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Original Article

Synthesis and characterization of ether-linked porphyrins

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Abstract

The ether-linked porphyrin dimers in this research work were prepared from coupling reaction between suitable porphyrin precursors and linkers in the presence of potassium carbonate. The structures of all synthesized compounds were characterized by spectroscopic methods. The UV/Visible absorption maxima and extinction coefficients did not show any significant difference among these porphyrin dimers. This indicates that the length of the linker did not affect the absorption property of the dimers. However, different metal ions bonding to the porphyrin moiety affect the different absorption maxima of the porphyrin dimers. It was also found that the position of the linker on the phenyl ring of porphyrin does not affect the visible absorption pattern or the proton chemical shifts of the porphyrin core as found in the case of Zn_2(*meta*)C-dimer (**13**) (compared with the data obtained for Zn_2C_2-dimer (**3**)).

Keywords: ether-linked porphyrin, porphyrin dimer, covalently-linked porphyrin

1. Introduction

Tetrapyrrolic macrocycles play a number of critical biological roles such as molecular binding reaction catalysis, energy and electron transfer, and light harvesting. The importance of these functions has provided the impetus for intensive research toward artificial tetrapyrrolic macrocycle systems that may be able to model or mimic their natural counterparts. However, the synthesis of suitable tetrapyrrolic macrocycles and assemblies of tetrapyrrolic macrocycles has been proved to be problematic.

Nature uses a myriad of biosynthetic pathways to make both the tetrapyrrolic macrocycles and the associated proteins and then to assemble them into arrays for energy and electron-transfer purposes (Kaim and Schwederski, 1994). The tetrapyrrolic macrocycles are bound to the proteins by a variety of interactions such as covalent thioether bonds, metal-ligand axial coordination, hydrophobic or hydrophilic interactions, and hydrogen bonding. It is virtually impossible to synthetically reproduce the intricate and specific protein matrix.

While some research groups have produced porphyrin-peptide conjugate assemblies as a model for natural systems (Geier III and Sasaki, 1997), many researchers who are interested in mimicking these systems have constructed a variety of artificial porphyrin arrays such as covalently linked conjugated oligomer (Officer *et al.*, 1996), non-conjugated oligomer (Dubowchick and Hamilton, 1986; Takeuchi *et al.*,1996), coordination polymer (Sharma *et al.*, 2000), and dendrimers (Norsten and Branda, 1998). The purpose of porphyrin array construction is to shift porphyrin absorption maxima to the lower energy region. This may help to produce photosensitizer for photovoltaic cells (Imahori *et al.*, 2004; Shimidzu and Segawa, 1996) and in photodynamic therapy (Zhang *et al.*, 2003). This research work will focus on the synthesis of ether-linked porphyrins. These may show inter-

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esting optical properties which can be used as photosensitizers for photovoltaic cells.

2. Materials and Methods

2.1 Apparatus

The NMR spectra were recorded using Bruker Avance 300 spectrophotometer. The deuterated solvents used were $CDCl_3$, d_6-DMSO. The internal reference for ^1H NMR is tetramethylsilane. UV/Visible spectra were measured in methylenechloride solutions with an HP-8453 UV/Vis spectrophotometer.

2.2 Reagents

All chemicals were reagent grade quality, purchased commercially and used without further purification. All solvents used in this experiment were dried and purified pior to use. Thin layer chromatographic plates were purchased from Merck, consisting of 20x20 cm plate coated with a 0.25 mm of Merck Kieselgel 60 F_{254} silica gel, while preparative thin layer chromatographic plates were prepared in this laboratory. Silica gel for column chromatography was Merck Kieselgel 60(0.063-0.2 mm).

2.2.1 Synthesis of 5- (4- hydroxyphenyl)- 10, 15, 20- tritolylporphyrinatozinc(II) (1)

A mixture of 4- tolualdehyde (2.56 g, 0.021 mol) and 4- hydroxybenzal-dehyde (0.91 g, 0.007 mol) in propionic acid was heated to 100°C. Freshly distilled pyrrole (2.00 g, 0.029 mol) was then added and the resulting mixture was refluxed for 4 hours. The mixture was allowed to stand for one day. The precipitate was filtered off and washed with propionic acid and then ethanol. The solid residue was dissolved in a small amount of CH_2Cl_2 (10 mL) and purified by column chromatography using CH_2Cl_2/hexane (1:1 v/v) as an eluent to obtain *meso*- tetra(4- tolyl)porphyrin. The column was then eluted with CH_2Cl_2 to obtain 5- (4- hydroxyphenyl)- 10, 15, 20- tritolylporphyrin (550 mg, 11.70%). 5- (4- Hydroxyphenyl)- 10, 15, 20- tri(4- tolyl)-porphyrin (550 mg, 0.82 mmol) was dissolved in CH_2Cl_2/MeOH (1:1 v/v) and $Zn(CH_3COO)_2.2H_2O$ (360 mg, 1.640 mmol) was subsequently added. The mixture was refluxed for 3 hours. The reaction mixture was filtered off. The filtrate was washed with water. The product was extracted with CH_2Cl_2 and dried over anh. Na_2SO_4. The solvent was removed under reduced pressure. The residue was crystallized from CH_2Cl_2/MeOH to give **1** as purple crystals (600 mg, 99.70%). UV/Visible (CH_2Cl_2) : λ_{max} (log ε) 424 (5.50), 553 (4.11), 595 (3.67) nm. ^1H NMR (300 MHz , $CDCl_3$) d 2.73 (s, 9H, CH_3), 7.20 (d, 2H, ^3J=8.5 Hz , $H_{m\text{-Ph}}$ (-OPh)) , 7.57 (d, 6H, ^3J=7.7 Hz, $H_{m\text{-Ph}}$(tolyl)), 8.09 (d, 2H, ^3J=8.5 Hz, $H_{o\text{-Ph}}$(-OPh)), 8.13 (d, 6H, ^3J=7.7 Hz, $H_{o\text{-Ph}}$(tolyl)), 8.98 (d, 8H, ^3J=0.7 Hz, $H_{pyrrole}$). MALDI-TOF MS: m/z 734.3, calcd for $C_{47}H_{34}N_4OZn$ 736.2.

2.2.2 Synthesis of 5- (4- [2- (tosyloxy)ethyleneoxy]phenyl)- 10, 15, 20- tri(4-tolyl)porphyrinatozinc(II)(2) and Zn_2C_2 dimer (3)

5- (4- Hydroxyphenyl)- 10, 15, 20- tri(4- tolyl)porphyrinatozinc(II) (**1**) (400 mg, 0.543 mmol) was dissolved in CH_3CN (50 mL). Then 1, 2- ditosyloxyethane (201 mg, 0.543 mmol) and K_2CO_3 (300 mg, 2.171 mmol) were added. The mixture was refluxed for 3 hours. The solvent was removed under reduced pressure. The residue was washed with water. The product was extracted with CH_2Cl_2 and dried over anh.Na_2SO_4. After solvent was evaporated, the residue was purified by TLC using CH_2Cl_2/hexane (1:1 v/v) as an eluent. The least polar compound was identified by ^1H NMR spectroscopy as a dimer (**3**) (R_f=0.8, 170 mg, 40.52%). The second compound was identified as 5- (4- [2- (tosyloxy) ethyleneoxy]phenyl)- 10, 15, 20-tri(4-tolyl)porphy-rinatozinc(II)(**2**) (R_f=0.7, 234 mg , 46.04%).

Compound (**2**): UV/Visible (CH_2Cl_2) : λ_{max} (log ε) 425 (5.68), 553 (4.27), 595 (3.81) nm. ^1H NMR (300 MHz, $CDCl_3$) : δ 2.48 (s, 3H, CH_3(-OTs)), 2.71(s, 9H, CH_3(tolyl)), 4.46 (m, 2H, -CH_2-OTs), 4.58 (m, 2H, -CH_2-OPh), 7.16 (d, 2H,^3J=8.6 Hz, $H_{m\text{-Ph}}$ (-OPh)), 7.44 (d, 2H,^3J=8.1 Hz, H_{Ph} (OTs), 7.56(d, 6H,^3J=7.8 Hz, $H_{m\text{-Ph}}$(tolyl) , 7.96 (d, 2H, ^3J= 8.1 Hz, H_{Ph}(-OTs), 8.09 (d, 2H, ^3J= 8.6 Hz, $H_{o\text{-Ph}}$ (-OPh), 8.10 (d, 6H, ^3J=7.8 Hz, $H_{o\text{-Ph}}$(tolyl)), 8.91 (d, 2H, ^3J=4.7 Hz, $H_{pyrrole}$), 8.96 (s, 4H, $H_{pyrrole}$), 8.97 (d, 2H, ^3J=4.7 Hz, $H_{pyrrole}$). MALDI-TOF MS: m/z 933.5, calcd for $C_{56}H_{44}N_4O_4ZnS$ 934.4.

Compound (**3**): UV/Visible (CH_2Cl_2) : λ_{max} (log ε) 425 (5.95), 553 (4.58), 596 (4.14) nm. ^1H NMR (300MHz, $CDCl_3$) : δ 2.67 (s sh, 18H, CH_3), 4.78 (s, 4H, -OCH_2CH_2O-), 7.39 (d, 4H, ^3J=8.6 Hz, $H_{m\text{-Ph}}$ (-OPh)), 7.51 (d, 12H, ^3J=7.8 Hz, $H_{m\text{-Ph}}$ (tolyl)), 8.08 (d, 12H, ^3J=7.8 Hz, $H_{o\text{-Ph}}$ (tolyl)), 8.16 (d, 4H, ^3J=8.6 Hz, $H_{o\text{-Ph}}$(-OPh)), 8.91 (s, 8H, $H_{pyrrole}$), 8.94 (d, 4H, ^3J=4.7 Hz, $H_{pyrrole}$), 8.96 (d, 4H, ^3J=4.7 Hz, $H_{pyrrole}$). MALDI-TOF MS: m/z 1497.8, calcd for $C_{96}H_{70}N_8O_2Zn_2$ 1498.4.

2.2.3 Synthesis of 5- (4- [2- (tosyloxy)ethyleneoxy]phenyl)- 10, 15, 20- tri(4- tolyl)- porphyrin (4)

5- (4- [2- (Tosyloxy)ethyleneoxy]phenyl)- 10, 15, 20-tri(4- tolyl)porphyrinato-zinc(II) (**2**) (201 mg, 0.215 mmol) was dissolved in CH_2Cl_2 (100 mL) and 1 M HCl (2 mL) was subsequently added. The mixture was refluxed for 3 hours. The solvent was removed under reduced pressure. The residue was washed with water. The product was extracted with CH_2Cl_2 and dried over anh.Na_2SO_4. After solvent was evaporated, the solid residue was crystallized from CH_2Cl_2/MeOH to yield 5- (4- [2- (tosyloxy)ethyleneoxy]phenyl)- 10, 15, 20-tri(4-tolyl)porphyrin as purple crystals (150 mg, 80.56%). UV/Visible (CH_2Cl_2) : λ_{max} (log ε) 421 (5.68), 517 (4.23), 553 (4.04), 592 (3.76), 648 (3.66) nm. ^1H NMR (300 MHz, $CDCl_3$) : δ -2.77 (s, 2H, NH), 2.50 (s, 3H, CH_3-(OTs)), 2.73 (s, 9H, CH_3(tolyl)), 4.48 (m, 2H, -CH_2-OTs), 4.58 (m, 2H, -CH_2-OPh), 7.18 (d, 2H, ^3J=8.7 Hz, H_{Ph}(-OPh)) , 7.46 (d, 2H,

^3J=8.4 Hz, H_{Ph}(OTs)), 7.58 (d, 6H, ^3J=7.8 Hz, $H_{m\text{-}Ph}$(tolyl)), 7.97 (d, 2H, ^3J=8.4 Hz, H_{Ph} (OTs)), 8.10 (d, 2H, ^3J=8.7 Hz, H_{Ph} (-OPh)), 8.11(d, 6H, ^3J=7.8 Hz, $H_{o\text{-}Ph}$(tolyl)) , 8.83 (d, 2H, ^3J=4.8 Hz, $H_{pyrrole}$), 8.87 (s, 4H, $H_{pyrrole}$), 8.88 (d, 2H, ^3J= 4.8 Hz, $H_{pyrrole}$). MALDI-TOF MS: m/z 871.0, calcd for $C_{56}H_{46}N_4O_4S$ 871.1.

2.2.4 Synthesis of Zn_2C- dimer (5)

5- (4- Hydroxyphenyl)- 10, 15, 20- tri(4- tolyl)porphyrinatozinc(II) (**1**) (226 mg, 0.308 mmol) was dissolved in CH_3CN (50 mL). Then CH_2Br_2 (27 mg, 0.154 mmol) and K_2CO_3 (170mg, 1.230 mmol) were added. The mixture was refluxed overnight. The solvent was removed under reduced pressure. The residue was washed with water. The product was extracted with CH_2Cl_2 and dried over anh.Na_2SO_4. After solvent was evaporated, the residue was purified by TLC using CH_2Cl_2/ hexane (1:1 v/v) as an eluent. Zn_2C- dimer (**5**) was obtained (R_f= 0.75, 156 mg, 68.18%). UV/Visible (CH_2Cl_2) : λ_{max} (log ε) 425 (5.92), 553 (4.57), 595 (4.11) nm. ^{1}H NMR (300MHz, $CDCl_3$) : δ 2.71(s, 18H, -CH_3), 6.33 (s, 2H, -OCH_2O-), 7.55 (d, 12H, ^3J= 0.03 Hz, $H_{m\text{-}Ph}$ (tolyl)), 7.68 (d, 4H, ^3J= 0.03 Hz, H_{Ph} (-OPh), 8.11 (d, 12H, ^3J= 0.03 Hz, $H_{o\text{-}Ph}$ (tolyl)), 8.26 (d, 4H, ^3J= 0.03Hz, H_{Ph}(-OPh)), 8.92 (s, 8H, $H_{pyrrole}$), 8.94 (d, 4H, ^3J= 0.02 Hz, $H_{pyrrole}$), 9.00 (d, 4H, ^3J= 0.02 Hz, $H_{pyrrole}$). MALDI-TOF MS: m/z 1483.9, calcd for $C_{95}H_{68}N_8O_2Zn_2$ 1484.4.

2.2.5 Synthesis of Zn_2C_8-dimer (6)

5- (4- Hydroxyphenyl)- 10, 15, 20- tri(4- tolyl)porphyrinatozinc(II) (**1**) (255 mg, 0.347 mmol) was dissloved in CH_3CN (50 mL). Then α, α′- dichloro- *p*- xylene (30 mg, 0.174 mmol) and K_2CO_3 (192 mg, 1.389 mmol) were added. The mixture was refluxed overnight. The solvent was removed under reduced pressure. The residue was washed with water. The product was extracted with CH_2Cl_2 and dried over anh.Na_2SO_4. After solvent was evaporated, the residue was purified by TLC using CH_2Cl_2/hexane (1:1 v/v) as an eluent. The least polar compound was identified as a dimer (**6**) (R_f= 0.8). The porphyrin dimer was crystallized from CH_2Cl_2/MeOH to give purple crystals (56 mg, 20.69%). UV/ Visible (CH_2Cl_2) : λ_{max} (log ε) 425 (5.71), 553 (4.32), 596 (3.88) nm.^{1}H NMR (300 MHz, $CDCl_3$) : δ 2.66 (s, 18H, CH_3), 5.42 (s, 4H, -OCH_2-), 7.37 (d, 4H, ^3J=8.6 Hz, $H_{m\text{-}Ph}$(-OPh)), 7.50 (d, 12H, ^3J=7.9 Hz, $H_{m\text{-}Ph}$(tolyl)), 7.74 (s, 4H, -$C_6\underline{H}_4$-), 8.05 (d, 12H, ^3J=7.9 Hz, $H_{o\text{-}Ph}$(tolyl)), 8.12 (d, 4H, ^3J=8.6 Hz, $H_{o\text{-}Ph}$(-OPh)), 8.85 (s, 8H, $H_{pyrrole}$), 8.87 (d, 4H, ^3J=4.7 Hz, $H_{pyrrole}$), 8.89 (d, 4H, ^3J=4.7 Hz, $H_{pyrrole}$). MALDI-TOF MS: m/z 1574.0, calcd for $C_{102}H_{74}N_8O_2Zn_2$ 1574.5.

2.2.6 Synthesis of H_2C_2- dimer (7)

The porphyrin dimer (**3**) (170 mg, 0.113 mmol) was dissolved in CH_2Cl_2 (100 mL) and 1 M HCl (2.00 mL) was then added. The mixture was refluxed for 3 hours. The solvent was removed under reduced pressure and washed with water. The product was extracted with CH_2Cl_2 and dried over anh.Na_2SO_4. After solvent was evaporated, H_2C_2- dimer (**7**) was yielded (140 mg, 90.26%). UV/Visible (CH_2Cl_2) : λ_{max} (log ε) 421 (5.95), 517 (4.55), 553 (4.31), 592 (4.05), 648 (4.02) nm. ^{1}H NMR (300 MHz, $CDCl_3$) : δ -2.75 (s, 4H, NH), 2.70 (s(sh), 18H, CH_3), 4.80 (s, 4H, -OCH_2CH_2O-), 7.45 (d, 4H, ^3J=8.6 Hz, $H_{m\text{-}Ph}$(-OPh)), 7.56 (d, 12H, ^3J=7.9 Hz, $H_{m\text{-}Ph}$(tolyl)), 8.11 (d, 12H, ^3J=7.9 Hz, $H_{o\text{-}Ph}$ (tolyl)), 8.21 (d, 4H, ^3J=8.6 Hz, $H_{o\text{-}Ph}$(-OPh)), 8.87 (s, 8H, $H_{pyrrole}$), 8.89 (d, 4H, ^3J=4.8 Hz, $H_{pyrrole}$), 8.92 (d, 4H, ^3J=4.8 Hz, $H_{pyrrole}$). MALDI-TOF MS: m/z 1370.9, calcd for $C_{96}H_{74}N_8O_2$ 1371.7.

2.2.7 Synthesis of Ni_2C_2-dimer (8)

The porphyrin dimer (**7**) (140 mg, 0.102 mmol) was dissolved in DMF (20 mL) and then $Ni(CH_3COO)_2.4H_2O$ (76 mg, 0.306 mmol) was added. The resulting mixture was refluxed overnight. The reaction mixture was washed with water and the product was extracted with CH_2Cl_2 and dried over anh.Na_2SO_4. After solvent evaporation, the solid residue was crystallized from CH_2Cl_2/MeOH to give porphyrin dimer (**8**) as purple crystals (120 mg, 79.41%). UV/Visible (CH_2Cl_2) : λ_{max} (log ε) 419 (5.70), 529 (4.49) nm. ^{1}H NMR (300MHz, $CDCl_3$) : δ 2.66 (s(sh), 18H, -CH_3), 4.75 (s, 4H, -OCH_2CH_2O-), 7.38 (d, 4H, ^3J=8.6 Hz, $H_{m\text{-}Ph}$ (-OPh)), 7.50 (d, 12H, ^3J=8.0 Hz, $H_{m\text{-}Ph}$ (tolyl), 7.92 (d, 12H, ^3J=8.0 Hz, $H_{o\text{-}Ph}$ (tolyl)), 8.00 (d, 4H, ^3J=8.6 Hz, $H_{o\text{-}Ph}$(-OPh)), 8.78 (s, 8H, $H_{pyrrole}$), 8.79 (d, 4H, ^3J=5.0 Hz, $H_{pyrrole}$), 8.82 (d, 4H, ^3J= 5.0 Hz, $H_{pyrrole}$). MALDI-TOF MS: m/z 1483.3, calcd for $C_{96}H_{70}N_8O_2Ni_2$ 1485.0.

2.2.8 Synthesis of Ni_2C-dimer (10)

5- (4- Hydroxyphenyl)-10, 15, 20- tri(4- tolyl)porphyrin (120 mg, 0.163 mmol) was dissolved in DMF (20 mL) and $Ni(CH_3COO)_2.4H_2O$ (81 mg, 0.326 mmol) was then added. The resulting mixture was refluxed overnight. The reaction mixture was washed with water. The product was extracted with CH_2Cl_2 and dried over anh.Na_2SO_4. After solvent was evaporated, the solid residue was crystallized from CH_2Cl_2/MeOH to give 5- (4- hydroxyphenyl)- 10, 15, 20- tri(4-tolyl)porphyrinato-nickel(II) (**9**) as purple crystals (112 mg, 94.48%).

5- (4- Hydroxyphenyl)- 10, 15, 20- tri(4- tolyl)porphyrinatonickel(II) (112 mg, 0.154 mmol) was dissolved in CH_3CN (50 mL). Then CH_2Br_2 (13 mg, 0.077 mmol) and K_2CO_3 (85 mg, 0.615 mmol) were added. The resulting mixture was refluxed overnight. The solvent was removed under reduced pressure. The residue was washed with water. The product was extracted with CH_2Cl_2 and dried over anh.Na_2SO_4. After solvent was evaporated, the residue was purified by TLC using CH_2Cl_2/hexane (1:1 v/v) as an eluent. The least polar band was identified as a dimer (**10**) (R_f=0.75, 76 mg, 67.53%). UV/Visible (CH_2Cl_2) : λ_{max} (log ε) 418 (5.62), 529 (4.48) nm. ^{1}H NMR (300 MHz, $CDCl_3$) : δ 2.66

(s(sh), 18H, -CH_3), 6.02 (s, 2H, -OCH_2O-), 7.36 (d, 4H, ^3J=8.8 Hz, $H_{m\text{-Ph}}$ (-OPh)), 7.50 (d, 12H, ^3J=7.8 Hz, $H_{m\text{-Ph}}$ (tolyl), 7.91 (d, 12H , ^3J=7.8 Hz, $H_{o\text{-Ph}}$ (tolyl)), 7.96 (d, 4H, ^3J=8.8 Hz, $H_{o\text{-Ph}}$(-OPh)), 8.77 (s(br), 16H, $H_{pyrrole}$). MALDI-TOF MS: m/z 1469.5, calcd for $C_{95}H_{68}N_8O_2Ni_2$ 1471.0.

2.2.9 Synthesis of $ZnNiC_2$-dimer (11)

5- (4- Hydroxyphenyl)- 10, 15, 20- tri(4- tolyl)porphyrinatonickel(II) (**9**) (112 mg, 0.154 mmol) was dissloved in CH_3CN (50 mL) then 5- (4- [2- (tosyloxy) ethyleneoxy] phenyl)- 10, 15, 20- tri(4- tolyl)porphyrinatozinc(II) (**2**) (144 mg, 0.154 mmol) and K_2CO_3 (85 mg, 0.615 mmol) were added. The resulting mixture was refluxed overnight. The solvent was removed under reduced pressure. The residue was washed with water. The product was extracted with CH_2Cl_2 and dried over anh.Na_2SO_4. After solvent was evaporated, the residue was purified by TLC using CH_2Cl_2/hexane (1:1 v/v) as an eluent. The least polar compound was identified as a dimer (R_f= 0.8). The porphyrin dimer was crystallized from CH_2Cl_2/MeOH to give purple crystals (30 mg, 13.06%). UV/Visible (CH_2Cl_2) : λ_{max} (log ε) 424 (5.78), 549 (4.37), 530 (sh, 4.30), 595 (3.88) nm. ^{1}H NMR (300MHz, $CDCl_3$) : δ 2.64 (s(sh), 9H, CH_3(Ni^{2+} Por)), 2.71 (s(sh), 9H, CH_3(Zn^{2+} Por)), 4.80 (m, 4H, -OCH_2CH_2O-), 7.39 (d, 2H, ^3J=8.6 Hz, $H_{m\text{-Ph}}$ (-OPh of Zn^{2+} Por)), 7.44 (d, 2H, ^3J=7.8 Hz, $H_{m\text{-Ph}}$ (-OPh of Ni^{2+} Por)), 7.48 (d, 6H, ^3J=7.8 Hz, $H_{m\text{-Ph}}$ (tolyl of Ni^{2+} Por)), 7.55 (d, 6H, ^3J=8.1 Hz, $H_{m\text{-Ph}}$ (tolyl of Zn^{2+} Por)), 7.90 (d, 6H, ^3J=7.8 Hz, $H_{o\text{-Ph}}$(tolyl of Ni^{2+} Por)), 8.01 (d, 2H, ^3J=8.5 Hz, $H_{o\text{-Ph}}$ (-OPh of Ni^{2+} Por)), 8.11 (d, 6H, ^3J=8.1 Hz, $H_{o\text{-Ph}}$ (tolyl of Zn^{2+} Por)), 8.20 (d, 2H, ^3J=8.6 Hz, $H_{o\text{-Ph}}$(-OPh of Zn^{2+} Por)), 8.76 (s, 4H, $H_{pyrrole}$ (Ni^{2+} Por), 8.78 (d, 2H, ^3J=5.0 Hz, $H_{pyrrole}$ (Ni^{2+} Por), 8.82 (d, 2H, ^3J= 5.0 Hz, $H_{pyrrole}$ (Ni^{2+} Por), 8.96 (s, 4H, $H_{pyrrole}$ (Zn^{2+} Por)), 8.98 (d, 2H, ^3J=4.7 Hz, $H_{pyrrole}$ (Zn^{2+} Por)), 9.00 (d, 2H, ^3J=4.7 Hz, $H_{pyrrole}$ (Zn^{2+} Por)**)**. MALDI-TOF MS: m/z 1491.8, calcd for $C_{96}H_{70}N_8O_2ZnNi$ 1491.7.

2.2.10 Synthesis of 5- (3- hydroxyphenyl)- 10, 15, 20- tri (4-tolyl)porphyrinato-zinc(II)(12)

A mixture of 4- tolualdehyde (2.56 g, 0.021mol) and 3-hydroxybenzal-dehyde(0.91 g, 0.007 mol) in propionic acid was heated at 100°C. Freshly distilled pyrrole (2.00 g, 0.030 mol) was then added and the resulting mixture was refluxed for 4 hours. The mixture was allowed to stand for one day. The precipitate was filtered off and washed with propionic acid and then ethanol. The solid residue was dissolved in a small amount of CH_2Cl_2 (10 mL) and was purified by column chromatography using CH_2Cl_2/hexane (1:1 v/v) as an eluent. The first fraction eluted was *meso*- tetra(4-tolyl)porphyrin. The column was then eluted with CH_2Cl_2 to obtain 5- (3- hydroxyphenyl)- 10, 15, 20- tri(4- tolyl) porphyrin (486 mg, 10.34%). 5- (3-Hydroxyphenyl)-10, 15, 20- tri(4- tolyl)porphyrin (486 mg, 0.724 mmol) was dissolved in CH_2Cl_2/MeOH (1:1 v/v) and $Zn(CH_3COO)_2.2H_2O$ (318 mg, 1.449 mmol) was then added. The mixture was refluxed for 3 hours. The reaction mixture was then filtered off. The filtrate was washed with water and dried over anh. Na_2SO_4. The solvent was removed under reduced pressure. The solid residue was crystallized from CH_2Cl_2/MeOH to give 5- (3- hydroxyphenyl)- 10, 15, 20- tri(4-tolyl)porphyrinato-zinc(II) (**12**) as purple crystals (480 mg, 90.01%). UV/ Visible (CH_2Cl_2) : λ_{max} (log ε) 420 (5.42), 549 (4.20), 587 (3.74), 512 (3.26) nm. ^{1}H NMR (300MHz, $CDCl_3$) : δ 2.73 (s, 9H, -CH_3), 5.61(brs, 1H, -OH), 7.16 (dd, 1H, H_{Ph}(Ph-OH)), 7.53-7.62 (m, 8H, $H_{m\text{-Ph}}$(tolyl) + H_{Ph}(Ph-OH)), 7.78(m, 1H, H_{Ph} (Ph-OH)), 8.09-8.13 (m, 6H, $H_{o\text{-Ph}}$(tolyl)), 8.96 (s, 4H, $H_{pyrrole}$), 8.98 (s, 4H, $H_{pyrrole}$). MALDI-TOF MS: m/z 733.6, calcd for $C_{47}H_{34}N_4OZn$ 736.2.

2.2.11 Synthesis of Zn_2(*meta*)C-dimer (13)

5- (3- Hydroxyphenyl)- 10, 15, 20- tri(4- tolyl)porphyrinatozinc(II) (**12**) (286 mg, 0.389 mmol) was dissolved in CH_3CN (50 mL). Then CH_2Br_2 (34 mg, 0.195 mmol) and K_2CO_3 (215 mg, 1.556 mmol) were added. The mixture was refluxed overnight. The solvent was removed under reduced pressure and was washed with water. The product was extracted with CH_2Cl_2 and dried over anh. Na_2SO_4. After solvent was evaporated, the residue was purified by TLC using CH_2Cl_2/hexane (1:1 v/v) as an eluent. The least polar compound was identified as a dimmer (R_f= 0.8). The porphyrin dimer was crystallized from CH_2Cl_2/MeOH to give a purple crystals (150 mg, 51.95%). UV/Visible (CH_2Cl_2) : λ_{max} (log ε) 424 (5.90), 553 (4.58), 595 (4.08) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.66 (s, 12H, -CH_3), 2.73 (s, 6H, -CH_3), 6.08 (s, 2H, -OCH_2O-), 7.45 – 7.52 (m, 8H, $H_{m,p\text{-Ph}}$), 7.57 (d, 6H, ^3J=7.9 Hz, $H_{m,p\text{-Ph}}$), 7.69 (t, 2H, ^3J=8.1 Hz, $H_{m\text{-Ph}}$), 7.94 (d, 2H, ^3J=7.2 Hz, $H_{o\text{-Ph}}$), 8.02 -8.14 (m, 14H, $H_{o\text{-Ph}}$), 8.93-9.02 (m, 16H, $H_{pyrrole}$). MALDI-TOF MS: m/z 1484.0, calcd for $C_{95}H_{68}N_8O_2Zn_2$ 1484.4.

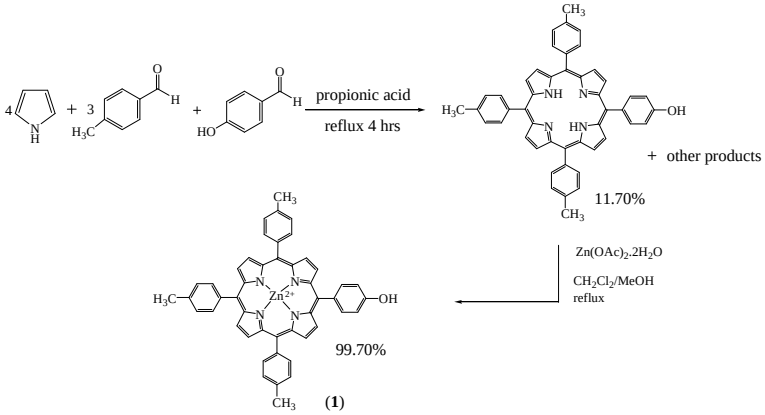
3. Results and Discussion

3.1 Synthesis and characterization of the porphyrin precursor

Reacting tolualdehyde and 4-hydroxybenzaldehyde with pyrrole in refluxing propionic acid yielded 5- (4-hydroxyphenyl)- 10, 15, 20-tritolylporphyrin which was further reacted with $Zn(CH_3COO)_2.2H_2O$ in CH_2Cl_2/MeOH to produce the target precursor, 5- (4- hydroxyphenyl)- 10, 15, 20-tritolylporphyrinatozinc(II) (**1**) as in Scheme 1. The synthesis of 5- (3- hydroxyphenyl)-10, 15, 20- tritolylporphyrinato-zinc(II) (**12**) was similarly performed (see Scheme 3).

3.2 Synthesis of the dimers

All porphyrin dimers were synthesized by base-catalyzed coupling reaction between the suitable porphyrin



Scheme 1

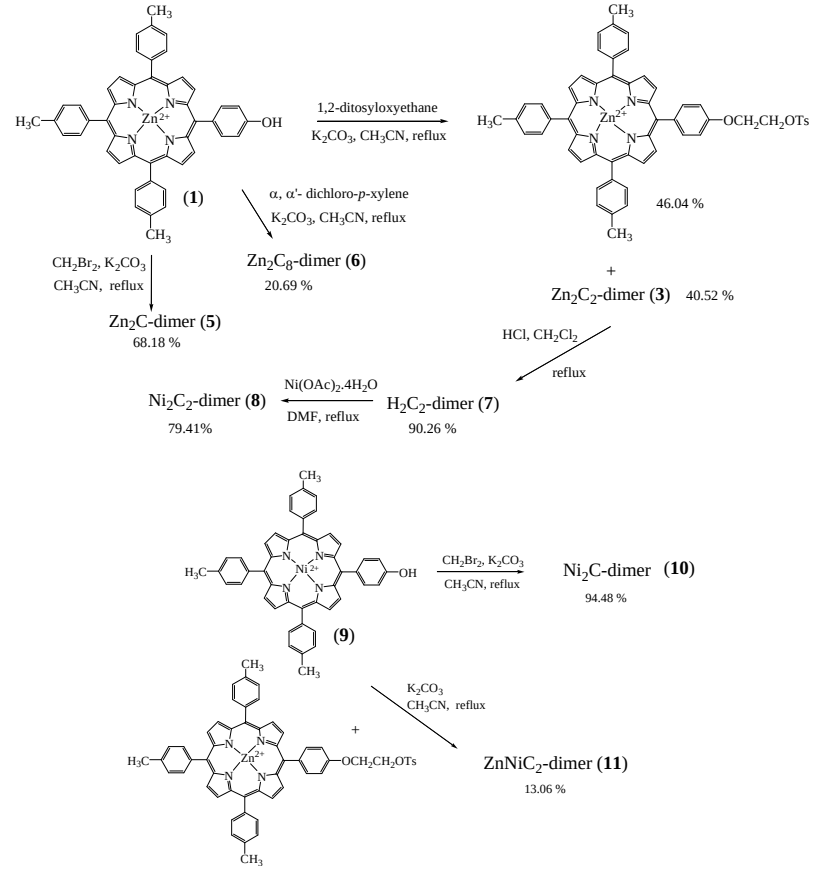
precursor and the linkers as summarized in Scheme 2 and Scheme 3. From the synthetic studies of Zn_2C_2-dimer, reacting 5- (4- hydroxyphenyl)- 10, 15, 20-tritolylporphyrinatozinc(II) (**1**) with 1, 2- ditosyloxyethane in the presence of potassium carbonate yielded 5- (4- [2- (tosyloxy)ethyleneoxy]phenyl)- 10, 15, 20- tritolylporphyrinatozinc(II) (**2**) (46.04%) and Zn_2C_2-dimer (**3**) (40.52%) as in Scheme 2. The acidic hydrogen of phenolic group on porphyrin ring is very reactive towards base to form phenolate anion. The phenolate anion is very reactive for the reaction with 1,2-ditosyloxyethane. Two products were obtained from the reaction. The yield of the dimer (**3**) depends on the stoichiometric amount between 5- (4- hydroxyphenyl)-10,15, 20-tritolylporphyrinatozinc(II) (**1**) and 1,2-ditosyloxyethane. The optimum mole ratio between compound **1** and the linker to obtain the best yield of the dimer is 2 :1. Attempts to react compound **1** with 1, 2- dichloroethane resulted in the formation of 5- (4- [2-chloroethyleneoxy]-phenyl)- 10, 15, 20-tritelylpor-phyrinatozinc(II). While the Zn_2C_2-dimer was not obtained. This may be good evidence showing the greater lability of tosylate group compared to chloride.

From Scheme 2, Zn_2C-dimer (**5**) was obtained in 68.18% by treating 5- (4- hydroxyphenyl)- 10, 15, 20- tritolylporphyrinatozinc(II) (**1**) with dibromomethane. This obviously shows that bromide is a good leaving group especially for this dimer synthesis. It was also attempted to react compound **1** with α, α′-dichloro-*p*- xylene. Zn_2C_8-dimer (**6**) was the main product. Ni_2C_2-dimer (**8**) was synthesized by removing Zn^{2+} from Zn_2C_2-dimer using HCl and subsequently adding nickel(II) acetate in refluxing *N,N´*-dimethylformamide. Ni_2C-dimer was prepared by a similar method to that for the preparation of Zn_2C-dimer (**5**). The mixed metal porphyrin dimer, $ZnNiC_2$-dimer (**11**) was obtained by reacting 5- {4-[2-(tosyloxy)ethyleneoxy]phenyl}- 10, 15, 20- tritolylporphyrinatozinc(II)(**2**) with 5-(4-hydroxyphenyl)- 10, 15, 20- tritolylporphyrinatonickel(II) (**9**) in the presence of potassium carbonate (Scheme 2). Zn_2(*meta*)C-dimer (**13**) was prepared by reacting 5- (3- hydroxyphenyl)-10, 15, 20-tritolylporphyrinatozinc(II) (**12**) with dibromomethane in the presence of potassium carbonate. This dimer gave a 51.95% yield (Scheme 3).

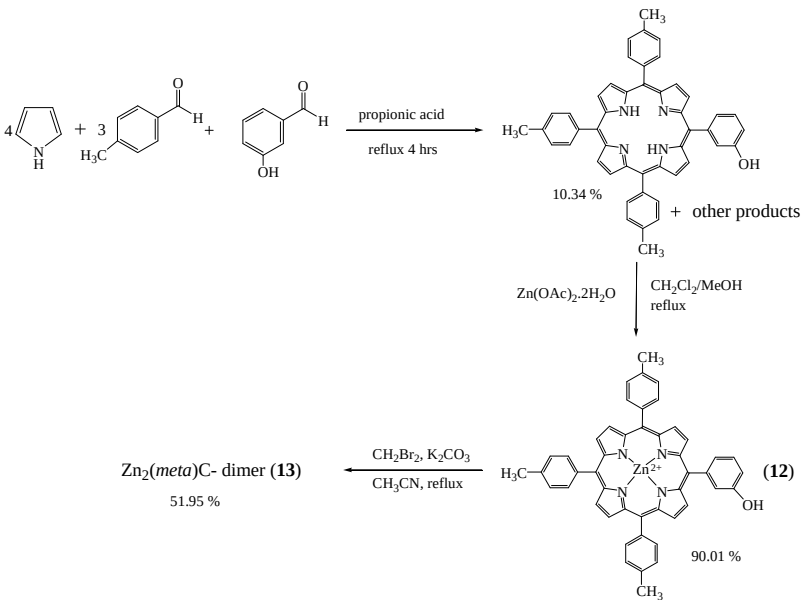
3.3 Structural characterization of the dimers

The ^{1}H-NMR spectra of Zn_2C_2-dimer (**3**), Zn_2C-dimer (**5**), Zn_2C_8-dimer (**6**)**,** Ni_2C_2-dimer (**8**)**,** Ni_2C-dimer (**10**) and $ZnNiC_2$-dimer (**11**) correspond to the structure in Figure 1. From ^{1}H-NMR data, it was found that the longer the linker, the lower the chemical shift of X (Zn_2C-dimer, δ 6.33; Zn_2C_2-dimer, δ 4.78; Ni_2C-dimer, δ 6.02; Ni_2C_2-dimer, δ 4.75). This is due to the electron withdrawing power of the oxygen atom. However, the chemical shift of -CH_2- in X of Zn_2C_8-dimer (**6**) was observed at δ 5.42 ppm which is a lower field than that in Zn_2C_2-dimer. The reason is the ring current effect of phenyl ring of X in Zn_2C_8-dimer (**6**). The chemical shifts of all the phenyl protons under the influence of ring current effect of porphyrin ring such as H_1, H_3 and H_5, were affected by the type of the metal ion in the porphyrin ring as seen in the case of Zn_2C_2-dimer and Ni_2C_2-dimer. The chemical shifts of pyrrole protons in Zn_2C_2-dimer, Zn_2C-dimer and Zn_2C_8-dimer are in the lower field region (δ = 8.85-9.00 ppm) compared to those of Ni_2C_2-dimer and Ni_2C-dimer. The chemical shift difference of H_7 and H_8 could be observed in the NMR spectrum of all dimers except Ni_2C-dimer. It is quite difficult to confidently locate the chemical shift of H_7 and H_8. It can only be presumed that the chemical shift of H_8 should be close to that of H_9 and H_{10}. The pyrrole protons of Ni_2C-dimer are quite similar resulting in the broad singlet at 8.77 ppm. This is quite different when compared to pyrrole protons of other dimers.

For mixed metal dimer, $ZnNiC_2$-dimer, it is clearly shown that the chemical shift of each proton is affected partly by the metal ion bonded to the porphyrin ring. Zinc (II) ion shows a greater electropositive effect than nickel (II) ion and this resulted in the low field shift of the protons of the porphyrin ring. The electropositive power of Zn^{2+} ion on one porphyrin ring does not affect much the proton chemical shift of the Ni^{2+}-porphyrin ring. This is observed from the small difference of chemical shift of each proton on M^{2+}-porphyrin moiety (M = Ni^{2+}, Zn^{2+}) in $ZnNiC_2$-dimer and M_2C_2-dimer.



Scheme 2



Scheme 3

Each proton on M^{2+}-porphyrin unit can keep its own identity.

The ^{1}H spectrum of Zn_2(*meta*)C-dimer (**13**) is very complicated especially in the aromatic region (7-8 ppm). Therefore, to identify proton signals of this compound, various NMR techniques, ^{13}C NMR, 2D COSY, 2D HMQC and 2D HMBC were performed. From HMBC data, the long range coupling between C and H in Zn_2(*meta*)C-dimer (**13**) was found as represented in Figure 2. The chemical shifts of

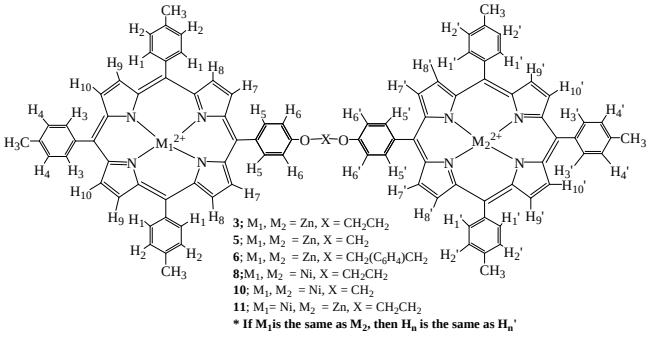


Figure 1. The structure of the dimers

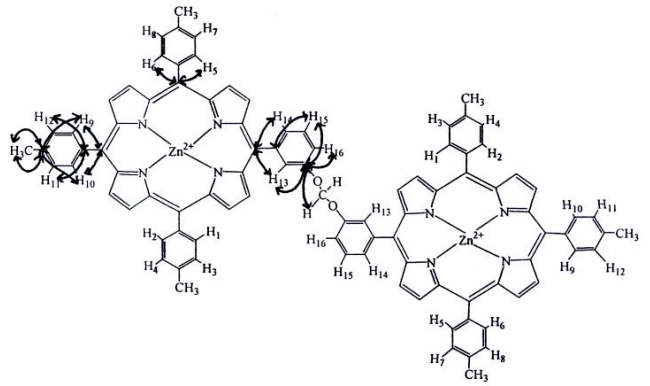


Figure 2. The long range coupling between C and H in Zn_2(*meta*) C-dimer (**13**)

each proton signal of Zn_2(*meta*)C-dimer (**13**) are tabulated in Table 1.

3.4 UV/Visible absorption of the dimers

Porphyrin dimers were characterized by UV/Visible spectroscopy. The UV/Visible absorption maxima and extinction coefficients of all compounds are shown in Table 2. The data in Table 2 indicate that the length of the linker does not affect the absorption patterns of the dimers in the visible region. The type of metal center affects more strongly the position of the Soret bands and also the peak pattern. The Soret bands of Ni_2C_2-dimer and Ni_2C-dimer are blue-shifted compared to those of Zn_2C_2-dimer and Zn_2C-dimer. The Soret band of $ZnNiC_2$-dimer is observed at 424 nm which is red-shifted compared to Ni_2C_2-dimer but blue-shifted compared to Zn_2C_2-dimer, whereas the Q bands show absorption at 530 (sh, log ε = 4.30), 549 (log ε = 4.37) and 595 nm (log ε = 3.88). These signals are the mixed Q bands of Zn-porphyrin and Ni-porphyrin moieties. This clearly shows that the metal ion bonded to the porphyrin ring affects the visible absorption of the porphyrin ring, whereas the position of the linker on the phenyl ring does not affect the visible absorption pattern as observed in Zn_2(*meta*)C-dimer and Zn_2C-dimer.

Table 1. The proton chemical shifts of Zn_2(*meta*)C-dimer (13)

δ (ppm)	Proton Type
2.66	s, 12H, $-CH_3$
2.73	s, 6H, $-CH_3$
6.08	s, 2H, $-OCH_2O-$
7.45-7.52	m, 8H, $2H_3$, $2H_4$, $2H_7$, $2H_8$
7.57	d, 6H, ^3J=7.9 Hz, $2H_{11}$, $2H_{12}$, $2H_{16}$
7.69	t, 2H, ^3J=8.1 Hz, $2H_{15}$
7.94	d, 2H, ^3J=7.2 Hz, $2H_{14}$
8.02-8.14	m, 14H, $2H_1$, $2H_2$, $2H_5$, $2H_6$, $2H_9$, $2H_{10}$, $2H_{13}$
8.93-9.02	m, 16H , $H_{pyrrole}$

Table 2 UV/Visible absorption maxima and extinction coefficients for dimers and trimer

Compound	λ_{max} (log ε) in CH_2Cl_2 (nm)
Zn_2C_2-dimer	425 (5.95), 553 (4.58), 596 (4.14)
Zn_2C-dimer	425 (5.92), 553 (4.57), 595 (4.11)
Zn_2C_8-dimer	425 (5.71), 553 (4.32), 596 (3.88)
Ni_2C_2-dimer	419 (5.70), 529 (4.49)
Ni_2C-dimer	418 (5.62), 529 (4.48)
$ZnNiC_2$-dimer	424 (5.78), 530(sh, 4.30), 549 (4.37), 595 (3.88)
Zn_2(*meta*)C-dimer	424(5.90), 553(4.58), 595(4.08)

4. Conclusions

The ether-linked porphyrin dimers were successfully prepared by coupling reaction between the suitable porphyrin precursor and the linker in the presence of base. The base used in this work was potassium carbonate and the linking agents were 1, 2- ditosyloxyethane, dibromomethane and α,α′-dichloro-*p*-xylene. The bromide acts as a good leaving group for this kind of coupling reaction. The length of the linker does not strongly affect the absorption maxima and the absorption ability of the dimer. The NMR data indicate that the proton signals of the porphyrin moiety are not affected by the length of the linker.

The mixed metal porphyrin dimer, $ZnNiC_2$-dimer (**11**) was also synthesized. The Soret band of this dimer is red-shifted compared to Ni_2C_2-dimer but blue-shifted compared to Zn_2C_2-dimer. The NMR data show that the electropositive power of Zn^{2+} ion on one porphyrin ring does not have much influence on the proton chemical shift of the Ni^{2+}-porphyrin ring. Each proton on M^{2+}-porphyrin unit can keep its own identity.

The position of the linker on the phenyl ring of porphyrin does not affect the visible absorption pattern or the proton chemical shifts of the porphyrin core as found in the case of Zn_2(*meta*)C-dimer (**13**) (compared with the data obtained for Zn_2C_2-dimer (**3**)).

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