

Thermal behavior and the solvent effects of ρ -Methoxy Tetraphenylporphyrin (TOMPP), Copper Porphyrin (CuTOMPP), and Nitroporphyrin (CuTOMPP-NO₂)

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Abstract. In this work, ρ -methoxy tetraphenylporphyrin (TOMPP) Copper porphyrin (CuTOMPP) and nitroporphyrin (CuTOMPP-NO₂) are synthesized following Adler Longo method by the reaction of pyrrole with and ρ -anisaldehyde. These compounds have been characterized by UV-Vis, fluorescence spectroscopy and thermogravimetric analysis (TGA). The ρ -methoxy tetraphenylporphyrin (TOMPP) was obtained in 26% yield. Reactions of TOMPP with copper ions gave CuTOMPP in 85% yield. Moreover, the nitration of CuTOMPP gave CuTOMPP-NO₂ in 0.03% yield. The absorption spectra for TOMPP exhibited one S-band (416 nm) and four Q-bands (518, 555, 593 and 650 nm) in dichloromethane solvent. The absorption band of copper porphyrin and nitroporphyrin displays one S band (415 and 423) and two Q bands (range from 550 – 600 nm). When excited to 530-570 nm, the fluorescence spectra show only one emission band at 645-654 nm for TOMPP and copper complexes. The results confirmed the solvent effect on the electronic absorption as found a small red shift from 414 nm (chloroform) to 417 nm (ethyl acetate) for TOMPP. The thermal behaviors including the possible phase transition of porphyrins were studied during the heating process at temperature of 298-973 K. Copper complexes exhibits the thermal stability from 653.3 K, which is slightly lower than that of the free base porphyrin ligand (TOMPP 703.9 K).

1 Introduction

Porphyrins were heterocyclic macrocycle organic compounds which were found in nature. Naturally occurring porphyrins played an important in the maintenance of the animal and plant bodies [1, 2]. Hemoglobin, cytochromes and chlorophylls were the best known porphyrin pigments [3, 4]. Hemoglobin and cytochromes contain iron(II) ion and chlorophylls contained magnesium(II) ion in the metal center hole [5, 6].

Free base porphyrins are known as substances with a great capability to form highly stable metalloporphyrins, having a great potential as corrosion inhibitors. Their planar molecules containing four pyrrole subunits present bonding sites for complexes formation at the nitrogen atoms. The whole molecule structure shows conjugated double bonds due to the -CH= bridging groups and thus, a very mobile electronic system. These properties are very important in the adsorption process of these compounds on diverse metals surfaces [7].

Synthesis of porphyrins and their metal complexes have received much attention. This has been mainly due to the use of these compounds in catalysis [8], as materials with novel electrical properties [9] and as biomimetic model systems of primary processes of natural photosynthesis [10]. They can be used as photosensitizing drugs in photodynamic therapy (PDT).

Photodynamic therapy is emerging as an important treatment for many diseases. Many applications of PDT involve killing undesirable disease-causing cells such as malignant cancer cells or pathogenic microorganisms [11]. PDT is also used for destroy unwanted tissues such as tumors [12], new blood vessels [13], and atherosclerotic plaques [14]. An extra stable porphyrin occurs by complexation with transition metal ions explained by the macrocyclic effect [15]. Porphyrins and their derivatives have well-known technological applications. Concerning to it can be applied as dyes in solar cells to improve efficiency [16]. Porphyrins have the characteristic properties and can be applied in many applications such as molecular electronic devices.

In the present work, the application of Adler Longo synthesis method was selected to study for the free base porphyrins ligand (TOMPP). The ρ -Methoxy tetraphenylporphyrin (TOMPP) and metalloporphyrins were prepared and purified polar characterization. The complexes were characterized by IR spectroscopy, ¹H and ¹³C NMR spectroscopy, mass spectrometry (MS), CHN analysis, thermogravimetric analysis (TGA), UV-Vis and fluorescence spectroscopy. To study the effect of solvent, the absorption spectra and emission spectra of free base porphyrin were analyzed by using UV-Vis spectrophotometry and spectrofluorometer, in dichloromethane, toluene, ethyl acetate and chloroform. The thermal gravimetric analysis results would represent

the stability of complexes, when it was prepared in real application such as coating on ITO glass.

2 Experimental

2.1 Measurements

Properties of ρ -methoxy tetraphenylporphyrin (TOMPP), copper porphyrin (CuTOMPP) and nitro porphyrin (CuTOMPP-NO₂) were characterized by UV-Vis spectroscopy in the wavelength range of 200-800 nm and fluorescence spectroscopy in the wavelength range of 530-700 nm. UV-Visible spectra were obtained on Shimadzu UV-spectrometer (UV-1700). Fluorescence spectra were recorded on Jasco spectrofluorometer (FP-6200). The FT-IR spectra were recorded on Perkin Elmer infrared spectrophotometer (spectrum GX). ¹H and ¹³C NMR spectra were recorded with a Bruker (FT-NMR advance 400 MHz) spectrometer in chloroform-d with tetramethylsilane (Me₄Si) as an internal standard. Mass spectra were obtained on Thermo Finnigan (LCQ Advantage) using CH₂Cl₂. CHN analysis was carried out on Perkin Elmer (2400) elemental analyzer. TGA were recorded on Perkin Elmer (TGA7).

2.2 Synthesis of ρ -methoxy tetraphenyl porphyrin, its metal complexes, and nitro derivative

General procedure: The ρ -methoxy tetraphenylporphyrin (TOMPP), were synthesized by refluxing pyrrole with ρ -anisaldehyde in propionic acid. The product has methoxy groups on para position of each TPP ring, as shown in Fig. 1. The metalloporphyrin were prepared by refluxing TOMPP ligand with metal acetate in DMF (Fig. 2). Lastly nitro group have been insert in CuTOMPP via reaction between CuTOMPP and copper nitrate (Fig. 3.). The crude products were purified by silica column chromatography with dichloromethane and hexane. There derivative were synthesized similarly.

Synthesis of ρ -methoxy tetraphenylporphyrin (TOMPP): The procedure was started by refluxing pyrrole (1 mL, 14.3 mmol) and ρ -anisaldehyde (1.5 mL, 15.6 mmol) in propionic acid (100 mL). The reaction was stirred at 363 K for 1 h. The title compound was isolated by column chromatography (silica gel, hexane: dichloromethane) as a purple solid (26% yield). IR (NaCl): 3435, 3053, 2987, 1606, 1550, 1265, 1163, 1017, 895 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ 8.88 (8H, Pyrrole, β -H), 8.13 (8H, Phenyl,o-H), 7.35 (8H, Phenyl, m-H), 4.22 (12H, -OCH₃), -2.82 (2H, Pyrrole, N-H). ¹³C-NMR (100 MHz, CDCl₃): δ 128.79 (Cmeso), 159.45 (C α , pyrrole ring), 130.81 (C β , pyrrole ring), 135.56, 134.87 (-C₆H₄), 134.72, 130.81 (phenyl ring), 55.56 (-OCH₃). Elemental analysis calcd (%) for C₄₈H₃₈N₄O₄ (734.84): C 78.45, H 5.21, N 7.62; found: C 76.42, H 5.75, N 7.42. The lower carbon contents many related to solvent in the compound, which need further characterization. Mass m/z (ESI): found 735.38.

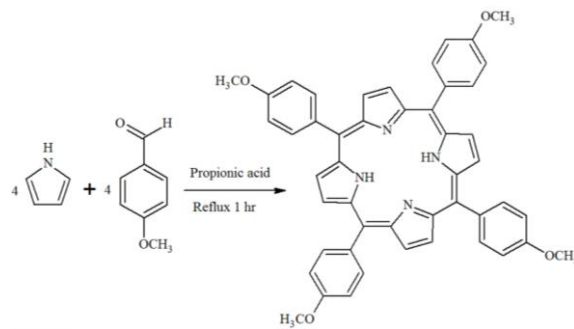


Figure 1. Synthesis of ρ -methoxy tetraphenylporphyrin (TOMPP).

The ρ -methoxy tetraphenylporphyrin (0.1 g, 0.14 mmol) and copper acetate (0.1 g, 0.55 mmol) were heated under reflux in DMF (20 mL). The CuTOMPP was purified by column chromatography (silica gel, hexane: dichloromethane) and gelled as a purple solid (85% yield). ¹H-NMR (400 MHz, CDCl₃): δ 8.88 (8H, Pyrrole, β -H), 8.14 (8H, Phenyl,o-H), 7.35 (8H, Phenyl, m-H), 4.21 (12H, -OCH₃). IR (NaCl): 3055, 2987, 1604, 1551, 1262, 1150, 896 cm⁻¹. Elemental analysis calcd (%) for CuC₄₈H₃₆N₄O₄ (796.37): C 72.39, H 4.56, N 7.04; found: C 71.78, H 4.65, N 7.02. Mass m/z (ESI): found 797.46.

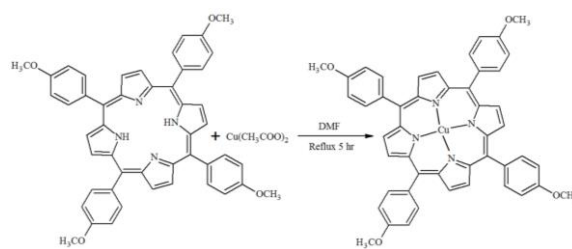


Figure 2. Synthesis of copper porphyrin complex (CuTOMPP)

Synthesis of 2-nitro-methoxy tetraphenylporphyrinato copper(II) (CuTOMPP-NO₂): The general procedure was magnetically stirred CuTOMPP (0.2 g, 3 mmol) and excess copper nitrate in chloroform (100 mL) and acetic anhydride (9 mL) for 48 hours at room temperature. The title compound was isolated by column chromatography (silica gel, hexane: dichloromethane) as a purple solid (0.03% yield) ¹H-NMR (400 MHz, CDCl₃): δ 7.26 (20H, Phenyl), 3.98 (12H, -OCH₃). IR (NaCl): 2928, 2831, 1606, 1501, 1463, 1340, 1248, 1174, 800 cm⁻¹. Mass m/z (ESI): found 842.65.

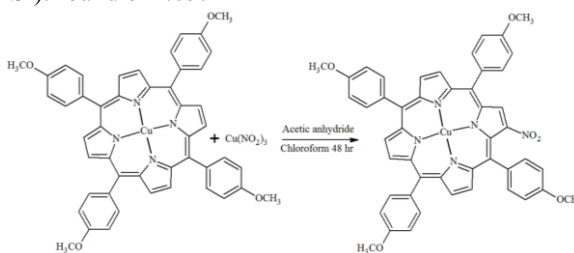


Figure 3. Synthesis of copper nitro porphyrin complex (CuTOMPP-NO₂)

3 Results and discussion

Table 1. The absorption data of TOMPP in various solvents.

Solvent	TOMPP				
	Soret band (nm), ϵ ($M^{-1}cm^{-1}$)	Q band (nm), ϵ ($M^{-1}cm^{-1}$)			
Dichloromethane	416, 29129	518, 5414	555, 3793	593, 1778	650, 2400
Toluene	416, 21088	518, 2881	555, 1962	596, 856	653, 1255
Ethyl acetate	417, 33034	516, 6468	558, 4565	594, 1976	651, 2750
Chloroform	414, 39198	519, 8313	556, 5683	594, 2770	651, 3429

* All solution was prepared in the concentration of 1×10^{-4} mol/L, (n =3, %RSD \leq 1.4)

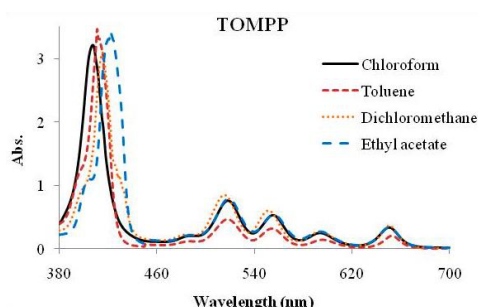


Figure 4. UV-Vis spectra of TOMPP in various solvents

Table 2. The absorption data of TOMPP, CuTOMPP, and CuTOMPP-NO₂ in dichloromethane.

Porphyrins	Dichloromethane				
	Soret band (nm), ϵ ($M^{-1}cm^{-1}$)	Q band (nm), ϵ ($M^{-1}cm^{-1}$)			
TOMPP	416, 404283	518, 15986	555, 10937	593, 5468	650, 6731
CuTOMPP	415, 510297	-	541, 7993	585, 5468	-
CuTOMPP-NO ₂	423, 224227	-	551, 17248	597, 13882	-

*All solution were prepared in the concentration of 2.38×10^{-6} mol/L, (n =3, %RSD \leq 1.6)

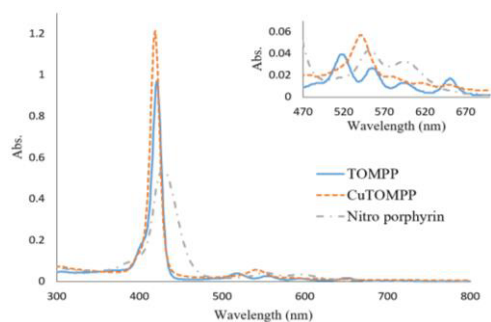


Figure 5. UV-Vis spectra of TOMPP, CuTOMPP, and CuTOMPP-NO₂ in dichloromethane

The intense colour of porphyrins was derived from the highly conjugated π -electron systems. The most attraction feature of porphyrins was their characteristic UV-Visible

spectra that consist of two distinct regions; in the near ultraviolet is called the Soret band (380-450 nm) and in the visible region is called Q-band (500-700 nm). The absorption spectra of the free base porphyrin showed significant characteristics of one soret band and four Q-bands, as shown in Fig. 4. The electronic spectra of the TOMPP in various solvents were investigated and the λ_{max} values were given in Table 1. In metalloporphyrin, the proton on NH group of porphyrin were deprotonated and then nitrogen atom binds with metal ion to give the metal-porphyrin. The metal ions acting as Lewis acids interact with the lone-pair electrons of porphyrin ligand. The intense absorption band, related due to absorption(s) with in the porphyrin ligands, involving the excitation of electrons from π to π^* porphyrin ring orbital [17], as shown in Fig. 5. The absorption band of metalloporphyrin displays only two Q-bands. The results were shown in Table 2 due to difference energy levels.

The solvent are effected on electronic absorption of TOMPP, as found a small red shift from 414 nm (chloroform) to 417 nm (ethyl acetate). The lower energy gap found in ethyl acetate solvent are related to the smaller HOMO-LUMO gap of the complexes. The further information for solvent effect on metalloporphyrins are needed to be studied. Similar result on the solvent on lower Q-band intensity for metalloporphyrins are found and reported as solvatochromism. Those complexes show linear correlation between polarity of solvent and dipole moments of complexes [18]. However, those results confirmed the solvent effect on the electronic absorption. Furthermore the weak coordination between each metalloporphyrin and solvent were clearly found. The sign of solvatochromism depends on the variation of the dipole moment of complexes and the absorption spectra with solvent polarity. When comparing with free base porphyrin (TOMPP) with metal complexes the soret band was little shifted while the Q-bands showed only 2 band Q-bands (Table 2). The absorption spectrum of Q-bands was changed relating to symmetry effect. The change in the spectrum (fewer peak in Table 2) on metal added is due to increased symmetry relative to the free base porphyrin similar to the previous reported by Boudif [19]. The two hydrogen atoms on the nitrogen atom in the free base porphyrins reduce the ring symmetry.

Fluorescence spectroscopy of TOMPP and metalloporphyrins were characterized in dichloromethane and the results were shown in Table 3. The enlargement of the π -conjugation yields the emission characteristics at the emission range from 645-654 nm when excited at 530-570 nm. This is manifested in a blue shift of the emission maximum compared to the free base ligand as the π -delocalization increases. This finding is consistent with the similar trend observed in the absorption spectra as above.

The term of band gap refers to the energy difference between the top of the valence band to the bottom of the conduction band, electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition, called the band gap energy [20]. The estimated energy gap

determined from an intersection of UV-Vis absorption (Q4-band) and fluorescence emission spectrum [21]. The calculated energy gap of TOMPP was 1.902 eV. The intersection of spectra of TOMPP showed in Fig. 6.

Table 3. The excitation and emission wavelength of TOMPP and copper complexes.

Porphyrin	CH ₂ Cl ₂		Toluene		Ethyl acetate		CHCl ₃	
	Ex.	Em.	Ex.	Em.	Ex.	Em.	Ex.	Em.
TOMPP	530	654	530	655	530	654	530	652
CuTOMPP	570	654	570	656	560	571, 654	560	653

All solution were prepared in the concentration of 1×10^{-4} mol/L, (n=3, %RSD \leq 1.5)

*Ex.; Excitation wavelength (nm), Em.; Emission wavelength (nm)

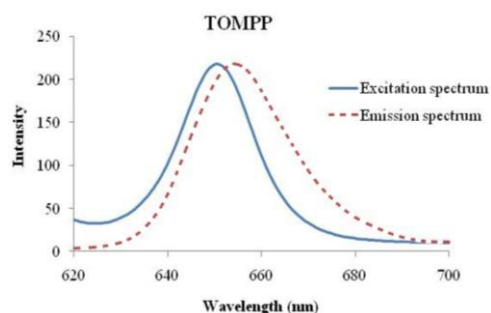


Figure 6. Excitation spectrum and emission spectrum of TOMPP in dichloromethane

Under the conditions that the thermogravimetry measurements were performed (open cells and nitrogen flow), the first observation is that decomposition temperature of the free base porphyrin TOMPP, is really high compared to metalloporphyrin. The condensation of pyrrole with ρ -anisaldehyde will afford the remarkable stability to TOMPP, which decompose at $T = 703.9$ K. The greater thermal stability may be related to the bond between metal ion and ligand in complexes and be a good choice. The metalloporphyrin complexes show the greater thermal stability from Cu-TOMPP (shown in Table 4 and Fig. 7.). Consider with TGA, metal complexes were interesting to use in alternative energy of solar cell [22]. However, the metal complexes show the lower thermal stability than pure ligand that may be related to weaker bond in metal complexes.

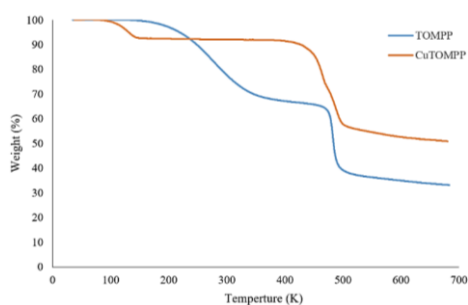


Figure 7. Themogravimetry curve of TOMPP and CuTOMPP

Table 4. Temperture of decomposition of TOMPP and CuTOMPP.

Compounds	I		II	
	T decomp (K)	Weight loss%	T decomp (K)	Weight loss%
TOMPP	443.2	31.3	703.9	29.8
Cu-TOMPP	348.4*	7.9	653.3	37.3

*water vapor

4 Conclusions

ρ -Methoxy tetraphenylporphyrin (TOMPP) and metalloporphyrins have been successfully synthesized and their identities were confirmed by mass spectrometry (MS), CHN elemental analysis, ¹H, ¹³C NMR, FT-IR spectra, thermogravimetric analysis (TGA), UV-Vis and fluorescence spectroscopy. The free base ligand (TOMPP) at optimal condition (refluxing in propionic acid) was obtained 26% yield. Reactions of TOMPP with metal ions (Cu²⁺) gave CuTOMPP in 85% yield. The nitration reaction provided CuTOMPP-NO₂ in 0.03% yield. The UV-Vis absorption spectra for TOMPP exhibited a single S-band with four Q-band, which the metalloporphyrin complexes and insertion nitrocomplex show a single S-band couple with only two Q-band. Excited the synthesized complexes, the product show the fluorescence spectra, emitted range 652-655 nm for TOMPP and emitted range 645-654 nm for metal complexes. The thermal behaviours including the possible phase transition of porphyrins were studied during the heating process at lower temperature (298-973 K). The CuTOMPP exhibit lower thermal stability compared with TOMPP. However, free base ligand and metalloporphyrins are stable enough for real applications, especially in ITO coating process for solar cell.

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