# CHAPTER II

# EXPERIMENTS

## 2.1 Chemicals

Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck Kieselgol 60 $F_{254}$) (Merck KgaA, Darmstadt, Germany). Column chromatography was performed in silicas gel (0.06-0.2 mm, 70-230 mesh ASTM) and Scharlau Chemie S. A. (Barcelona, Spin). Chloroform used in column chromatography were reagent grades, Dichloromethane and methanol were distilled from commercial grade prior to use. Solvents used in synthesis were reagent or analytical grades. The reagents used for synthesizing were purchased from the following vendors:

- Aldrich Chemical Company (Steinheim, Germany): copper(II) acetate
- Acros: propionic acid, pyrrole
- Carlo Erba: pyridine
- Fluka Chemical Company (Buchs, Switzerland): benzaldehyde, cobalt(II) acetate tetrahydrate, *N,N*-dimethylformamide, manganese(II) acetate tetrahydrate, nickel(II) tetrahydrate, propionic acid, 4-pyridinecarboxaldehyde, pyrrole, zinc(II) acetate dihydrate
- Labscan (Bangkok, Thailand): chloroform, hydrochloric acid, tetrahydrofuran, toluene
- Merck Co. Ltd. (Darmstadt, Germany): ethanol, acetone, anhydrous sodium hydrogencarbonate
- Riedel-de Haën: anhydrous iron(III) chloride, anhydrous sodium sulfate
- Wilmad (New Jersey, USA): deuterated Chloroform, hexadeuterated dimethylsulfoxide

## 2.2 Instruments and Equipments

All reported $^1$H NMR spectra were obtained in deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-$d_6$) using a Nuclear Magnetic Resonance Spectrometer (Varian Mercury plus 400) operated at 399.84 MHz for $^1$H and 100.54 MHz for $^{13}$C nuclei (Varian Company, CA, USA). The chemical shifts are listed in

parts per million (ppm) with respect to the reference peak of the deuterated solvent. UV-Visible absorption spectra were recorded on UV-Visible Spectrophotometer: UV-2550 (Shimadzu Corporation, Kyoto, Japan) and HP 8453 (Agilent Technologies, U.S.A.). Mass spectra were performed on a Matrix Assisted Laser Desorption/Ionization Time Of Fight (MALDI-TOF): Microflex mass spectrometer (Bruker Daltonik GmbH, Germany). The instrument was equipped with a nitrogen laser to desorb and ionize the samples. A stainless steel target was used as the MALDI substrate on which the samples are deposited. Dithranol matrix solution for porphyrins was prepared as a 10 mg $mL^{-1}$ solution in tetrahydrofuran.

## 2.3 Synthesis of Tetraphenylporphyrin and Their Complexes

### 2.3.1 Preparation of 5,10,15,20-tetraphenylporphyrin (TPP, 1)

Benzaldehyde (1.62 mL, 16 mmol) and freshly distilled pyrrole (1.11 mL, 16 mmol) were added to 100 mL of boiling propionic acid. The reaction mixture was refluxed for 1 hour, cooled down to ambient temperature and letting stand overnight. Purple crystals of 5,10,15,20-tetraphenylporphyrin (**1**) (0.584 g, 24% yield) were filtered off and washed with cold methanol. $^1$H NMR ($CDCl_3$, 400 MHz): δ -2.73 (s, 2 H, internal NH), 7.75-7.81 (m, 12 H, *m*-, *p*-phenyl), 8.23-8.25 (m, 8 H, *o*-phenyl), 8.88 (s, 8 H, β-pyrrole),; UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 418 (Soret), 516, 550, 592, and 648 (Q); MALDI-TOF MS (dithranol) *m/z* $[M]^+$. Calcd: 614.749; Found: 614.635.

### 2.3.2 Preparation of 5,10,15,20-tetraphenylporphyrinatozinc(II) (ZnTPP, 2)

To a boiling solution of 5,10,15,20-tetraphenylporphyrin (**1**) (0.76 g, 1.24 mmol) in chloroform (150 mL) was added a saturated solution of zinc acetate dihydrate (0.41 g, 1.86 mmol) in methanol (3 mL). The reaction mixture was refluxed for 0.5 hour, cooled down, and extracted twice with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight. Purple crystals of ZnTPP (**2**) (0.83 g, 99.0%) were collected on a filter and washed with cold methanol. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.75-7.77 (m, 12 H, *m*-, *p*-phenyl), 8.23-8.25 (m, 8 H, *o*-phenyl), 8.96 (s, 8 H, β-pyrrole); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 423 (Soret), 554 and 598 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 678.123; Found: 677.492.

### 2.3.3 Preparation of 5,10,15,20-tetraphenylporphyrinatocopper(II) (CuTPP, 3)

To a boiling solution of 5,10,15,20-tetraphenylporphyrin (**1**) (0.47 g, 0.76 mmol) in chloroform (100 mL) was added a saturated solution of copper acetate (0.21 g, 1.14 mmol) in methanol (2 mL). The reaction mixture was refluxed for 0.5 hour, cooled down, and extracted twice with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight. Bright purple crystals of CuTPP (**3**) (0.506 g, 99%) were collected on a filter and washed with cold methanol. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.50 (br), 7.65 (br); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 416 (Soret), 539 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 676.189; Found: 676.367.

### 2.3.4 Preparation of 5,10,15,20-tetraphenylporphyrinatonickel(II) (NiTPP, 4)

To a boiling solution of 5,10,15,20-tetraphenylporphyrin (**1**) (0.020 g, 0.0325 mmol) in *N,N*-dimethylformamide (6 mL) was added a saturated solution of nickel acetate tetrahydrate (0.04 g, 0.163 mmol) in methanol (1 mL). The reaction mixture was refluxed for 3 hours, cooled down, and extracted three times with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight at 0°C. Purple crystals of NiTPP (**4**) (0.019 g, 87%) were collected on a filter and washed with cold methanol. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.71 (m, 12 H, *m*-, *p*-phenyl), 8.00-8.02 (m, 8 H, *o*-phenyl), 8.74 (s, 8 H, β-pyrrole); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 415 (Soret), 528 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 671.426; Found: 671.400.

### 2.3.5 Preparation of 5,10,15,20-tetraphenylporphyrinatocobalt(II) (CoTPP, 5)

To a boiling solution of 5,10,15,20-tetraphenylporphyrin (**1**) (0.123 g, 0.20 mmol) in chloroform (40 mL) was added a saturated solution of cobalt acetate tetrahydrate (0.073 g, 0.29 mmol) in methanol (2 mL). The reaction mixture was refluxed for 1 hour, cooled down and extracted twice with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered

off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight at 0°C. Purple powder of CoTPP (**5**) (0.134 g, 94%) were collected on a filter and washed with cold methanol. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.75 (br), 8.22 (br), 8.67 (br); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 410 (Soret), 528 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 671.666; Found: 670.561.

### 2.3.6 Preparation of 5,10,15,20-tetraphenylporphyrinatoiron(III) ((Cl)FeTPP, 6)

To a boiling solution of 5,10,15,20-tetraphenylporphyrin (**1**) (0.020 g, 0.0325 mmol) in (6 mL) was added a saturated solution of iron(III) chloride anhydrous (0.026 g, 0.163 mmol) in methanol (1 mL). Pyridine was added a few drop in the solution. The reaction mixture was refluxed for 20 hours, cooled down, extracted with 0.5% dilute HCl, and extracted twice with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of cold methanol and letting stand overnight at 0°C. Purple crystals of (Cl)FeTPP (**6**) (0.0197 g, 91%) were collected on a filter and washed with cold methanol. $^1$H NMR ($CDCl_3$, 400 MHz,): δ 6.44 (br); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 416 (Soret), 510 and 580 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 704.031; Found: 702.281. *m/z* $[M\text{-}Cl]^+$. Calcd: 668.578; Found: 667.244.

### 2.3.7 Preparation of 5,10,15,20-tetraphenylporphyrinatomanganese(III) (MnTPP, 7)

To a boiling solution of 5,10,15,20-tetraphenylporphyrin (**1**) (0.022 g, 0.036 mmol) in dimethylformamide (6 mL) was added a saturated solution of manganese acetate tetrahydrate (0.013 g, 0.054 mmol) in methanol (1 mL). The reaction mixture was refluxed for 1 hour, cooled down, and extracted three times with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of cold hexane and letting stand overnight at 0°C. Green powder of MnTPP (**7**) (0.023 g, 96%) was collected on a filter and washed with cold hexane. $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.29 (br); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 474 (Soret), 578 and 614 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 667.671; Found: 666.275.

## 2.4 Synthesis of Pyridylporphyrin and Their Complexes

### 2.4.1 Preparation of arylporphyrins

Arylporphyrins were prepared according to the method described in the literature with a slight modification [31]. Benzaldehyde (0.81 mL, 8 mmol), 4-pyridine carboxaldehyde (0.75 mL, 8 mmol) and freshly distilled pyrrole (1.11 mL, 16 mmol) were added to 50 mL of boiling propionic acid in a round bottom flask. The reaction mixture was refluxed for 1 hour, cooled to ambient temperature, and allowed to sit overnight. Purple crystals of mixture products (0.48 g, 20%) were filtered and washed with cold methanol. Thin layer chromatography (mobile phase was a 98:2 chloroform/ ethanol) of crude products yielded a mixture of six possible porphyrin isomers. The $R_f$ values of the isomers were 0.88 (TPP, **1**), 0.46 (MPyTPP, **8**), 0.38 (*trans*-DPyDPP, **9**), 0.28 (*cis*-DPyDPP, **10**), 0.21 (TPyMPP, **11**), and 0.12 (TPyP, **18**). The isomers were purified using column chromatography. First column, was packed with silica gel (4×12 cm), $CH_2Cl_2$ was used to remove TPP (**1**) (0.126 g, 26%) in the first band. The remaining fractions were combined and the mixture was passed through another column. The second column was packed with silica gel (4×15 cm). The crude mixture products from the first column were eluted with a 98:2 chloroform/ ethanol. Each isomer was isolated, characterized, and the structure confirmed by $^1$H NMR spectroscopy, UV/Visible spectroscopy, and MALDI-TOF MS spectrometry and the data of which are as listed below:

**2.4.1.1 5-(Pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, 8)** was isolated as purple crystals (0.171 g, 36%); $^1$H NMR ($CDCl_3$, 400 MHz): δ -2.80 (s, 2 H, internal NH), 7.74-7.81 (m, 9 H, *m*-, *p*-phenyl), 8.17-8.19 (m, 2 H, 3,5-pyridyl), 8.21-8.23 (m, 6 H, *o*-phenyl), 8.79 (d, 2 H, β-pyrrole), 8.87 (s, 4 H, β-pyrrole), 8.89 (d, 2 H, β-pyrrole), 9.03 (d, 2 H, 2,6-pyridyl); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 418 (Soret), 515, 550, 590, and 646 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 615.737; Found: 615.587.

**2.4.1.2 5,15-(Dipyridyl)-10,20-diphenylporphyrin (*trans*-DPyDPP, 9)** was isolated as purple crystals (0.029 g, 6%); $^1$H NMR ($CDCl_3$, 400 MHz): δ -2.84 (s, 2 H, internal NH), 7.76-7.82 (m, 6 H, *m*-, *p*-phenyl), 8.20-8.22 (m, 4 H, *o*-phenyl, 4 H, 3,5-pyridyl ), 8.80 (d, 4 H, β-pyrrole), 8.91 (d, 4 H, β-pyrrole), 9.05 (d, 4 H, 2,6-pyridyl); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 418 (Soret), 515, 549, 590, and 648 (Q); MALDI-TOF- MS (dithranol) *m/z* $[M]^+$. Calcd: 616.725; Found: 616.423.

**2.4.1.3 5,10-(Dipyridyl)-15,20-diphenylporphyrin (*cis*-DPyDPP, 10)** was isolated as purple crystals (0.083 g, 17%); $^1$H NMR ($CDCl_3$, 400 MHz): δ -2.83 (s, 2 H, internal NH), 7.76-7.82 (m, 6 H, *m*-, *p*-phenyl), 8.21-8.23 (m, 8 H, *o*-phenyl and 3,5-pyridyl), 8.80 (d, 2 H, β-pyrrole), 8.85 (s, 2 H, β-pyrrole), 8.88 (s, 2 H, β-pyrrole), 8.92 (d, 2 H, β-pyrrole), 9.05 (d, 4 H, 2,6-pyridyl); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 418 (Soret), 515, 549, 590, and 647 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 616.725; Found: 616.508.

**2.4.1.4 5,10,15-(Tripyridyl)-20-phenylporphyrin (TPyMPP, 11)** was isolated as purple powder (0.04 g, 8%); $^1$H NMR ($CDCl_3$, 400 MHz): δ-2.88 (s, 2 H, internal NH), 7.76-7.84 (m, 3 H, *m*-, *p*-phenyl), 8.19-8.21 (m, 8 H, *o*-phenyl and 3,5-pyridyl), 8.81 (d, 2 H, β-pyrrole), 8.86 (s, 4 H, β-pyrrole), 8.92 (d, 2 H, β-pyrrole), 9.06 (d, 6 H, 2,6-pyridyl); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 417 (Soret), 513, 545, 586, and 648 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 617.713; Found: 617.401.

**2.4.1.5** 5,10,15,20-Tetrapyridylporphyrin (TPyP) (0.02 g, 4%) was isolated as purple powder in a small amount. The spectroscopic data will be presented later (*vide infra*)

### 2.4.2 Preparation of 5-(pyridyl)-10,15,20-triphenylporphyrinatozinc(II) (ZnMPyTPP, 12)

To a boiling solution of 5-(pyridyl)-10,15,20-triphenylporphyrin (**8**) (0.020 g, 0.0325 mmol) in *N,N*-dimethylformamide (5 mL) was added a saturated solution of zinc acetate dihydrate (0.0136 g, 0.065 mmol) in methanol (0.5 mL). The reaction mixture was refluxed for 1 hour, cooled down, and extracted three times with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight. Purple crystals of ZnMPyTPP (**12**) (0.022 g, 94%) were collected on a filter and washed with cold methanol. $^1$H NMR (DMSO, 400 MHz): δ 7.81 (m, 9 H, *m*-, *p*-phenyl), 8.18-8.21 (m, 8 H, *o*-phenyl, 3,5-pyridyl), 8.77-8.81 (m, 8 H, β-pyrrole), 8.97 (m, 2 H, 2,6-pyridyl); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 424 (Soret), 555 and 597 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 679.111; Found: 677.739.

### 2.4.3 Preparation of 5-(pyridyl)-10,15,20-triphenylporphyrinatocopper(II) (CuMPyTPP, 13)

To a boiling solution of 5-(pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, **8**) (0.020 g, 0.0325 mmol) in *N,N*-dimethylformamide (5 mL) was added a saturated solution of copper acetate (0.0118 g, 0.065 mmol) in methanol (0.5 mL). The reaction mixture was refluxed for 1 hour, cooled down, and extracted twice with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight. Purple crystals of CuMPyTPP (**13**) (0.0229 g, 99%) were collected on a filter and washed with cold methanol. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.52 (br), 7.66 (br); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 415 (Soret), 539 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 677.267; Found: 676.730.

### 2.4.4 Preparation of 5-(pyridyl)-10,15,20-triphenylporphyrinatonickel(II) (NiMPyTPP, 14)

To a boiling solution of 5-(pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, **8**) (0.005 g, 0.0081 mmol) in *N,N*-dimethylformamide (4 mL) was added a saturated solution of nickel acetate tetrahydrate (0.010 mg, 0.041 mmol) in methanol (1 mL). The reaction mixture was refluxed for 3 hours, cooled down, and extracted three times with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight at 0°C. Purple crystals of NiMPyTPP (**14**) (0.0051 g, 94%) were collected on a filter and washed with cold methanol. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.67-7.73 (m, 9 H, *m*-, *p*-phenyl), 7.99-8.01 (m, 8 H, *o*-phenyl and 3,5-pyridyl), 8.55-8.64 (m, 4 H, β-pyrrole and 2,6-pyridyl), 8.77 (m, 4 H, β-pyrrole), 8.86 (m, 2 H, β-pyrrole),; UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 416 (Soret) 529 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 672.414; Found: 670.098.

### 2.4.5 Preparation of 5-(pyridyl)-10,15,20-triphenylporphyrinatocobalt(II) (CoMPyTPP, 15)

To a boiling solution of 5-(pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, **8**) (0.025 g, 0.041 mmol) in *N,N*-dimethylformamide (8 mL) was added a saturated solution of cobalt acetate tetrahydrate (0.020 g, 0.081 mmol) in methanol (1 mL). The

reaction mixture was refluxed for 2 hours, cooled down, and extracted three times with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight at 0°C. Purple powder of CoMPyTPP (**15**) (0.027 g, 99%) were collected on a filter and washed with cold methanol. $^1$H NMR ($CDCl_3$, 400 MHz): δ broad peaks at 7.70-9.58; UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 410 (Soret), 528 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 672.654; Found: 672.668.

### 2.4.6 Preparation of 5-(pyridyl)-10,15,20-triphenylporphyrinatoiron(III) ((Cl)FeMPyTPP, 16)

To a boiling solution of 5-(pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, **8**) (0.020 g, 0.0325 mmol) in chloroform (8 mL) was added a saturated solution of iron(III) chloride anhydrous (0.0105 g, 0.065 mmol) in methanol (1 mL). Pyridine was added a few drop in the solution. The reaction mixture was refluxed for 8 hours, cooled down, extracted with 0.5% dilute HCl, and three times with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight at 0°C. Purple crystals of (Cl)FeMPyTPP (**16**) (0.020 g, 92%) were collected on a filter and washed with cold methanol. NMR ($CDCl_3$, 400 MHz): δ 6.56 (br); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 416 (Soret), 509 and 574 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 705.019; Found: 704.343. *m/z* $[M\text{-}Cl]^+$. Calcd: 669.566; Found: 669.380.

### 2.4.7 Preparation of 5-(pyridyl)-10,15,20-triphenylporphyrinato manganese(III) (MnMPyTPP, 17)

To a boiling solution of 5-(pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, **8**) (0.020 g, 0.0325 mmol) in *N,N*-dimethylformamide (8 mL) was added a saturated solution of manganese acetate tetrahydrate (0.0159 g, 0.065 mmol) in methanol (1 mL). The reaction mixture was refluxed for 2 hours, cooled down, and extracted three times with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition

of cold hexane and letting stand overnight at 0°C. Green powder of MnMPyTPP (**17**) (0.021 g, 97%) were collected on a filter and washed with cold hexane. $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.22 (br); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 473 (Soret), 577 and 612 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 668.659; Found: 667.664.

## 2.5 Synthesis of Tetrapyridylporphyrin and Their Complexes

### 2.5.1 Preparation of 5,10,15,20-tetrapyridylporphyrin (TPyP, 18)

Freshly distilled pyrrole (0.28 mL, 4 mmol) and 4-pyridinecarboxaldehyde (0.38 mL, 4 mmol) were added to 100 mL of boiling propionic acid in a round bottom flask. The reaction mixture was refluxed for 2 hours, cooled to 0°C, and allow to standing overnight. Purple powder of TPyP (**18**) (0.12 g, 19% yield) were filtered off and washed with cold methanol. $^1$H NMR ($CDCl_3$, 400 MHz): δ -2.93 (s, 2 H, internal NH), 8.16 (m, 8 H, 3,5-pyridyl), 8.87 (m, 8 H, β-pyrrole), 9.06 (m, 8 H, 2,6-pyridyl); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 418 (Soret), 513, 546, 588, and 644 (Q); MALDI-TOF- MS (dithranol) *m/z* $[M]^+$. Calcd: 618.701; Found: 618.577.

### 2.5.2 Preparation of 5,10,15,20-tetrapyridylporphyrinatozinc(II) (ZnTPyP, 19)

To a boiling solution of 5,10,15,20-tetrapyridylporphyrin (TPyP, **18**) (0.025 g, 0.04 mmol) in chloroform (10 mL) was added a saturated solution of zinc acetate dihydrate (0.018 g, 0.081 mmol) in methanol (1 mL). The reaction mixture was refluxed for 1 hour, cooled down and extracted three times with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight. Purple powder of ZnTPyP (**19**) (0.0248 g, 91%) were collected on a filter and washed with cold methanol. $^1$H NMR (DMSO, 400 MHz): δ 8.22 (m, 8 H, 3,5-pyridyl), 8.84 (m, 8 H, β-pyrrole), 9.02 (m, 8 H, 2,6-pyridyl); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 424 (Soret), 555 and 593 (Q); MALDI-TOF-MS (dithranol) *m/z* $[M]^+$. Calcd: 682.076; Found: 680.567.

## 2.6 Synthesis of Bismonopyridyltriphenylporphyrin Metal Assemblies

### 2.6.1 Cu(II)(CuMPyTPP)$_2$ (20)

A solution of 5-(pyridyl)-10,15,20-triphenylporphyrinatocopper(II) (CuMPyTPP, **13**) (0.007 g, 0.010 mmol) in toluene (20 mL) was added a saturated solution of copper acetate (0.0094 g, 0.052 mmol) in methanol (1 mL). The reaction mixture was stirred for 2 days at room temperature and extracted three times with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The purple crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.50 (br), 7.65 (br); UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 415 (Soret), 540 (Q); MALDI-TOF-MS (neat) *m/z* $[M]^+$. Calcd: 1418.08; Found: 1419.45.

### 2.6.2 Pd(II)(MPyTPP)$_2$ (21)

To a boiling solution of 5-(pyridyl)-10,15,20-triphenylporphyrin (MPyTPP, **8**) (0.005 g, 0.008 mmol) in toluene (20 mL) was added a saturated solution of palladium acetate (0.0036 g, 0.016 mmol) in methanol (1 mL). The reaction mixture was refluxed for 24 hrs and extracted three times with distilled water. The organic solution was dried over anhydrous sodium sulfate and the drying agent was filtered off. The volume of solution was reduced *in vacuo*. The purple crude product precipitated from the concentrated solution after an addition of methanol and letting stand overnight. UV/Visible ($CHCl_3$, nm): $\lambda_{max}$ 417 (Soret), 514, 549, 588, and 644 (Q); MALDI-TOF-MS (neat) *m/z* $[M]^+$. Calcd: 1337.894; Found: not observed.

## 2.7 Synthesis of Side to Face Complexation of Porphyrin Units

### 2.7.1 Zn(TPP)(MPyTPP), (22)

MPyTPP (**8**) (2.3 mg, 3.7 μmol) was added to an NMR tube containing ZnTPP (**2**) (2.5 mg, 3.7 μmol) in 0.5 mL $CDCl_3$. The progress of the reaction was monitored by NMR spectroscopy immediately, and after 24 hours at room temperature. $^1$H NMR ($CDCl_3$, 400 MHz): δ -3.12 (s, 2H, internal NH), 7.70-7.72 (m, 9 H, *m*-, *p*-phenyl of MPyTPP), 7.77-7.74 (m, 12 H, *m*-, *p*-phenyl of ZnTPP), 8.07 (d, 4 H, *o*-phenyl of MPyTPP), 8.12 (d, 2 H, *o*'-phenyl of MPyTPP), 8.31 (m, 8 H, *o*-phenyl of ZnTPP), 8.60 (m, 2 H, $\beta_2$ of MPyTPP), 8.76 (m, 4 H, $\beta_3$ and $\beta_4$ of MPyTPP), 8.99 (m, 8 H, β-

pyrrole of ZnTPP); MALDI-TOF-MS (neat) *m/z* $[M]^+$. Calcd: 1293.86; Found: 1293.987.

### 2.7.2 Co(TPP)(MPyTPP), (23)

MPyTPP (**8**) (2.3 mg, 3.7 μmol) was added to an NMR tube containing CoTPP (**5**) (2.5 mg, 3.7 μmol) in 0.5 mL $CDCl_3$. The progress of the reaction was monitored by NMR spectroscopy immediately, and after 24 hours at room temperature. $^1$H NMR ($CDCl_3$, 400 MHz): δ -3.31 (s, 1 H, internal NH), -3.24 (s, 1 H, internal NH), 1.27 (d, 1 H, 2,6-pyridyl), 1.49 (d, 1 H, 2,6-pyridyl), 5.76 (d, 1 H, 3,5-pyridyl), 6.04 (d, 1 H, 3,5-pyridyl), 7.12 (d, 1 H, $\beta_{1a}$ of MPyTPP), 7.20 (d, 1 H, $\beta_{1b}$ of MPyTPP), 8.45 (d, 1 H, $\beta_{2a}$ of MPyTPP), 8.53 (d, 1 H, $\beta_{2b}$ of MPyTPP), 8.53 (m, 4 H, $\beta_{3a}$ and $\beta_{4a}$ of MPyTPP), 8.74 (m, 4 H, $\beta_{3b}$ and $\beta_{4b}$ of MPyTPP); MALDI-TOF-MS (neat) *m/z* $[M]^+$. Calcd: 1287.403; Found: 1287.255.

### 2.7.3 Ni(TPP)(MPyTPP), (24)

MPyTPP (**8**) (2.3 mg, 3.7 μmol) was added to an NMR tube containing NiTPP (**4**) (2.5 mg, 3.7 μmol) in 0.5 mL $CDCl_3$. The progress of the reaction was monitored by NMR spectroscopy immediately, and after 24 hours at room temperature. $^1$H NMR ($CDCl_3$, 400 MHz): δ -2.81 (d, 2 H, internal NH), 7.65-7.71 (m, 12 H, *m*-, *p*-phenyl of NiTPP), 7.74-7.81 (m, 9 H, *m*-, *p*-phenyl of MPyTPP), 8.00-8.02 (m, 8 H, *o*-phenyl of NiTPP), 8.20-8.22 (m, 6 H, *o*-phenyl of MPyTPP, 2 H, 3,5-pyridyl of MPyTPP), 8.74 (s, 8 H, β-pyrrole of NiTPP), 8.80 (d, 2 H, β-pyrrole of MPyTPP), 8.86 (s, 4 H, β-pyrrole of MPyTPP), 8.90 (d, 2 H, β-pyrrole of MPyTPP), 9.04 (br, 2 H , 2,6-pyridyl of MPyTPP); MALDI-TOF-MS (neat) *m/z* $[M]^+$. Calcd: 1287.163; Found: not observed.

## 2.8 Optical Gas Sensor of 5,10,15,20-Tetraphenylporphyrinatozinc(II) (ZnTPP, 2)

The result in this section has been provided by Uttiya, S. and co-workers (menuscript in preparation). The 5,10,15,20-tetraphenylporphyrinatozinc(II) (ZnTPP, **2**) organic thin film was prepared by the spin-coating technique. The chloroform solution of **2** at 0.007 molar concentration was spin-coated onto glass slides at 1000 rpm for 30 sec. An improvement in the ZnTPP sensing properties has been achieved by thermal annealing in a furnace under a flow argon gas and heated at the heating/cooling rate of 5°C/min until reaching 340°C. Responses of the films to

methanol, ethanol, isopropanol, and Thai whisky were monitored at room temperature and at normal incidence in the range of 340-795 nm by optical absorption spectroscopy (Appendix B).