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APPENDICES

APPENDIX A

Spectroscopic Data

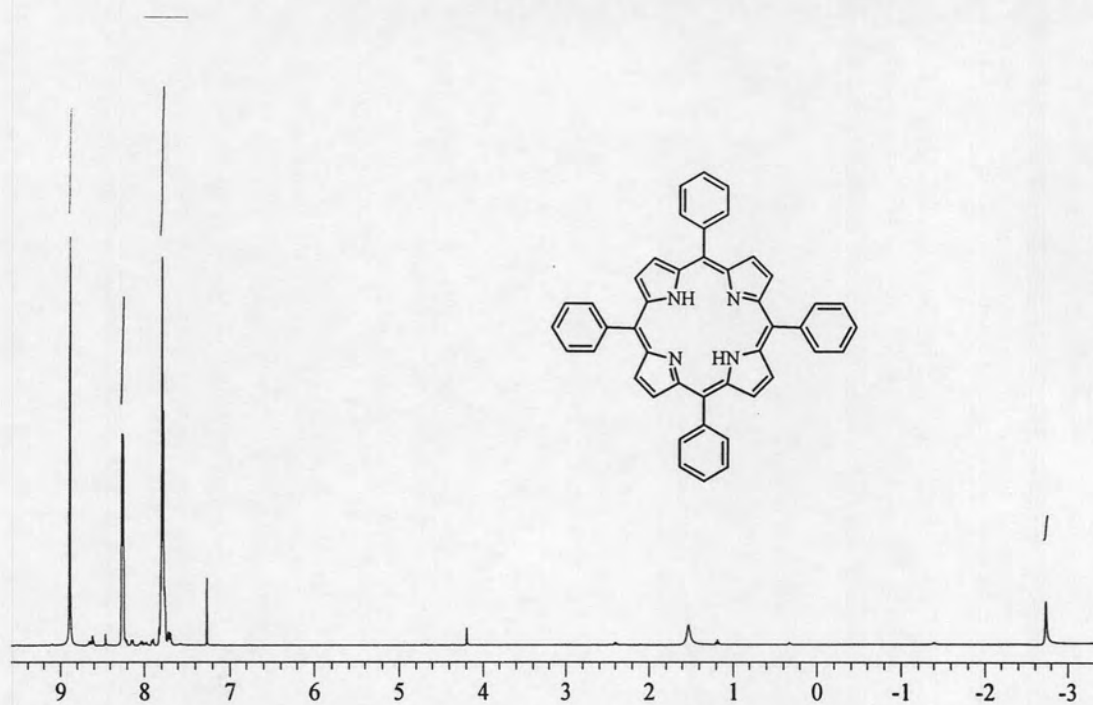


Figure A-1 The ^1H NMR spectrum of 5,10,15,20-tetraphenylporphyrin (TPP, 1)

Absorbance

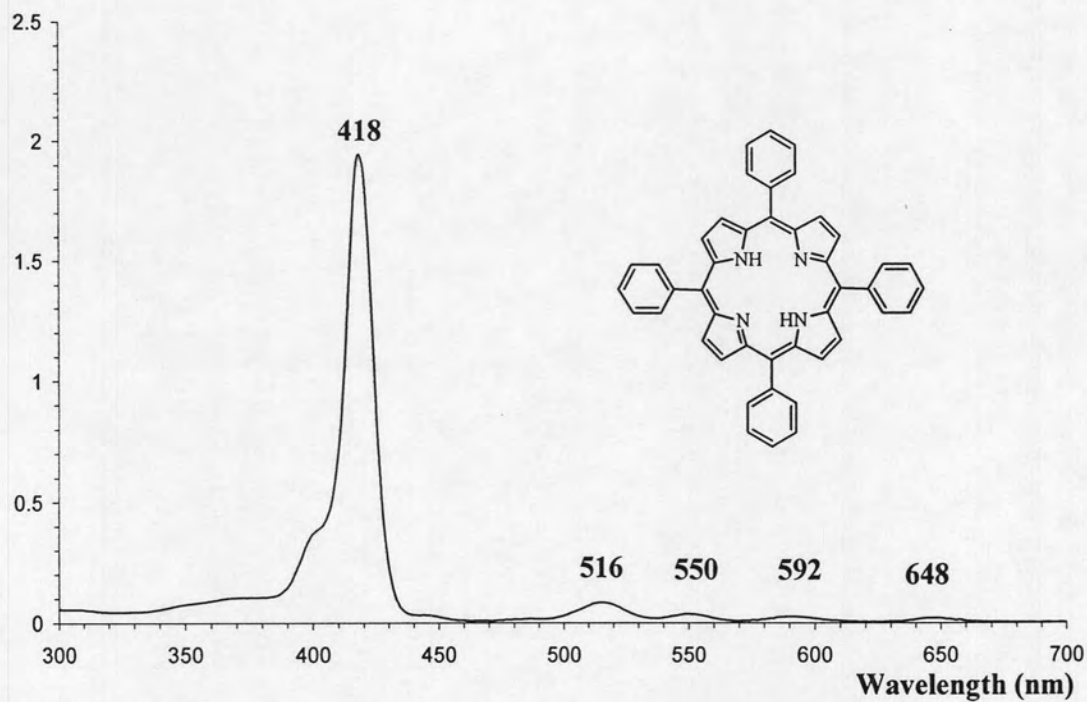


Figure A-2 UV/Visible spectrum of 5,10,15,20-tetraphenylporphyrin (TPP, 1)

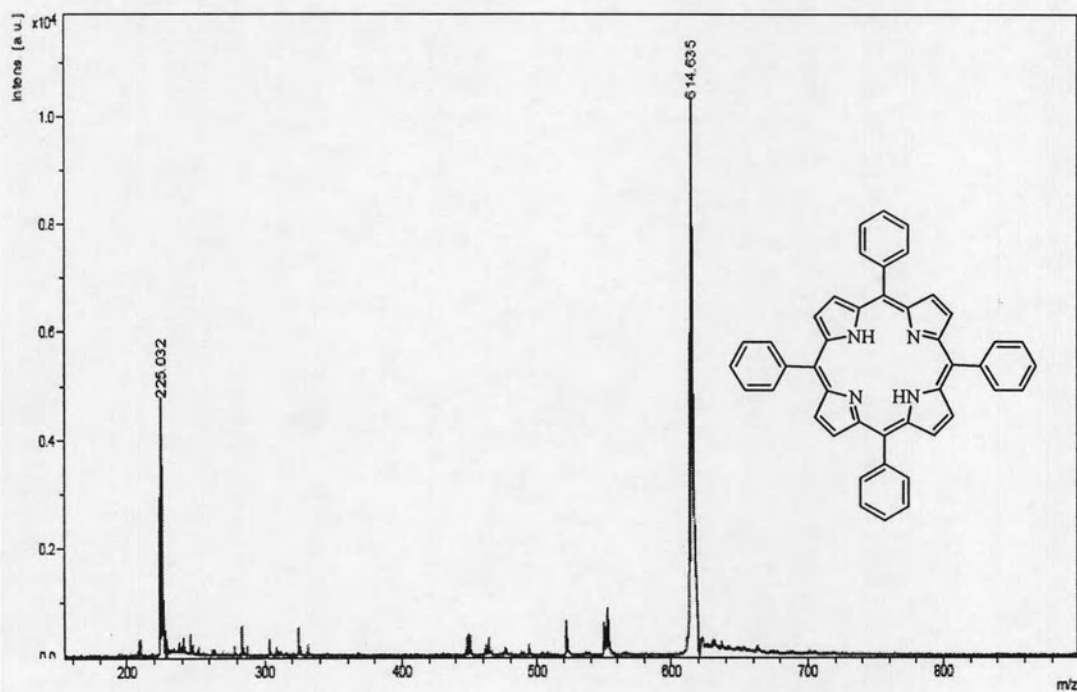


Figure A-3 MALDI-TOF mass spectrum of 5,10,15,20-tetraphenylporphyrin (TPP, 1)

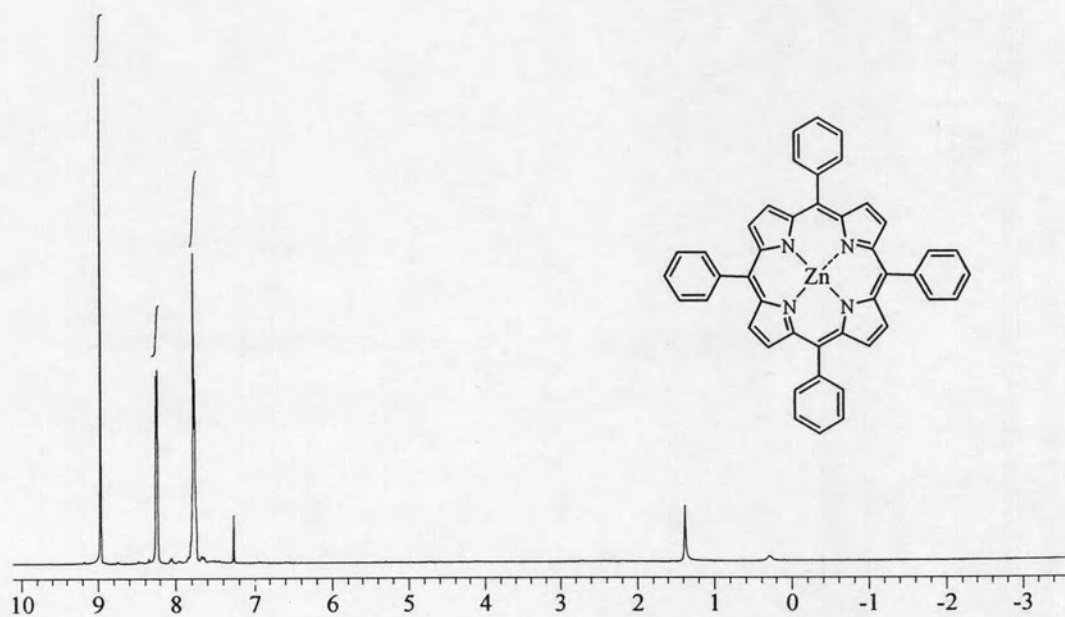


Figure A-4 The ¹H NMR spectrum of 5,10,15,20-tetraphenylporphyrinatozinc(II) (ZnTPP, 2)

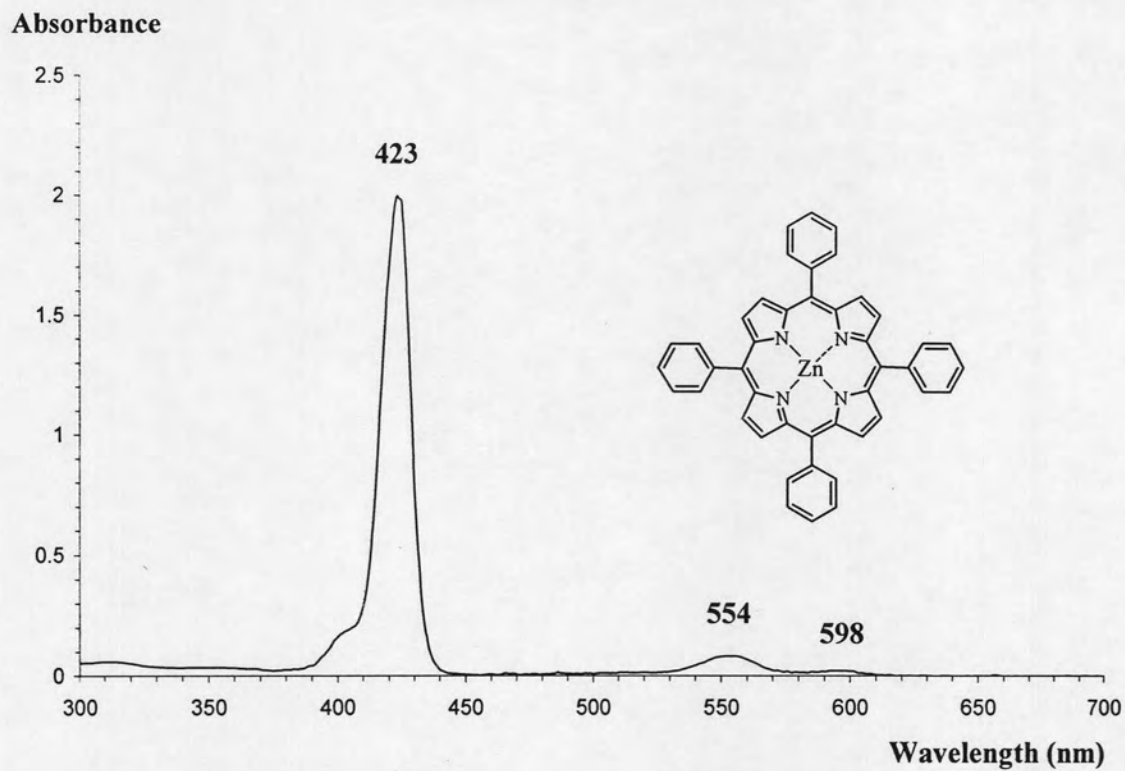


Figure A-5 UV/Visible spectrum of 5,10,15,20-tetraphenylporphyrinatozinc(II) (ZnTPP, **2**)

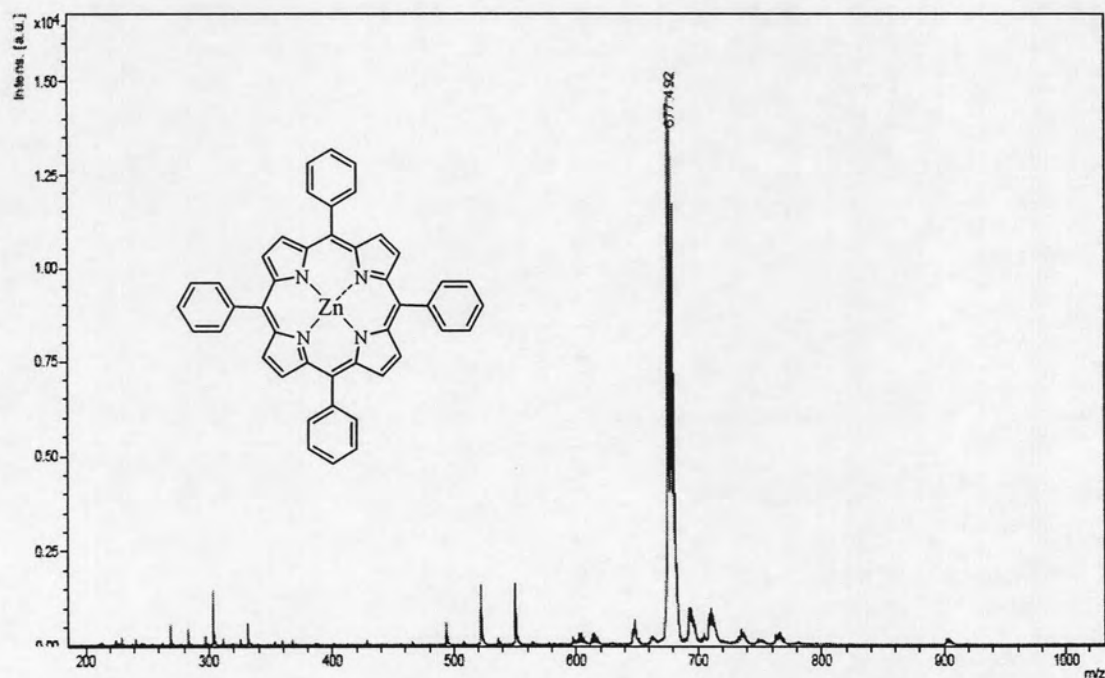


Figure A-6 MALDI-TOF mass spectrum of 5,10,15,20-tetraphenyl porphyrinatozinc(II) (ZnTPP, **2**)

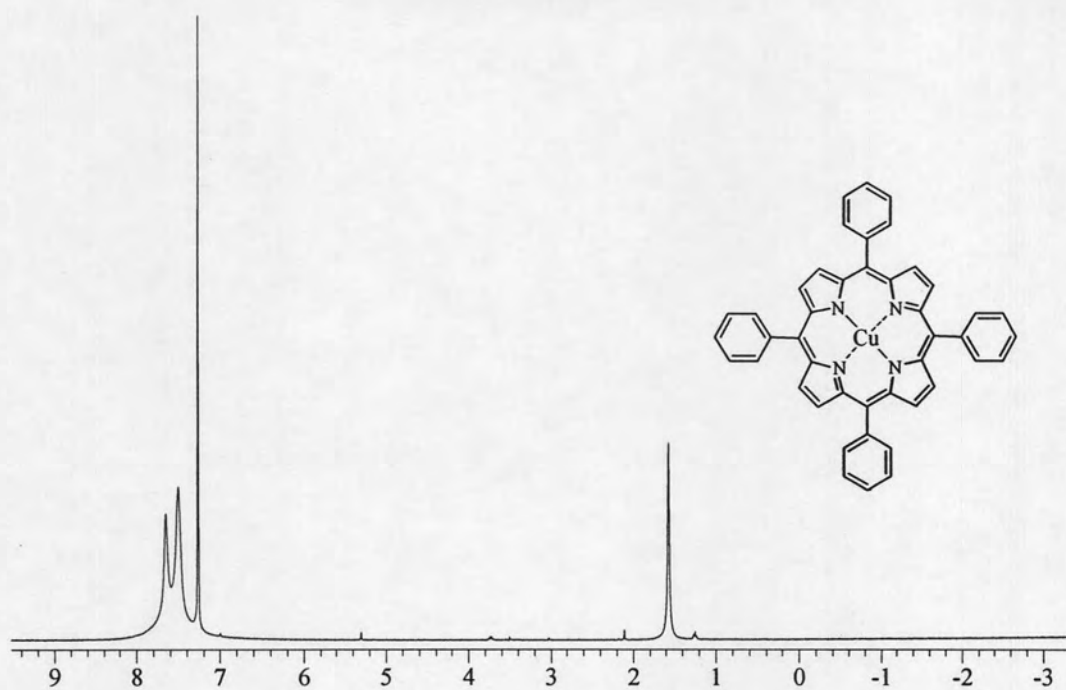


Figure A-7 The ^1H NMR spectrum of 5,10,15,20-tetraphenylporphyrinatocopper(II) (CuTPP, 3)

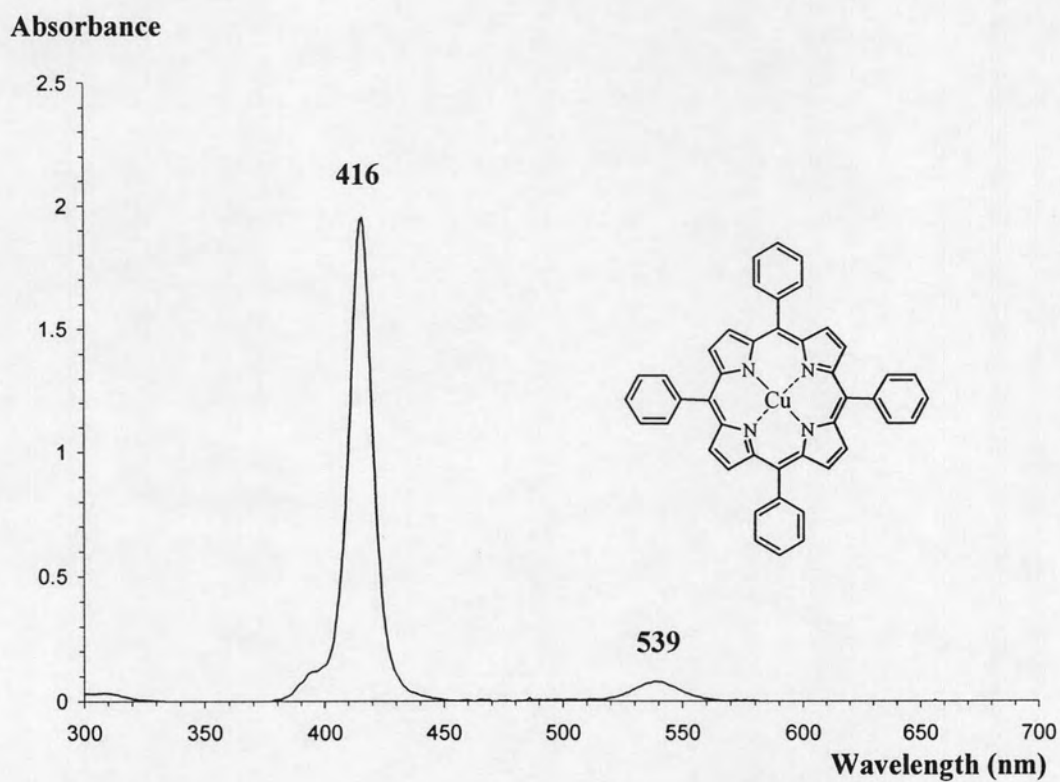


Figure A-8 UV/Visible spectrum of 5,10,15,20-tetraphenylporphyrinatocopper(II) (CuTPP, 3)

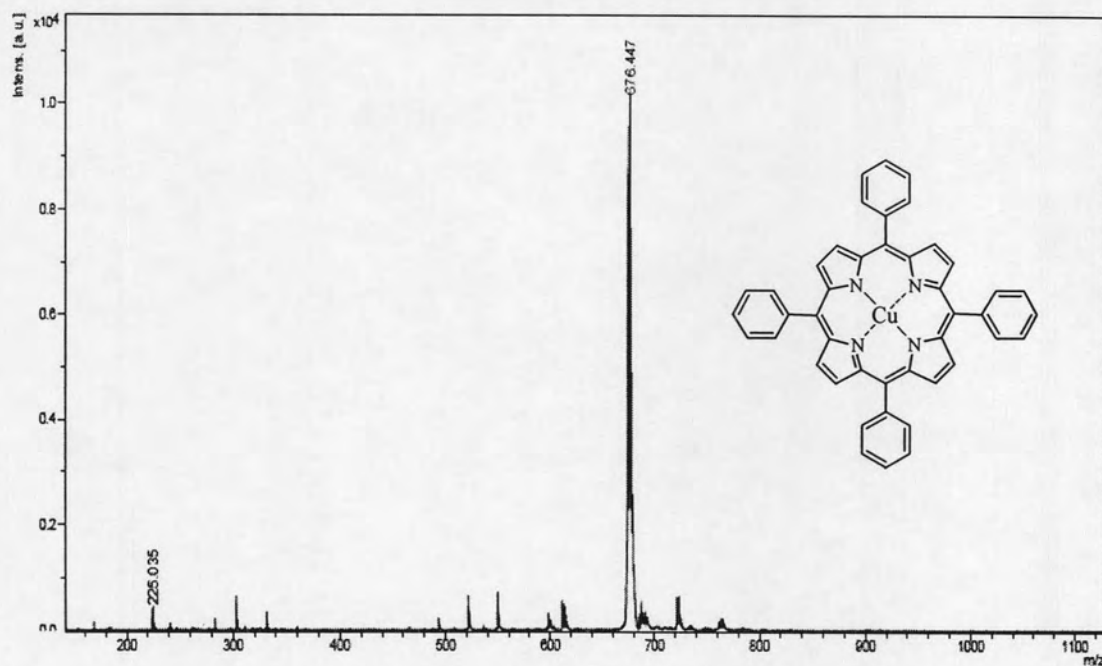


Figure A-9 MALDI-TOF mass spectrum of 5,10,15,20-tetraphenyl porphyrinatocopper(II) (CuTPP, 3)

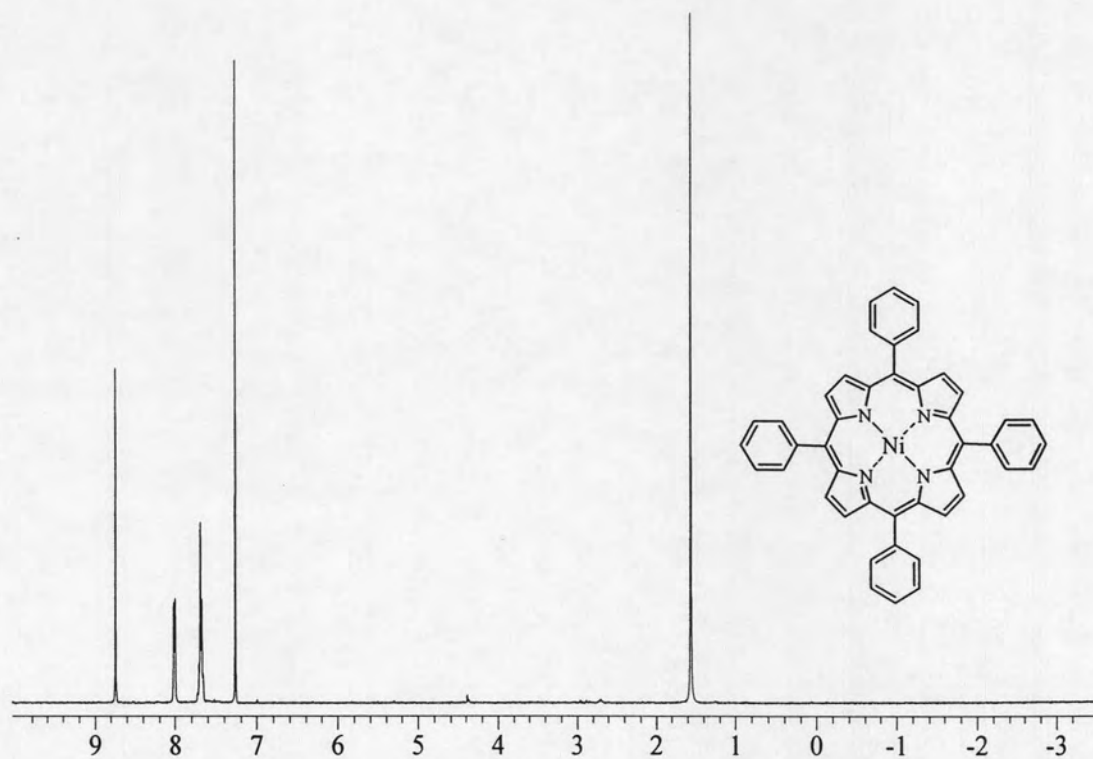


Figure A-10 The ¹H NMR spectrum of 5,10,15,20-tetraphenyl porphyrinatonicel(II) (NiTPP, 4)

Absorbance

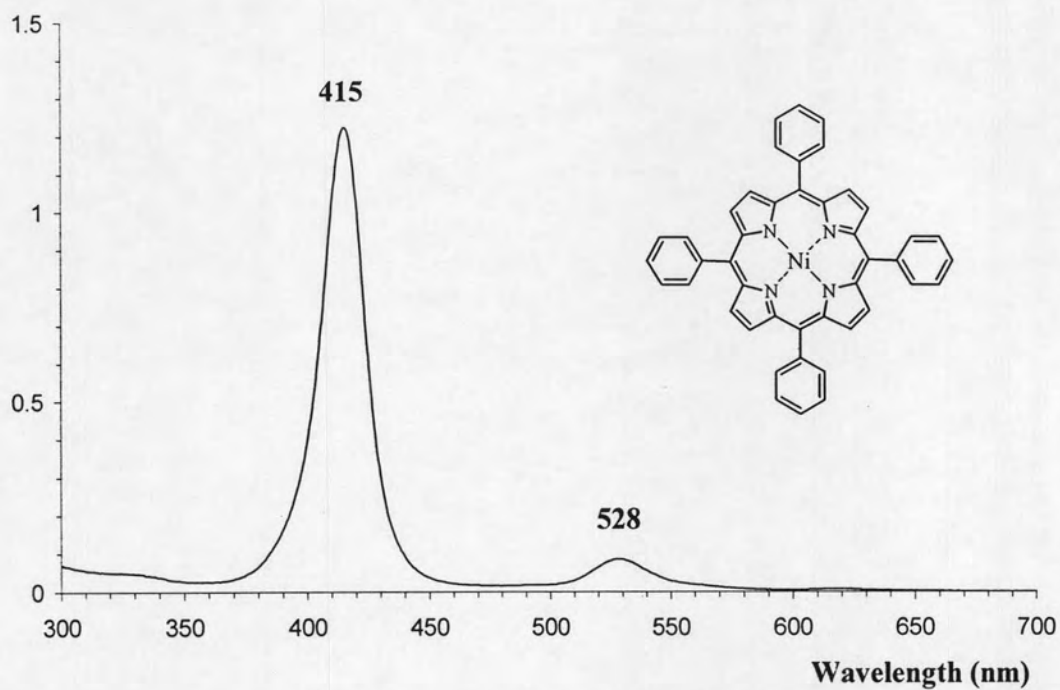


Figure A-11 UV/Visible spectrum of 5,10,15,20-tetraphenylporphyrinatonicell(II) (NiTPP, 4)

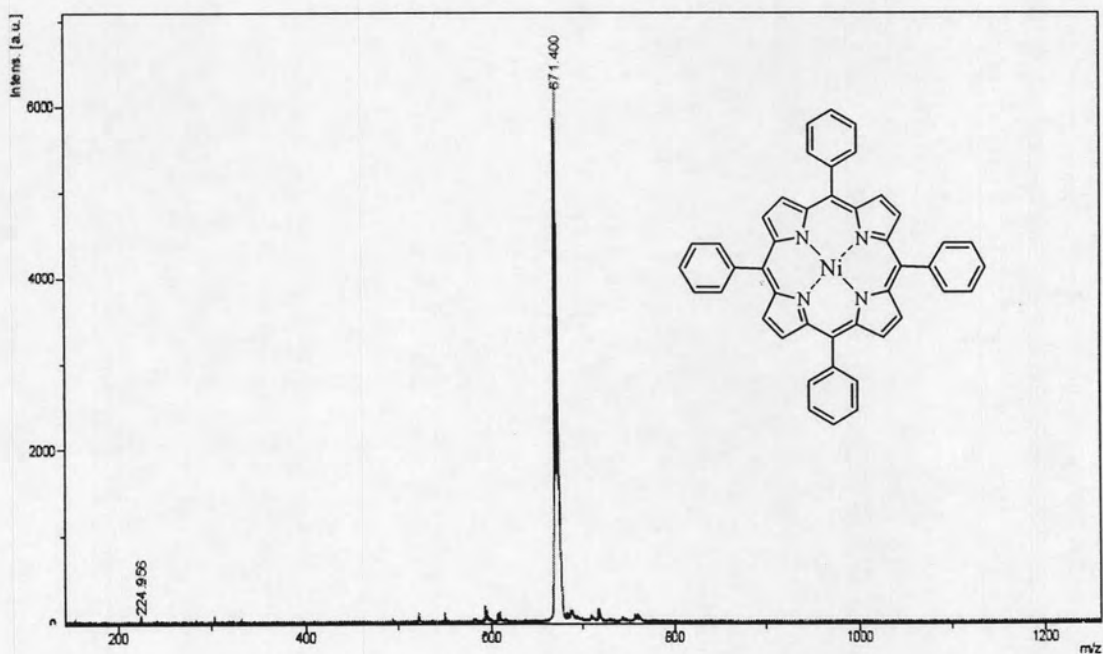


Figure A-12 MALDI-TOF mass spectrum of 5,10,15,20-tetraphenylporphyrinatonicell(II) (NiTPP, 4)

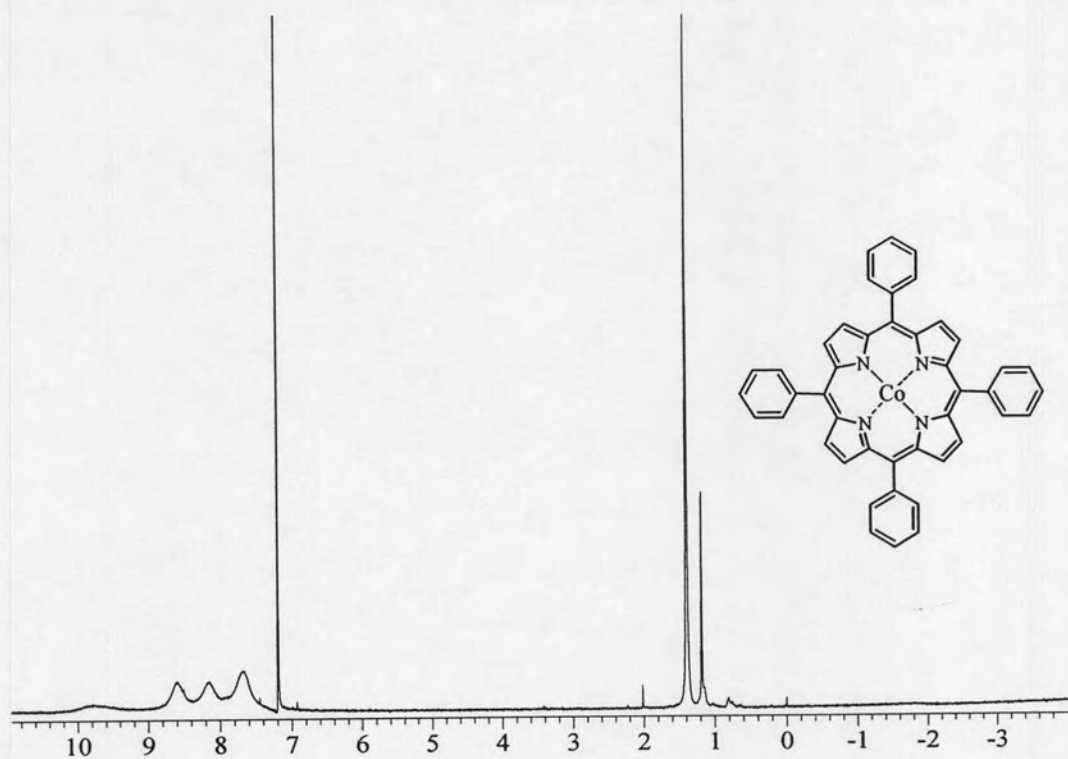


Figure A-13 The ^1H NMR spectrum of 5,10,15,20-tetraphenylporphyrinatocobalt(II) (CoTPP, 5)

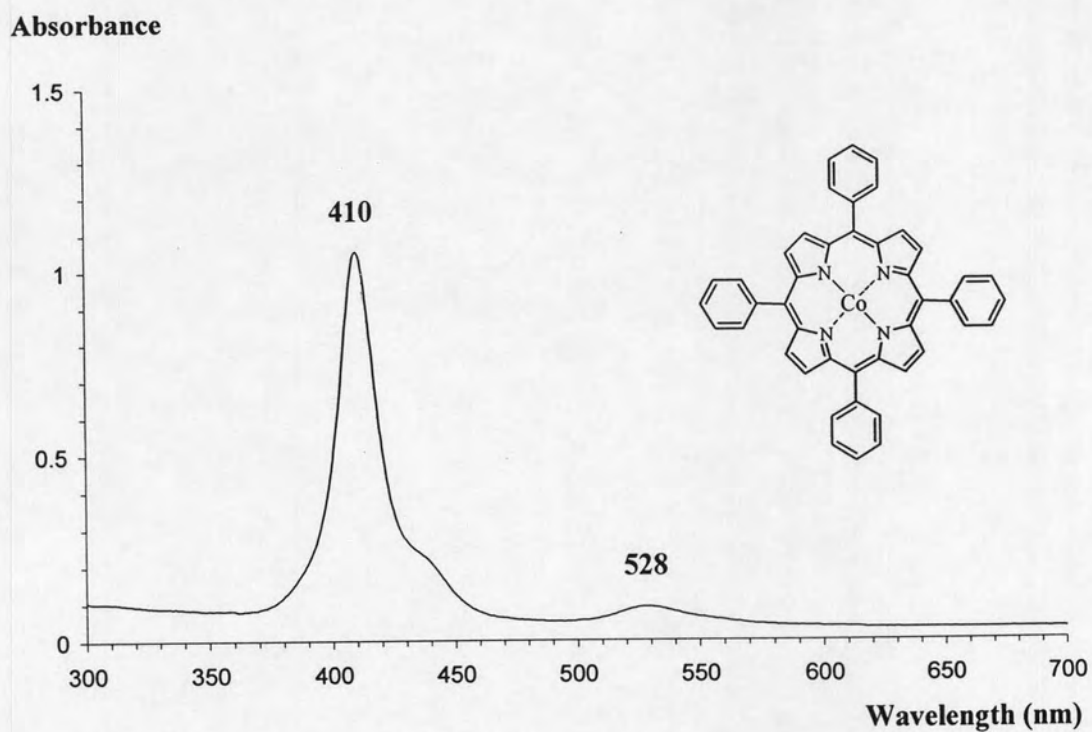


Figure A-14 UV/Visible spectrum of 5,10,15,20-tetraphenylporphyrinatocobalt(II) (CoTPP, 5)

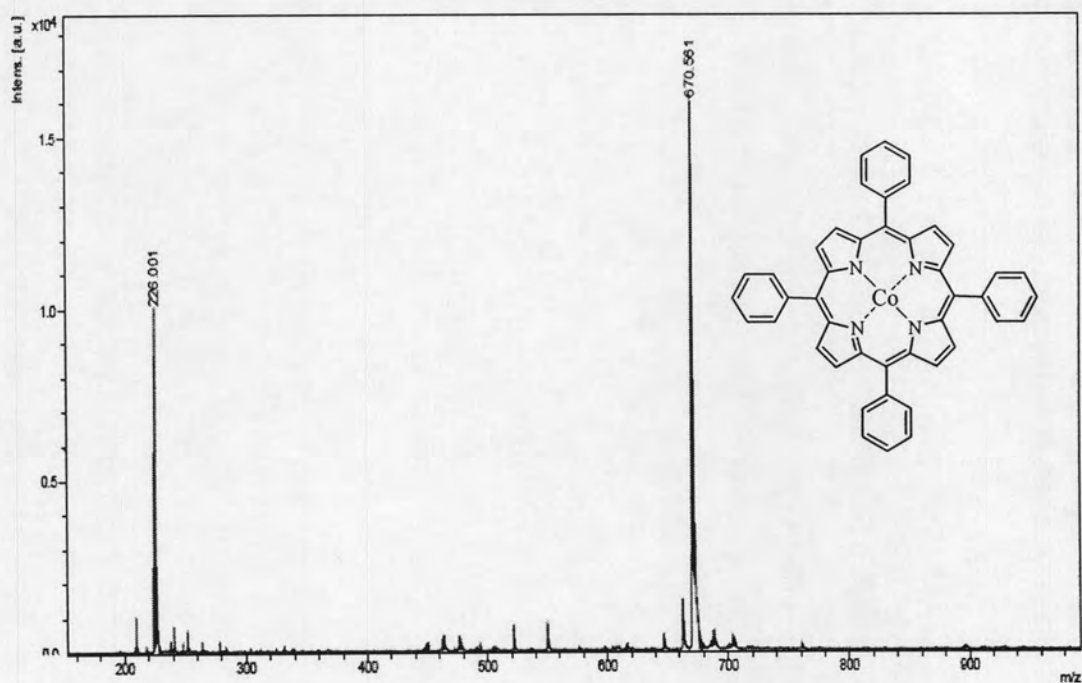


Figure A-15 MALDI-TOF mass spectrum of 5,10,15,20-tetraphenylporphyrinatocobalt(II) (CoTPP, 5)

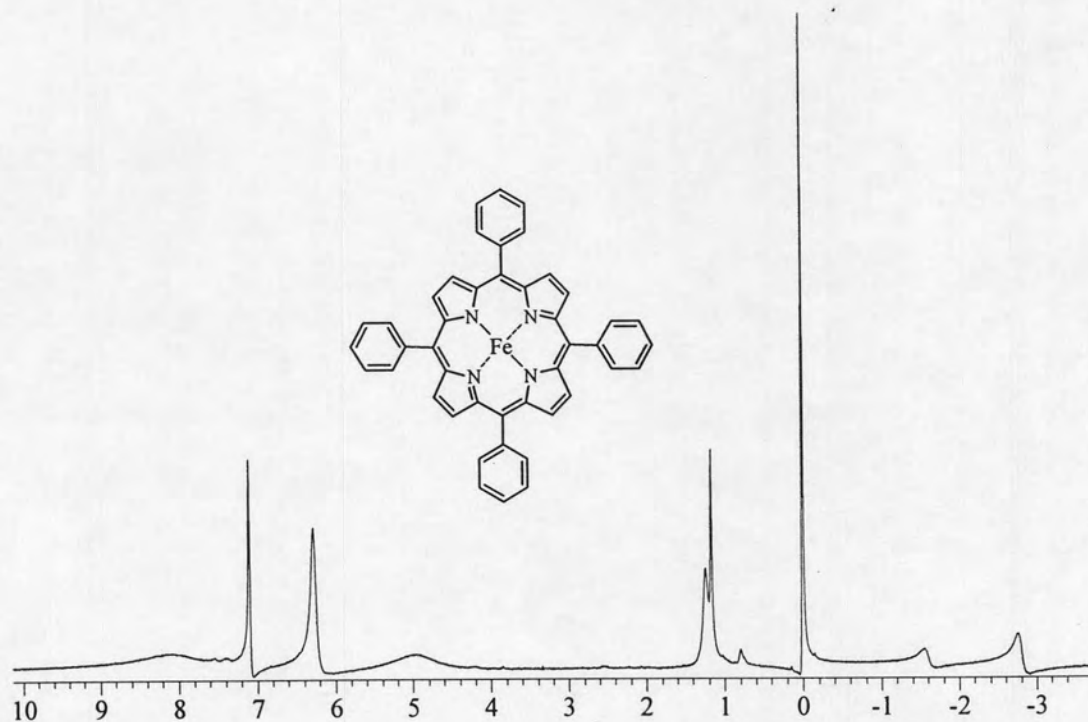


Figure A-16 The ^1H NMR spectrum of 5,10,15,20-tetraphenylporphyrinatoiron(III) ((Cl)FeTPP, 6)

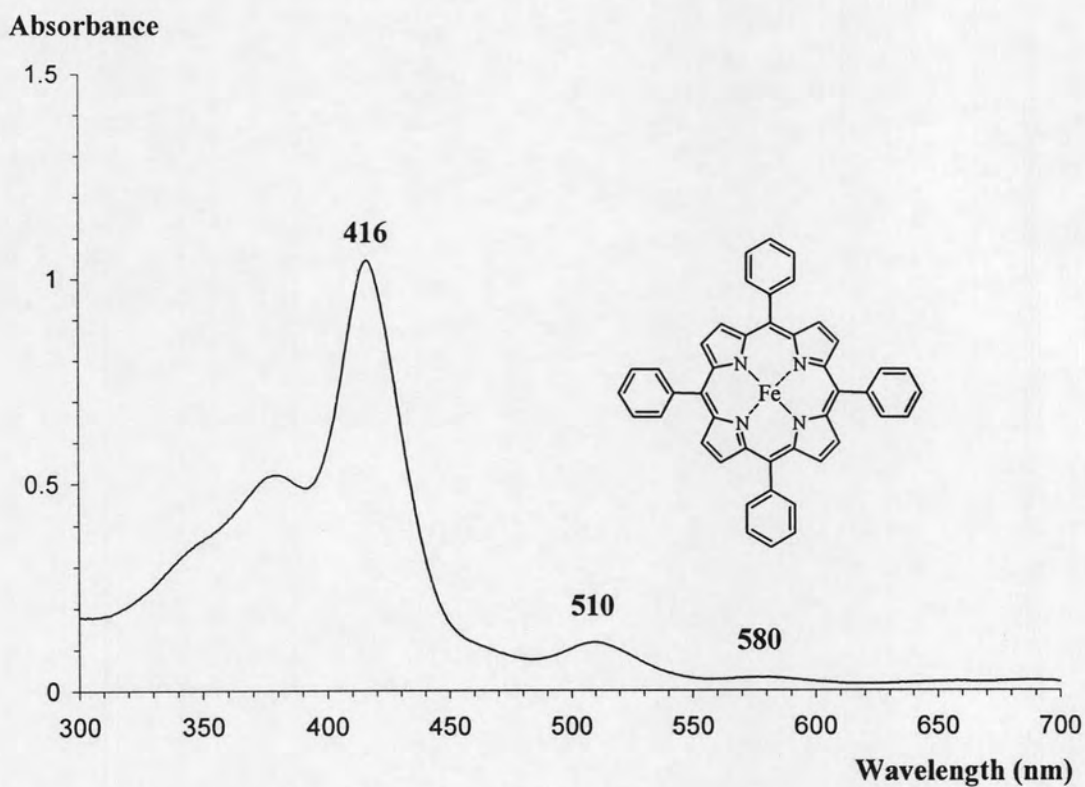


Figure A-17 UV/Visible spectrum of 5,10,15,20-tetraphenylporphyrinatoiron(III) ((Cl)FeTPP, 6)

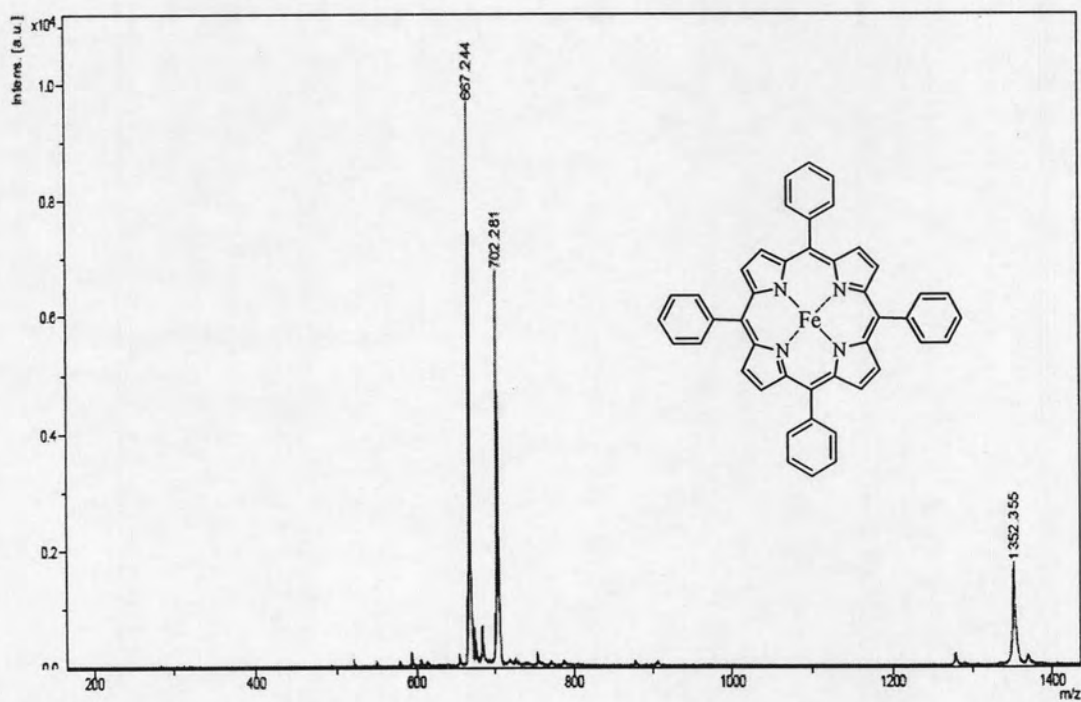


Figure A-18 MALDI-TOF mass spectrum of 5,10,15,20-tetraphenylporphyrinatoiron(III) ((Cl)FeTPP, 6)

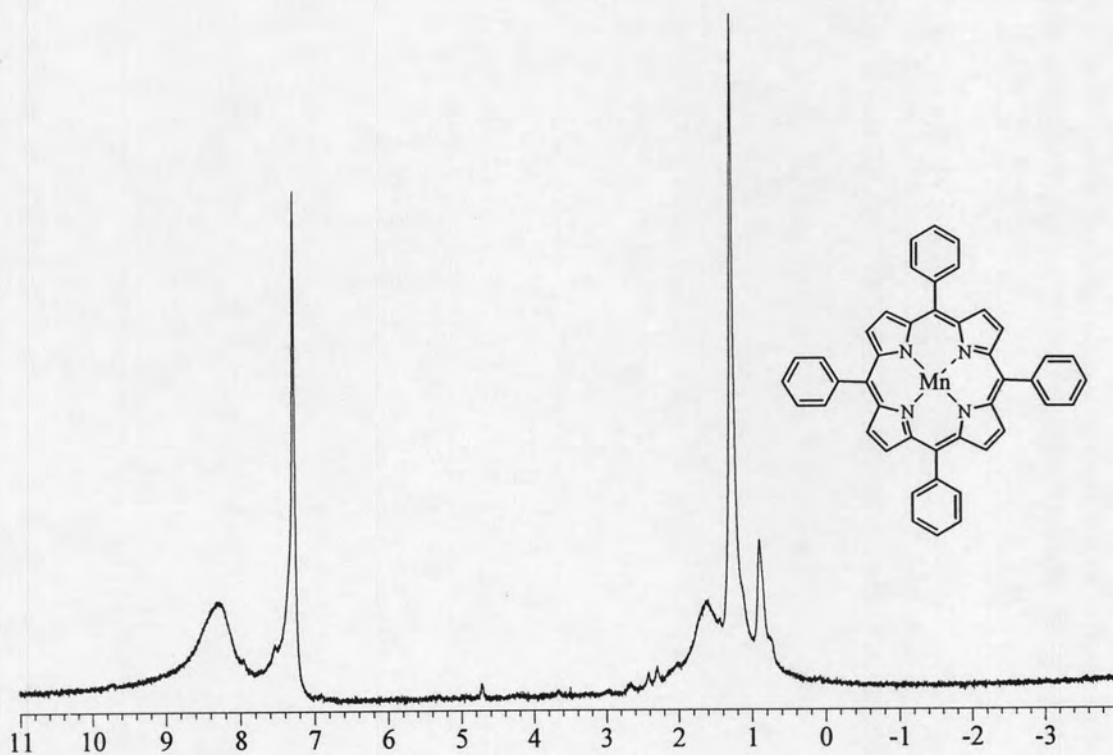


Figure A-19 The ^1H NMR spectrum of 5,10,15,20-tetraphenyl porphyrinat manganese(III) (MnTPP, 7)

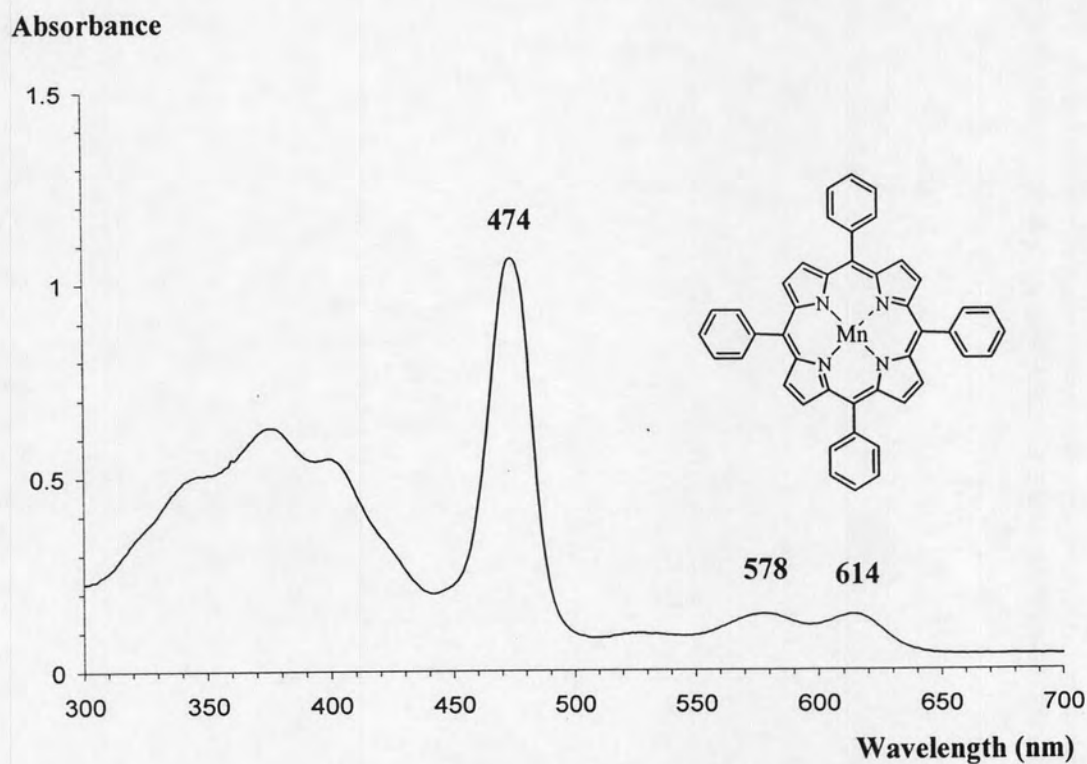


Figure A-20 UV/Visible spectrum of 5,10,15,20-tetraphenylporphyrinato manganese(III) (MnTPP, 7)

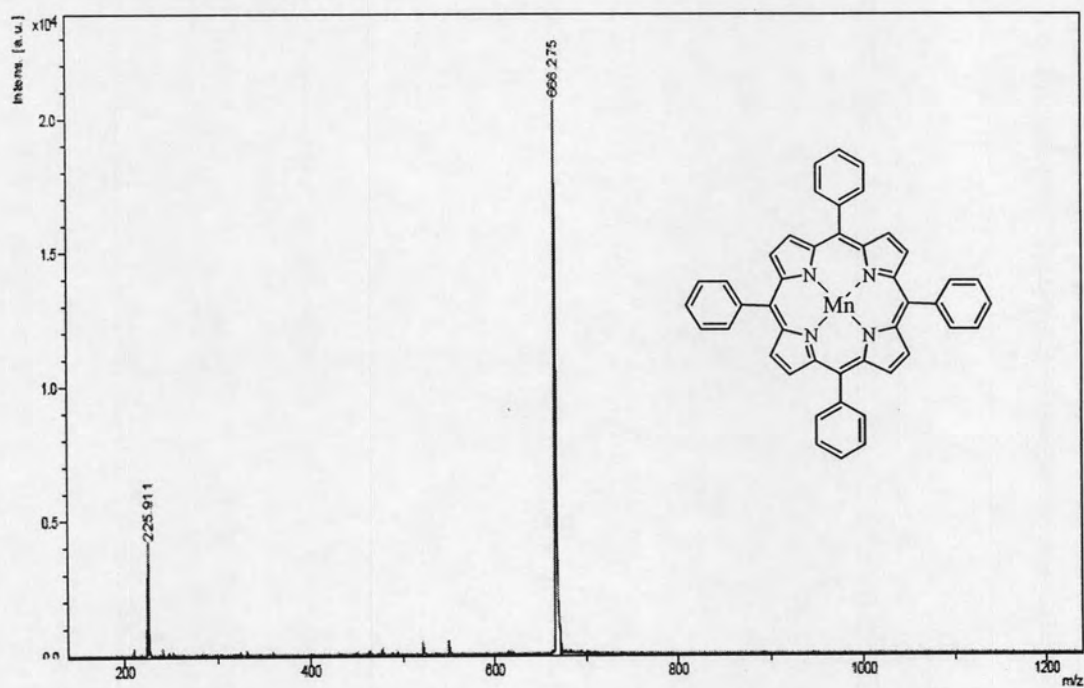


Figure A-21 MALDI-TOF mass spectrum of 5,10,15,20-tetraphenylporphyrinato manganese(III) (MnTPP, 7)

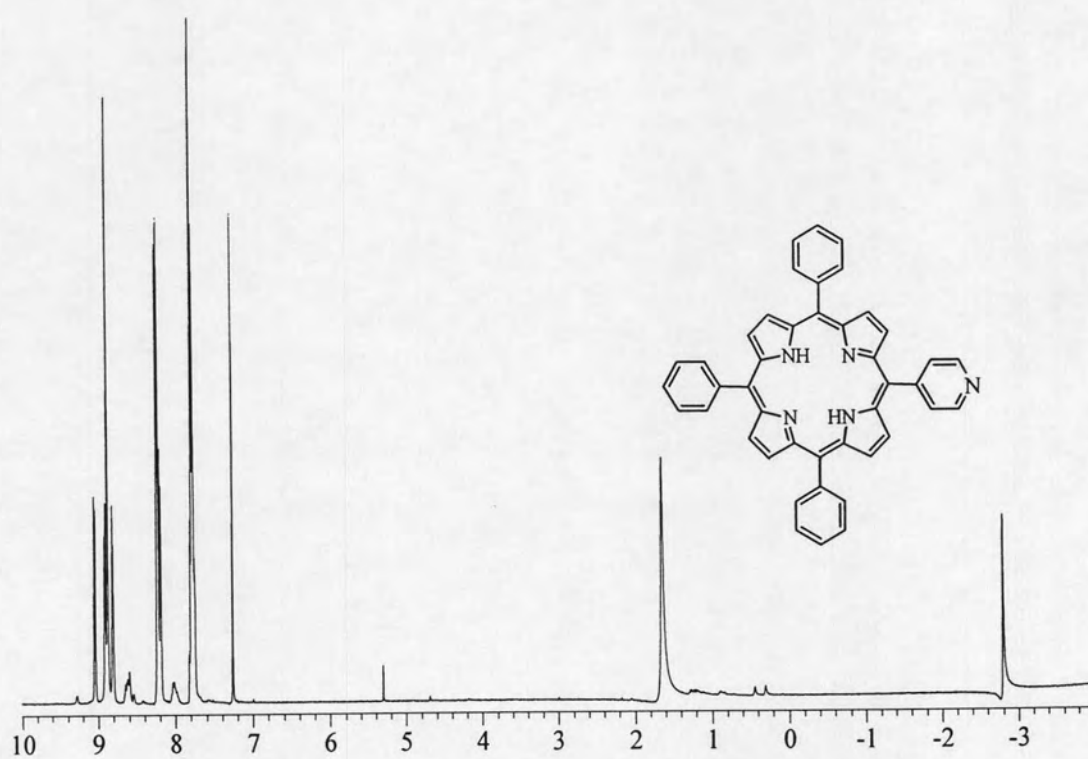


Figure A-22 The ¹H NMR spectrum of 5-(pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, 8)

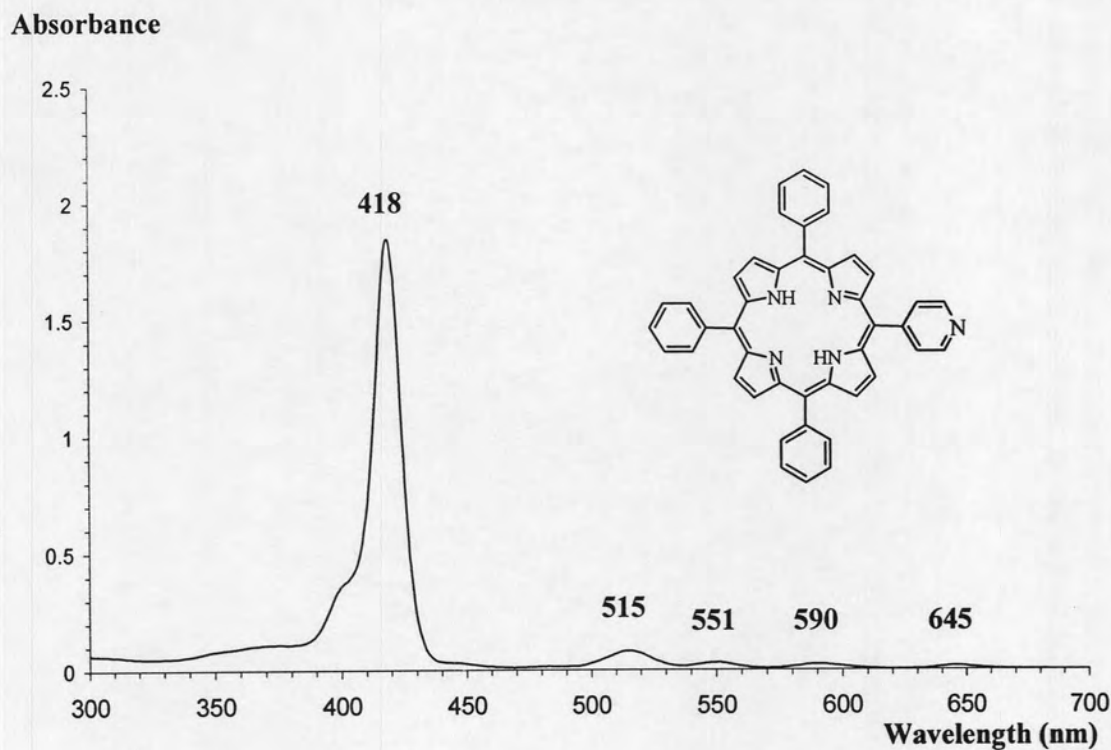


Figure A-23 UV/Visible spectrum of 5-(pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, **8**)

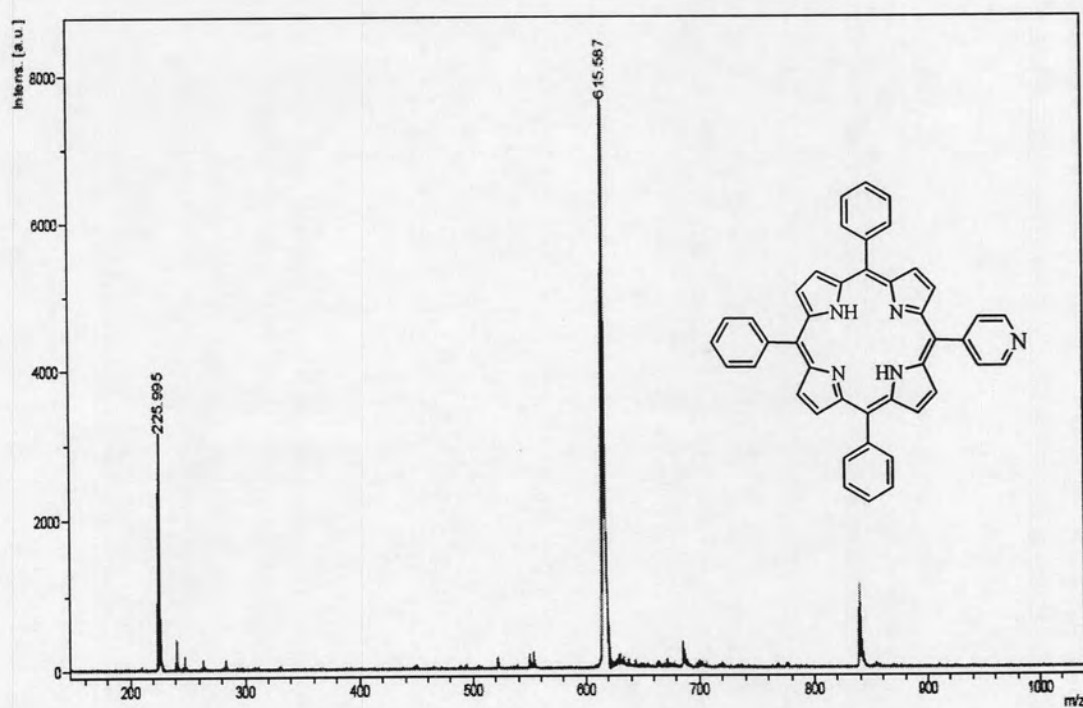


Figure A-24 MALDI-TOF mass spectrum of 5-(pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, **8**)

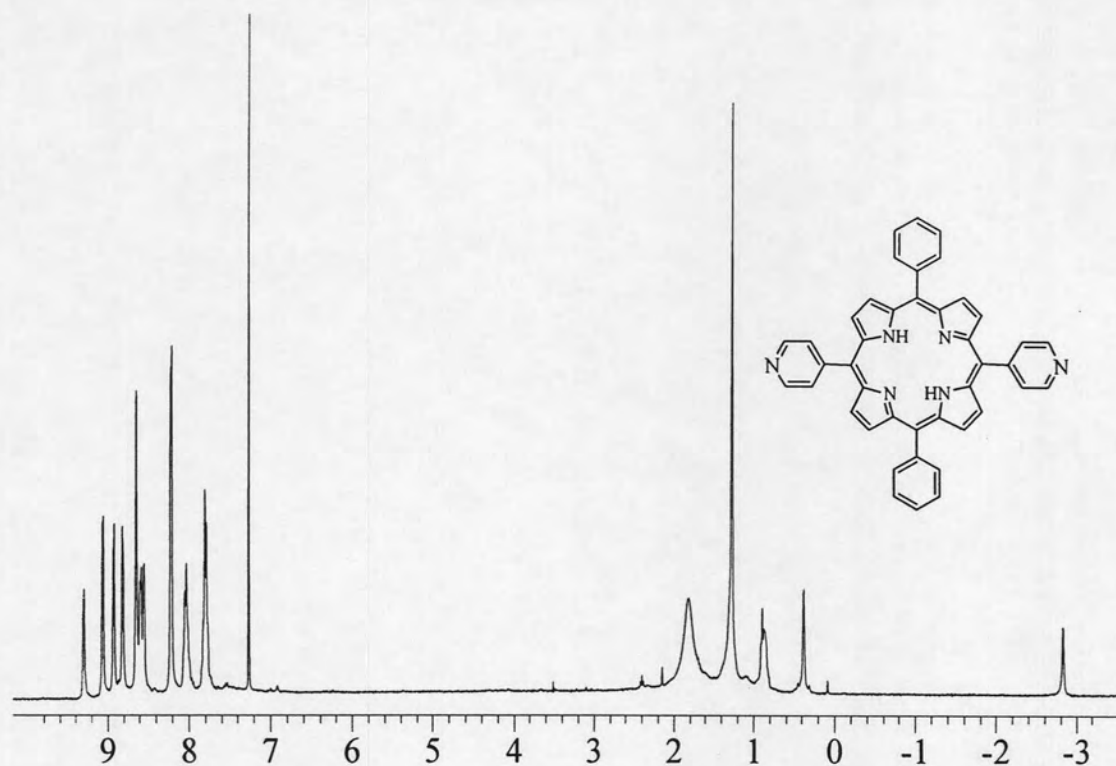


Figure A-25 The ^1H NMR spectrum of 5,15-(dipyridyl)-10,20-diphenylporphyrin (*trans*-DPyDPP, 9)

Absorbance

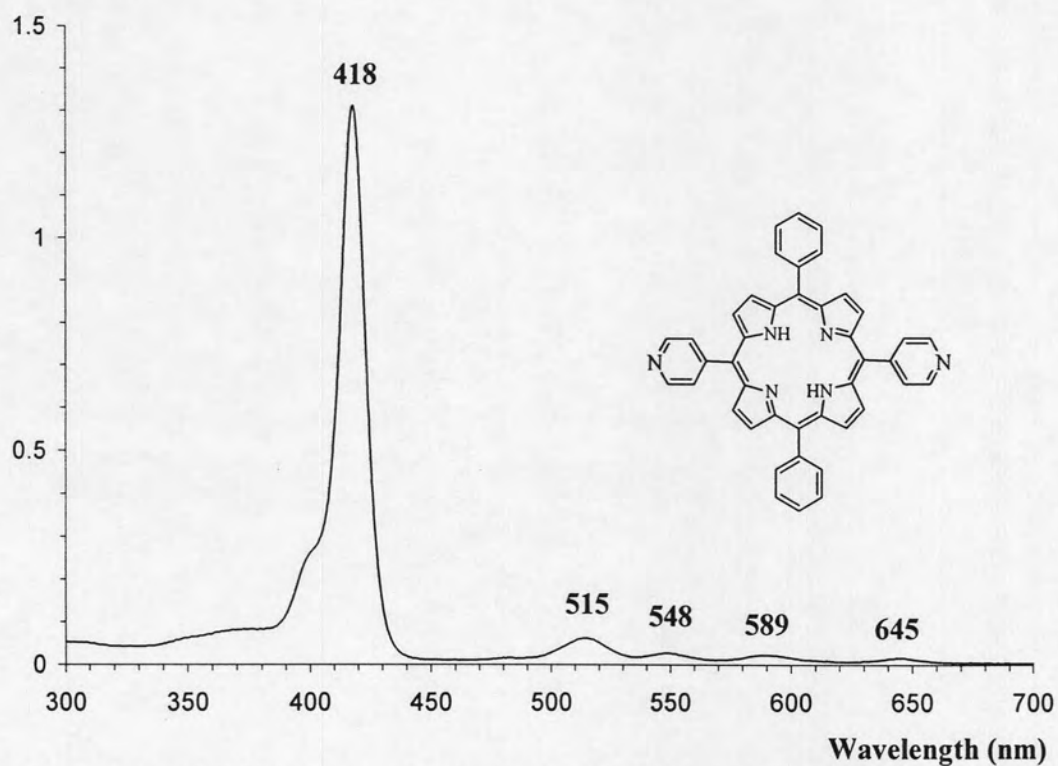


Figure A-26 UV/Visible spectrum of 5,15-(dipyridyl)-10,20-diphenylporphyrin (*trans*-DPyDPP, 9)

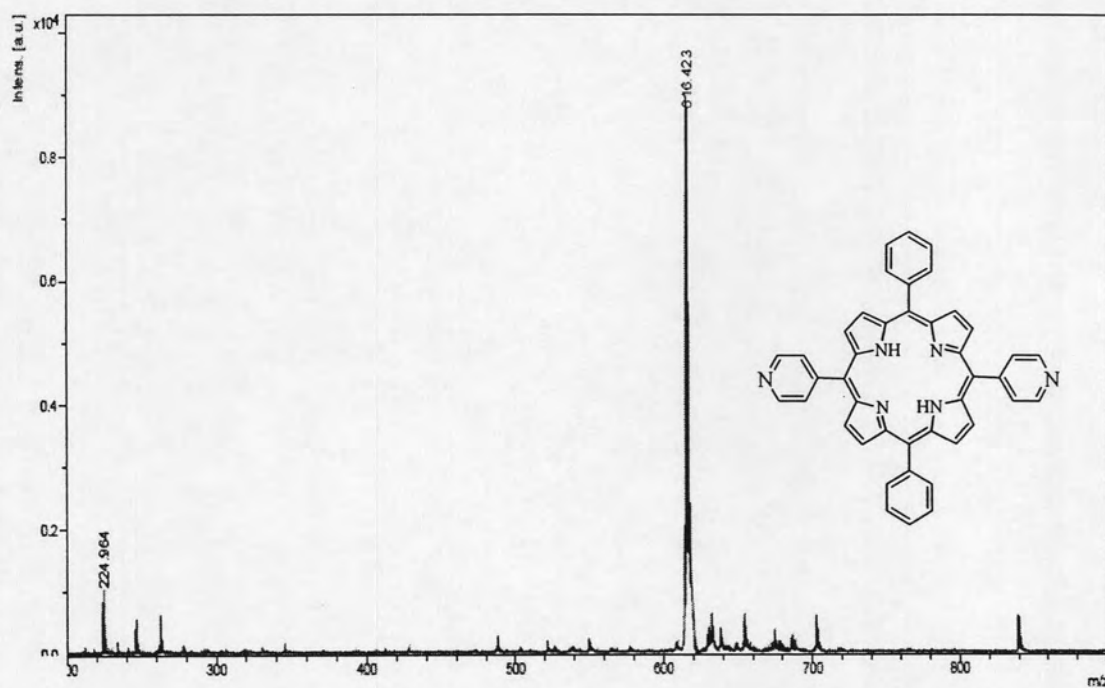


Figure A-27 MALDI-TOF mass spectrum of 5,15-(dipyridyl)-10,20-diphenyl porphyrin (*trans*-DPyDPP, **9**)

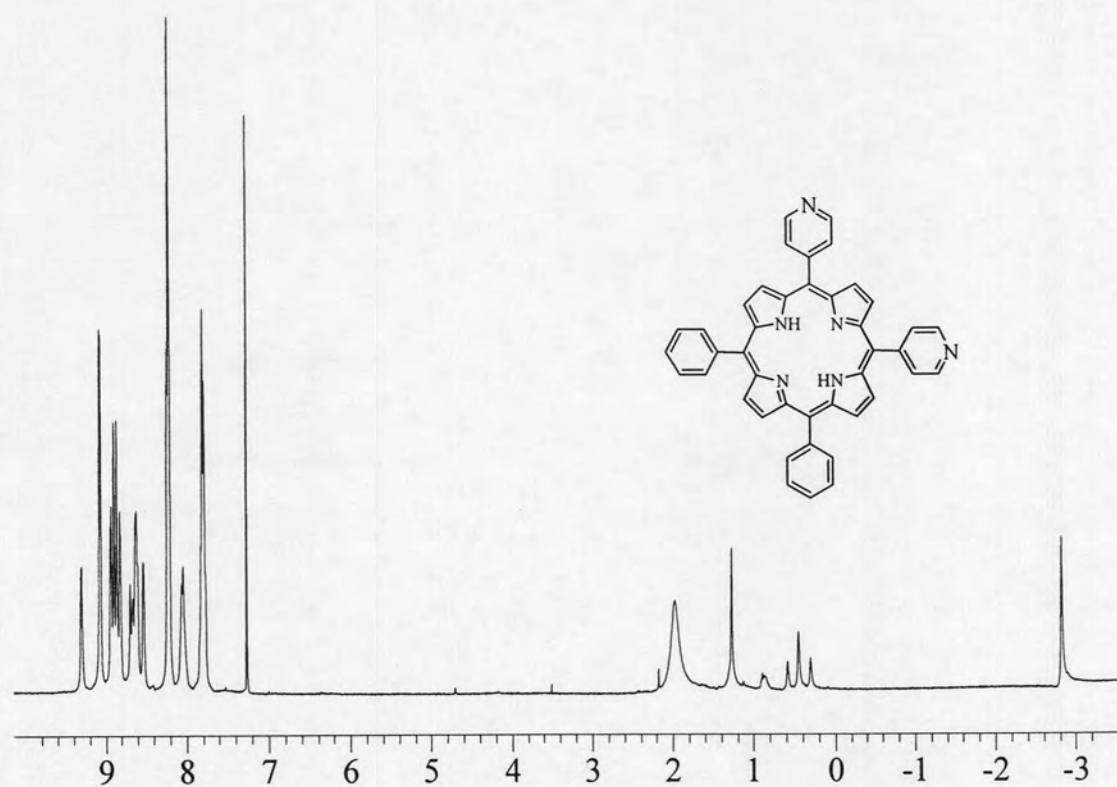


Figure A-28 The ¹H NMR spectrum of 5,10-(dipyridyl)-15,20-diphenylporphyrin (*cis*-DPyDPP, **10**)

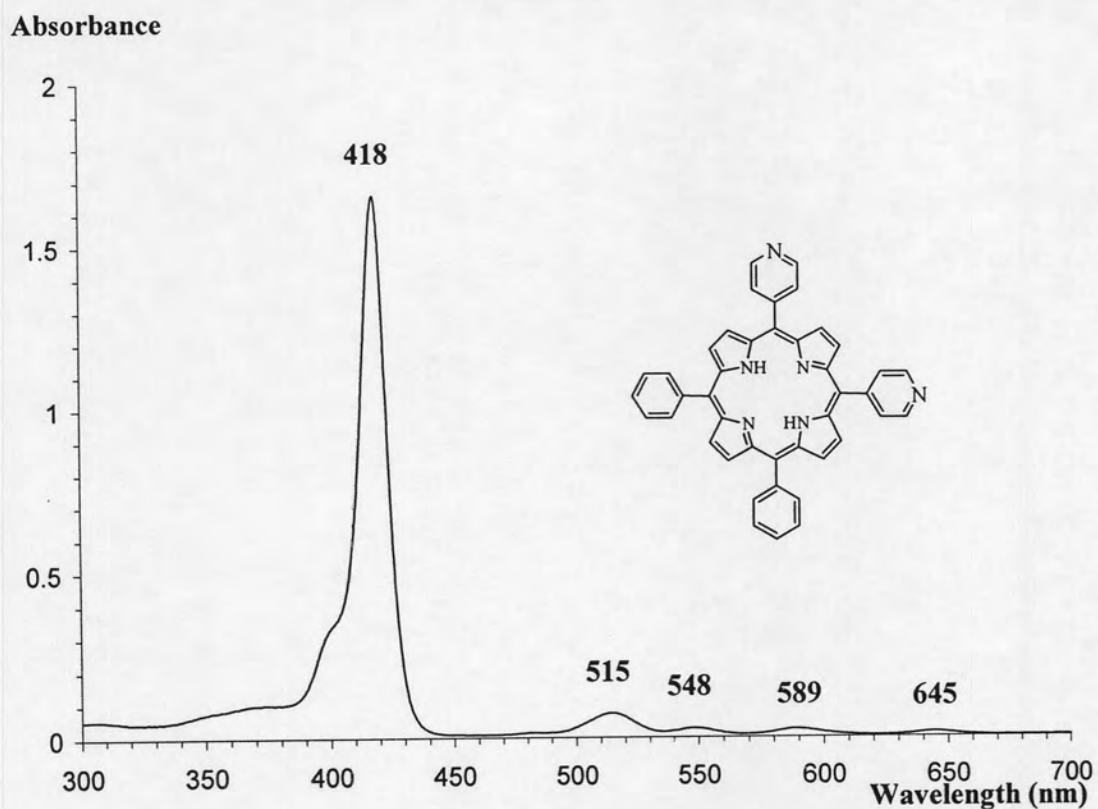


Figure A-29 UV/Visible spectrum of 5,10-(dipyridyl)-15,20-diphenylporphyrin (*cis*-DPyDPP, 10)

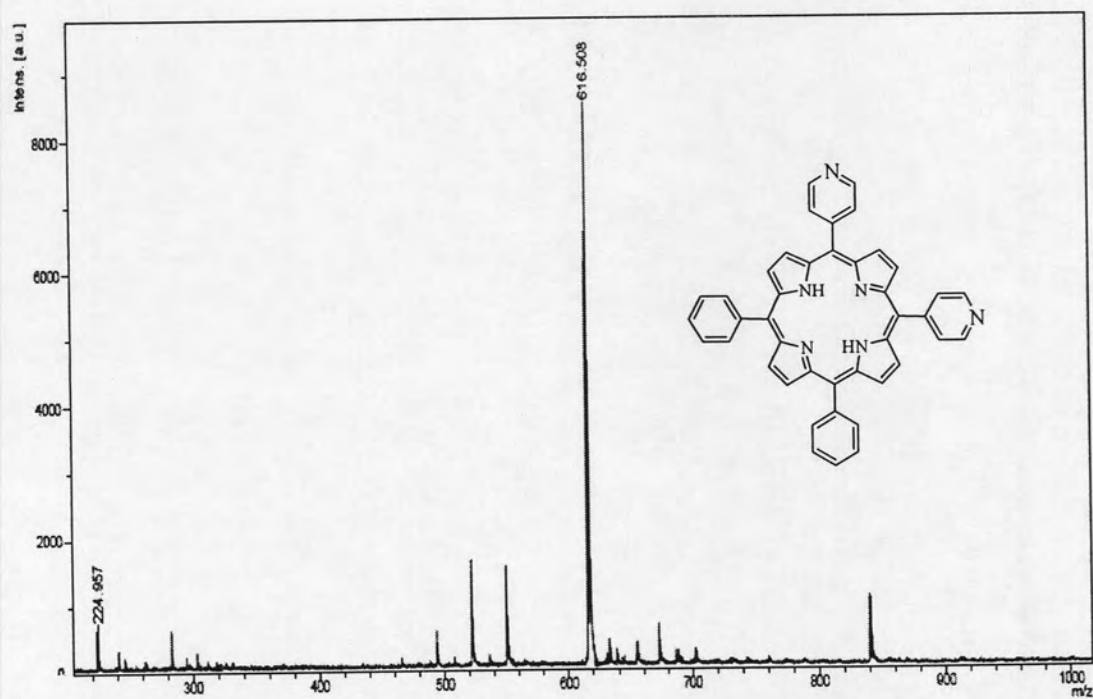


Figure A-30 MALDI-TOF mass spectrum of 5,10-(dipyridyl)-15,20-diphenyl porphyrin (*cis*-DPyDPP, 10)

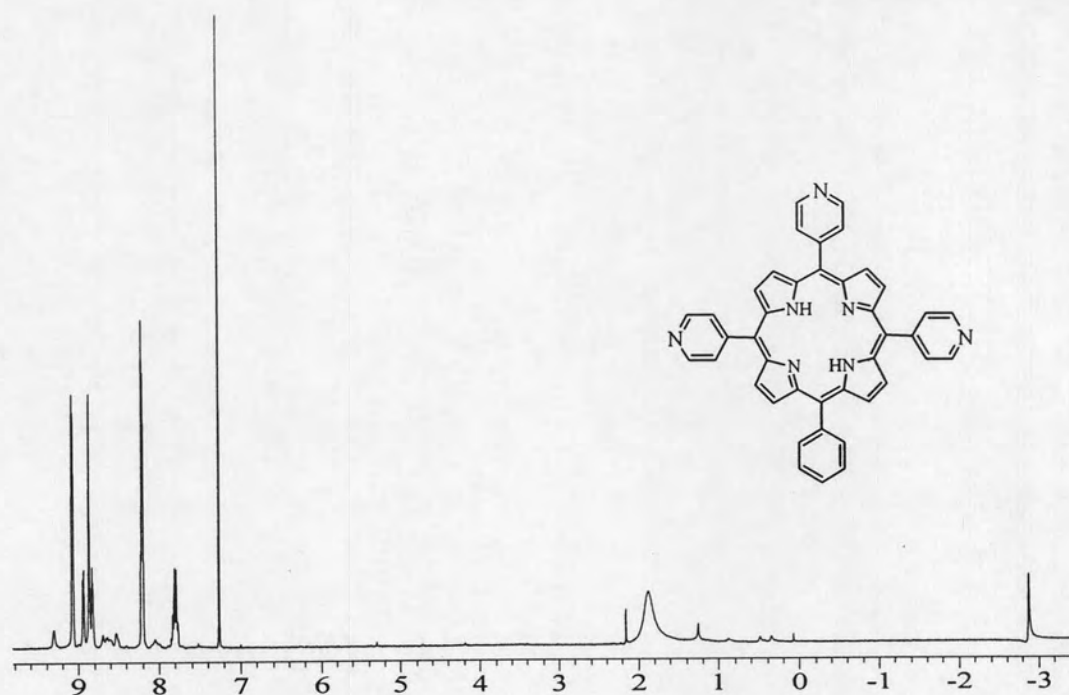


Figure A-31 The ^1H NMR spectrum of 5,10,15-(tripyridyl)-20-phenylporphyrin (TPyMPP, 11)

Absorbance

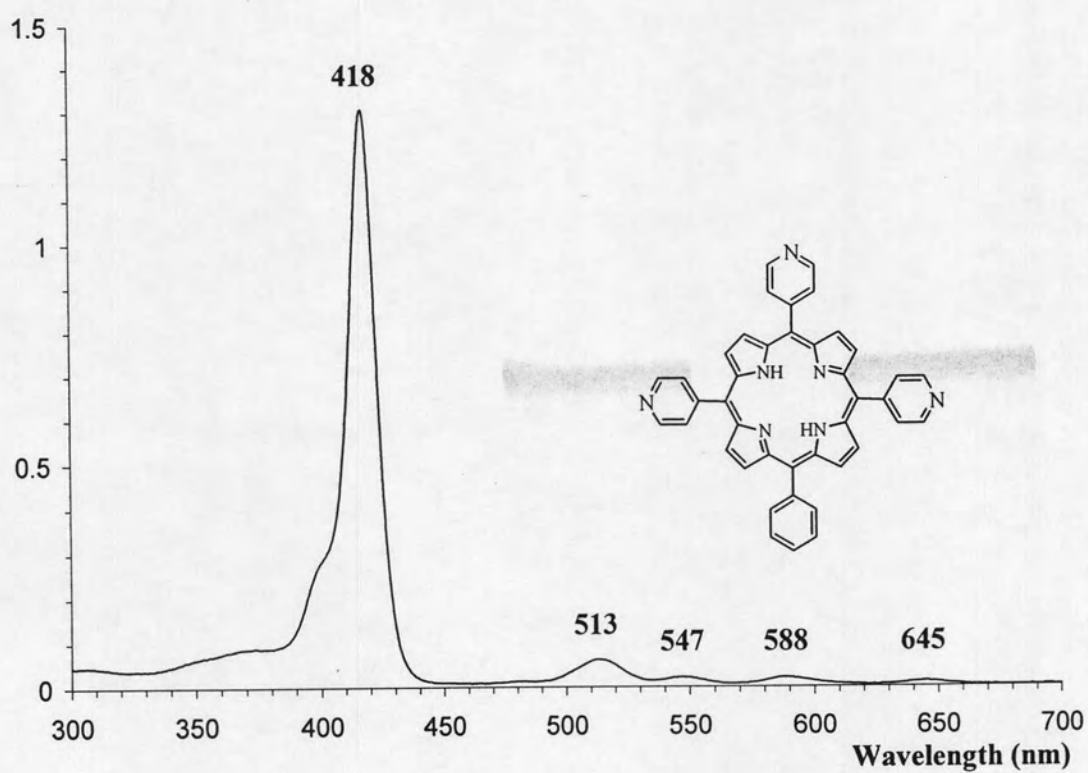


Figure A-32 UV/Visible spectrum of 5,10,15-(tripyridyl)-20-phenylporphyrin (TPyMPP, 11)

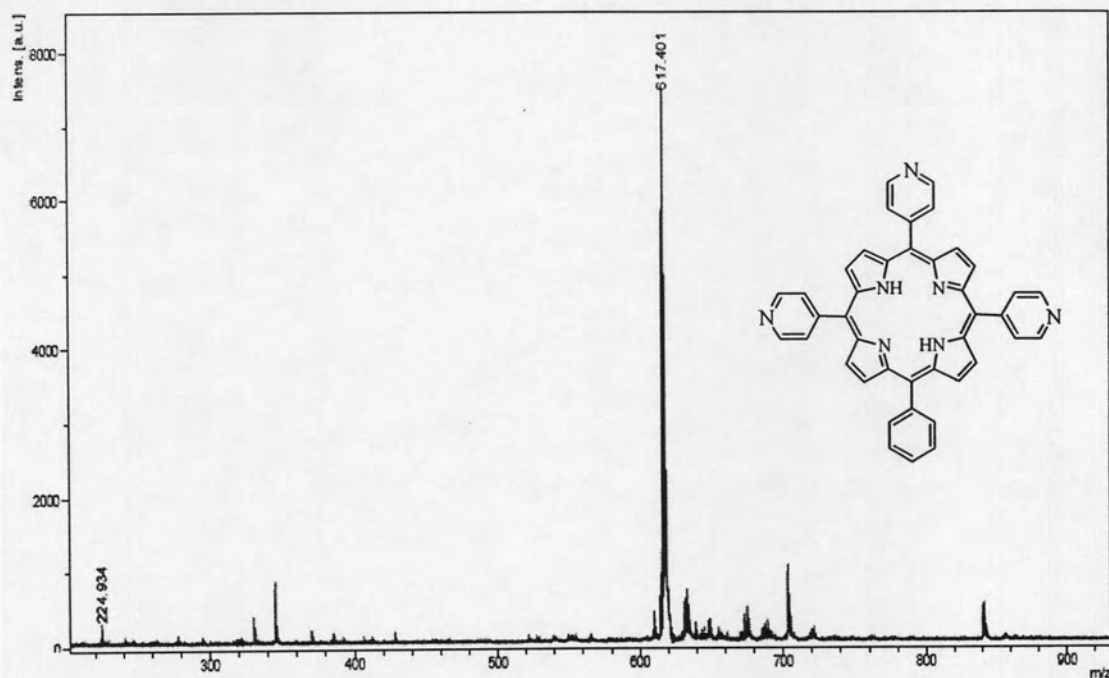


Figure A-33 MALDI-TOF mass spectrum of 5,10,15-(tripyridyl)-20-phenyl porphyrin (TPyMPP, 11)

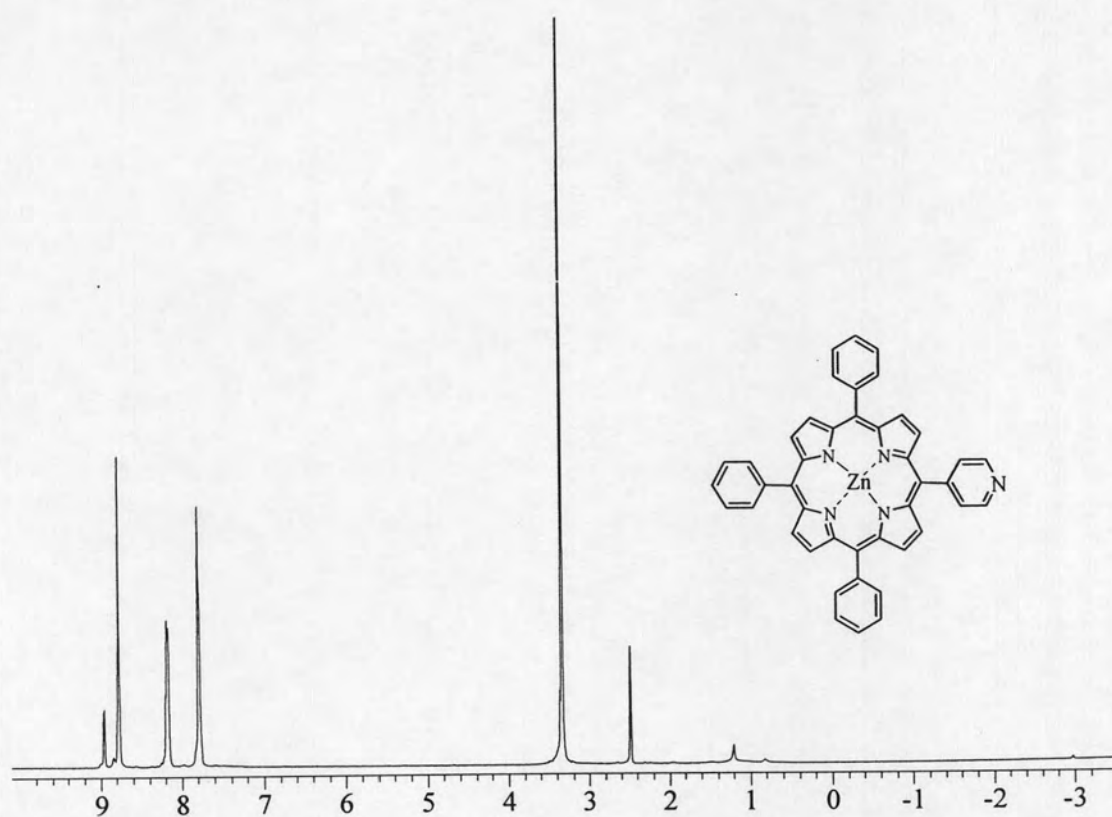


Figure A-34 The ^1H NMR spectrum of 5-(pyridyl)-10,15,20-triphenyl porphyrinatozinc(II) (ZnMPyTPP, 12)

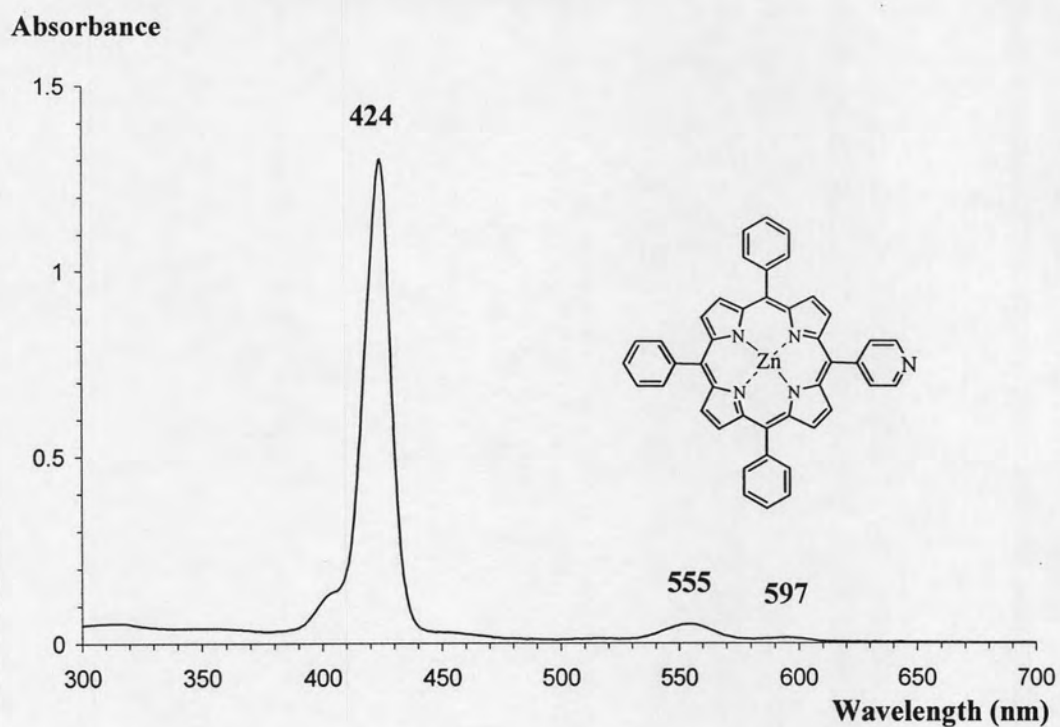


Figure A-35 UV/Visible spectrum of 5-(pyridyl)-10,15,20-triphenylporphyrinato zinc(II) (ZnMPyTPP, 12)

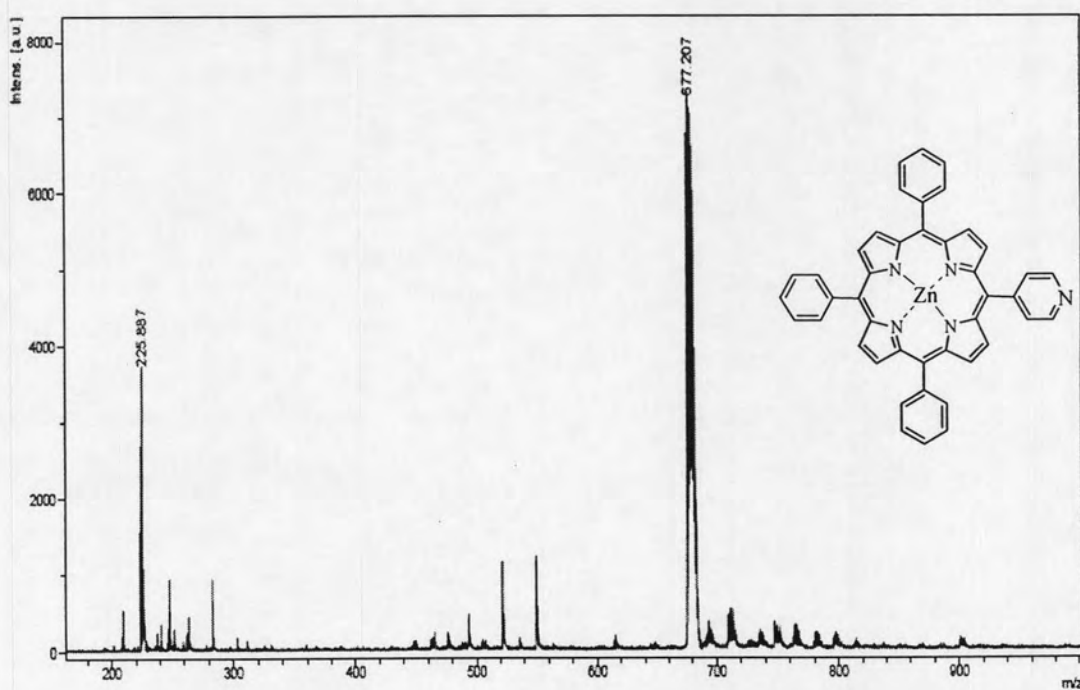


Figure A-36 MALDI-TOF mass spectrum of 5-(pyridyl)-10,15,20-triphenyl porphyrinatozinc(II) (ZnMPyTPP, 12)

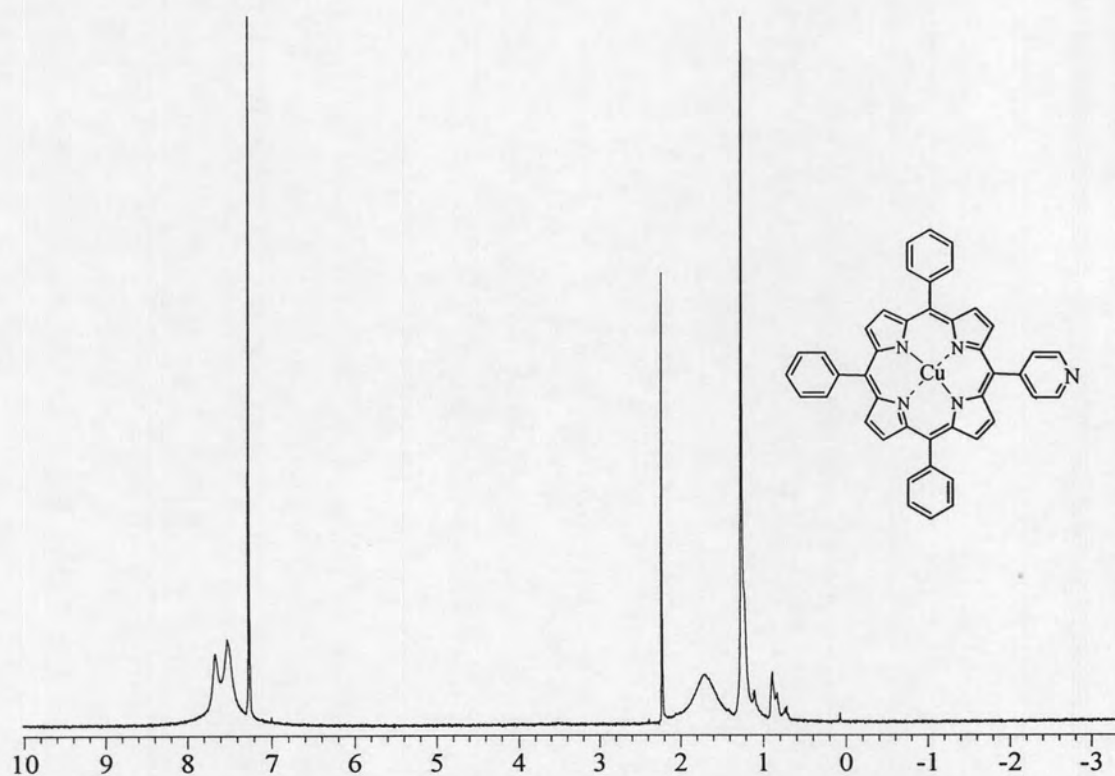


Figure A-37 The ^1H NMR spectrum of 5-(pyridyl)-10,15,20-triphenyl porphyrinatocopper(II) (CuMPyTPP, 13)

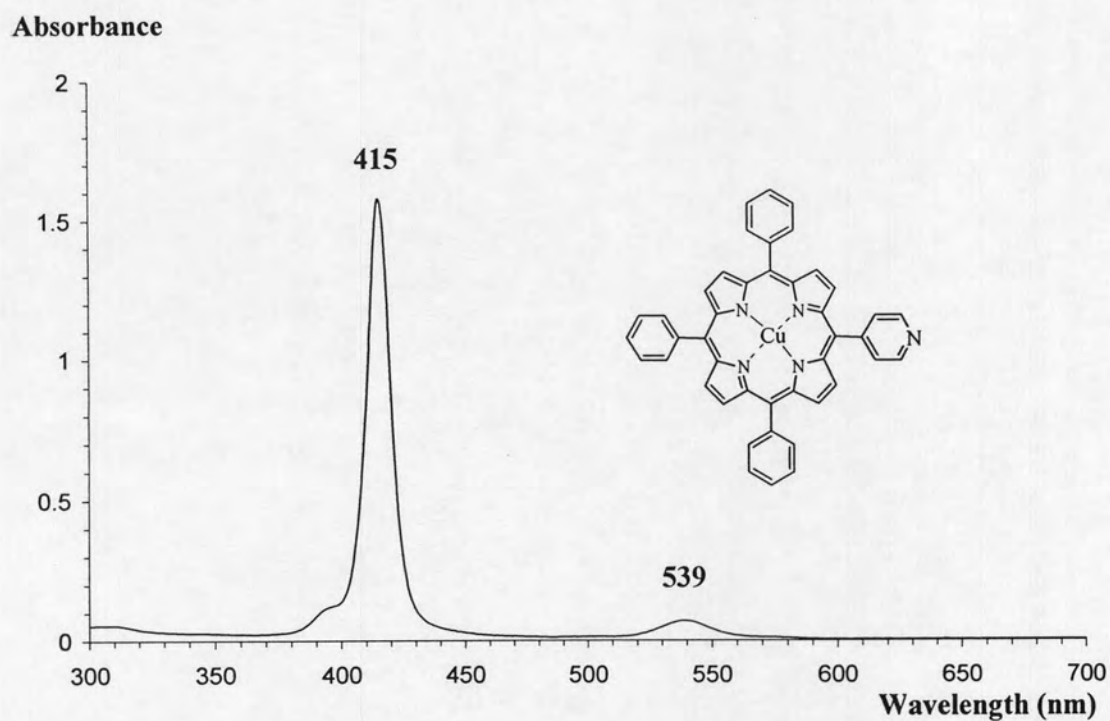


Figure A-38 UV/Visible spectrum of 5-(pyridyl)-10,15,20-triphenylporphyrinato copper(II) (CuMPyTPP, 13)

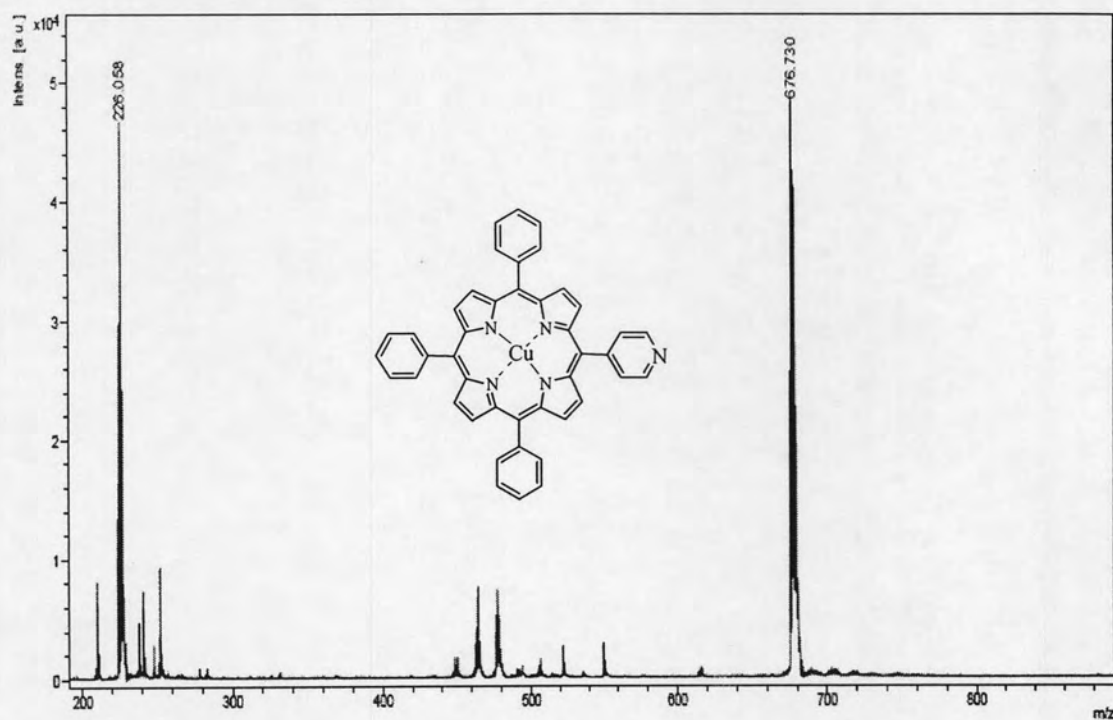


Figure A-39 MALDI-TOF mass spectrum of 5-(pyridyl)-10,15,20-triphenyl porphyrinatocopper(II) (CuMPyTPP, 13)

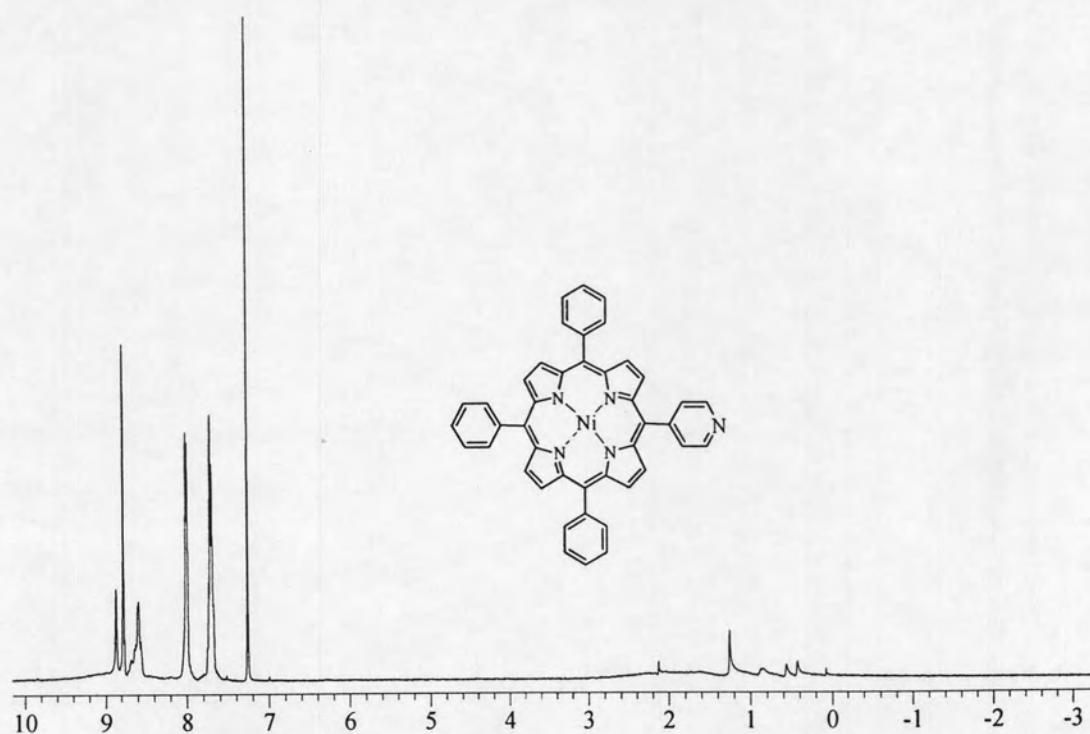


Figure A-40 The ¹H NMR spectrum of 5-(pyridyl)-10,15,20-triphenyl porphyrinatonicel(II) (NiMPyTPP, 14)

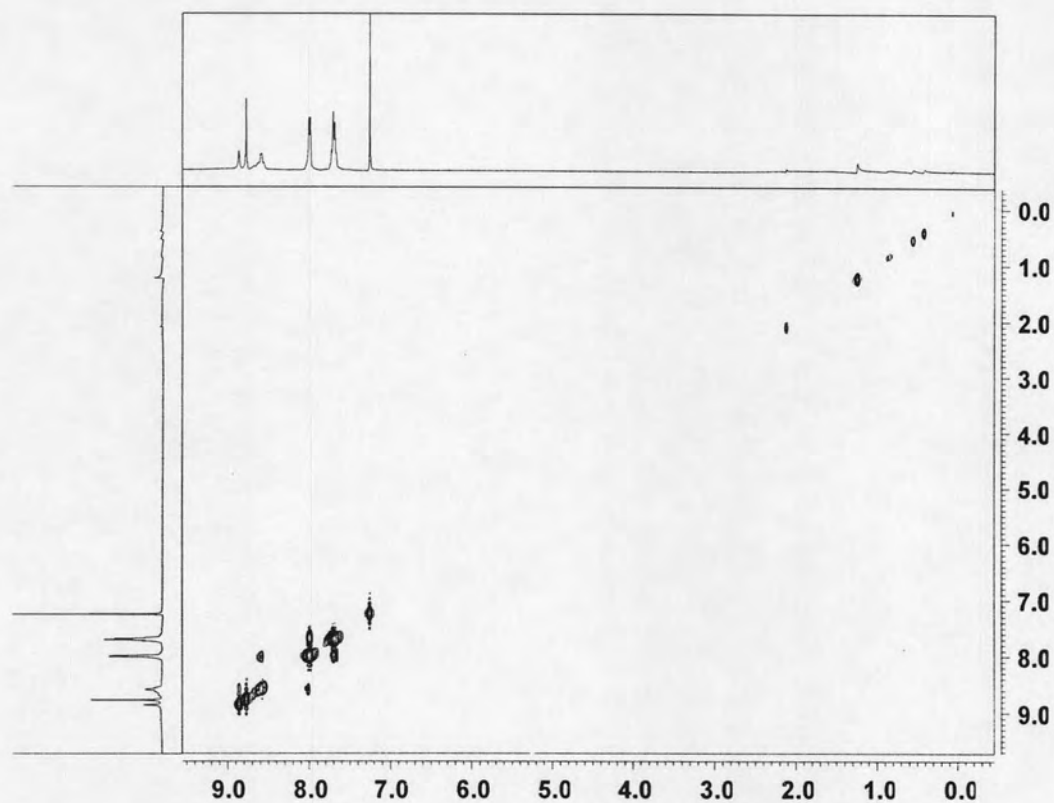


Figure A-41 The ^1H - ^1H COSY spectrum of 5-(pyridyl)-10,15,20-triphenylporphyrinato nickel(II) (NiMPyTPP, **14**)

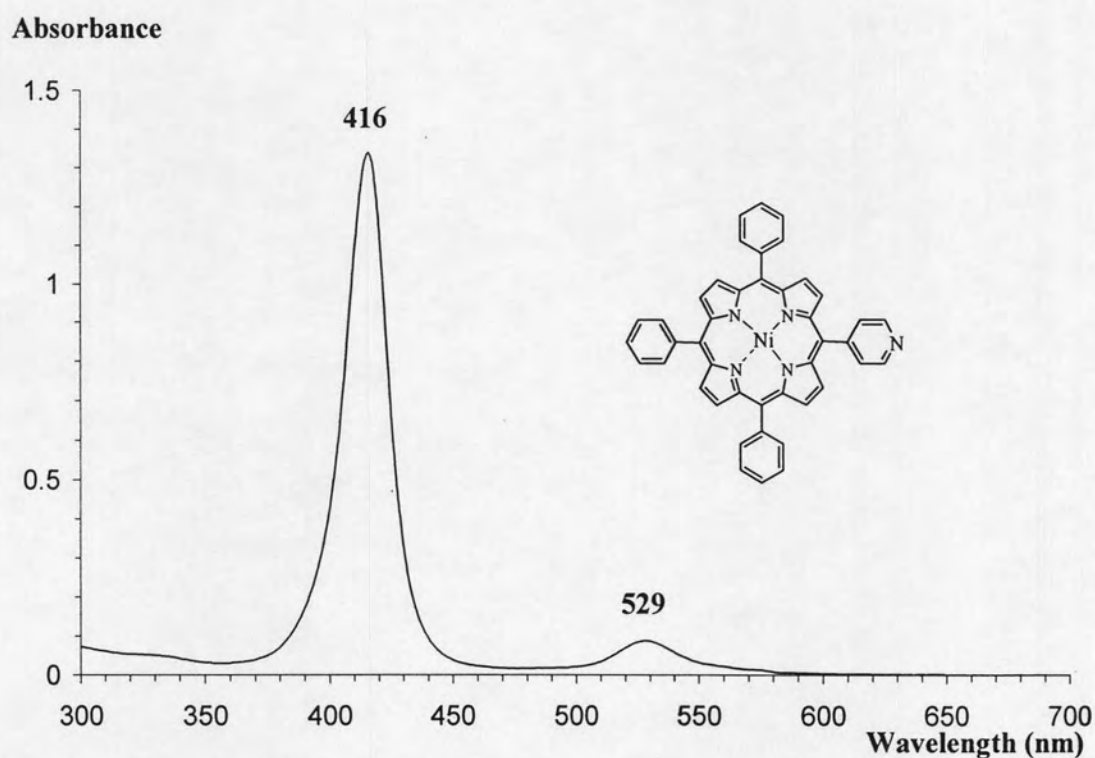


Figure A-42 UV/Visible spectrum of 5-(pyridyl)-10,15,20-triphenylporphyrinato nickel(II) (NiMPyTPP, **14**)

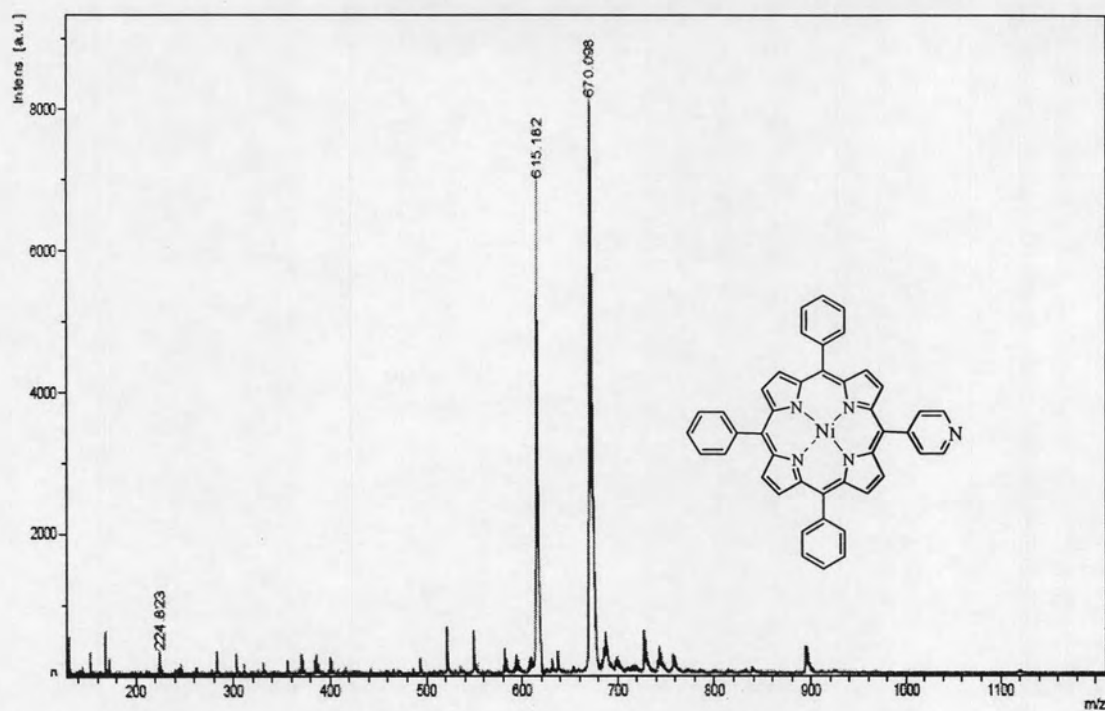


Figure A-43 MALDI-TOF mass spectrum of 5-(pyridyl)-10,15,20-triphenyl porphyrinatonicell(II) (NiMPyTPP, 14)

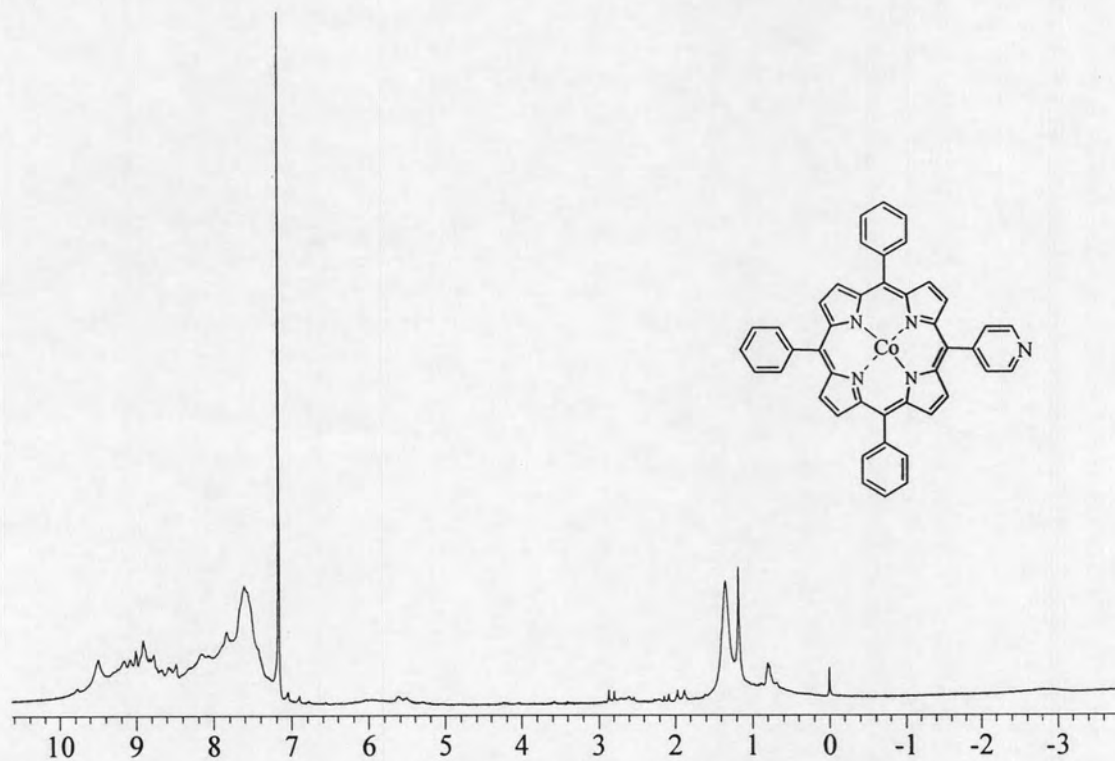


Figure A-44 The ¹H NMR spectrum of 5-(pyridyl)-10,15,20-triphenyl porphyrinatocobalt(II) (CoMPyTPP, 15)

Absorbance

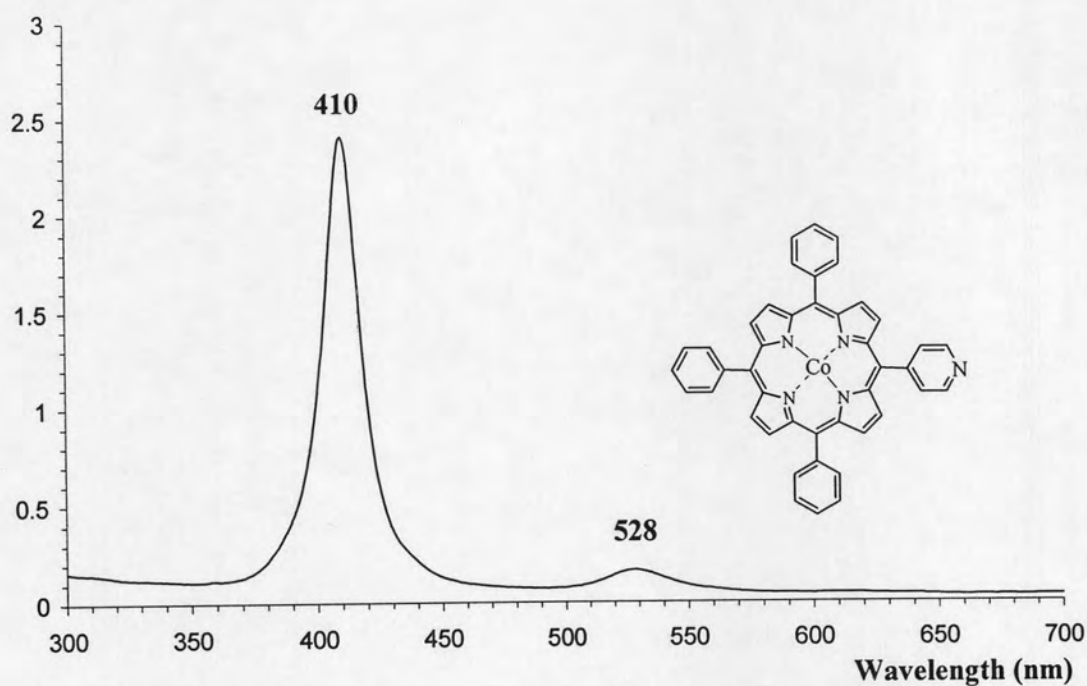


Figure A-45 UV/Visible spectrum of 5-pyridyl-10,15,20-triphenylporphyrinato cobalt(II) (CoMPyTPP, 15)

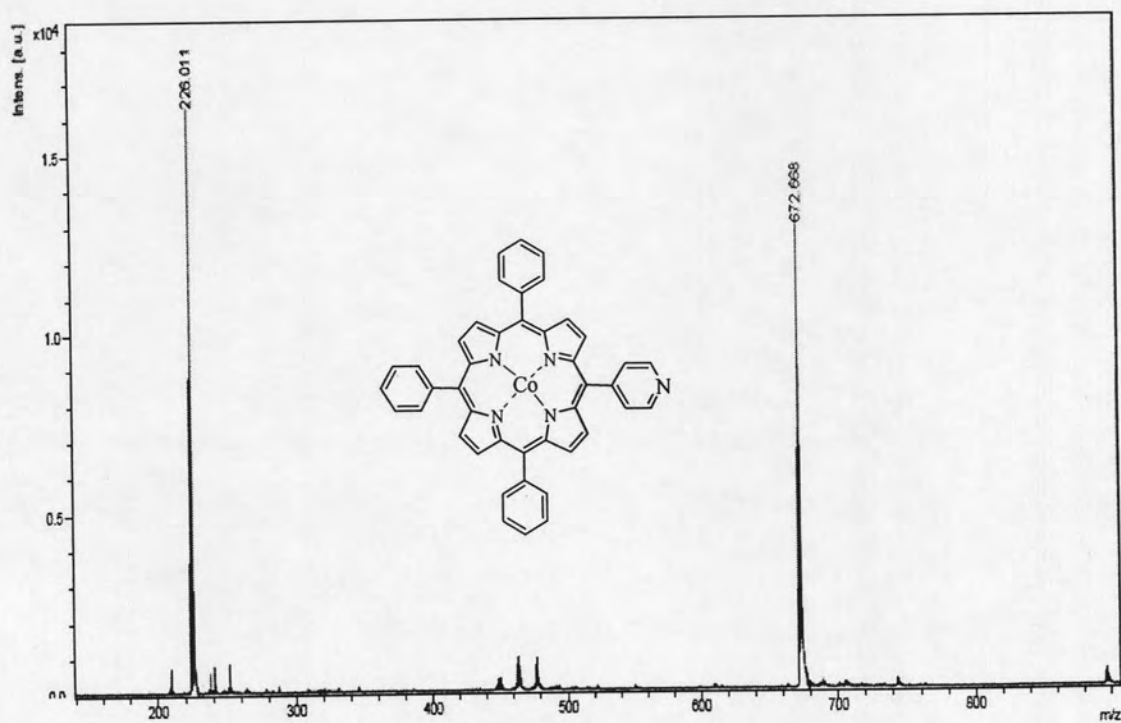


Figure A-46 MALDI-TOF mass spectrum of 5-(pyridyl)-10,15,20-triphenylporphyrinatocobalt(II) (CoMPyTPP, 15)

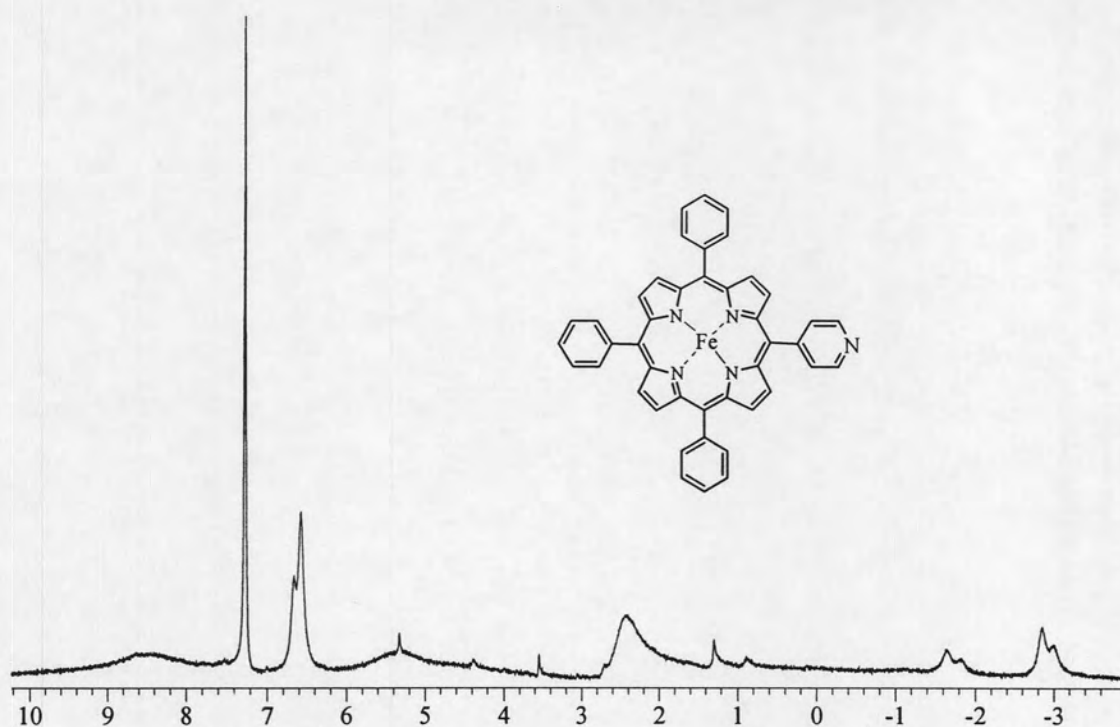


Figure A-47 The ^1H NMR spectrum of 5-pyridyl-10,15,20-triphenylporphyrinatoiron(III) ((Cl)FeMPyTPP, 16)

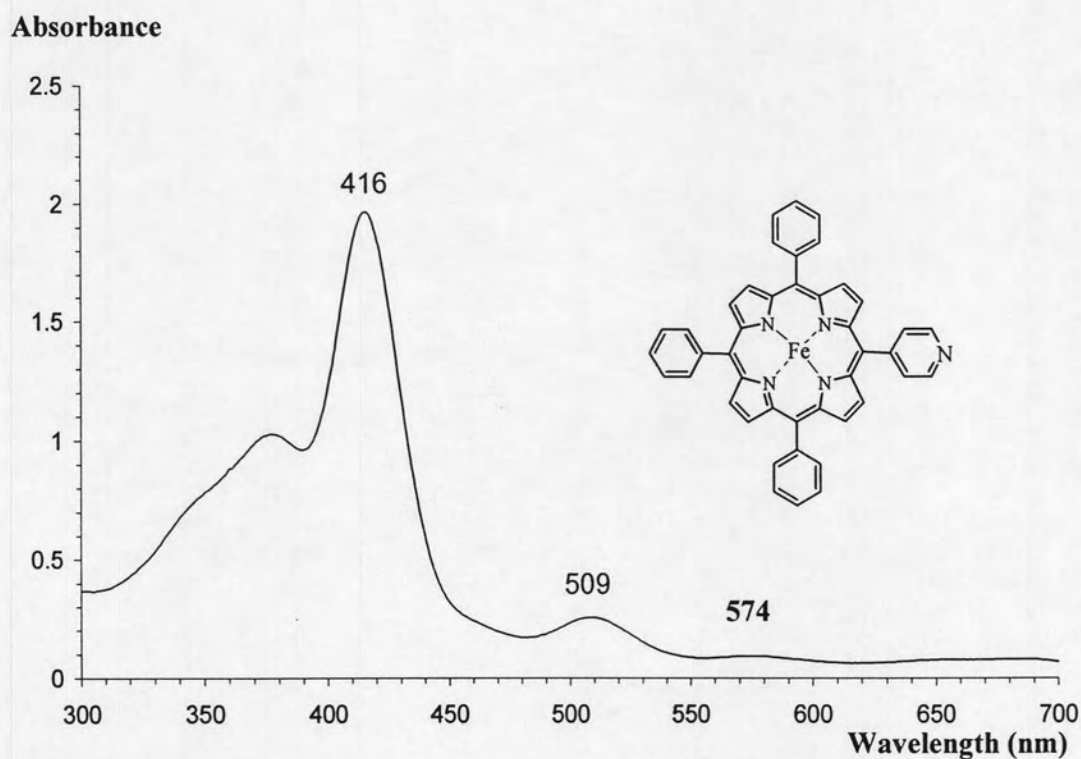
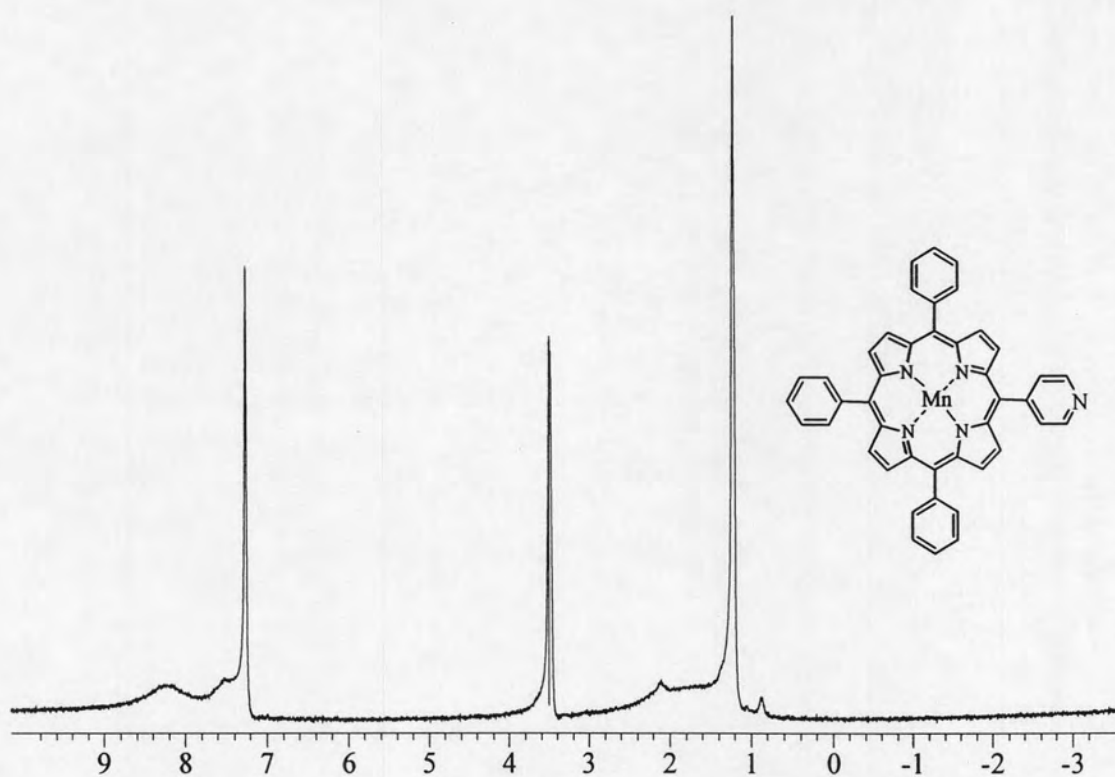
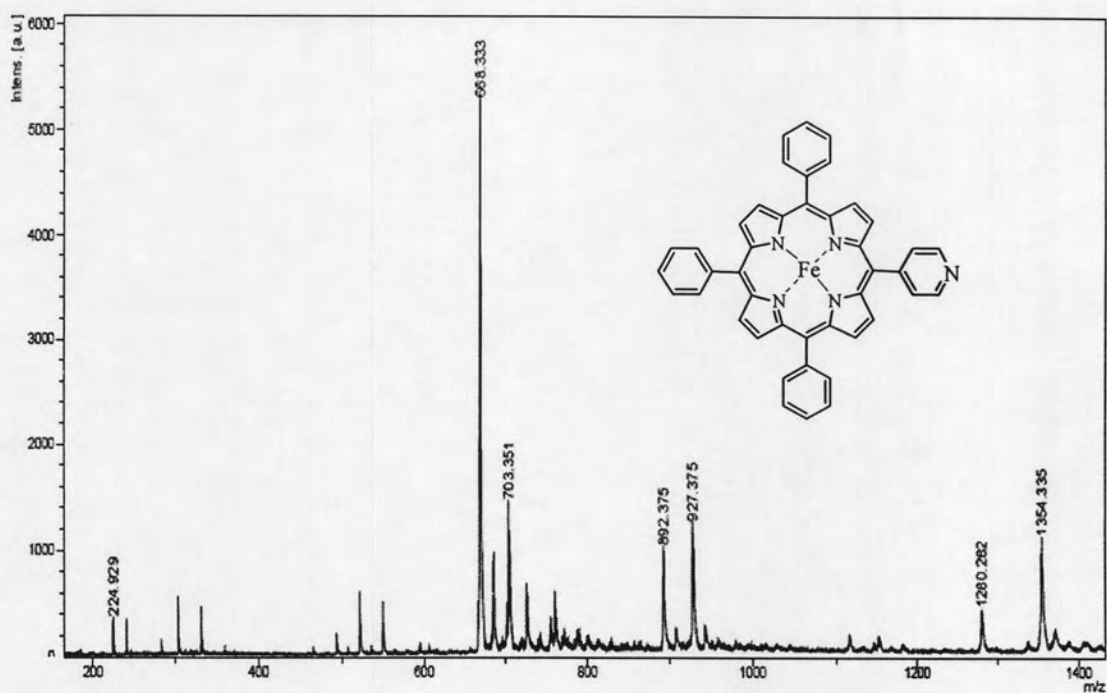


Figure A-48 UV/Visible spectrum of 5-pyridyl-10,15,20-triphenylporphyrinatoiron(III) ((Cl)FeMPyTPP, 16)



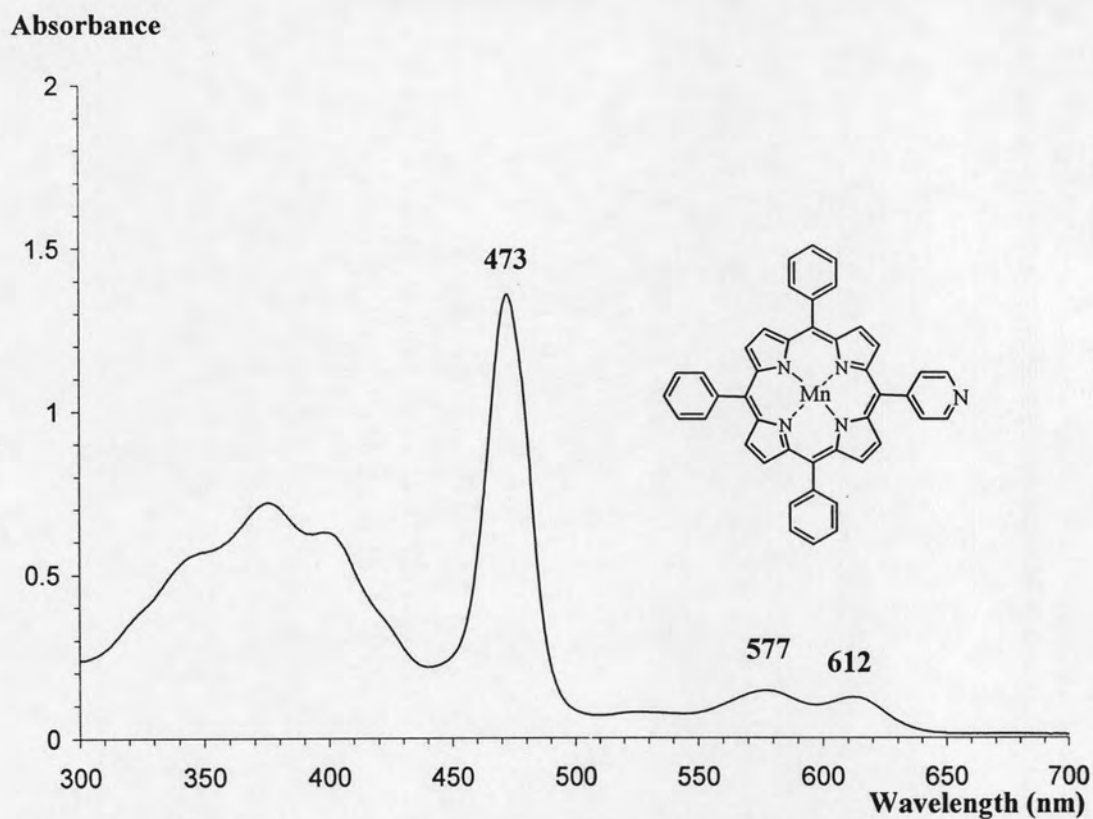


Figure A-51 UV/Visible spectrum of 5-(pyridyl)-10,15,20-triphenyl porphyrinat manganese(III) (MnMPyTPP, 17)

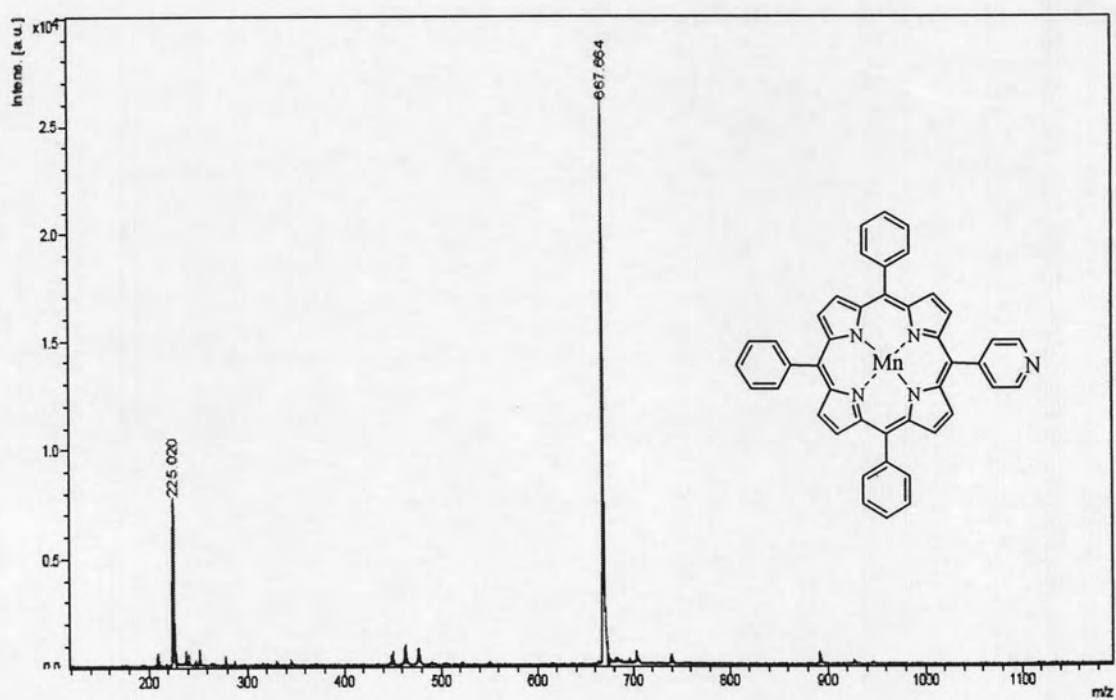


Figure A-52 MALDI-TOF mass spectrum of 5-(pyridyl)-10,15,20-triphenyl porphyrinat manganese(III) (MnMPyTPP, 17)

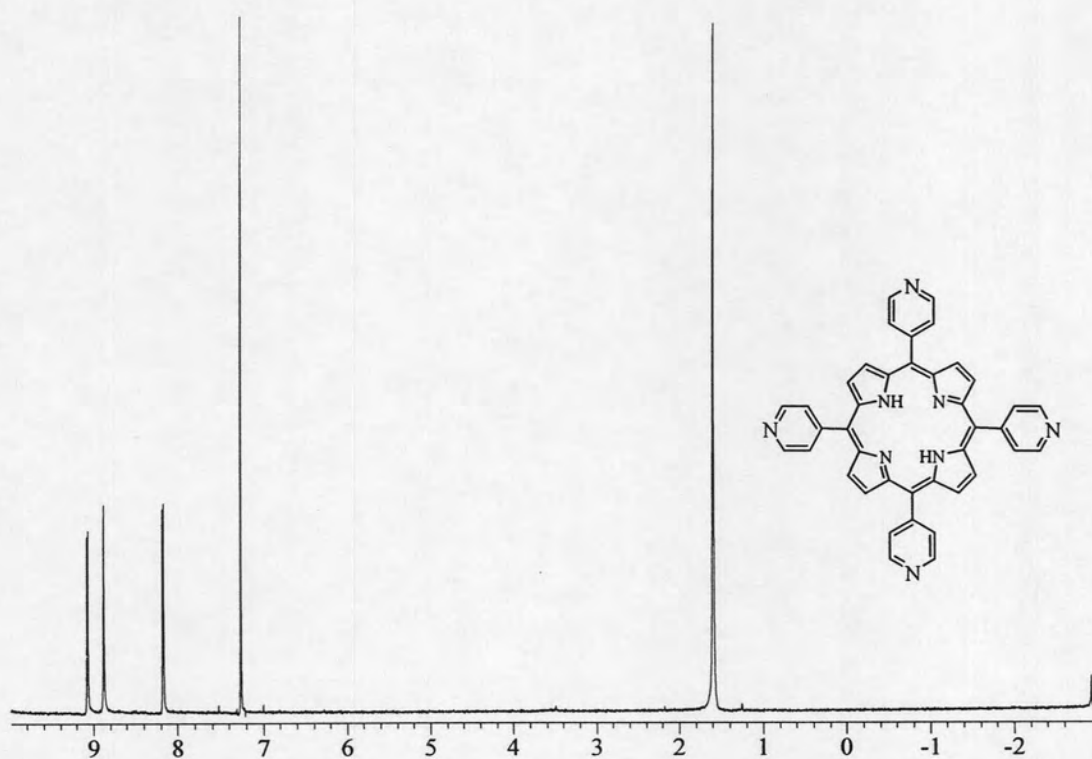


Figure A-53 The ^1H NMR spectrum of 5,10,15,20-tetrapyrrolylporphyrin (TPyP, 18)

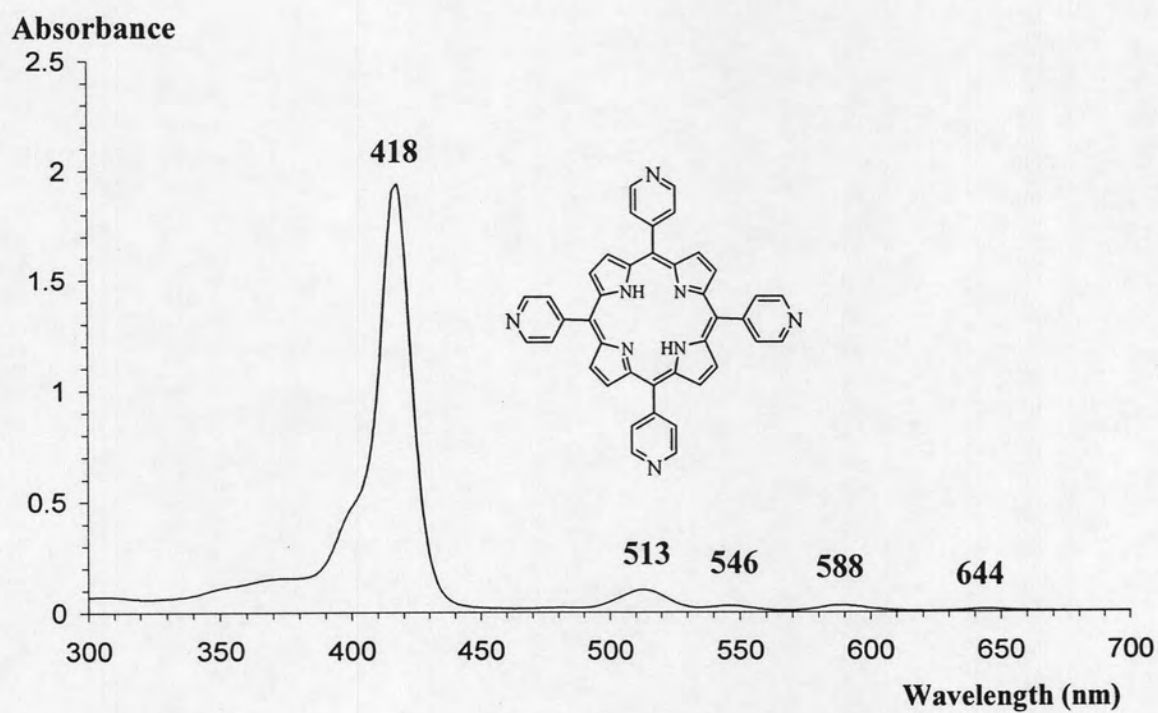


Figure A-54 UV/Visible spectrum of 5,10,15,20-tetrapyrrolylporphyrin (TPyP, 18)

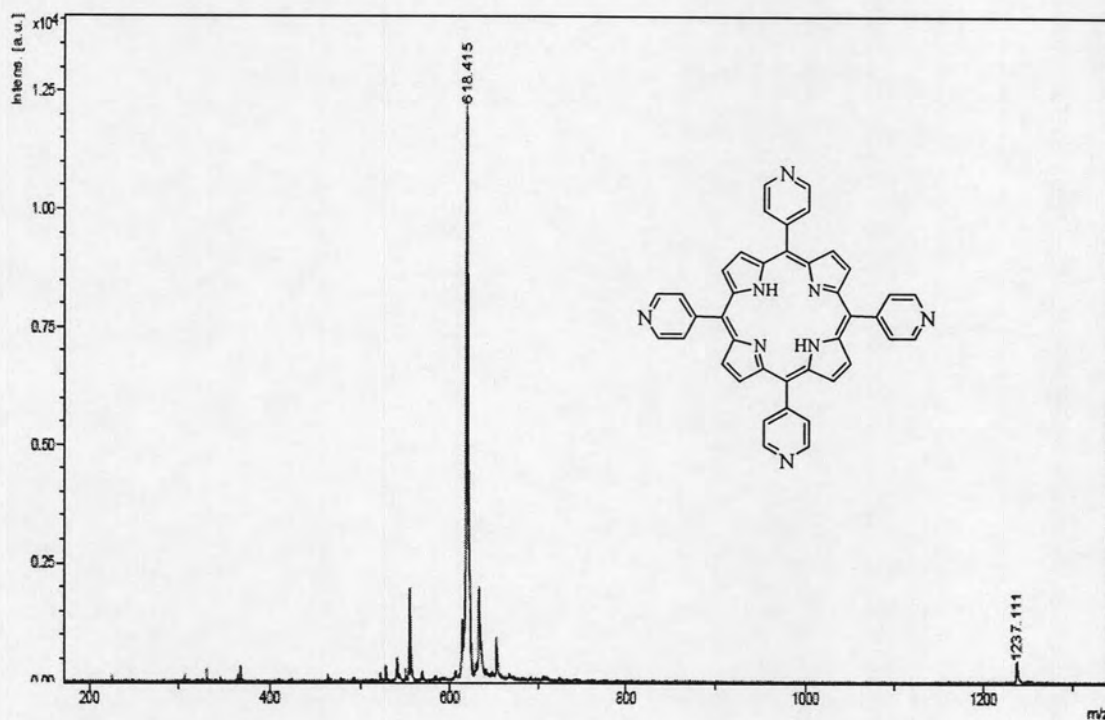


Figure A-55 MALDI-TOF mass spectrum of 5,10,15,20-tetrapyridylporphyrin (TPyP, 18)

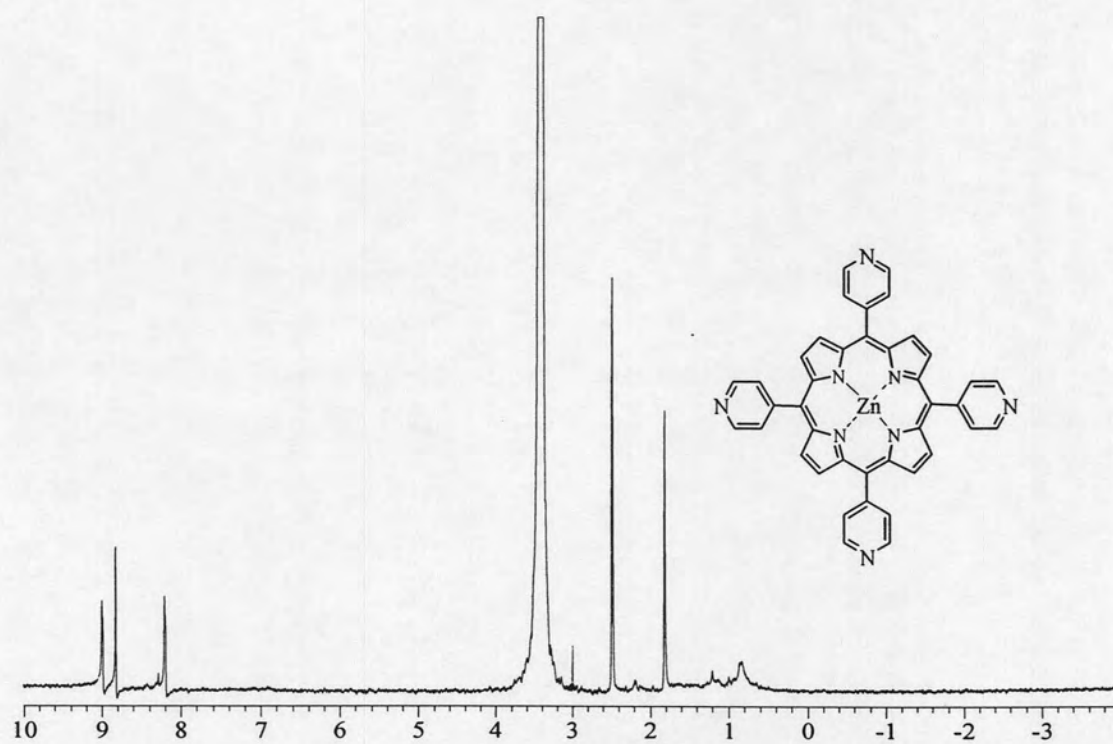


Figure A-56 The ^1H NMR spectrum of 5,10,15,20-tetrapyridylporphyrinatozinc(II) (ZnTPyP, 19)

Absorbance

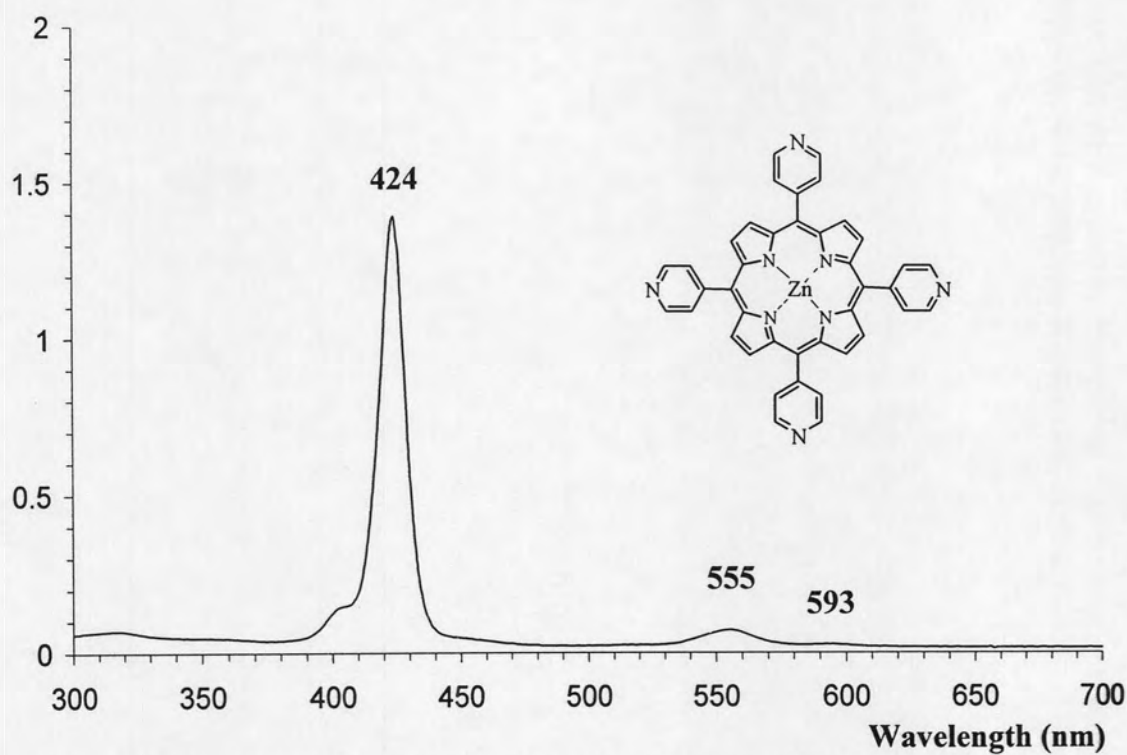


Figure A-57 UV/Visible spectrum of 5,10,15,20-tetrapyrridylporphyrinatozinc(II) (ZnTPyP, 19)

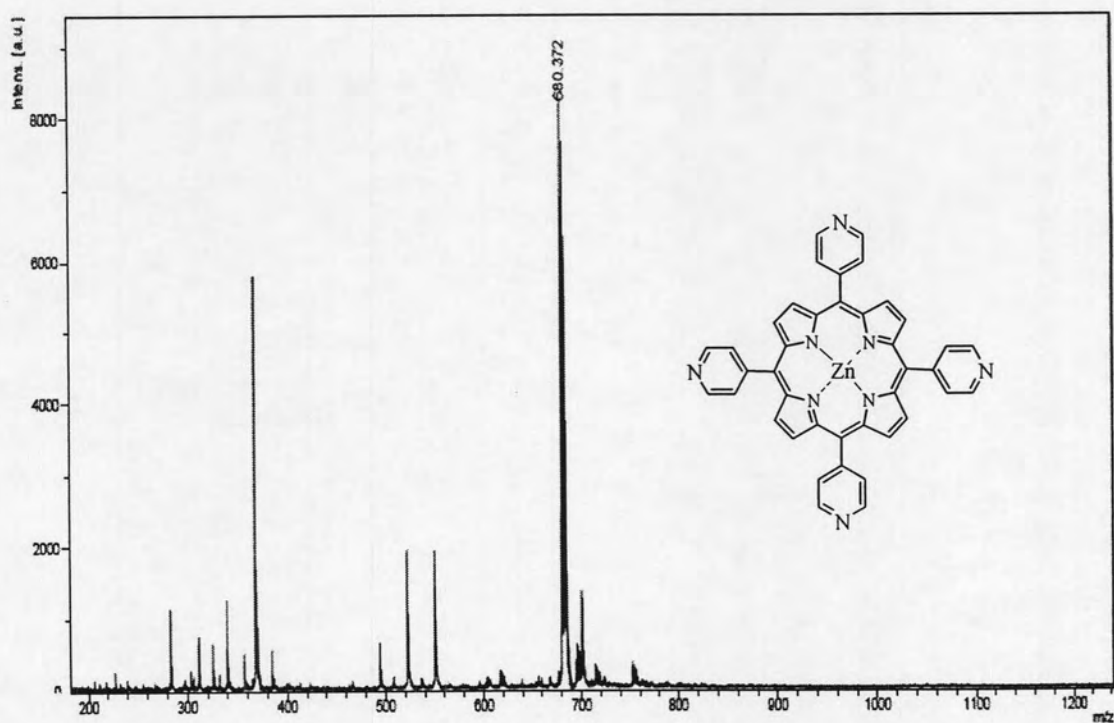


Figure A-58 MALDI-TOF mass spectrum of 5,10,15,20-tetrapyrridyl porphyrinatozinc(II) (ZnTPyP, 19)

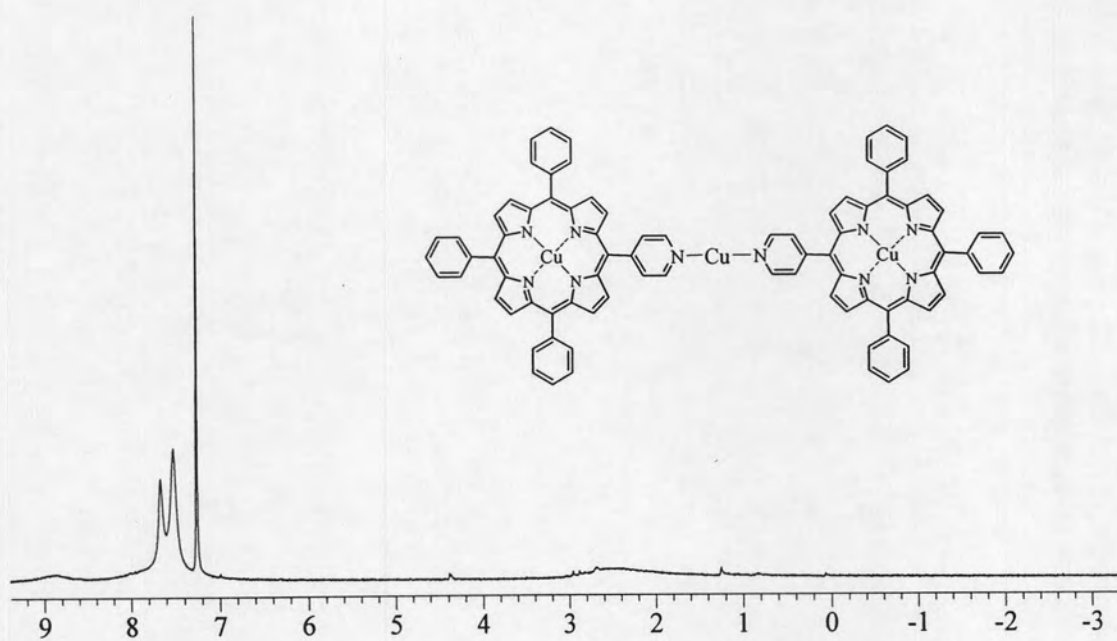


Figure A-59 The ^1H NMR spectrum of $\text{Cu(II)(CuMPyTPP)}_2$ (20)

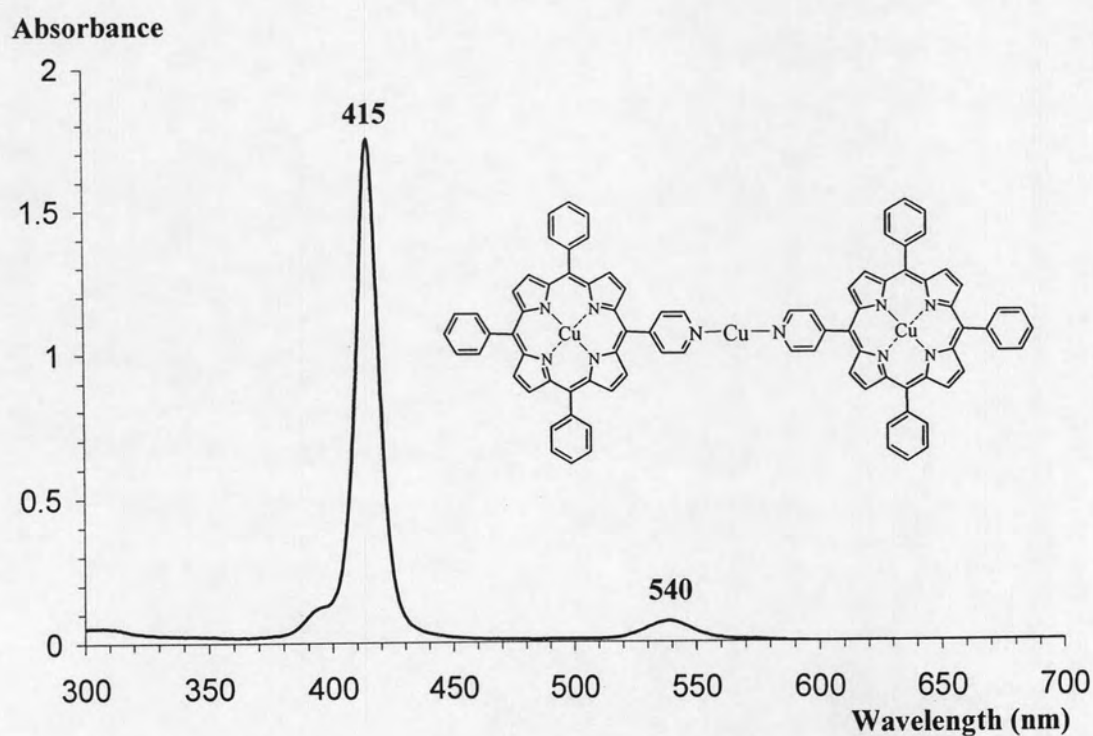


Figure A-60 UV/Visible spectrum of $\text{Cu(II)(CuMPyTPP)}_2$ (20)

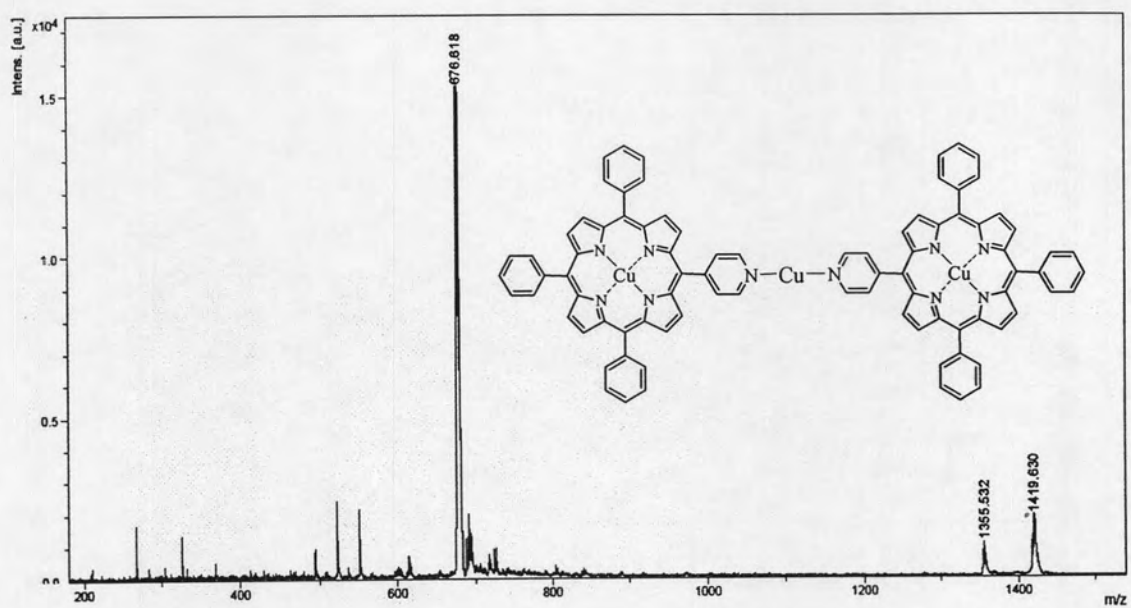


Figure A-61 MALDI-TOF mass spectrum of $\text{Cu(II)(CuMPyTPP)}_2$ (**20**)

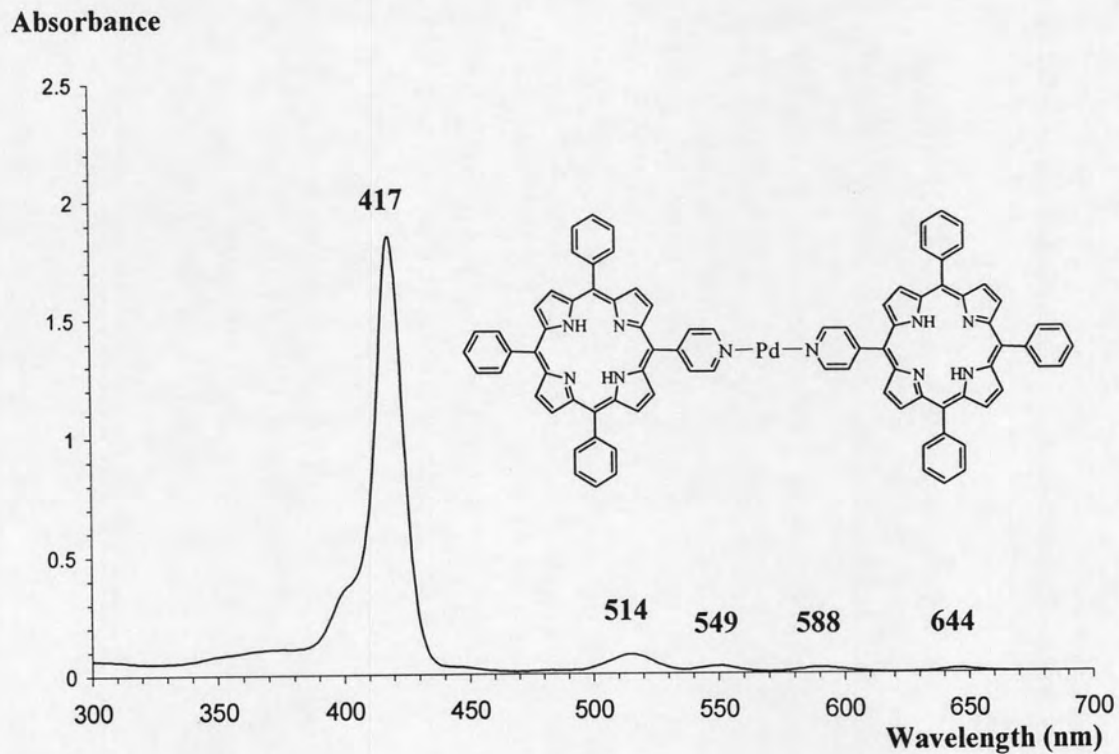


Figure A-62 UV/Visible spectrum of Pd(II)(MPyTPP)_2 (**21**)

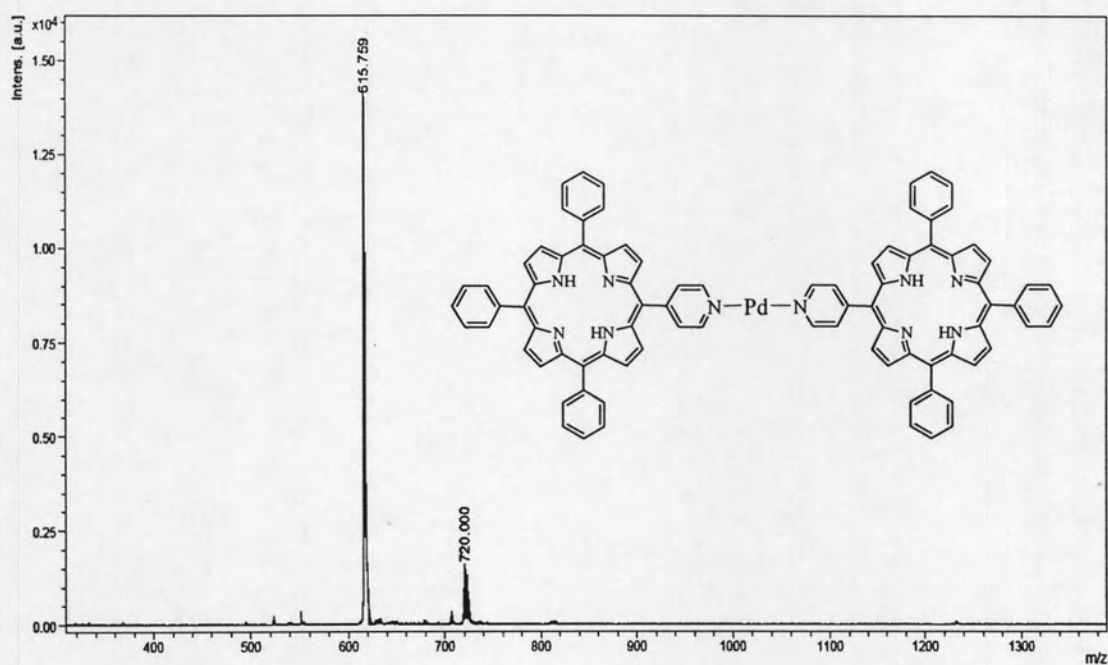


Figure A-63 MALDI-TOF mass spectrum of Pd(II)(MPyTPP)₂ (**21**)

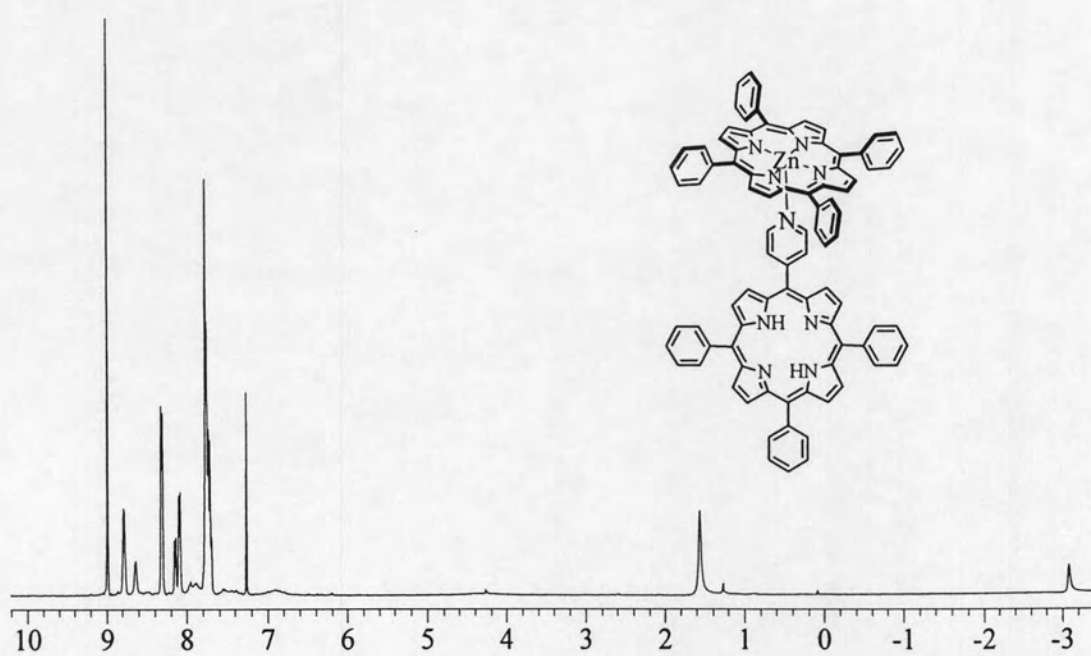


Figure A-64 The ¹H NMR spectrum of Zn(TPP)(MPyTPP), (**22**)

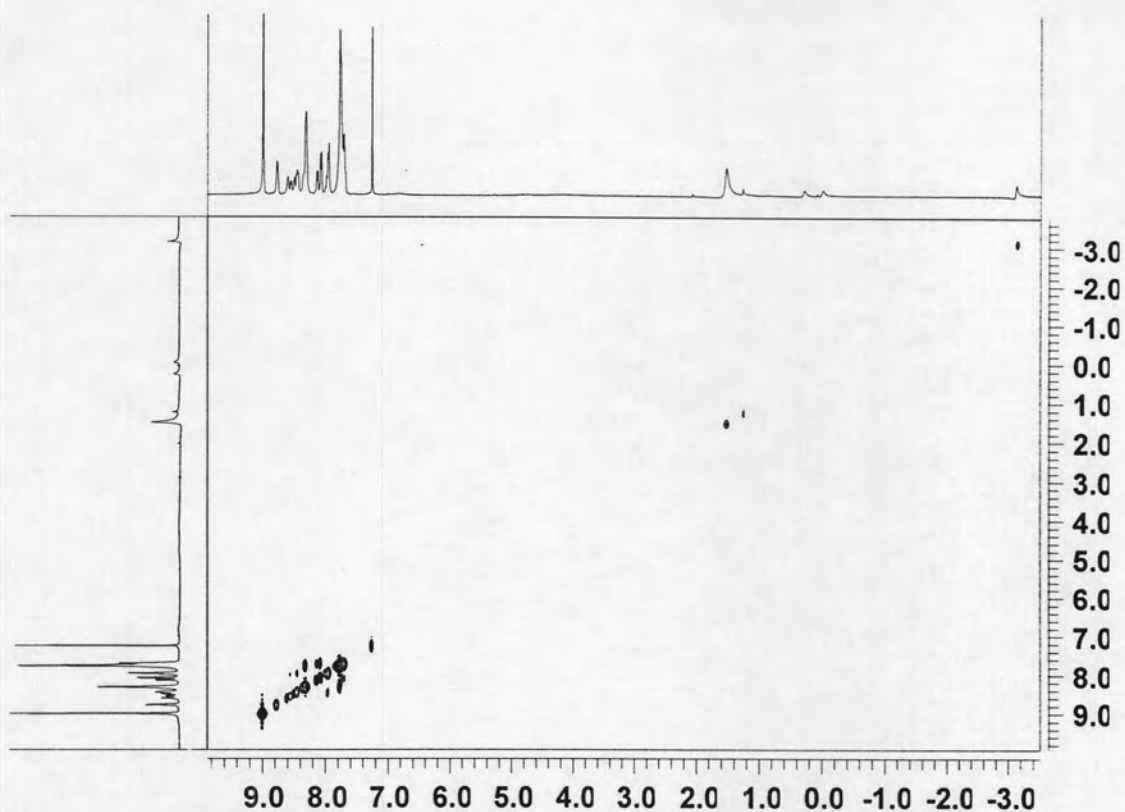


Figure A-65 The ^1H - ^1H COSY spectrum of $\text{Zn}(\text{TPP})(\text{MPyTPP})$, (22)

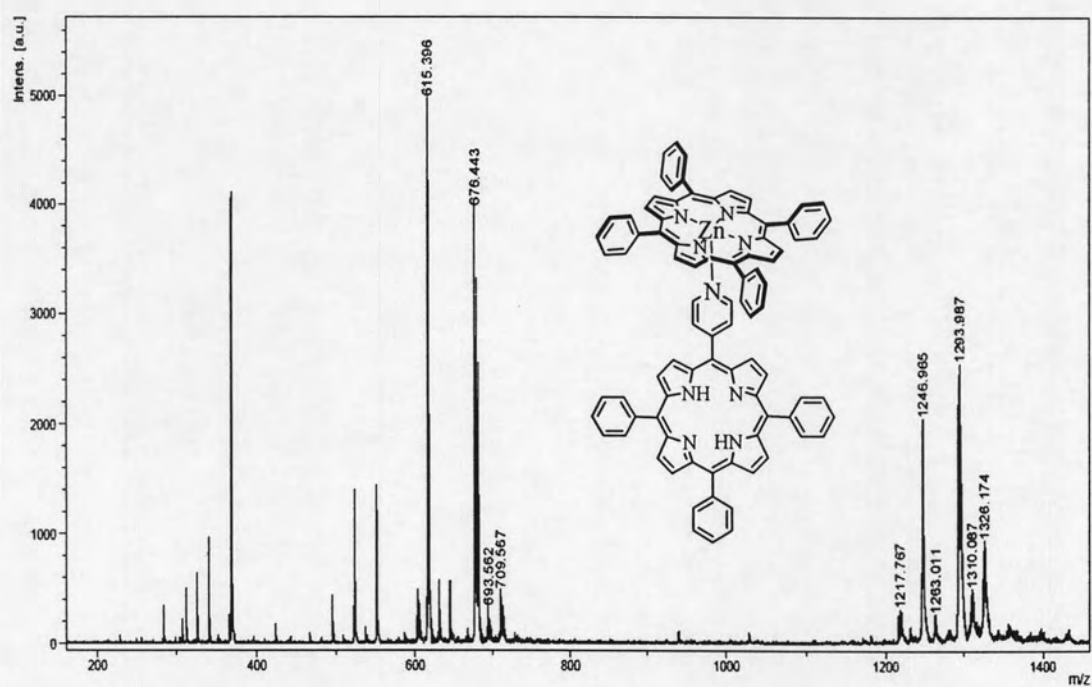


Figure A-66 MALDI-TOF mass spectrum of $\text{Zn}(\text{TPP})(\text{MPyTPP})$, (22)

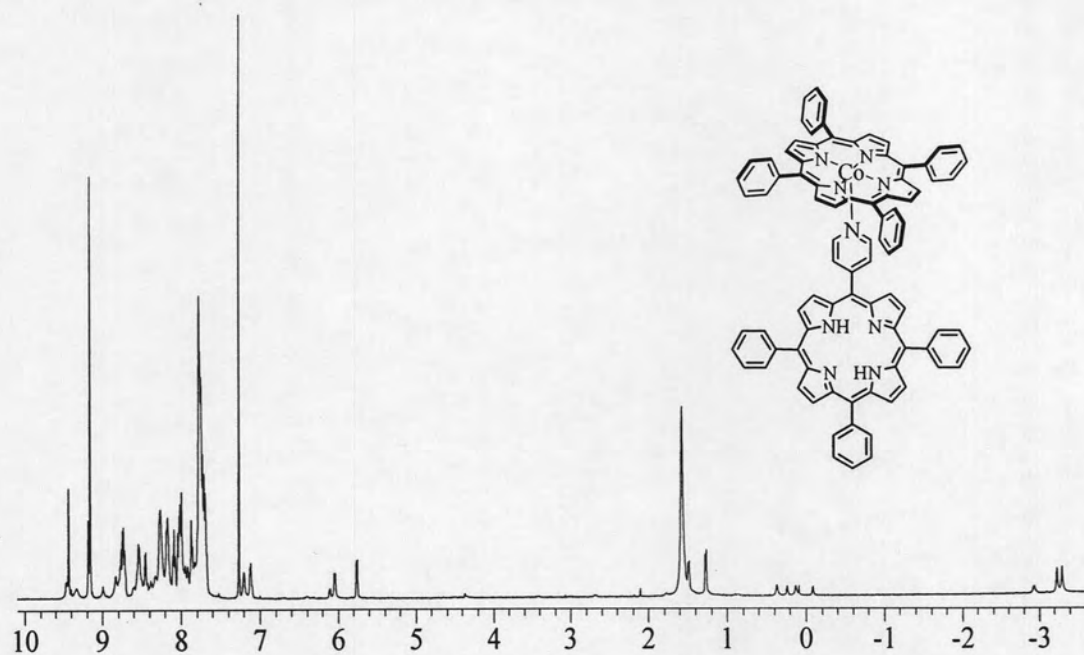


Figure A-67 The ^1H NMR spectrum of $\text{Co}(\text{TPP})(\text{MPyTPP})$, (23)

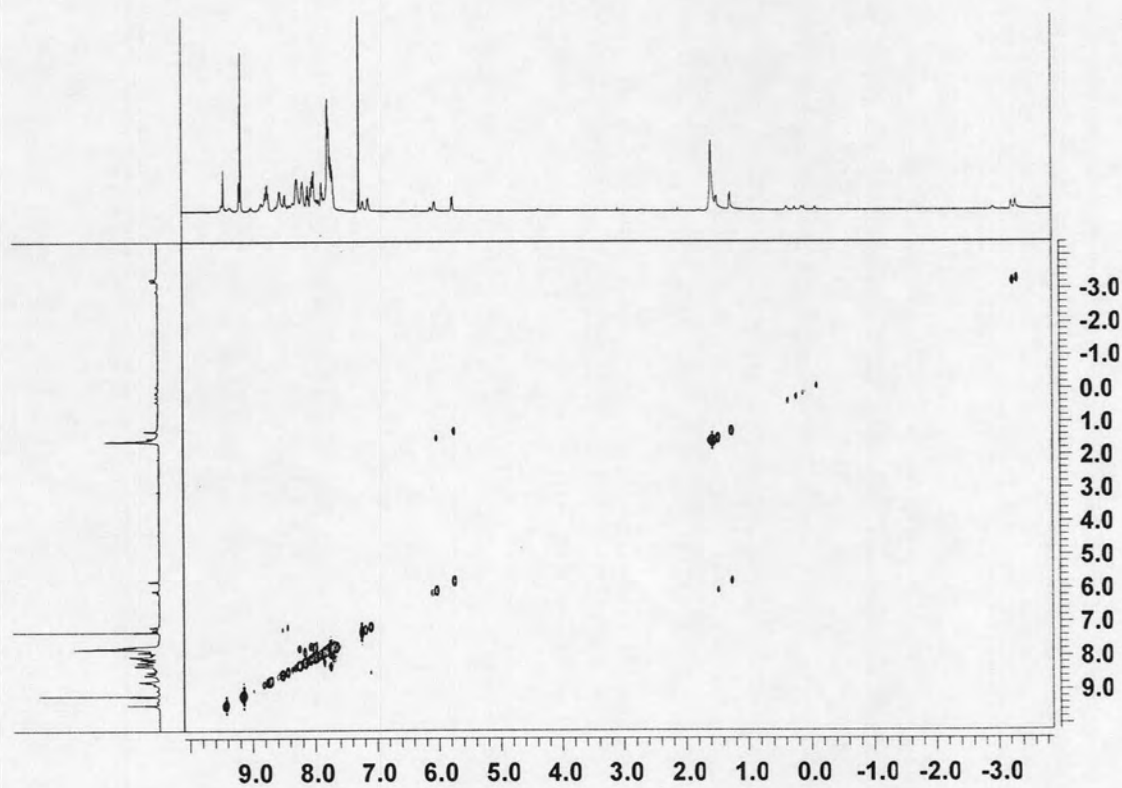


Figure A-68 The ^1H - ^1H COSY spectrum of $\text{Co}(\text{TPP})(\text{MPyTPP})$, (23)

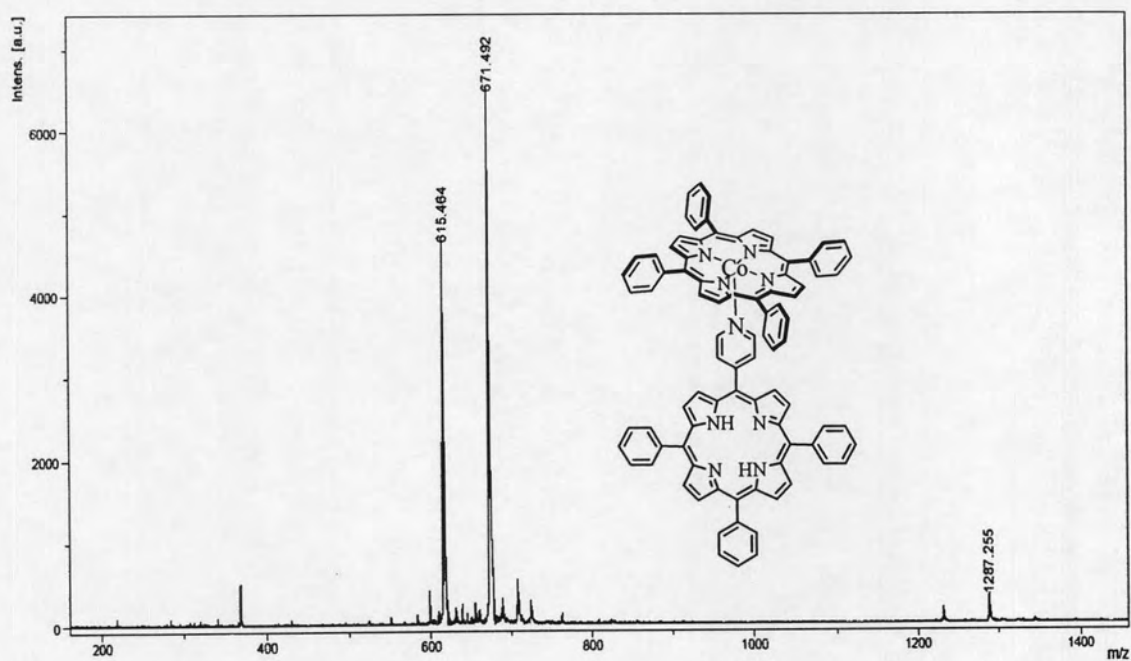


Figure A-69 MALDI-TOF mass spectrum of Co(TPP)(MPyTPP), (**23**)

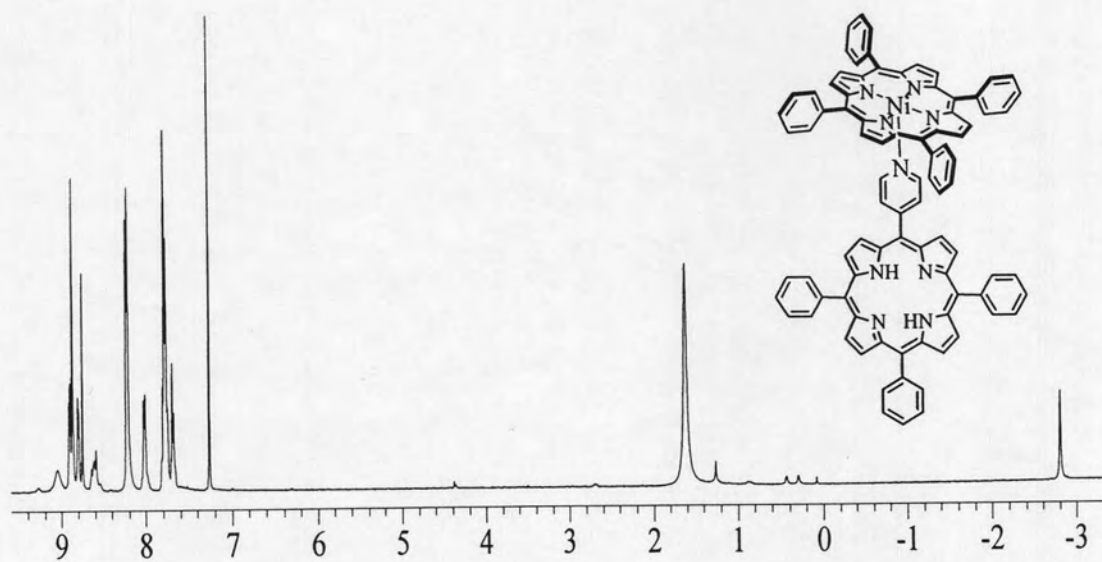


Figure A-70 The ^1H NMR spectrum of Ni(TPP)(MPyTPP), (**24**)

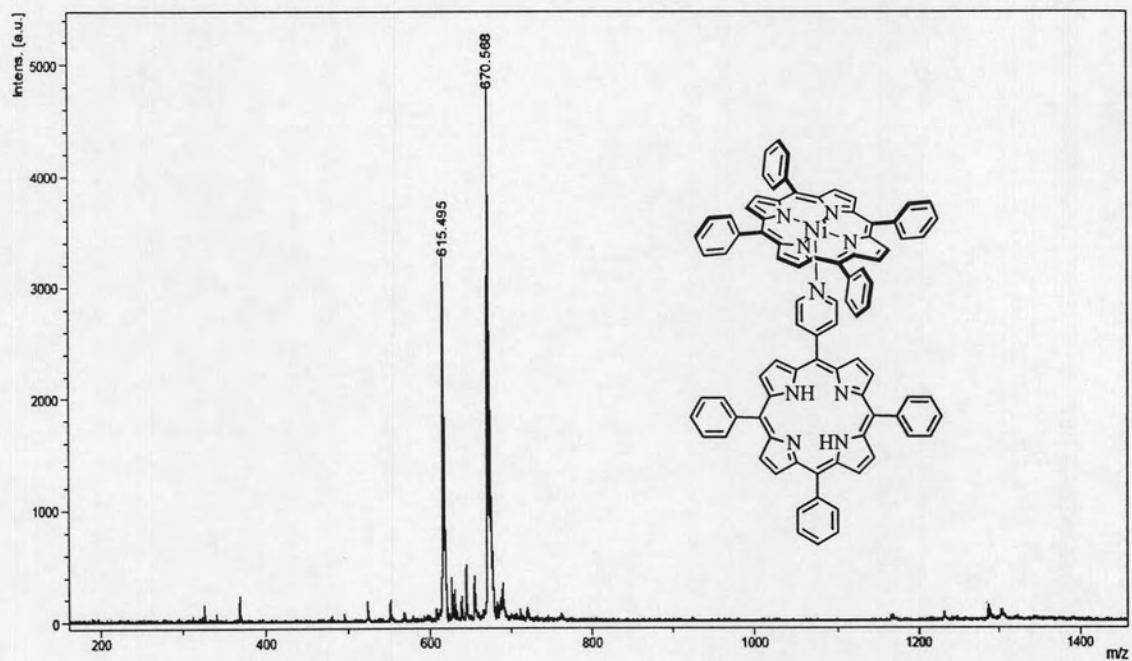


Figure A-71 MALDI-TOF mass spectrum of Ni(TPP)(MPyTPP), (24)

APPENDIX B

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

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : singlet at -2.73, 2 H_5 , signal of internal NH protons
 (Figure A-1, Appendix A) multiplet at 7.75-7.81, 8 H_3 signal of *m*-phenyl protons and 4 H_4 signal of *p*-phenyl protons
 multiplet at 8.23-8.25, 8 H_2 , signal of *o*-phenyl protons
 singlet at 8.88, 8 H_1 , signal of β -pyrrole protons

UV/Visible (CHCl_3 , nm) λ_{max} : 418 (Soret band)

(Figure A-2, Appendix A) 516, 550, 592, and 648 (Q bands)

MALDI-TOF MS (dithranol) m/z $[M]^+$ Calcd: 614.749; Found: 614.635.

(Figure A-3, Appendix A)

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

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : multiplet at 7.75-7.77, 8 H_3 signal of *m*-phenyl protons and 4 H_4 signal of *p*-phenyl protons
 (Figure A-4, Appendix A) multiplet at 8.23-8.25, 8 H_2 , signal of *o*-phenyl protons
 singlet at 8.96, 8 H_1 , signal of β -pyrrole protons

UV/Visible (CHCl_3 , nm) λ_{max} : 423 (Soret band)

(Figure A-5, Appendix A) 554 and 598 (Q bands)

MALDI-TOF MS (dithranol) m/z $[M]^+$ Calcd: 678.123; Found: 677.492.

(Figure A-6, Appendix A)

3. 5,10,15,20-Tetraphenylporphyrinatonickel(II) (NiTPP, 4)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : multiplet at 7.75-7.77, 8 H_3 signal of *m*-phenyl protons and 4 H_4 signal of *p*-phenyl protons
 (Figure A-10, Appendix A) multiplet at 8.23-8.25, 8 H_2 , signal of *o*-phenyl protons
 singlet at 8.96, 8 H_1 , signal of β -pyrrole protons

UV/Visible (CHCl_3 , nm) λ_{max} : 415 (Soret band)

(Figure A-11, Appendix A) 528 (Q band)

MALDI-TOF MS (dithranol) m/z $[M]^+$ Calcd: 671.426; Found: 671.400.

(Figure A-12, Appendix A)

6. 5,10-(Dipyridyl)-15,20-diphenyl porphyrin (*cis*-DPyDPP, 10)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : singlet at -2.84, 2 H_{10} , signal of internal NH protons
 (Figure A-28, Appendix A) multiplet at 7.76-7.82, 4 H_8 , signal of *m*-phenyl protons and 2 H_9 signal of *p*-phenyl protons
 multiplet at 8.21-8.23, 4 H_6 , signal of *o*-phenyl protons and 4 H_7 signal of 3,5-pyridyl protons
 doublet at 8.80, 2 H_5 , signal of β -pyrrole protons
 singlet at 8.85, 2 H_4 , signal of β -pyrrole protons
 singlet at 8.88, 2 H_3 , signal of β -pyrrole protons
 doublet at 8.92, 2 H_2 , signal of β -pyrrole protons
 doublet at 9.05, 4 H_1 , signal of 2,6-pyridyl protons

UV/Visible (CHCl_3 , nm) λ_{max} : 418 (Soret band)

(Figure A-29, Appendix A) 515, 549, 590, and 647 (Q band)

MALDI-TOF MS (dithranol) m/z [M] $^+$ Calcd: 616.725; Found: 616.508.

(Figure A-30, Appendix)

7. 5,10,15-(Tripyridyl)-20-phenylporphyrin (TPyMPP, 11)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : singlet at -2.88, 2 H_9 , signal of internal NH protons
 (Figure A-31, Appendix A) multiplet at 7.76-7.84, 2 H_7 , signal of *m*-phenyl protons and 1 H_8 signal of *p*-phenyl protons
 multiplet at 8.19-8.21, 2 H_5 , signal of *o*-phenyl protons and 6 H_6 signal of 3,5-pyridyl protons
 doublet at 8.81, 2 H_4 , signal of β -pyrrole protons
 singlet at 8.86, 4 H_3 , signal of β -pyrrole protons
 doublet at 8.92, 2 H_2 , signal of β -pyrrole protons
 doublet at 9.06, 6 H_1 , signal of 2,6-pyridyl protons

UV/Visible (CHCl_3 , nm) λ_{max} : 417 (Soret band)

(Figure A-32, Appendix A) 513, 545, 586, and 648 (Q bands)

MALDI-TOF MS (dithranol) m/z [M] $^+$ Calcd: 617.713; Found: 617.401.

(Figure A-33, Appendix A)

8. 5-(Pyridyl)-10,15,20-triphenylporphyrinatozinc(II) (ZnMPyTPP, 12)

^1H NMR (DMSO, 400 MHz) δ : multiplet at 7.81, 6 H₇, signal of *m*-phenyl protons
(Figure A-34, Appendix A) and 3 H₈ signal of *p*-phenyl protons
multiplet at 8.18-8.21, 6 H₅, signal of *o*-phenyl
protons and 2 H₆ signal of 3,5-pyridyl protons
multiplet at 8.77-8.81, 2 H₂, 4 H₃, 2 H₄, signal of
 β -pyrrole protons
multiplet at 8.97, 2 H₁, signal of 2,6-pyridyl protons

UV/Visible (CHCl₃, nm) λ_{max} : 424 (Soret band)

(Figure A-35, Appendix A) 555 and 597 (Q bands)

MALDI-TOF MS (dithranol) m/z [M]⁺ Calcd: 679.111; Found: 677.739.

(Figure A-36, Appendix A)

9. 5-(Pyridyl)-10,15,20-triphenylporphyrinatonickel(II) (NiMPyTPP, 14)

^1H NMR (CDCl₃, 400 MHz) δ : multiplet at 8.86, 2 H₂, signal of β -pyrrole protons
(Figure A-40, Appendix A) multiplet at 8.77, 4 H₃, signal of β -pyrrole protons
multiplet at 8.64-8.55, 2 H₄ signal of β -pyrrole
protons and 2 H₁ signal of 2,6-pyridyl protons
multiplet at 8.01-7.99, 6 H₅ signal of *o*-phenyl
protons and 2 H₆ signal of 3,5-pyridyl protons
multiplet at 7.73-7.67, 6 H₇ signal of *m*-phenyl
protons and 3 H₈ signal of *p*-phenyl protons

UV/Visible (CHCl₃, nm) λ_{max} : 416 (Soret band)

(Figure A-41, Appendix A) 529 (Q band)

MALDI-TOF MS (dithranol) m/z [M]⁺ Calcd: 672.414; Found: 670.098.

(Figure A-42, Appendix A)

10. 5,10,15,20-Tetrapyridylporphyrin (TPyP, 18)

^1H NMR (CDCl₃, 400 MHz) δ : multiplet at 9.06, 8 H₁, signal of 2,6-pyridyl protons
(Figure A-52, Appendix A) multiplet at 8.87, 8 H₂, signal of β -pyrrole protons
multiplet at 8.16, 8 H₃, signal of 3,5-pyridyl protons
singlet at -2.93, 2 H₄, signal of internal NH protons

UV/Visible (CHCl₃, nm) λ_{max} : 418 (Soret band)

(Figure A-53, Appendix A) 513, 546, 588, and 644 (Q bands)

MALDI-TOF MS (dithranol) m/z $[M]^+$ Calcd: 618.701; Found: 618.577.

(Figure A-54, Appendix A)

11. 5,10,15,20-Tetrapyridylporphyrinatozinc(II) (ZnTPyP, 19)

^1H NMR (DMSO, 400 MHz) δ : multiplet at 9.02, 8 H₁, signal of 2,6-pyridyl protons

(Figure A-55, Appendix A) multiplet at 8.84, 8 H₁, signal of β -pyrrole protons

multiplet at 8.22, 8 H₂, signal of 3,5-pyridyl protons

UV/Visible (CHCl₃, nm) λ_{max} : 424 (Soret band)

(Figure A-56, Appendix A) 555 and 593 (Q bands)

MALDI-TOF MS (dithranol) m/z $[M]^+$ Calcd: 682.076; Found: 680.567.

(Figure A-57, Appendix A)

Optical Gas Sensor of 5,10,15,20-tetraphenylporphyrinatozinc(II) (ZnTPP, 2)

The thin film ZnTPP absorption spectrum is signified by the intense Soret band at 433 nm and Q band at 551 nm. The optical absorption spectrum was selectively divided into five intervals, covering the entire range for observable changes, as R1:340-415, R2:415-565, R3:565-625, R4:625-635, and R5:635-795 nm. The alcohol sensing capability of the ZnTPP films has been investigated under dynamic conditions by using a home-built stainless steel chamber with quartz windows for optical measurements. The test was conducted under a flow system at a constant rate of 755 mL/min by using 99.9% nitrogen as both a carrier and a reference gas. The dynamic optical response was monitored by recording the absorbance intensity at fixed interval of 10 min during alcohol exposure and another 10 min during recovery under a nitrogen flow.

The optical absorption response $\Delta A/A_{\text{ZnTPP}}$ for each interval was calculated from $(A-A_0)/A_{\text{ZnTPP}}$, where A and A_0 are the area integrals measured during alcohol vapor exposure and during the nitrogen gas flow, respectively, and A_{ZnTPP} are the initial area integral of ZnTPP. The typical dynamic responses of alcohol vapor of ZnTPP were similar to what was reported in the literature [54]. The spectral regions of methanol, ethanol, isopropanol, and Thai whisky vapor corresponding to the R3 (565-625 nm) have a positive response, different from the other ranges, which show a negative. The average response ΔS was calculated from the average of $S-S_0$ for all

observable response pulses, where S is the dynamic sensor signal during alcohol vapor exposure and S_0 is the base sensor signal in nitrogen gas flow. The responses of ZnTPP films to alcohols produce the strongest response with Thai whisky in R3 (565-625 nm).

VITA

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