

CHAPTER III

RESULTS AND DISCUSSION

3.1 Synthesis and Structural Characterization of Tetraphenylporphyrin and Their Complexes

3.1.1 5,10,15,20-Tetraphenylporphyrin (TPP, 1)

5,10,15,20-Tetraphenylporphyrin (TPP, 1) was synthesized according to Adler and Longo's method [13]. After a workup, the compound was obtained as purple crystals in 24% yield, relatively close to what was reported in the literature ($20\pm 3\%$). The compound was then characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy and MALDI-TOF mass spectrometry. ^1H NMR spectrum (Appendix B) showed signals corresponding to the structure shown in **Figure 3.1**.

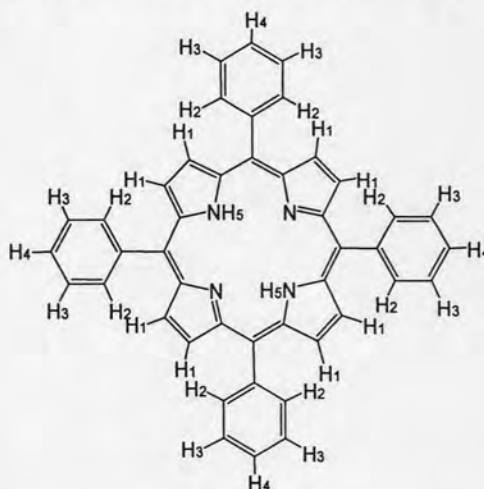


Figure 3.1 Structure of 5,10,15,20-tetraphenylporphyrin (TPP, 1)

The ^1H NMR data were consistent with those reported in the literature [39]. Free-base tetraphenyl porphyrin showed three multiplet series in aromatic region at δ 7.76-7.78, 8.23-8.25, and 8.88 ppm which correspond to the signals of *m*-, *p*-phenyl, and *o*-phenyl, and β -pyrrole protons, respectively. The upfield singlet signal at -2.73 ppm refers to internal N-H protons within the inner core of porphyrin rings (**Figure A-1**, Appendix A). UV/Visible absorption spectrum of the product showed a strong Soret band at 418 nm and four weaker Q-bands at 516, 550, 592, and 648 nm, respectively (**Figure A-2**, Appendix A). Molecular ion peak $[M]^+$ found at 614.635 by

MALDI-TOF-MS technique employing dithranol as a matrix was consistent with calculated molecular ion of 614.749 (**Figure A-3**, Appendix A).

3.1.2 5,10,15,20-Tetraphenylporphyrinatozinc(II) (ZnTPP, **2**)

A saturated zinc acetate dihydrate solution in methanol was reacted with a chloroform solution of TPP at reflux to afford 5,10,15,20-tetraphenylporphyrinatozinc(II) (ZnTPP, **2**). Only after a half an hour of reflux, zinc ion was inserted very easily into the core of the free-base TPP as indicated by a change in the color of the solution from deep to bright purple. After a routine workup the purple crystals were obtained in a quantitative yield. The product was characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy, and MALDI-TOF mass spectrometry. The ^1H NMR spectrum (Appendix B) showed signals corresponding to the structure in **Figure 3.2**.

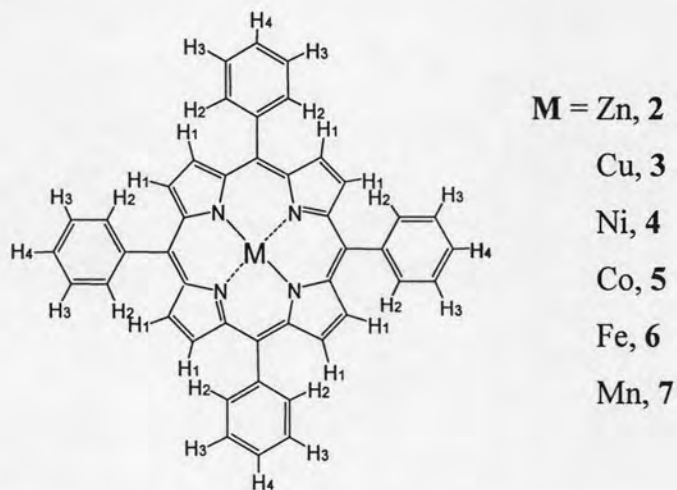


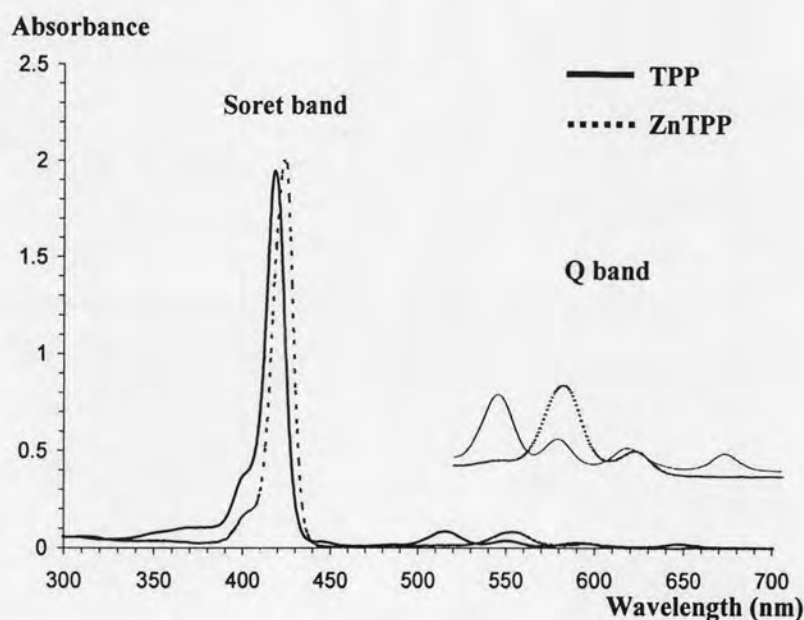
Figure 3.2 Structure of TPP complexes, 2-7

The ^1H NMR spectrum of ZnTPP (**2**) showed relatively similar proton signals to that of the free-base 5,10,15,20-tetraphenylporphyrin (**1**) with the β -pyrrole protons shifted from 8.88 to 8.96 ppm (**Table 3.1**). However, the characteristic signal of the internal NH protons observed in the spectrum of the free-base **1** at -2.73 ppm had disappeared.

Table 3.1 Comparison of ^1H NMR chemical shifts between TPP (1) and ZnTPP (2)

Compounds	Chemical shifts of the protons (δ , ppm)			
	β -pyrrole (H1)	<i>o</i> -phenyl (H2)	<i>m</i> -, <i>p</i> -phenyl (H3,H4)	internal NH (H5)
TPP, 1	8.88	8.23-8.25	7.76-7.78	-2.73
ZnTPP, 2	8.96	8.23-8.25	7.76-7.78	not observed

In order to confirm that the Zn complex was formed a UV/Visible absorption was measured. Compared to the spectrum of the free-base parent (1), UV/Visible spectrum of the ZnTPP (2) showed a red shift of the λ_{max} of the Soret band from 418 nm to 423 nm. In addition, the characteristics of metallated porphyrin were observed. While four Q bands were observed in the free-base porphyrins, only two peaks at 554 and 598 nm were present in the Zn complex (Figure 3.3). Results from MALDI-TOF-MS analysis also confirmed the formation of ZnTPP (2) with the molecular ion peak found at 677.492 which was consistent with calculated molecular ion of 678.123 (Figure A-6, Appendix A).

**Figure 3.3** An overlay of UV/Visible absorption spectra of free-base TPP and ZnTPP showing a red shift and a difference in the number of peaks in Q band

3.1.3 5,10,15,20-Tetraphenylporphyrinatocopper(II) (CuTPP, 3)

5,10,15,20-Tetraphenylporphyrinatocopper(II) (CuTPP, 3) was synthesized from a reaction of anhydrous copper acetate and TPP. The desired compound was obtained as bright purple crystals in 99% yield. Characterization by ^1H NMR spectroscopy, UV/Visible spectroscopy, and MALDI-TOF mass spectrometry were carried out.

The ^1H NMR spectrum of CuTPP (3) showed broad signals of aromatic protons resonance at δ 7.50 and 7.65 ppm. Although signals in the aromatic region were not fully resolved, the significant signal of internal NH protons between -2.70 to -2.90 ppm was absent. This strongly supported that copper(II) ion had completely replaced the inner protons (Figure A-7, Appendix A). The electronic absorption spectrum in chloroform showed a slight blue shift of the Soret band λ_{max} from 418 nm in free-base TPP to 416 nm in the complex. The Q-band signals have decreased from four to one peak at 539 nm when transformed from the free-base to the complex (Figure A-8, Appendix A). MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak at 676.367 which was consistent with calculated molecular weight of 676.189 (Figure A-9, Appendix A).

3.1.4 5,10,15,20-Tetraphenylporphyrinatonicel(II) (NiTPP, 4)

Attempts have been made to synthesize 5,10,15,20-tetraphenylporphyrinatonicel(II) (NiTPP, 4) by reacting TPP with 2 equivalents of nickel acetate tetrahydrate in chloroform. This resulted in an incomplete reaction even though the reaction was carried out for a long time. The condition was modified by increasing the amount of the nickel salt to 5 equivalents. The solvent was changed to DMF. As a result, the reaction was complete within 3 hours. It was noteworthy that NiTPP partially precipitated after the solution was cooled down. After a workup, purple crystals precipitated in 87% yield. The product was characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy, and MALDI-TOF mass spectrometry. The ^1H NMR spectrum (Appendix B) showed signals corresponding to the structure in Figure 3.2.

The ^1H NMR spectrum of NiTPP (4) showed peaks of aromatic protons resonance at δ 7.75-7.77, 8.23-8.25, and 8.96 ppm which were assigned to signals of *m*- and *p*-phenyl protons, *o*-phenyl protons, and β -pyrrole protons, respectively. As

anticipated, the characteristic signal of internal NH protons of the free-base porphyrin between -2.70 to -2.90 ppm had disappeared indicating that nickel(II) inner nitrogen coordination had taken place (**Figure A-10**, Appendix A). UV/Visible absorption spectrum showed a slight blue shift of the Soret band λ_{\max} from 418 nm in the free-base TPP to 415 nm in the complex. Moreover, absorption peaks in the Q-band were reduced from four to one peak at 528 nm (**Figure A-11**, Appendix A). Molecular ion peak of 671.400 which was consistent with the calculated value of 671.426 was found in the MALDI- TOF-MS analysis (**Figure A-12**, Appendix A).

3.1.5 5,10,15,20-Tetraphenylporphyrinatocobalt(II) (CoTPP, 5)

5,10,15,20-Tetraphenylporphyrinatocobalt(II) (CoTPP, 5) was prepared by a reaction of cobalt acetate tetrahydrate in methanol and TPP in chloroform. The color of the free-base porphyrin solution gradually changed from deep purple to brown as the complexation proceeded. After workup, purple powder of CoTPP was afforded in 99% yield. The product was characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy, and MALDI-TOF mass spectrometry. The structure of CoTPP showed in **Figure 3.2**.

The ^1H NMR spectrum of CoTPP (5) showed broad signals of aromatic proton resonance, which made it uncertain to be identify as the desired product. Nevertheless, the characteristic signal of the internal NH protons of the free base at -2.70 to -2.90 ppm was absent, supporting that cobalt(II) ion has replaced these inner protons (**Figure A-13**, Appendix A). In addition, the electronic absorption spectrum in chloroform showed blue shifts of the Soret band (λ_{\max}) from 418 nm in free-base TPP to 410 nm. The numbers of Q-band signals have decreased from four to one peak at 528 nm (**Figure A-14**, Appendix A). MALDI-TOF-MS spectrum confirmed molecular ion peak of 670.561 which was relatively close to the calculated molecular ion of 671.666 (**Figure A-15**, Appendix A).

3.1.6 5,10,15,20-Tetraphenylporphyrinatoiron(III) ((Cl)FeTPP, 6)

The synthesis of 5,10,15,20-tetraphenylporphyrinatoiron(III) ((Cl)FeTPP, 6) using saturated iron (III) chloride anhydrous 5 equivalent in methanol was carried out in a boiling chloroform solution of TPP. Neutralizing the reaction by adding a few drops of pyridine cause a color change from brown to green. Purple crystals of the

product were obtained in 90.8% yield after a workup and recrystallization. The product was characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy and MALDI-TOF mass spectrometry. The structure of $(\text{Cl})\text{FeTPP}$ showed in **Figure 3.2**.

Similar to the ^1H NMR spectrum of CoTPP (**5**), that of $(\text{Cl})\text{FeTPP}$ (**6**) showed broad peaks of aromatic proton resonances, (**Figure A-16**, Appendix A), Nevertheless, the characteristic signal of the internal NH protons of the free base at -2.70 to -2.90 ppm was absent, supporting that iron(III) ion has replaced these inner protons. The electronic absorption spectrum in chloroform showed slightly blue shifts of the Soret band (λ_{max}) from 418 nm in free base TPP to 416 nm and only two Q-band at 510 and 580 nm (**Figure A-17**, Appendix A) were observed. MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak of $(\text{Cl})\text{FeTPP}$ at 702.281 In addition, another peak at 667.244 identified as FeTPP was observed which were consistent with calculated molecular ion of 668.578 (**Figure 3.4**, **Figure A-18**, Appendix A).

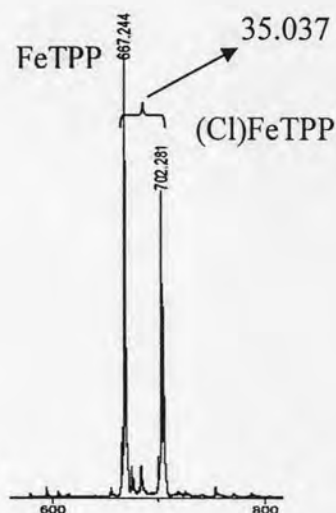


Figure 3.4 Molecular ion peaks of FeTPP and $(\text{Cl})\text{FeTPP}$.

3.1.7 5,10,15,20-Tetraphenylporphyrinat manganese(III) (MnTPP , **7**)

5,10,15,20-Tetraphenylporphyrinat manganese(III) (MnTPP , **7**) was synthesized from manganese acetate tetrahydrate. The colour of the mixture changed from deep purple to green solution. After workup, hexane was added into the concentrated chloroform reaction solution which was used instead of methanol for recrystallization because the product was soluble in methanol. A green powder was obtained in 97% yield and characterized by ^1H NMR spectroscopy, UV/Visible

spectroscopy and MALDI-TOF mass spectrometry. The structure of MnTPP showed in **Figure 2**.

The ^1H NMR spectrum of MnTPP (**6**) showed broad peaks of aromatic protons resonance (**Figure A-19**, Appendix A). An absence of the characteristic signal of the internal NH protons of the free base at -2.70 to -2.90 ppm was an evidence that manganese(III) ion has replaced these inner protons. The electronic absorption spectrum in chloroform showed a red shift of the Soret band (λ_{max}) from 418 nm in free-base TPP to 474 nm in the complex and Q-band reduced to two peaks at 578 and 614 nm (**Figure A-20**, Appendix A). MALDI-TOF-MS spectrum confirmed molecular ion peak of 666.275 which was relatively close to the calculated molecular ion of 667.671 (**Figure A-21**, Appendix A).

Table 3.2 UV-Visible absorption of TPP and its metal complexes

Product	Soret band	Q band
TPP	418	516, 550, 592, and 648
ZnTPP	423	554, 598
CuTPP	416	539
NiTPP	415	528
CoTPP	410	528
FeTPP	416	510 and 580
MnTPP	474	578 and 614

3.2 Synthesis of Pyridylporphyrin and Their Complexes

3.2.1 4-Pyridyl/phenyl porphyrins

Tetraarylporphyrins were prepared according to standard literature method by Fleischer and coworkers [39]. Typically, tetraphenylporphyrin was synthesized by reacting benzaldehyde with equal equivalence of pyrrole in refluxing propionic acid. In the case of 4-pyridyl/phenyl porphyrins possessing different number of the 4-pyridyl group reported by Fleischer, the synthesis was at first performed similarly by using the ratio of pyrrole, benzaldehyde, and 4-pyridinecarboxaldehyde at 4:3:1. The products were obtained as a mixture consisted of 30% TPP, 20% MPyTPP, 2% *trans*-DPyDPP, 8% *cis*-DPyDPP, 15% TPyMPP, and 25% TPyP. Since MPyTPP was the

desired product in this work, the above ratio of the starting materials was modified to be 4:2:2 to increase the amount of MPyTPP. A mixture products consisting of six porphyrin isomers was obtained in 20% yield. Yield of the desired product had increased from that literature which reported at only 13%. Thin layer chromatography (mobile phase = 98:2 chloroform/ethanol) was performed. The R_f values of the isomers were 0.88 (TPP), 0.46 (MPyTPP), 0.38 (*trans*-DPyDPP), 0.28 (*cis*-DPyDPP), 0.21 (TPyMPP), and 0.12 (TPyP). The isomers were separated using column chromatography with TPP (**1**) (0.126 g, 26%) being the first to be eluted from the mixture with CH_2Cl_2 . The rest of the mixture was subjected to another column chromatography purification employing a 98:2 chloroform/ethanol as a mobile phase which yielded other fractions. The products isolated from this column consisted of 5-(pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, **8**) (0.171 g, 36%), 5,15-(dipyridyl)-10,20-diphenylporphyrin (*trans*-DPyDPP, **9**) (0.029 g, 6%), 5,10-(dipyridyl)-15,20-diphenylporphyrin (*cis*-DPyDPP, **10**) (0.083 g, 17%), 5,10,15-(tripyrindyl)-20-phenylporphyrin (TPyMPP, **11**) (0.04 g, 8%) and 5,10,15,20-tetrapyrindylporphyrin (TPyP, **18**) (0.02 g, 4%) structures of which are shown in **Figure 3.5**. The amount of each isomer found here differs from those reported by Fleischer [39]. Apparently a modification of this method had resulted in an increase of almost double percentage of MPyTPP from 20% to 36%. The identities of MPyTPP, *trans*-DPyDPP, *cis*-DPyDPP, and TPyMPP were characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy and MALDI-TOF mass spectrometry and confirmed by comparison to literature data [56].

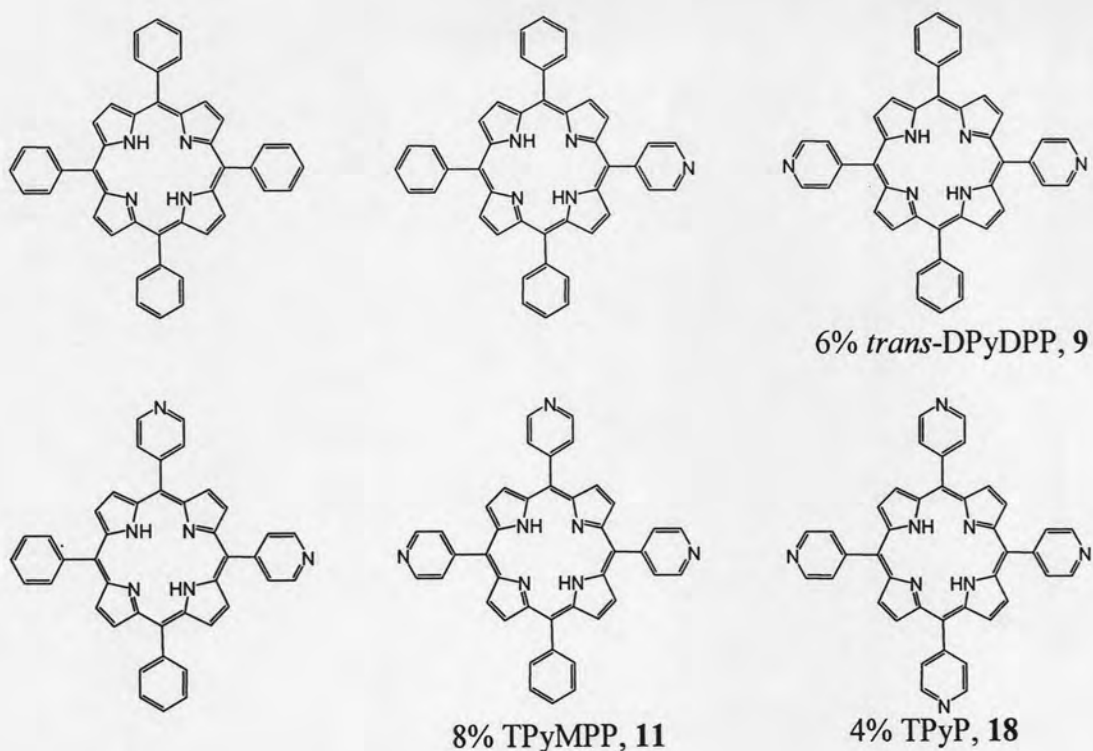


Figure 3.5 Structures and % yield of six porphyrin isomers

3.2.1.1 5-(Pyridyl)-10,15,20-triphenylporphyrin (MPyTTP, 8)

The ^1H NMR spectrum of MPyTTP (8) showed signals corresponding to the structure in Figure 3.6 (Appendix B).

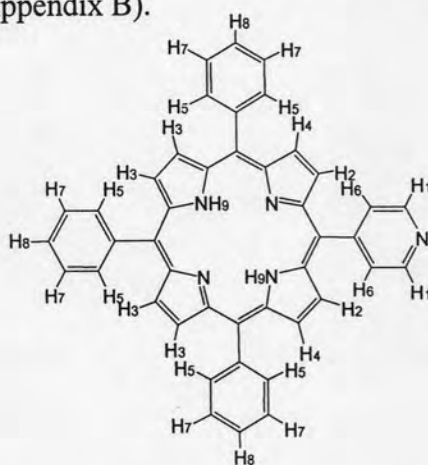


Figure 3.6 Structure of 5-(pyridyl)-10,15,20-triphenylporphyrin (MPyTTP, 8)

The ^1H NMR spectrum of MPyTTP (8) revealed a significantly lowfield doublet signal of the 2,6-pyridyl group at 9.03 ppm. In addition, β -pyrrole protons were split into three signals at 8.79, 8.87, and 8.89 ppm. Internal N-H protons were observed upfield as a singlet at -2.80 ppm (**Figure A-22**, Appendix A). UV/Visible absorption showed a similar spectral pattern as that of TPP, *i.e.*, a strong Soret band

(λ_{\max}) at 418 nm and, at a much lower intensity, four Q-bands at 515, 550, 590, and 646, respectively (**Figure A-23**, Appendix A). MALDI-TOF-MS spectrum confirmed the molecular ion peak of 615.587 which was consistent with calculated molecular weight of 615.737 (**Figure A-24**, Appendix A).

3.2.1.2 5,15-(Dipyridyl)-10,20-diphenylporphyrin (*trans*-DPyDPP, **9**)

The ^1H NMR spectrum of *trans*-DPyDPP (**9**) showed the signals corresponding to the structure in **Figure 3.7** (Appendix B).

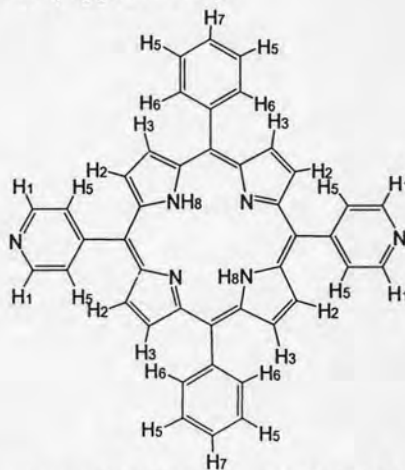


Figure 3.7 Structure of 5,15-(dipyridyl)-10,20-diphenylporphyrin (*trans*-DPyDPP, **9**)

The ^1H NMR spectrum of *trans*-DPyDPP (**9**) showed characteristic four proton signals of the 2,6-pyridyl group at 9.05 ppm. The signal of β -pyrrole protons appeared in such a way to indicate that they were under two distinguishable environments. The peaks were split into two doublets at 8.80 and 8.91 ppm. The upfield singlet resonance at -2.84 ppm was assigned to internal NH protons in the porphyrin ring (**Figure A-25**, Appendix A). The UV/Visible spectrum of *trans*-DPyDPP showed identical λ_{\max} to TPP at 418 nm in Soret band and 515, 549, 590, and 648 in Q band (**Figure A-26**, Appendix A). MALDI-TOF-MS spectrum confirmed the structure by showing the molecular ion peak at 616.423 which was consistent with calculated molecular weight of 616.725 (**Figure A-27**, Appendix A).

3.2.1.3 5,10-(Dipyridyl)-15,20-diphenyl porphyrin (*cis*-DPyDPP, **10**)

The ^1H NMR spectrum of *cis*-DPyDPP (**10**) showed the signals corresponding to the structure in **Figure 3.8** (Appendix B).

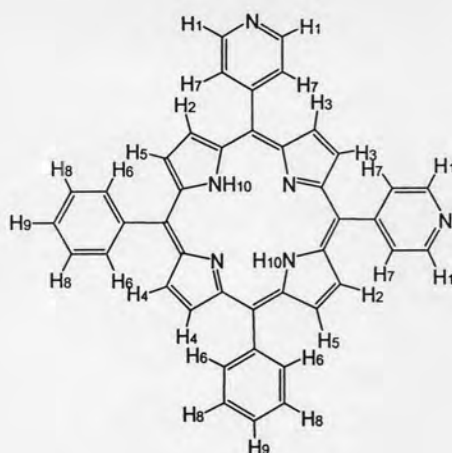


Figure 3.8 Structure of 5,10-(dipyridyl)-15,20-diphenylporphyrin (*cis*-DPyDPP, **10**)

cis-DPyDPP (**10**) showed significant ^1H NMR signals at 9.05 ppm refer to four protons of the 2,6-pyridyl group. The β -pyrrole protons were split into two doublets at 8.80 and 8.92 ppm, and two singlets at 8.88 and 8.85 ppm. Internal N-H protons were observed upfield as an singlet signal at -2.83 ppm (**Figure A-28**, Appendix A). UV/Visible absorption showed similar spectrum as that of TPP with a strong Soret band (λ_{max}) at 418 nm and intensity four Q-bands of lower at 515, 549, 590, and 647, respectively (**Figure A-29**, Appendix A). MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak at 616.508 which was consistent with calculated molecular weight of 616.725 (**Figure A-30**, Appendix A).

3.2.1.4 5,10,15-(Tripyridyl)-20-phenylporphyrin (TPyMPP, **11**)

The ^1H NMR spectrum of TPyMPP showed signals corresponding to the structure in **Figure 3.9** (Appendix B).

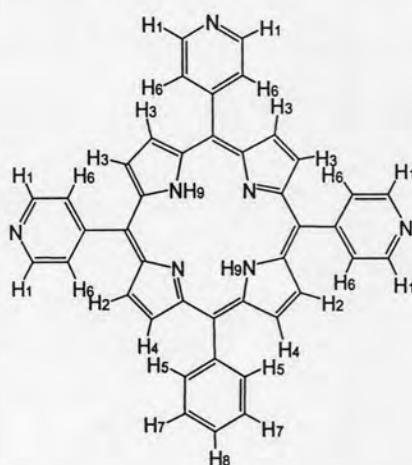
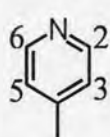
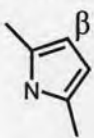
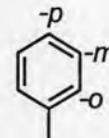
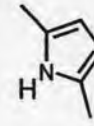


Figure 3.9 Structure of 5,10,15-(tripyrindyl)-20-phenylporphyrin (TPyMPP, **11**)

The ^1H NMR spectrum of TPyMPP (**11**) showed characteristic protons resonance of the 2,6-pyridyl group at 9.06 ppm. Moreover, the β -pyrrole protons signal were split into three signals at 8.81, 8.86, and 8.92 ppm. N-H protons at the inner core of the porphyrin ring were found as a singlet signal slightly shifted upfield at -2.88 ppm (**Figure A-31**, Appendix A). The electronic absorption in chloroform showed a strong Soret band (λ_{max}) at about 417 nm and four Q bands at 513, 545, 586, and 648 nm (**Figure A-32**, Appendix A). MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak at 617.401 which was consistent with calculated molecular weight of 617.713 (**Figure A-33**, Appendix A).

Table 3.3 Comparison of ^1H NMR chemical shifts of six isomers

Product	2,6-pyridyl	3,5-pyridyl	β -pyrrole	<i>o</i> -phenyl	<i>m</i> -, <i>p</i> -phenyl	internal NH
TPP	-	-	8.88	8.23-8.25	7.76-7.78	-2.73
MPyTPP	9.03	8.17-8.19	8.79, 8.87	8.21-8.23	7.74-7.81	-2.80
<i>trans</i> -DPyDPP	9.05	8.20-8.22	8.80, 8.91	8.20-8.22	7.76-7.82	-2.84
<i>cis</i> -DPyDPP	9.05	8.21-8.23	8.80, 8.85	8.21-8.23	7.76-7.82	-2.83
TPyMPP	9.06	8.19-8.21	8.81, 8.86 8.88, 8.92	8.19-8.21	7.76-7.84	-2.88
TPyP	9.06	8.16	8.87	-	-	-2.93

3.2.2 5-(Pyridyl)-10,15,20-triphenylporphyrinatozinc(II) (ZnMPyTPP, **12**)

The synthesis of 5-(pyridyl)-10,15,20-triphenylporphyrinatozinc(II) (ZnMPyTPP, **12**) using saturated zinc acetate dihydrate in methanol was carried out in a boiling DMF solution of MPyTPP. A purple powder was obtained in 94% yield. The product was characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy, and MALDI-TOF mass spectrometry. The ^1H NMR spectrum (Appendix B) showed signals corresponding to the structure in **Figure 3.10**.

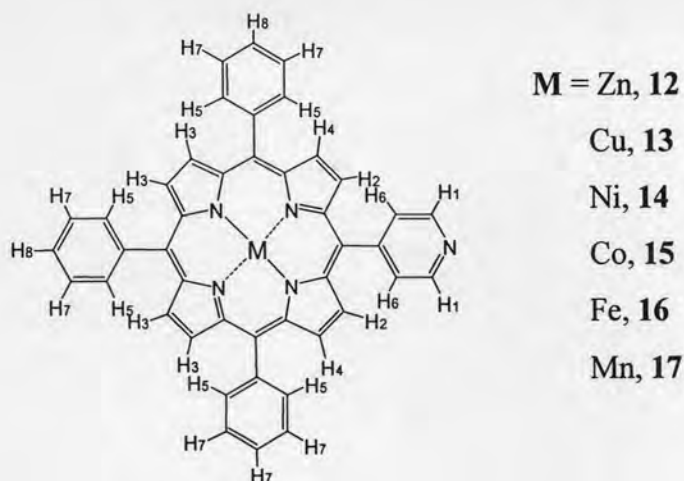


Figure 3.10 Structure of 5-(pyridyl)-10,15,20-triphenylporphyrin complexes, 12-17

^1H NMR spectrum of ZnMPyTPP (12) could not be measured in CDCl_3 because of the compound's low solubility. In addition, broad peaks of aromatic protons were observed. In $\text{DMSO}-d_6$, on the other hand, 2,6-pyridyl protons was found at δ 8.97 ppm. Furthermore, signals corresponding to β -pyrrole protons were observed at δ 8.77-8.81 ppm, while *o*-phenyl and 3,5-pyridyl at δ 8.18-8.21 ppm, and *m*-, *p*-phenyl at δ 7.81 ppm. The disappearance of the internal NH protons signal between δ -2.70 to -2.90 ppm indicated that zinc(II) ion had inserted into inner free-base MPyTPP (Figure A-34, Appendix A). UV/Visible spectrum showed a red shift of the Soret band (λ_{max}) from 418 nm in MPyTPP to 424 nm. In addition, Q absorption bands which were characteristics for metallated porphyrin appeared as two peaks at 554 and 597 nm (Figure A-35, Appendix A) as opposed to the four Q bands of the free-based porphyrin. The absorption spectrum highly resembling to that reported by Fleischer and coworkers showed the Soret band (λ_{max}) at 422 nm and Q band at 564 and 606 nm. MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak at 677.739 which was consistent with calculated molecular weight of 679.111 (Figure A-36, Appendix A).

3.2.3 5-(Pyridyl)-10,15,20-triphenylporphyrinatocopper(II) (CuMPyTPP, 13)

5-(Pyridyl)-10,15,20-triphenylporphyrinatocopper(II) (CuMPyTPP, 13) was synthesized by adding a saturated solution of anhydrous copper acetate in methanol into a DMF solution of MPyTPP. The product was obtained in 99% yield and subsequently characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy and

MALDI-TOF mass spectrometry. The structure of CuMPyTPP is as shown in **Figure 3.10**.

The ^1H NMR spectrum of CuMPyTPP (**13**) showed broad peaks of aromatic proton resonances at δ 7.38-7.75 ppm. The characteristic signal of internal NH protons at between -2.70 to -2.90 ppm was absent which is supportive of a placement of the inner protons by a copper(II) ion (**Figure A-37**, Appendix A). The electronic absorption spectrum in chloroform showed a slight blue shifts of the Soret band (λ_{max}) from 418 nm in the free-base MPyTPP to 415 nm in the complex and Q-band reduced to only one peak at 539 nm (**Figure A-38**, Appendix A). MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak at 676.730 which was consistent with calculated molecular weight of 677.267 (**Figure A-39**, Appendix A).

3.2.4 5-(Pyridyl)-10,15,20-triphenylporphyrinatonickel(II) (NiMPyTPP, **14**)

The synthesis of 5-(pyridyl)-10,15,20-triphenylporphyrinatonickel(II) (NiMPyTPP, **14**) using 5 equivalents of nickel acetate tetrahydrate in methanol carried out in a boiling DMF solution of MPyTPP and the reddish brown solution was refluxed for 3 hours. It was observed that NiMPyTPP partially precipitated out after the solution was cooled down. Eventually, purple crystals were obtained in 94% yield. The product was characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy and MALDI-TOF mass spectrometry. The ^1H NMR spectrum (Appendix B) showed the signals corresponding to the structure in **Figure 3.10**.

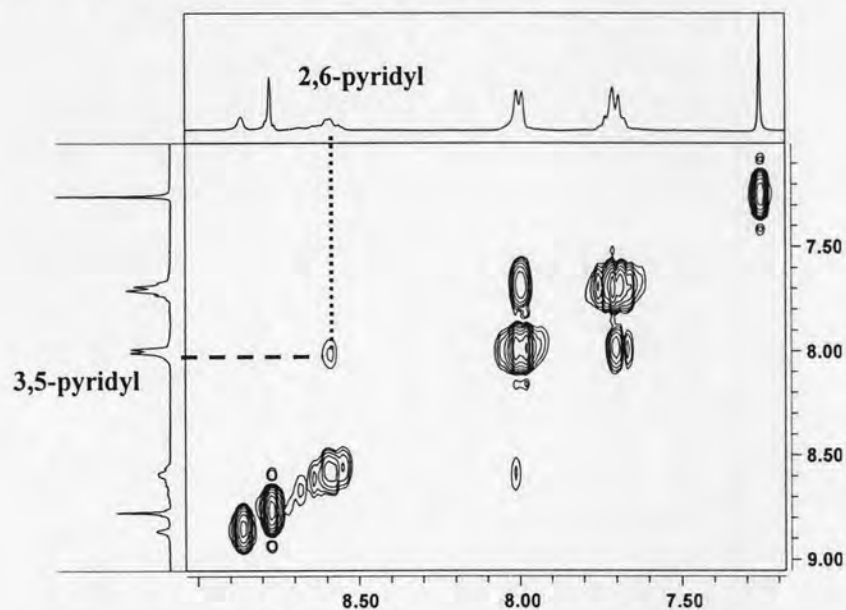


Figure 3.11 ^1H - ^1H COSY spectrum of NiMPyTPP (**14**)

The ^1H NMR spectrum of NiMPyTPP (**14**) showed signal of β -pyrrole protons at 8.55-8.64, 8.77, and 8.86, respectively (**Figure A-40**, Appendix A). ^1H - ^1H COSY signal of 2,6-pyridyl protons (**Figure A-41**, Appendix A) showed an upfield shift which overlaps with β -pyrrole protons signals at δ 8.55-8.64 ppm (**Figure 3.11**). The significant signal of internal NH protons was not observed between -2.70 to -2.90 ppm indicating that nickel (II) ion has replaced the inner protons of MPyTPP. UV/Visible absorption spectrum showed a slightly blue shifts of the Soret band (λ_{max}) from 418 nm in MPyTPP to 416 nm and Q-band reduced to one peak at 529 nm (**Figure A-42**, Appendix A). MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak at 670.098 which was consistent with calculated molecular weight of 672.414. In addition, a peak at 615.182 which corresponds to the molecular weight of the free-base MPyTPP was also observed. This has been reasoned as some extent of the Ni-N bond cleavage from the inner core of MPyTPP by the energy of the employed MALDI-TOF technique (**Figure 3.12**, **Figure A-43**, Appendix A). The UV/Visible spectrum showed Q-band only one peak at 529 nm (**Figure 3.13**).

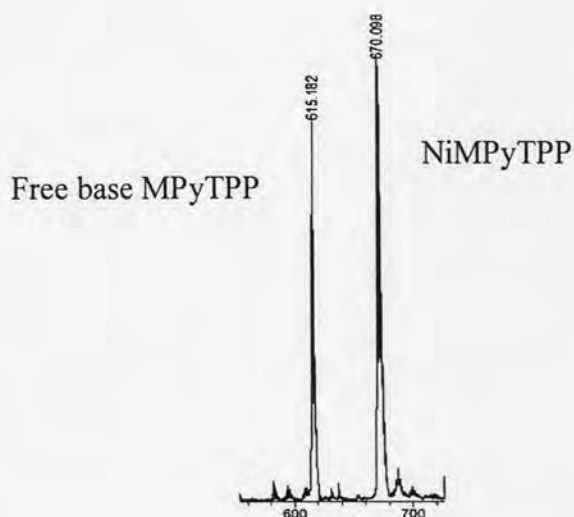


Figure 3.12 MALDI-TOF-MS spectrum of 5-(pyridyl)-10,15,20-triphenyl porphyrinatonickel(II) (NiMPyTPP, **14**)

3.2.5 5-(Pyridyl)-10,15,20-triphenylporphyrinatocobalt(II) (CoMPyTPP, **15**)

5-(Pyridyl)-10,15,20-triphenylporphyrinatocobalt(II) (CoMPyTPP, **15**) was synthesized by adding saturated cobalt acetate tetrahydrate in methanol into a DMF solution of MPyTPP. Purple crystals were obtained in 99% yield. The product was

characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy and MALDI-TOF mass spectrometry. The structure of CoMPyTPP showed in **Figure 10**.

The ^1H NMR spectrum of CoMPyTPP (**15**) showed broad peaks of aromatic proton resonances. The characteristics signal of internal NH protons at between -2.70 to -2.90 ppm disappeared which is supportive of cobalt (II) ion-nitrogen coordination instead of the N-H (**Figure A-44**, Appendix A). The electronic absorption spectrum in chloroform showed blue shifts of the Soret band (λ_{max}) from 418 nm in the free-base MPyTPP to 410 nm in the complex and Q-band reduced to one peak at 528 nm (**Figure A-45**, Appendix A). MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak at 672.668 which was consistent with calculated molecular weight of 672.654 (**Figure A-46**, Appendix A).

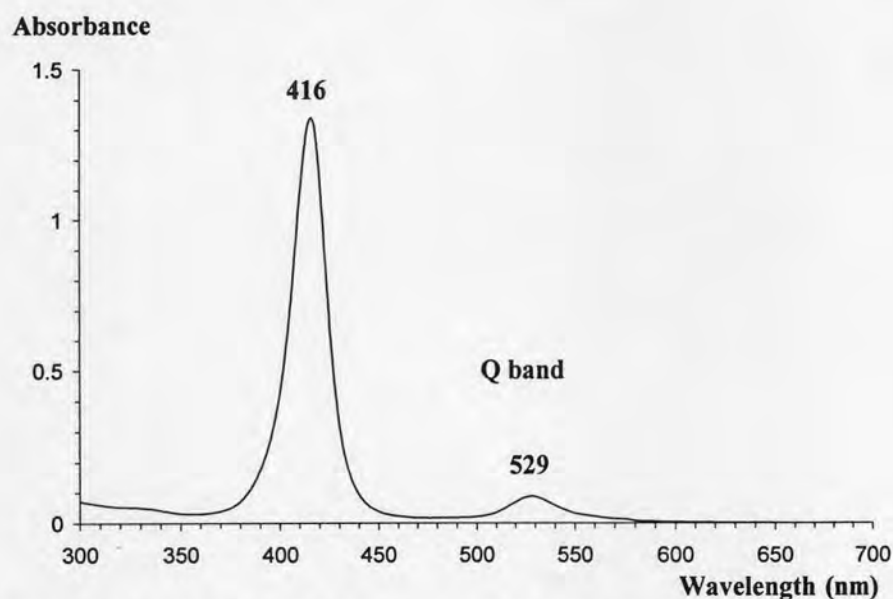


Figure 3.13 UV/Visible spectrum of 5-(pyridyl)-10,15,20-triphenyl porphyrinatonicel(II) (NiMPyTPP, **14**)

3.2.6 5-(Pyridyl)-10,15,20-triphenylporphyrinatoiron(III) ((Cl)FeMPyTPP, **16**)

The synthesis of 5-(pyridyl)-10,15,20-triphenylporphyrinatoiron(III) ((Cl)FeMPyTPP, **16**) was accomplished by reacting a solution of 5 equivalents of saturated anhydrous iron (III) chloride in methanol with a boiling chloroform solution of MPyTPP. During the reaction, the color of the solution changed from purple to a brown solution. When the reaction was carried out in DMF instead of chloroform the reaction was incomplete even with long reaction time). Neutralization of the reaction

by adding a few drops of pyridine caused a color change to green. Purple crystals were obtained in 92% yield and subsequently characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy and MALDI-TOF mass spectrometry. The structure of $(\text{Cl})\text{FeMPyTPP}$ is shown in **Figure 3.10**.

The ^1H NMR spectrum of $(\text{Cl})\text{FeMPyTPP}$ (**16**) showed broad peaks of aromatic protons resonance which made it uncertain to identify as product. Nevertheless, the characteristic signal of the internal NH protons of the free base at -2.70 to -2.90 ppm was absent, supporting that iron(III) ion has replaced these inner protons. (**Figure A-47**, Appendix A). The electronic absorption spectrum in chloroform showed a slight blue shift of the Soret band (λ_{max}) from 418 nm in the free-base MPyTPP to 416 nm in the complex and Q-band reduced to two peaks at 509 and 574 nm (**Figure A-48**, Appendix A). MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak of $(\text{Cl})\text{FeMPyTPP}$ at 704.343. Furthermore, another peak at 669.380, later identified as FeMPyTPP was detected. This was consistent with calculated molecular ion of 669.566 (**Figure 3.14**, **Figure A-49**, Appendix).

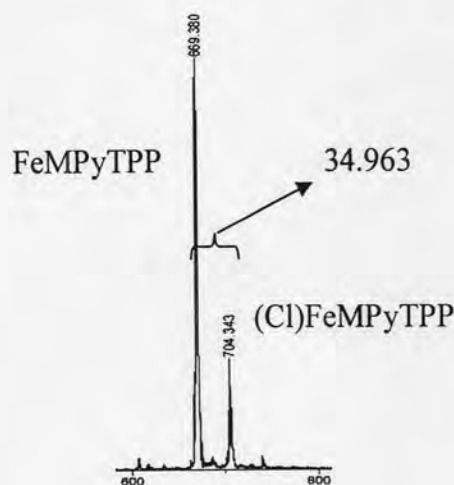


Figure 3.14 Molecular ion peaks of FeMPyTPP and $(\text{Cl})\text{FeMPyTPP}$.

3.2.7 5-(Pyridyl)-10,15,20-triphenylporphyrinatomanganese(III) (MnMPyTPP, **17**)

5-(Pyridyl)-10,15,20-triphenylporphyrinatomanganese(III) (MnMPyTPP, **17**) was synthesized by adding saturated manganese acetate tetrahydrate in methanol into DMF solution of MPyTPP. Green crystals were obtained in 97% yield. The product was characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy and MALDI-TOF mass spectrometry. The structure of MnMPyTPP showed in **Figure 3.10**.

The ^1H NMR spectrum of 5-(pyridyl)-10,15,20-triphenylporphyrinato manganese (III) (MnMPyTPP, **17**) showed broad peaks of aromatic proton resonances. The characteristic signal of internal NH protons at between -2.70 to -2.90 ppm was absent which is supportive of a replacement of the inner protons by a manganese(III) ion (**Figure A-50**, Appendix A). The electronic absorption spectrum in chloroform showed largely red shifts of the Soret band (λ_{max}) from 418 nm in the free-base MPyTPP to 473 nm in the complex and Q-band reduced to two peaks at 577 and 612 nm (**Figure A-51**, Appendix A). MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak at 667.664 which was consistent with calculated molecular weight of 668.659 (**Figure A-52**, Appendix A).

Table 3.4 UV-Visible absorption of MPyTPP and its metal complexed

Product	Soret band	Q band
MPyTPP	418	515, 550, 590, and 646
ZnMPyTPP	424	555, 597
CuMPyTPP	415	539
NiMPyTPP	416	529
CoMPyTPP	410	528
FeMPyTPP	416	509 and 574
MnMPyTPP	473	577 and 612

3.3 Synthesis of Tetrapyrrolylporphyrin and Their Complexes

3.3.1 5,10,15,20-Tetrapyrrolylporphyrin (TPyP, **18**)

5,10,15,20-Tetrapyrrolylporphyrin (TPyP, **18**) was synthesized by reacting 4-pyridinecarboxaldehyde with pyrrole (at a 1:1 ratio) in propionic acid at reflux. Dark purple crystals were obtained 19.0 % yield and the product was characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy and MALDI-TOF mass spectrometry. The ^1H NMR spectrum showed the signals corresponding to the structure in **Figure 3.15** (Appendix B).

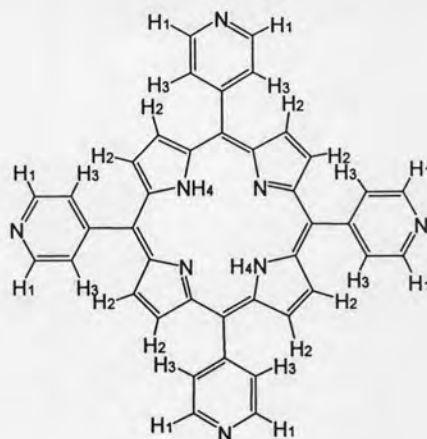


Figure 3.15 Structure of 5,10,15,20-tetrapyrridylporphyrin (TPyP, 18)

Free-base tetrapyrridylporphyrin ^1H NMR spectrum showed the characteristics eight protons at low-field doublet signal of the 2,6-pyridyl group at δ 9.06 ppm, β -pyrrole protons at δ 8.87 ppm and 3,5-pyridyl protons at δ 8.16 ppm. In addition, internal NH protons were again found as an upfield singlet signal at -2.93 ppm (**Figure A-53**, Appendix A). This was slightly further upfield than other free-base arylporphyrins. UV/Visible absorption showed strong Soret band at 418 nm and nearly low-intensity four Q-bands with TPP at 515, 550, 590, and 646 respectively (**Figure A-54**, Appendix A). MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak at 618.577 which was consistent with calculated molecular weight of 618.701 (**Figure A-55**, Appendix A).

3.3.2 5,10,15,20-Tetrapyrridylporphyrinatozinc(II) (ZnTPyP, 19)

The synthesis of 5,10,15,20-tetrapyrridylporphyrinatozinc(II) (ZnTPyP, 19) using saturated zinc acetate dihydrate in methanol was carried out in a boiling chloroform solution of TPyP. The product was afforded in 90.9% after recrystallization. The product was characterized by ^1H NMR spectroscopy, UV/Visible spectroscopy and MALDI-TOF mass spectroscopy. The ^1H NMR spectrum showed the signals corresponding to the structure in **Figure 3.16** (Appendix B).

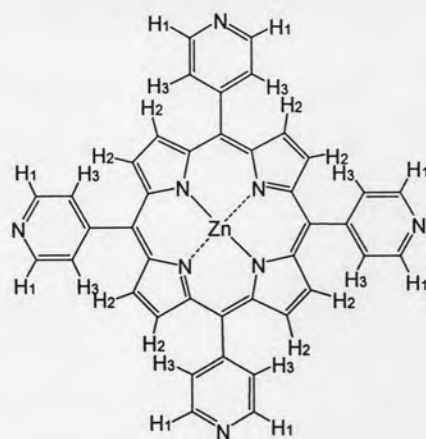


Figure 3.16 Structure of 5,10,15,20-tetrapyrridylporphyrinatozinc(II) (ZnTPyP, **19**)

Because ZnTPyP (**19**) has a low solubility in chloroform-*d* so the spectrum was measured in DMSO-*d*₆. The ¹H NMR spectrum showed the characteristics protons signals of 2,6-pyridyl, β-pyrrole and 3,5-pyridyl at 9.02, 8.84, and 8.22, respectively. Internal NH protons signals have disappeared which indicated that Zinc (II) ion coordinated with the inner nitrogens (**Figure A-56**, Appendix A). The electronic absorption spectrum in chloroform showed red shifts of the Soret band (λ_{max}), similar to other zinc complex porphyrins, *i.e.*, from 418 nm in TPyP to 424 nm. In addition, the numbers of signals in the Q-band region were reduced from four to two peaks at 555 and 593 nm (**Figure A-57**, Appendix A). MALDI-TOF-MS spectrum confirmed the molecular weight showing molecular ion peak at 680.567 which was consistent with calculated molecular weight of 682.076 (**Figure A-58**, Appendix A).

Table 3.5 summarizes the solubility of all derivatives in various organic solvents for the purpose of further manipulations.

Table 3.5 The solubility of all porphyrin products

Product	Colour solution	Solubility								
		Hex	CH ₂ Cl ₂	THF	CHCl ₃	EA	CH ₃ CN	DMF	DMSO	MeOH
TPP	deep purple	●	○	○	○	△	●	○	●	●
MPyTPP	deep purple	●	○	○	○	△	●	○	●	●
trans-DPyDPP	deep purple	●	○	○	○	△	●	○	●	●
cis-DPyDPP	deep purple	●	△	○	○	△	●	○	●	●
TPyMPP	deep purple	●	△	△	○	●	●	△	△	●
TPyP	deep purple	●	△	△	○	●	●	△	△	●
ZnTPP	bright purple	●	○	○	○	△	●	○	●	●
CuTPP	reddish purple	●	○	○	○	△	●	●	●	●
NiTPP	reddish brown	●	○	○	○	△	△	△	●	●
CoTPP	reddish brown	△	○	○	○	○	△	○	○	●
FeTPP	brown	●	○	○	○	△	△	○	○	△
MnTPP	green	△	○	○	○	○	○	○	○	○
ZnMPyTPP	bright purple	●	○	○	○	●	●	△	△	●
CuMPyTPP	reddish purple	●	○	○	○	●	●	△	△	●
NiMPyTPP	reddish brown	●	○	○	○	△	△	△	●	●
CoMPyTPP	reddish brown	●	○	○	○	△	●	○	○	△
FeMPyTPP	brown	●	○	○	○	△	△	○	○	△
MnMPyTPP	green	●	○	○	○	△	△	○	△	○
ZnTPyP	purple	●	△	△	△	●	●	△	△	●

○ Soluble

△ Partially soluble at room temperature

● Insoluble

3.4 Synthesis of Bismonopyridyltriphenylporphyrin Metal Assemblies

3.4.1 Cu(II)(CuMPyTPP)₂ (20)

Cu(II)(CuMPyTPP)₂ (20) were synthesized by adding a saturated solution of copper acetate in methanol to a toluene solution of CuMPyTPP (13). Regularly, ¹H NMR spectrum of coordination between metal and MPyTPP showed a downfield shift of 2,6-pyridyl protons signals which are similar to literature report [47]. In this case, Cu(II)(CuMPyTPP)₂ (20) showed broad signals of aromatic protons resonance, in a similar way to CuMPyTPP (13). Therefore, a clear assignment of 2,6-pyridyl protons signals was difficult (Figure A-59, Appendix A). The UV/Visible absorption spectrum showed a relatively similar pattern to that of CuMPyTPP (13), showing the Soret band (λ_{max}) at 415 nm and Q band at 540 nm (Figure A-60, Appendix A). MALDI-TOF MS (neat) spectrum revealed a molecular ion peak at 1419.630 which was consistent with calculated molecular ion of 1418.08. Another peak at 676.618 referring to CuMPyTPP (Figure A-61, Appendix A) was also observed.

3.4.2 Pd(II)(MPyTPP)₂ (21)

Pd(II)(MPyTPP)₂ (21) were synthesized by adding a saturated solution of palladium acetate in methanol to a toluene solution of MPyTPP (8). The UV/Visible absorption spectrum showed, relatively similar pattern to that of MPyTPP (8) with the Soret band (λ_{max}) at 417 nm and Q band at 514, 549, 588, and 644 nm (Figure A-62, Appendix A). No molecular ion peak (at 1337.894) was detected by MALDI-TOF MS (neat). Besides, another peak at 615.759 referring to MPyTPP also appeared (Figure A-63, Appendix A).

3.5 Side to Face Complexation of Porphyrin Units

3.5.1 Zn(TPP)(MPyTPP), (22)

We have had interest in preparing a larger porphyrin systems consisting of more than one porphyrin units. One of the most simple possibility is to assemble one metalloporphyrin unit with another porphyrin unit which has to possess an atom with coordinating ability. One can envisage a reaction between a ZnTPP unit together with a free-base MPyTPP. The latter, with a nitrogen of the pyridyl as a donor atom, is capable of coordinating to the Zn atom of ZnTPP. A metal-MPyTPP should not be used in this case to avoid a self-coordinating dimer of 2 molecules of the metal-MPyTPP as impurities.

MPyTPP (**8**) was added to an NMR tube containing ZnTPP (**2**) in CDCl_3 solution. The ^1H NMR spectrum of the presumably assembled $\text{Zn}(\text{TPP})(\text{MPyTPP})$, (**22**) (**Figure A-64**, Appendix A) was quite similar to that of the osmium analog that has been reported by Kariya and co-workers (**Figure 3.17**) [45].

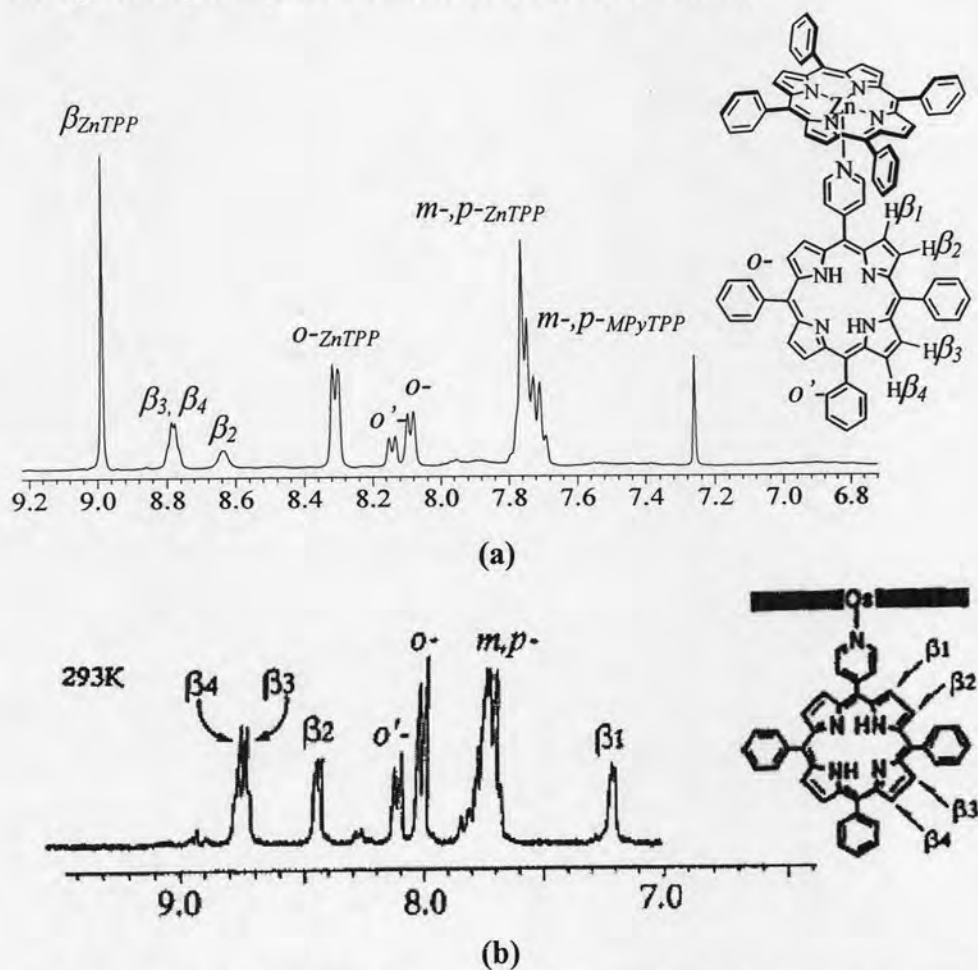


Figure 3.17 The ^1H NMR spectrum of (a) $\text{Zn}(\text{TPP})(\text{MPyTPP})$, (**22**) and (b) $\text{Os}(\text{OEP})(\text{CO})(\text{MPyTPP})$ (OEP = octaethylporphyrin)

Figure 3.17 (a) showed the aromatic region of ^1H NMR spectrum of $\text{Zn}(\text{TPP})(\text{MPyTPP})$, (**22**) at room temperature. The β_{MPyTPP} protons signal was split into a broad singlet at 8.60 ppm of β_2 protons and multiplet at 8.76 of β_3 , and β_4 protons. The signals showed relatively similar pattern of the β_{MPyTPP} protons to that of $\text{Os}(\text{OEP})(\text{CO})(\text{MPyTPP})$ (**Figure 3.17 (b)**). The phenyl protons signals of MPyTPP unit of **22** were confirmed by $^1\text{H}\text{-}^1\text{H}$ COSY (**Figure A-65**, Appendix A, **Figure 3.18**) which showed $o\text{-MPyTPP}$ and $o\text{'-MPyTPP}$ protons signals at 8.12 and 8.31 ppm together with $m, p\text{-MPyTPP}$ at 7.70-7.72 ppm. Although the β_1 , 2,6-pyridyl, and 3,5-pyridyl protons signal of $\text{Zn}(\text{TPP})(\text{MPyTPP})$, (**22**) disappeared in NMR tube reaction, the signals were observed in standard reaction. The internal NH protons slightly shifted

upfield from -2.80 ppm of free-base MPyTPP to -3.12 ppm. MALDI-TOF-MS (neat) spectra confirmed the molecular weight peak appeared at 1293.99 which was consistent with calculated molecular weight of 1293.86 (**Figure A-66**, Appendix A).

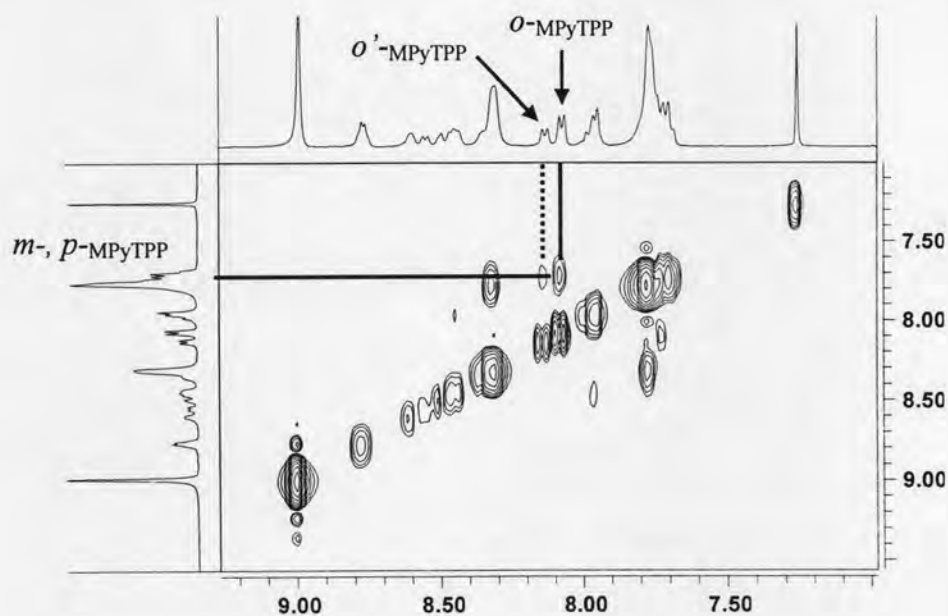


Figure 3.18 The ^1H - ^1H COSY of $\text{Zn}(\text{TPP})(\text{MPyTPP})$, (**22**)

3.5.2 $\text{Co}(\text{TPP})(\text{MPyTPP})$, (**23**)

MPyTPP (**8**) was added to an NMR tube containing CoTPP (**5**) in CDCl_3 solution. The ^1H NMR spectrum of expected $\text{Co}(\text{TPP})(\text{MPyTPP})$, (**23**) at room temperature (**Figure A-67**, Appendix A) showed largely upfield signals of 2,6-pyridyl protons at 1.27 and 1.49 ppm and of 3,5-pyridyl protons at 5.76 and 6.04 ppm because of the resonance effect of CoTPP ring. The coupling correlation between 2,6-pyridyl and 3,5-pyridyl protons signals were confirmed by ^1H - ^1H COSY (**Figure A-68**, Appendix A, **Figure 3.19**) which was consistent with the previous related report by Funatsu and co-workers [44], in which similar up field shifts and correlation were found in ^1H - ^1H COSY spectrum of $[\text{Ru}(4\text{-PyT}_3\text{P})(\text{CO})_4]$ complex. (4-PyT₃P = 5-(4-pyridyl)-10,15,20-tritolyly porphyrinato dianion) (**Figure 3.20**). The internal proton signals observed as into two singlets at -3.24 and -3.31 ppm because the rate of proton exchange over four nitrogens is sufficiently slow on the ^1H NMR time scale for the two kinds of N-H protons in the axial tetraarylporphyrins to be distinguished. The signal in upfield for **23** was assigned to the N-H on the pyrrole ring in I or II and the other signal to that on ring III or IV shown in **Figure 3.21**.

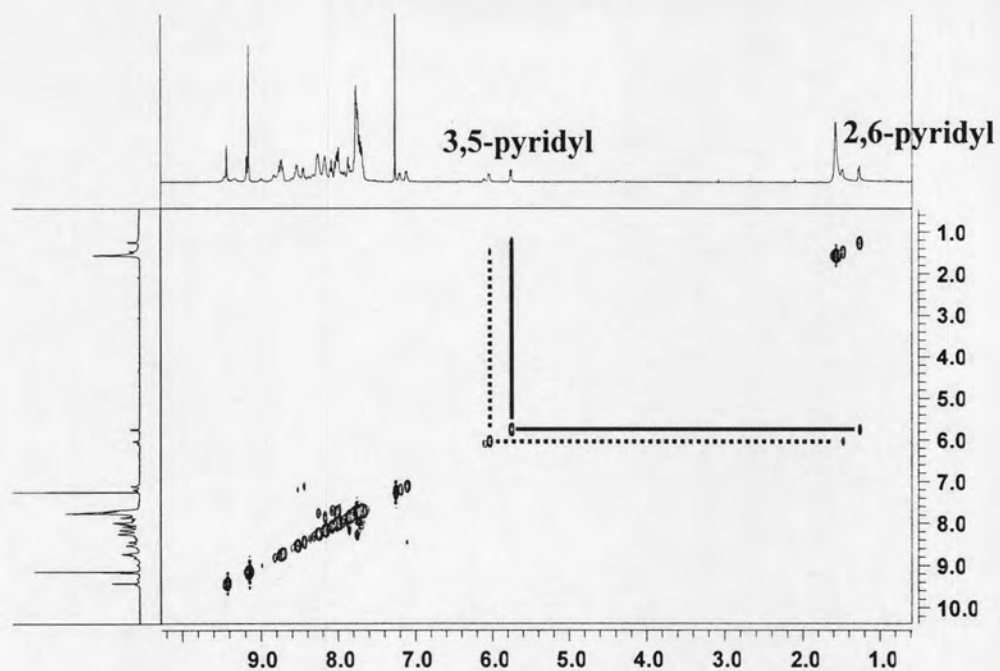


Figure 3.19 The ^1H - ^1H COSY of $\text{Co}(\text{TPP})(\text{MPyTPP})$, (**23**)

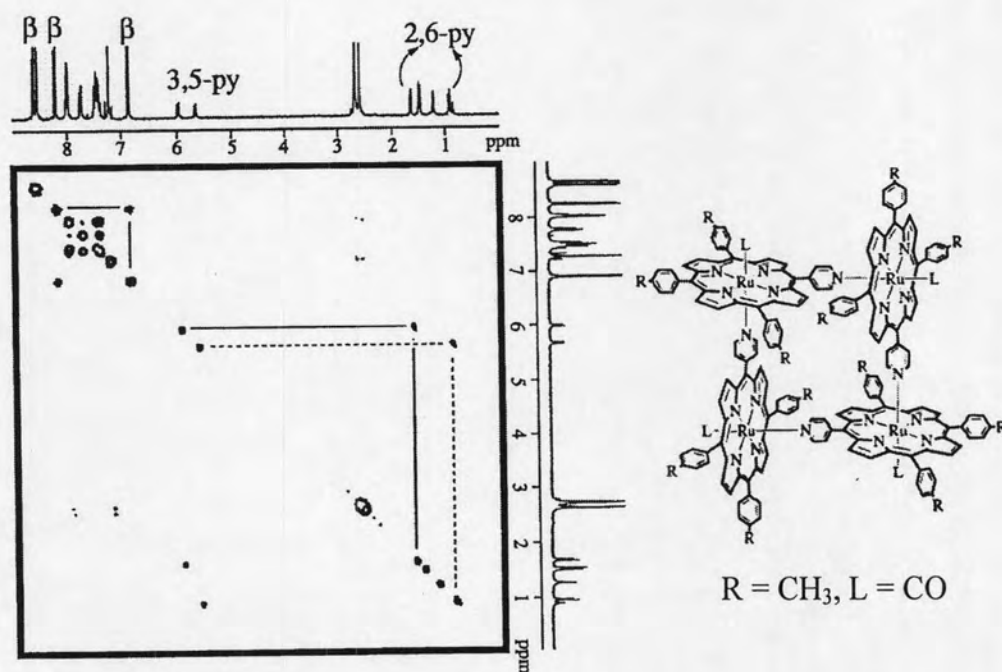


Figure 3.20 The ^1H - ^1H COSY of $[\text{Ru}(4\text{-PyT}_3\text{P})(\text{CO})]_4$

The minor signal at -2.94 ppm was the N-H proton of free-base MPyTPP which decomposed from $\text{Co}(\text{TPP})(\text{MPyTPP})$, (**23**) by the measurement process (Figure 3.21).

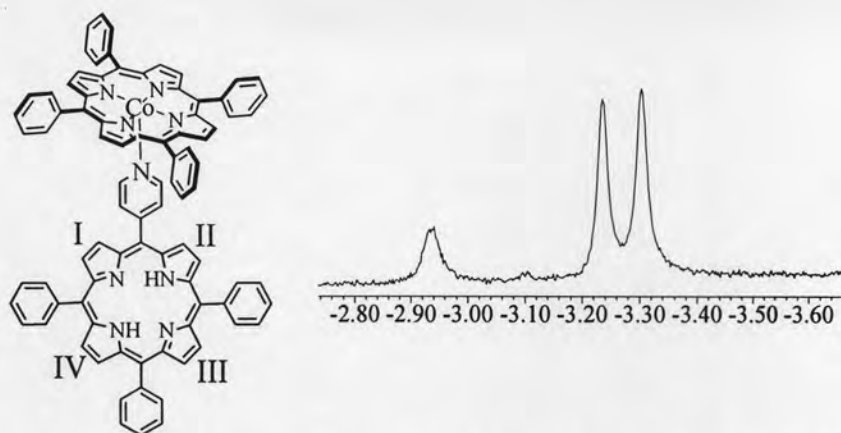


Figure 3.21 The ^1H NMR spectrum of the N-H protons of $\text{Co}(\text{TPP})(\text{MPyTPP})$, (**23**)

In addition, the β_{MPyTPP} protons signal were split into two doublets at 7.12 and 7.20 ppm (β_{1a} and β_{1b} protons), two doublets at 8.45 and 8.53 ppm (β_{2a} and β_{2b} protons), a multiplet at 8.53 ppm (β_{3a} and β_{4a} protons), and a multiplet at 8.74 ppm (β_{3b} and β_{4b} protons) (**Figure 3.22 (a)**). The signal pattern was relatively similar to β_{MPyTPP} protons of Kariya and coworkers' $\text{Os}(\text{OEP})(\text{CO})(\text{MPyTPP})$ [45] at 193 K (**Figure 3.22 (b)**).

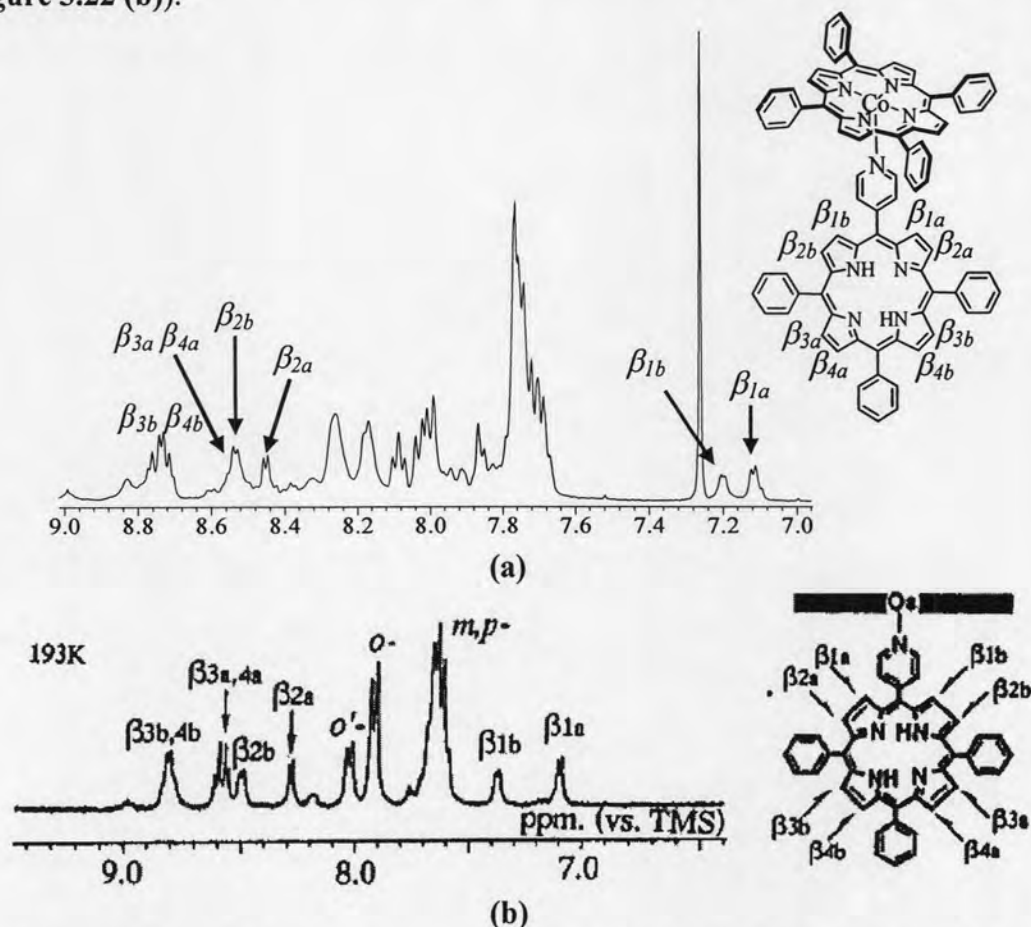


Figure 3.22 The ^1H NMR spectrum of (a) $\text{Co}(\text{TPP})(\text{MPyTPP})$, (**23**) and (b) $\text{Os}(\text{OEP})(\text{CO})(\text{MPyTPP})$ at 193 K

The pyrrole β -proton signals in the downfield region (β_{1b} and β_{2b} protons) were assigned to the β -proton of pyrrole rings with protonated Nitrogens. The others were assigned to those on the deprotonated pyrrole rings (β_{1a} and β_{2a} protons). The peaks in the downfield region were slightly broader, which indicates the long range coupling to the N-H protons. The coupling correlations of β_{1a} and β_{1b} protons with β_{2a} and β_{2b} protons were confirmed by ^1H - ^1H COSY (Figure 3.23). MALDI-TOF-MS (neat) spectrum showed the molecular weight peak at 1287.26 which was consistent with the calculated molecular weight of 1287.40 (Figure A-69, Appendix A).

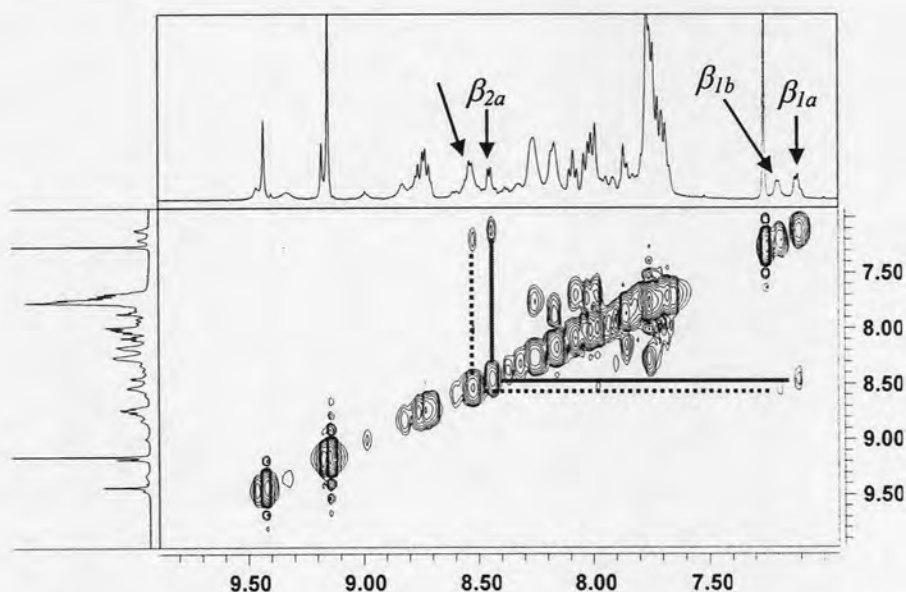


Figure 3.23 The aromatic region of ^1H - ^1H COSY spectrum of $\text{Co}(\text{TPP})(\text{MPyTPP})$, (**23**)

3.5.3 $\text{Ni}(\text{TPP})(\text{MPyTPP})$, (**24**)

MPyTPP (**8**) was added to an NMR tube containing NiTPP (**4**) in CDCl_3 solution. The ^1H NMR spectrum of $\text{Ni}(\text{TPP})(\text{MPyTPP})$, (**24**) (Figure A-70, Appendix A) showed relatively the same chemical shifts of the signals of both MPyTPP (**8**) and NiTPP (**4**) individually appeared (Figure 3.24). MALDI TOF-MS (neat) spectrum showed the molecular weight peaks of free MPyTPP (**8**) and NiTPP (**4**) at 615.495 and 670.568 respectively, with no molecular weight peak of the desired $\text{Ni}(\text{TPP})(\text{MPyTPP})$, (**24**) at 1287.163 observed (Figure A-71, Appendix A).



Figure 3.24 Comparison on the ^1H NMR spectra of NiTPP (**4**), MPyTPP (**8**), and Ni(TPP)(MPyTPP), (**24**)