

# An Undergraduate Experiment Using Microwave-Assisted Synthesis of First Row Metalloporphyrins: Characterizations and Spectroscopic Study

Muna Bufaroosha\*, Shaikha S. Al Neyadi, Mohamed A.R. Alnaqbi,  
Sayed A.M. Marzouk, Abdullah Al-Hemyari, Bashar Yousef Abuhattab, Dana Akram Adi

Department of Chemistry, College of Science, UAE University, Al-Ain, UAE

\*Corresponding author: [muna.bufaroosha@uaeu.ac.ae](mailto:muna.bufaroosha@uaeu.ac.ae)

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**Abstract** There is a notable absence in the practical inorganic curricula for experiments in which students can synthesize and characterize series of inorganic complexes. This is possibility attributed to the long required time which is not normally available in regular lab sessions. To address this absence, this paper describes a two-part experiment for chemistry major students in which they prepare series of metalloporphyrins using microwave-assisted technique. In addition to its attractive simplicity, microwave-assisted preparation substantially reduces the needed reaction time to suit the lab session duration. The first lab session is dedicated to the characterization of the 5,10,15,20-tetraphenylporphyrin (TPP) as well as the synthesis of the corresponding Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes. The second session involves the spectroscopic characterization (UV-vis, <sup>1</sup>H-NMR, and IR) of the prepared metalloporphyrins. The students relate the experimental results with the provided theoretical data based on quantum chemical calculations.

**Keywords:** Metalloporphyrins Frontiers Orbitals, metalloporphyrins electronic structure, metalloporphyrins microwave-assisted synthesis

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## 1. Introduction

Since metalloporphyrins play an essential role in the chemistry of the living entities [1,2,3], scientists have always found them fascinating to study, understand, and mimic. Therefore, synthetic metalloporphyrins possess substantial significance in our world. For example, to be capable of understanding the detailed biological reactions involved in enzymatic processes, we need biomimetic representatives of these complicated enzymatic molecules. Synthetic metalloporphyrins provide such biomimicry molecules; and nowadays, they play important roles in medicine [4] materials [5] catalyst [6] among others. In general, to demonstrate a relationship between the structures and certain properties in class of complexes, usually, it requires many experimental and quantum calculations studies. The time constraint in educational laboratories makes it difficult to introduce this kind of experiments at the undergraduate level. However, with the advances in microwave-assisted synthesis technique, it is possible to reduce the experimental time substantially.

This technique offers many advantages such as reduction in reaction time and increased product yield. [7]

In addition to the laboratory work, we provided results of quantum cautions for the series of the complexes in the experiment. To explain a chemical phenomenon by combining experimental results with computational data gives a great depth of comprehension of the studied phenomenon. Exposing undergraduate students to this type of experiments where interpreting theoretical findings are used to explain empirical data, raise their appreciation and understanding for theoretical and computational methods in chemistry and their usages. The two-session undergraduate laboratory experiments presented in this paper involves synthesis and spectroscopic analysis of the synthetic metalloporphyrins of the first-row transition metal (II) ions: Fe, Co, Ni, Cu, and Zn which will be prepared using microwave technique. The synthesized complexes will be characterized via UV-visible spectra, <sup>1</sup>H-NMR spectra, and infrared spectra. Because it is possible to conduct multi reactions at the same time in the multi-mode microwave providing that all the reaction requires the same conditions, therefore, it is achievable to prepare the whole series in the same time in

one laboratory session. Thus, with the availability of Microwave of multi-reaction tubes, it is possible to divide the students into small groups (two to three students per group) and assign one complex for each group to synthesize and carry out all the spectral studies for it. In the first session, the students will be given pre-prepared 5,10,15,20-tetraphenylporphyrin (TPP). The H<sub>2</sub>TPP synthesis procedure is provided in the Supporting Information. The students will perform spectroscopically characterizations, UV-vis, <sup>1</sup>H-NMR, and IR, on the free base to confirm its structure. The following task will be carrying out the TPP metallization as described in the Supporting Information via microwave-assisted synthesis technique. The second session involves the synthesis and characterization of metal (II) ions complexes of (Fe (II), Co(II), Ni(II), Cu(II) and Zn(II)) which are described in the Supporting Information. The students will be divided into five groups and each group will be responsible for the synthesis and characterizations of a specific complex. By the end of the two sessions, the students will acquire spectroscopic data for the five complexes. To explain these spectra, the students need to predict the structure of the complexes and their electron configurations. The students will notice that there are some differences between the predicted electron configurations and the resulted <sup>1</sup>HMR. The quantum chemical calculations usually offer good predictions regarding the order of the frontiers orbitals of the molecules. Referring to these quantum calculations sometimes provides a good explanation for the experimental results.

## 2. Materials and Methods

### 2.1. General

All reagents and chemicals were purchased from Sigma-Aldrich and used as received. Benzaldehyde (C<sub>7</sub>H<sub>6</sub>O), pyrrole (C<sub>4</sub>H<sub>5</sub>N), propionic acid (CH<sub>3</sub>CH<sub>2</sub>COOH), Zinc acetate dehydrate (Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·2H<sub>2</sub>O), Nickel(II) acetate tetrahydrate (Ni(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O), iron (III) sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O), Cobalt(II) chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O), Copper(II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O), chloroform-*d* (CDCl<sub>3</sub>) were purchased from Sigma-Aldrich Chemical Company (Sigma Chemical Co., St. Louis, MO, USA). Thin-layer chromatography (TLC) was performed on silica gel glass plates (Silica gel, 60 F254, Fluka) and spots were visualized under UV lamp. Column chromatography was performed on Kieselgel S (Silica gel S, 0.063-0.1mm). Melting points recorded on a Gallenkamp apparatus and are uncorrected. Infrared spectra were measured using KBr pellets on a Thermo Nicolet model 470 FT-IR spectrophotometer. <sup>1</sup>H-NMR spectra were recorded on Varian, 400 MHz instruments by using DMSO-*d*<sub>6</sub> and CDCl<sub>3</sub> solutions and tetramethylsilane (TMS) as an internal reference. Microwave-assisted reactions performed using a microwave reactor (one touch technology CEM- Matthews, NC, USA). Multimode reactor is use for running a single vessel (20 ml) or up to 40 in parallel. Absorption measurements were carried out using Agilent 8453 spectrophotometer supported with 1.0 cm quartz cells (Austria).

## 2.2. Synthesis

### 2.2.1. Synthesis of Meso-tetraphenylporphyrin (TPP) 3

A microwave vessel equipped with a standard cap (vessel commercially furnished by CEM Discover) was filled with 10 mmol of Benzaldehyde and 10 mmol of pyrrole. Then to this mixture propionic acid (3.5 mL) and nitrobenzene (1.5 mL) were added in the reaction vessel. After the vessel was sealed, the reaction mixture heated under microwave irradiation (150°C) for 10 min. The irradiation power was 600W. The progress of the reaction was monitored by TLC and after completion porphyrin was crystallized overnight from the concentrated crude product mixture by addition of methanol. The dark purple solid was then filtered off, washed with methanol, dried to give pure porphyrin in a good yield; dark purple solid; yield 68%; mp 300°C; IR (KBr, cm<sup>-1</sup>): 3314 (NH), 3052 and 2923 (ArH), 1472 and 1440 (NH bending), 698 (out of plane bending deformation, monosubstituted benzene), 1593 (C=C), 1490 (C=N); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: -2.74 (brs, 2H, -NH), 7.76 (m, 12H, aromatic), 8.23 (dd, 8H, aromatic, *J* = 8.0 Hz), 8.87 (s, 8H, H<sub>β</sub>-pyrrolic); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ ppm: 120.1, 126.7, 127.7, 128.8, 129.1, 134.6, 142.2.

### 2.2.2. Synthesis of Metalloporphyrin 3a-e

The *meso*-tetraphenylporphyrin (1 mmol) and the appropriate metal salts (5 mmol) were added to *N,N*-dimethylformamide (DMF) (5 mL) in 20 ml CEM Microwave vial. The reaction mixture heated under microwave irradiation (150°C) for 15 min and the irradiation power was 600W. The reaction was monitored over time by UV-vis absorption spectrophotometry until the typical degeneracy of the Q bands was observed. After cooling to room temperature, the crude product mixture was washed with ice-cold distilled water (50 mL) and the resulting suspension was refrigerated for a few hours. Filtration of the precipitate under reduced pressure followed by washing with distilled water (50 mL) and drying, firstly overnight in an oven at 120°C and then in vacuo at room temperature, yielded the metallo-porphyrins as crystalline solids **3a-e**.

#### 2.2.2.1. Iron (III) 5,10,15,20-tetraphenylporphyrin (FeTPP) (4a)

(0.163 mmol, 100 mg of H<sub>2</sub>TPP mixed with 0.815 mmol, 226 mg in 10 ml DMF), Reddish brown solid; yield 92%; mp > 300°C; IR (KBr, cm<sup>-1</sup>): 2918, 1478, 1596, 805, 750; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 6.6, 8.25 (8H, *o*-phenyl), 7.79 (4H, *p*-phenyl), 12.5, 13.7 (d, 8H, *m*-phenyl), 80.20 (s, 8H, H<sub>β</sub>-pyrrolic).

#### 2.2.2.2. Cobalt (II) 5,10,15,20-tetraphenylporphyrin (CuTPP) (3b)

(0.163 mmol, 100 mg of H<sub>2</sub>TPP mixed with 0.815 mmol, 194 mg in 10 ml DMF), purple solid; yield 93%; mp > 300°C; IR (KBr, cm<sup>-1</sup>): 2923, 1440, 1596, 805, 750; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 8.00 (4H, *p*-phenyl), 8.20 (8H, *m*-phenyl), 13.2 (8H, *o*-phenyl), 16.50 (s, 8H, H<sub>β</sub>-pyrrolic).

### 2.2.2.3. Nickel(II) 5,10,15,20-tetraphenylporphyrin (NiTPP) (3c)

This complex was prepared following the procedure in reference [8]. NiTPP is a dark purple solid; yield 94%; mp > 300°C; IR (KBr, cm<sup>-1</sup>): 1598, 1462, 1440, 1384, 1006, 793, 695; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 7.69 (m, 12H, aromatic), 8.00 (dd, 8H, aromatic, *J* = 8.0 Hz), 8.74 (s, 8H, H<sub>β</sub>-pyrrolic).

### 2.2.2.4. Copper (II) 5,10,15,20-tetraphenylporphyrin (CuTPP) (3d)

(0.163 mmol, 100 mg of H<sub>2</sub>TPP mixed with 0.815 mmol, 199 mg in 10 ml DMF), Purple solid; yield 93%; mp > 300°C; IR (KBr, cm<sup>-1</sup>): 2918, 1440, 1597, 799, 698; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 7.80 (m, 8H, aromatic), 8.24 (p, 4H, aromatic).

### 2.2.2.5. Zinc(II) 5,10,15,20-tetraphenylporphyrin (ZnTPP) (3e)

The complex was synthesized according to reference [8]. ZnTPP is Red-purple solid; yield 96%; mp > 300°C; IR (KBr, cm<sup>-1</sup>): 1596, 1482, 1439, 1339, 1002, 797, 752; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 7.77 (m, 12H, aromatic), 8.24 (dd, 8H, aromatic, *J* = 8.0 Hz), 8.96 (s, 8H, H<sub>β</sub>-pyrrolic).

## 2.3. UV-Vis Measurements

All the UV-Visible studies were performed using a UV-Visible spectrophotometer with 1 cm quartz cells in the range of 200-700 nm at room temperature. The stock solutions were prepared by dissolving appropriate amounts of each compound in dichloromethane to final concentrations of 10<sup>-6</sup> M.

## 3. Results and Discussions

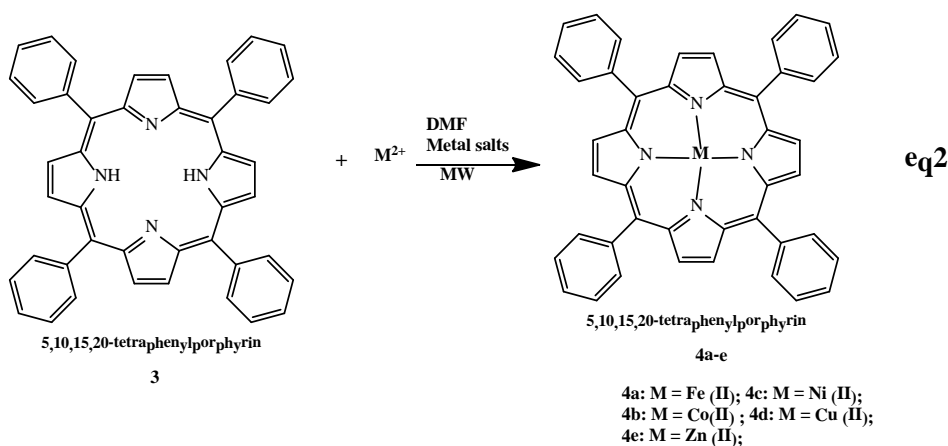
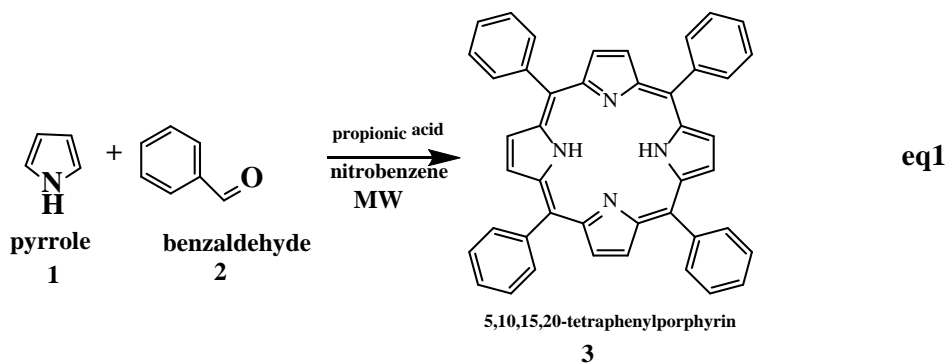
### 3.1. Synthesis

In this project, we are introducing students with microwave-assisted technique as a synthetic tool which is becoming very popular for synthesizing organic compounds in a quick and clean way. [9] The first step toward complexation started with the preparation of the free ligand. The synthesis of the H<sub>2</sub>TPP was conducted following Gonsalves *et al* procedure. [10] In this method, the acid of our choice was propionic acid and nitrobenzene as an oxidant. This choice of starting materials in combination with microwave technique yielded free chlorine porphyrin precipitate as given in (eq1).

Secondly, the preparation of a porphyrin complex was a one-step process, where the ligand and appropriate metal salts were reacted using microwave technique (eq2). The metalloporphyrins **4a-e** have been produced in relatively good yield (91-96%) (Table 1). Structures of the synthesized tetraphenylporphyrin **3** and its complexes **4a-e** were confirmed on the bases of <sup>1</sup>H NMR, IR and UV/Vis spectroscopy.

Table 1. Reaction time and percent yield of porphyrin H<sub>2</sub>TPP and the metalloporphyrins 4a-e

No.	Compound	Reaction time (min)	Yield %
3	H <sub>2</sub> TPP	5	68
4a	Fe (II)TPP	10	92
4b	Co (II)TPP	10	93
4c	Ni (II)TPP	10	94
4d	Cu (II)TPP	10	91
4e	Zn (II)TPP	10	96

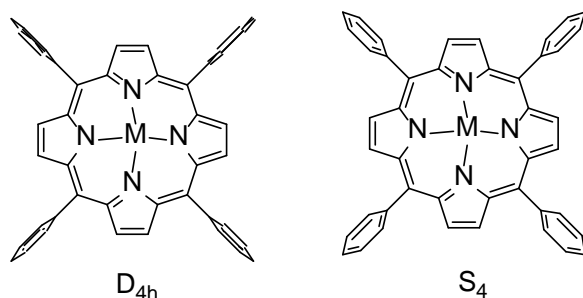


The metalloporphyrins (**4a-e**) were prepared by a very straightforward microwave-assisted experimental protocol, clearly demonstrating its synthetic potential when compared to other conventional synthetic methodologies used for the same purpose. The usefulness and convenience of the synthetic methods reported here arise from the use of a microwave oven, significant minimization of the reaction times, the amounts of solvents employed and the undemanding workups involved when compared with other method. For example Mamardashvili and coworkers [11] prepared Co(II)TPP conventionally by using equimolar of TPP and Co(II)salt in DMF with a reasonable yield of 72%. However, they used 70 mL of DMF to produce 0.04 g of the desired Co(II) complex. Their synthesis methodology is not economic or environment-friendly to be used in the educational laboratory due to the usage of the excess of solvent.

## 3.2. Structure and Spectroscopic Analysis

### 3.2.1. Structure

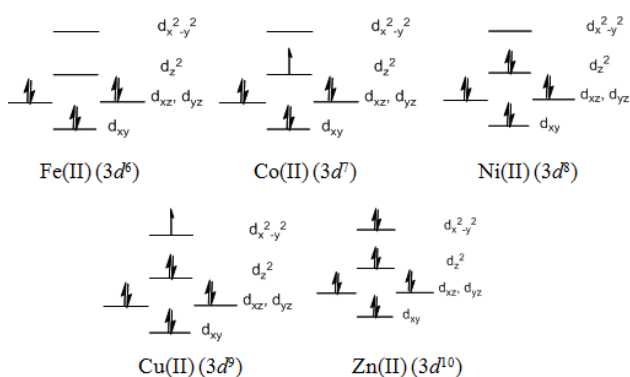
Although all the MTPP in this study are almost planar  $D_{4h}$  structures, some of them show some ruffling distortions  $S_4$  as depicted in Figure 1.



**Figure 1.**  $D_{4h}$  structure has the phenyl ring perpendicular to the porphyrin ring.  $S_4$  structure has the phenyl ring ruffled

#### 3.2.1.1. Electronic Structure

$TPP^{2-}$  is a tetradentate strong field ligand. Therefore, we are going to assume that all of our complexes are of low spin. Consequently, the valence electrons of the first row transition metals, which are Lewis acids, complexed with the Lewis base  $TPP^{2-}$  should be situated in the  $3d$  orbitals of the metal ions as illustrated in Figure 2.

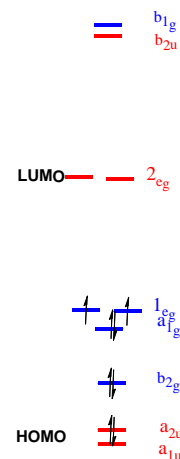


**Figure 2.** Metal d-orbital splitting in  $D_{4h}$  and Electron. Distributions in  $3d$  low spin metal ions

### 3.2.1.2. Frontiers Orbitals

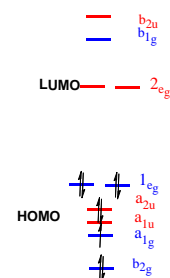
The energies of  $3d$  orbitals are decreasing in the direction of Fe to Zn. The most affected orbital by this trend of the five  $d$  orbitals in our complexes is  $d_{x^2-y^2}$  orbital. This explains why  $d_{x^2-y^2}$  orbital falls into the extent of the MOs of the porphyrin ligand in NiTPP and ZnTPP. Liao and coworkers, have computed the energies of the frontiers orbitals of MTPP complexes presented in this paper. They assumed that all of these complexes have  $D_{4h}$  symmetry, therefore, the  $3d$ -orbitals adopt the following symmetry:  $d_z^2(a_{1g})$ ,  $d_{x^2-y^2}(b_{1g})$ , ( $d_{xz}$  and  $d_{yz}$ ) ( $e_g$ ), and  $d_{xy}(b_{2g})$ . [12]

The HOMOs and LUMOs are not the same for all the complexes. Indeed, when closely examining the frontiers orbitals of our series we notice that they are different. In FeTPP the frontiers orbitals are the porphyrin ones, namely, the HOMO ( $a_{2u}$ ) and LUMO ( $2e_g(\pi^*)$ ) of TPP ligand and the  $3d$  of the metallic ion orbitals lay above the ring orbitals (See Figure 3). [12]



**Figure 3.** FeTPP Molecular Orbital Diagram according to theoretical calculations in reference [12]

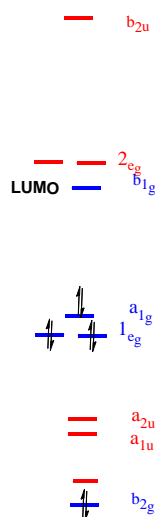
In CoTPP the  $d_z^2$  become lower in energy than  $d_{\pi}(d_{xz}, d_{yz})$ , hence,  $1e_g(d_{xz}, d_{yz})$  are the HOMO for the Co(II) complex and the LUMO is still the porphyrin's orbital set  $2e_g(\pi^*)$  (See Figure 4). [12]



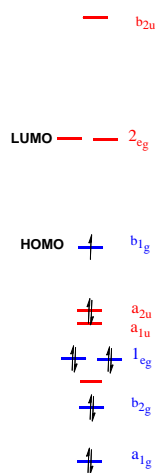
**Figure 4.** CoTPP Molecular Orbital Diagram according to theoretical calculations in reference [10]

The  $d_z^2$  orbital in NiTPP becomes higher in energy than  $1e_g(d_{xz}, d_{yz})$  and therefore it is the HOMO of it. (See Figure 5). [12]

While the  $d_{x^2-y^2}$  drop below the porphyrin  $2e_g(\pi^*)$  energy and becomes the LUMO of NiTPP. The  $d_{x^2-y^2}$  orbital is occupied in CuTPP, thus, becomes the HOMO and the LUMO is the  $2e_g(\pi^*)$  of the porphyrin (See Figure 6). [10]

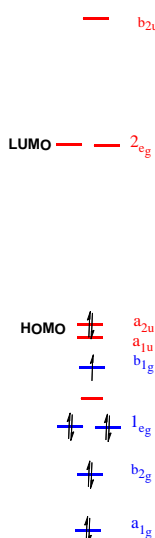


**Figure 5.** NiTPP Molecular Orbital Diagram according to theoretical calculations in reference [10]



**Figure 6.** NiTPP Molecular Orbital Diagram according to theoretical calculations in reference [12]

Finally, Zn (II) metal ion  $d$  orbitals are fully occupied and not involved in the HOMO- LUMO of the MOs of ZnTPP. Actually, the HOMO is  $a_{2u}$  and LUMO is  $2e_g$  ( $\pi^*$ ) of the porphyrin (See Figure 7). [12]

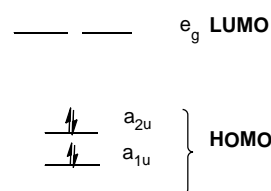


**Figure 7.** ZnTpp Molecular Orbital Diagram according to theoretical calculations in reference [12]

According to the above calculated values the electron configurations in the ground states of the complexes in reference [12] are: FeTPP  $\{(a_{1u})^2(a_{2u})^2(b_{2g})^2(a_{1g})^2(1e_g)^2\}$ , CoTPP  $\{(a_{1u})^2(a_{2u})^2(a_{1g})^1(1e_g)^4\}$ , NiTPP  $\{(a_{1u})^2(a_{2u})^2(1e_g)^4(a_{1g})^2\}$ , CuTPP  $\{(a_{1u})^2(a_{2u})^2(b_{1g})^1\}$ , ZnTPP  $\{(a_{1u})^2(a_{2u})^2\}$ .

Inspecting the frontiers orbitals of porphyrin ring shows that there are four outer molecular orbitals available to interact with the central metal ion. These orbitals are  $3e$  ( $\pi$ ),  $1a_{1u}$  ( $\pi$ ) or  $3a_{2u}$  ( $\pi$ ) which are the HOMO of the ligand and  $4e$  ( $\pi^*$ ) is the LUMO of this macrocycle molecule.

According to Gouterman's model [13] the four frontier orbitals for porphyrin are  $\pi$  ( $a_{1u}$  and  $a_{2u}$ ) and  $\pi^*$  ( $e_g$ ) orbitals. In this model the two (HOMO's) and two (LUMO's) with their symmetry is depicted in (Figure 8). Upon energy absorption, the ligand electrons are excited from  $\pi$  to  $\pi^*$  and this phenomenon is responsible for the metalloporphyrins colors.



**Figure 8.** Gouterman's model for porphyrin

In what follow we will discuss the covalent interaction of the porphyrin frontiers orbitals with metal ions center. The  $D_{4h}$  symmetry of the porphyrin does not allow for good interaction between the ring outer orbitals and the  $3d$  Fe ion. This is because the symmetries of the porphyrin outer orbitals are different than those of  $d_\pi$  of Fe (II) in this geometry. Actually, FeTPP was found to be distorted from  $D_{4h}$  to saddled conformation ( $D_{2d}$ ). [14,15] This saddled conformation enhance the covalent overlap between the metal-ligand (M-L) outer orbitals. The possible further interaction between Fe (II) and the porphyrin is the back-bonding from  $d_\pi$  of Fe  $\rightarrow$  Porphyrin  $4e$  ( $\pi^*$ ). Generally, This M-L back-bonding is possible when the metal ion has from one to three electrons in ( $d_{xz}$ ,  $d_{yz}$ ). [16]

### 3.2.2. UV-Vis Absorption Spectra

The absorption spectra of  $H_2TPP$  and MTPP complexes in this study were measured in dichloromethane within the spectral range 300-700nm.  $H_2TPP$  free base shows one intense band at 418 nm (Soret band ( $a_{1u}$  to  $e_g$ )) and four less intense Q ( $a_{2u}$  to  $e_g$ ) bands between 500 and 700 nm in agreement with the literature. [17] The placement of the metal ion in the cavity of the ligand results in the reduction of the Q bands to two peaks as listed in Table 2. As shown in Table 2, the absorption peaks for MTPP complexes are unique for each complex and the disappearance of 647 nm is an indication for complexation. For the spectra please refer to Supporting Information. Other than ZnTPP, the small interaction between the metal ions and the porphyrin does not change the merit of the spectra; however, there are minimal shifts in absorptions peaks are detected.

The spectral shifts in MTPP are due to that the insertion of the divalent metal ion into TPP2- affects the  $\pi$ - $\pi^*$  transition. This perturbation is due to the possible interactions between the metal and ligand such as



metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge (LMCT) transfer or d-d transfer.

The complexes Fe(II)TPP, Co(II)TPP, Ni(II)TPP and Cu(II)TPP peaks are shifted to shorter wavelengths due to the back bonding from metal center *d* (electrons) to the empty ligand frontier orbitals. Because Zn (II) ion in Zn(II)TPP (closed-shell porphyrin) has full *d* orbital ( $d^{10}$ ) it belongs to regular spectrum with no back bonding effect. In this case, *d* orbitals are relatively low in energy and have a smaller effect on the porphyrin HOMO-LUMO energy gap.

**Table 2. UV-vis data of free base porphyrins and metallated porphyrins**

Compound	Soret Band $\lambda_{nm}$	Q Bands			
		Q <sub>IV</sub> $\lambda_{nm}$	Q <sub>III</sub> $\lambda_{nm}$	Q <sub>II</sub> $\lambda_{nm}$	Q <sub>I</sub> $\lambda_{nm}$
H <sub>2</sub> TPP	418	516	551	589	645
FeTPP	409	512	570	--	623
CoTPP	407	--	527	--	--
NiTPP	416	--	523	--	--
CuTPP	416	--	539	--	--
ZnTPP	414	--	522	589	--

### 3.2.3. IR Studies

The range of 400-4000  $\text{cm}^{-1}$  was used to record the IR absorption frequencies for H<sub>2</sub>TPP and MTPP complexes. The IR /FTIR data are summarized in Table 3. For the spectra please refer to Supporting information. The comparison between the H<sub>2</sub>TPP and MTPP spectra reveals the disappearance of N-H bond stretching and bending frequencies ( $\sim 3314 \text{ cm}^{-1}$ )  $\delta$  N-H (in-planarity) and  $\delta$  N-H (out of planarity) absorption bands (964  $\text{cm}^{-1}$  and 798  $\text{cm}^{-1}$  respectively). The disappearance of N-H frequencies is attributed to the fact that the metallization of the porphyrin to occur, deprotonation of the two hydrogens of the ligand

must take place. For the spectra please refer to Supporting Information.

### 3.2.4. <sup>1</sup>H NMR Study

<sup>1</sup>H NMR spectral measurements have been conducted to verify the formation of porphyrin and its metalloporphyrins and to gain further insight toward their structures. Table 4 summarizes the characteristic <sup>1</sup>H NMR Shifts for H<sub>2</sub>PPT and MTPP complexes. The free porphyrin exhibits a singlet band for inner imino protons of the H<sub>2</sub>TPP. The singlet NH peak (due to the rapid exchange of -NH protons) set at a very high field (-2.74 ppm), since the two N-Hs lay within the shielded cavity of the porphyrin ring. The Multiple signals which resonate at  $\delta = 7.74$  ppm and integrated into 12 protons are assigned to aromatic protons. The two doublets of doublet appeared at  $\delta = 8.22$  ppm and  $\delta = 8.24$  ppm are correlated to the aromatic protons ( $J = 4.0 \text{ Hz}$ ) and integrated into 8 protons. The broad singlet band resonate at  $\delta = 8.87$  ppm due to  $\beta$ - protons of pyrrole ring and integrated into 8 protons. Metalloporphyrins <sup>1</sup>H-NMR spectra showed the disappearance of the NH peak at around -2.74 ppm which designates the formation of metalloporphyrins. Crystalline phase study by Hu C. and coworkers [14] showed that Fe(II)TPP has a very saddled symmetry. This explains why Fe(II) in TPP has two unpaired electrons in  $d_{x^2-y^2}$  and not as we predicted (see Figure 2). This confirms the theoretical results. This structure conformation was also seen in Co (II)TPP. The distinguishing features of paramagnetic complexes of Co (II) and Cu(II) ions are that all the proton signals are shifted to the downfield with the broadening of the resonance signals. Cu(II)TPP has the electronic configuration of  $(d_{xy})^2(d_{xz}, d_{yz})^4(d_z^2)^3(d_{x^2-y^2})^1$ . [18] The location of the unpaired electron in the plane of the porphyrin plane allows for spin delocalization through  $\sigma$  bond especially for the  $\beta$ -pyrrole. This delocalization is responsible for the extreme broadening seen for the  $\beta$ -pyrrole signals in this complex. [19]

**Table 3. IR/FIR data of free base porphyrins and metalloporphyrins**

Functional Group	Wavenumber ( $\text{cm}^{-1}$ )					
	H <sub>2</sub> TPP	Zn(II)TPP	Ni(II)TPP	Fe(II)TPP	Cu(II)TPP	Co(II)TPP
$\nu$ [NH]	3314	-	-	-	-	-
$\nu$ [=C-H]	2923	2923	2922	2923	2918	2923
$\nu$ [C=N]	1490	1339	1384	1384	1440	1440
$\nu$ [C=C]	1593	1596	1598	1596	1597	1596
$\delta$ [C-H]	798,698	797, 752	793, 695	798,698	799, 698	805, 750
$\delta$ [NH]	964	-	-	-	-	-

**Table 4. <sup>1</sup>H NMR chemical shifts ( $\delta$  in ppm) taken in CDCl<sub>3</sub> solution at 298 K**

Complexes	-NH	Pyrrole	Meso		
			Ortho	Meta	Para
H <sub>2</sub> TPP	-2.74	8.87	8.23	7.76	7.76
Fe(II)TPP	-	13.45	7.55	7.79	7.66
Co(II)TPP	-	16.50	13.20	8.20	8.00
Ni(II)TPP	-	8.74	8.00	7.69	7.69
Cu(II)TPP	-	a	a	7.80	8.24
Zn(II)TPP	-	8.96	8.24	7.77	7.77

a: Too broad to detect.

For the spectra please refer to Supporting Information.

## 4. Conclusion

Our conclusion for the above work can be summarized as follow:

1. Synthesis using microwave techniques can be used in educational laboratories to prepare some compounds in a fast and clean way. Multi-mode microwave that can be used to carry several reactions under the same conditions at the same time can be very advantageous in educational laboratories.

2. UV-Vis, IR/FTIR and <sup>1</sup>H NMR spectroscopies are powerful tools in detecting the complexation between the porphyrin ligand and metal ion and to check their purities.

3. <sup>1</sup>H NMR spectroscopy is a reasonable tool that can be utilized to gain some knowledge about the spin of the metal ion in metalloporphyrin complexes.

4. Correlating the results of theoretical studies such as the calculations of orbitals energies in the ground state with the experimental data gives deeper understanding of the electronic structure of the complexes in this study.

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