesis reactions have been successfully repeated several times with identical results.

**Determination of zinc:** The zinc *meso*-tetraphenylporphyrin complex was established, as soon as zinc acetate was added to a solution of *meso*-tetraphenylporphyrin in glacial acetic acid after 50-60 min at room temperature. The absorption band of the complex was diminished at 551 nm (Fig. 1).

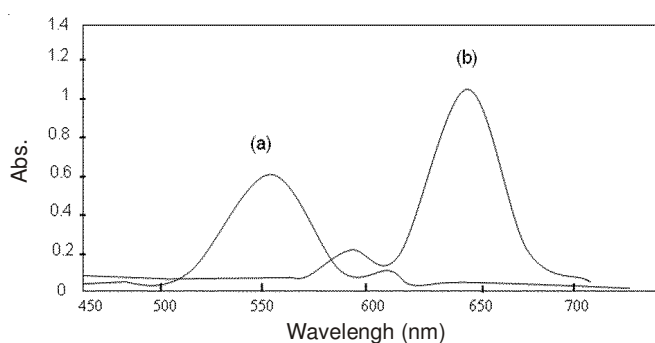


Fig. 1. (a) Absorption spectra of zinc tetraphenylporphyrin complex in glacial acetic acid; (b) Absorption spectra of *meso*-tetraphenylporphyrin complex in glacial acetic acid

The calibration curve was organized by transferring zinc acetate solution into series of 25 mL volumetric flasks and adding appropriate aliquots of the *meso*-tetraphenylporphyrin solution to each of them. Following 50 min the absorbance at 551 nm was read against a reference solution. The calibration curve parameters are given in Table-2.

Sample was dissolved and prepared to yield the same concentration, as was used in the calibration curve. The same amount of *meso*-tetraphenylporphyrin was added and after 1 h

the absorbance was read. Calibration curve was applied for determination of the zinc ion of the samples (Table-3).

TABLE-2  
PARAMETERS FOR CALIBRATION CURVE

Samples	Wavelength (nm)	Quantitative range (mg L <sup>-1</sup> )	R <sup>a</sup>	RSD <sup>b</sup> (%)
Zinc acetate	551	0.8-8.0	0.991	3.1
Zinc perchlorate	551	0.8-8.0	0.986	5.9

<sup>a</sup>Correlation coefficient; <sup>b</sup>Relative Standard Deviation

TABLE-3  
CONCENTRATIONS OF THE ZINC METAL IONS IN SAMPLES

Sample	Metal Zn <sup>2+</sup> (mg L <sup>-1</sup> )	
	Added	Founded
Sample a	2.00	2.50
Sample b	5.00	5.12
Sample c	7.00	6.93

**Interferences:** In this study interference of Mg(II), Co(II), Fe(II) and Cu(II) ions, which are likely to form complexes with *meso*-tetraphenylporphyrin in acetic acid was investigated (Table-4). In quantitative determination of zinc with complex formation, the most interaction was absorbed in presence of copper ions, Due to the similarity of the absorption spectra and also molar absorptivities of two metal complexes.

TABLE-4  
THE INTERFERENCE OF THE METAL IONS

Salt	Reagent	Wavelength (nm)	Tolerable level of interference concentration (mg L <sup>-1</sup> )			
			Cu(II)	Fe(II)	Co(II)	Mg(II)
Zinc acetate	TPP	551	N. D <sup>a</sup>	223	235	4.8

<sup>a</sup>Represents less than detection limit of method

**Effect of metal salt:** The absorbance of two identical solutions of *meso*-tetraphenylporphyrin with zinc acetate and *meso*-tetraphenylporphyrin with zinc perchlorate at 551 nm was compared. Consequently, as shown in Table-2, the absorbance was increased when zinc was added as zinc acetate. Moreover, according to the theory of solvent systems acetate salt functions as base and increases the concentration of the solvent anion<sup>15</sup>.

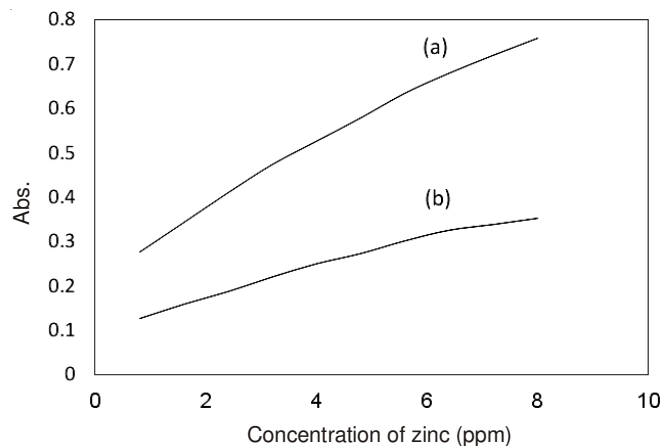


Fig. 2. (a) ZnTPP calibration curve with zinc acetate (b) ZnTPP calibration curve with zinc perchlorate

## Conclusion

*meso*-Tetraphenylporphyrin was synthesized by microwave irradiation with innovative, effective and available catalyst in 10 min with enhanced yield. Spectrophotometry property of the porphyrin was applied to obtain the concentration of zinc ions in the samples. Consequently, this study offers a simple and appropriate method for indirect spectrophotometric determination of metal ions, chelates, porphyrins and metalloporphyrins, which could be dissociated in acetic acid by effect on the complex formation equilibrium and changes in the absorbance at 551 nm.

## ACKNOWLEDGEMENTS

The authors are grateful to the Laboratory Complex of Islamic Azad University for valuable technical assistance.

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