CHAPTER II

EXPERIMENTAL

2.1 Materials and Chemicals

All reactions were performed in oven-dried glassware. The progress of the reactions and the isolation of products by column chromatography were monitored by thin layer chromatography (TLC) performed on Merck D.C. silica gel 60 F_{254} 0.2 mm precoated aluminium sheets and visualized using UV light (254 nm) or iodine. Column chromatography was performed on Merck 70-230 mesh ASTM silica gel, while flash column chromatography was performed on Merck 230-400 mesh ASTM silica gel.

Unless otherwise specified, solvents for reaction set ups including chloroform, dichloromethane, *N*,*N*-dimethylformamide (DMF), acetone, methanol, benzene, diethyl ether, and tetrahydrofuran (THF) were AR grade. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl under nitrogen atmosphere prior to use. Solvents for chromatographic purification including hexanes, dichloromethane, ethyl acetate, and methanol were commercial grade and were distilled before use.

All chemicals used in the reactions were reagent grade and were used as received without further purification. They were purchased from the following vendors:

- Aldrich Chemical Co., Inc. (Milwaukee, Wisconsin, USA) : phenylacetylene
- Carlo Erba Reagenti (Milan, Italy) : diethylamine
- Fluka Chemical Corp. (Buchs, Switzerland) : anhydrous magnesium sulfate, bis(triphenylphosphine)palladium(II) dichloride, boron trifluoride diethyl etherate, 4-bromobenzaldehyde, 4-bromobenzonitrile, 4-bromo-*N*,*N*-dimethylaniline, 4-bromonitrobenzene, *N*-bromosuccinimide (NBS), celite® 545, copper(I) iodide, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), *N*,*N*-dimethylformamide (DMF), heptaldehyde, 4-iodobenzoic acid, manganese(II) acetate tetrahydrate, mesitaldehyde, piperidine, pyrrole, tetrabutylammonium fluoride solution (TBAF; 1.0 M in THF), tetrakis(triphenylphosphine)palladium(0), triethylamine, trifluoroacetic acid

(TFA), trimethylsilylacetylene, triphenylphosphine, zinc(II) acetate dihydrate

- J.T. Baker Chemical Co. (Deventer, The Netherlands) : 37% formaldehyde solution
- Labscan Asia Co., Ltd. (Bangkok, Thailand) : chloroform, dichloromethane, tetrahydrofuran (THF)
- Merck Co., Ltd. (Darmstadt, Germany) : acetone, benzene, diethyl ether, diisopropylamine, methanol, pyridine, sodium hydroxide
- Riedel-de Haën AG (Seelze, Germany) : paraformaldehyde, potassium carbonate
- Sigma-Aldrich Chemical Co., Inc. (Steinheim, Germany) : magnesium bromide
- Sigma Chemical Co., Inc. (St. Louis, Missouri, USA) : dithranol
- Suksapan Panit (Bangkok, Thailand) : sodium hydrogen carbonate
- Wilmad LabGlass SP Industries, Inc. (New Jersey, USA) : deuterated chloroform, hexadeuterated dimethylsulfoxide

2.2 Instruments and Equipments

The weight of all chemical substances was determined on a Mettler Toledo AB204-S or a Precisa XT 220A electrical balance. Evaporation of solvents was carried out on a Büchi Rotavapor R-200 equipped with a Büchi Heating Bath B-490 and a Büchi Recirculating Chiller B-740.

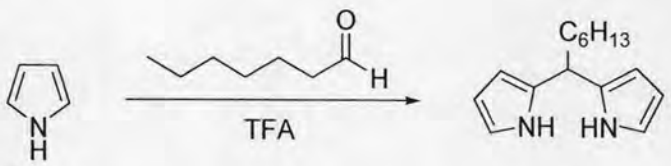
All reported proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury plus 400 operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C nuclei. Unless otherwise stated, the spectra were taken in deuterated chloroform ($CDCl_3$) or hexadeuterated dimethylsulfoxide (DMSO-d_6). The chemical shifts (δ) are reported in parts per million (ppm) and are relative to that of tetramethylsilane (TMS) or relative to the residual protonated signal of deuterated solvents as a reference. Coupling constants (J) are proton-proton coupling unless otherwise noted and were reported in hertz (Hz). Multiplicities were abbreviated as followed: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet and br = broad.

Mass spectra were carried out using Electrospray Ionization Mass Spectrometry (ESI-MS) by a Waters Micromass Quattro micro API Mass Spectrometer with an electrospray ion source, and ethyl acetate was used as a solvent. Mass spectroscopic data of porphyrin derivatives were obtained on a Bruker Microflex Matrix Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometer (MALDI-TOF-MS). The instrument was equipped with a nitrogen laser to desorb and ionize the samples. A stainless steel target was used as the substrate on which the samples were deposited. Samples were prepared as solutions in micromolar concentration in THF, and dithranol was utilized as the matrix.

UV-visible absorption spectra were recorded on a Varian Cary 100 Bio UV-Visible Spectrophotometer. Both the deuterium and the visible lamps were used as light sources in this instrument. Fluorescence emission spectra were acquired using a Varian Cary Eclipse Fluorescence Spectrophotometer. The light source is a pulsed xenon lamp and the detector is a photomultiplier tube.

2.3 Synthesis of Dipyrromethane Derivatives

2.3.1 Synthesis of 5-Hexyldipyrromethane (1) [53]



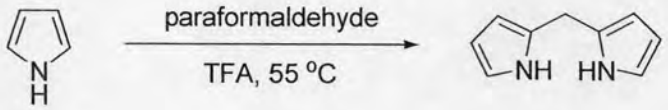
1

Pyrrole (25.0 mL, 361.12 mmol) and heptaldehyde (2.00 mL, 14.33 mmol) were added to a dried single-necked round-bottomed flask containing a magnetic stir bar. The solution was purged with a stream of N_2 for 10 min. TFA (214 μL, 2.79 mmol) was added, and the mixture was stirred under N_2 at room temperature for 20 min. The reaction was then quenched with 0.1 M NaOH (15 mL) and stirred for 5 min. After that, the reaction mixture was extracted with ethyl acetate. The organic phase was washed with water and dried over anhydrous $MgSO_4$. The drying agent was filtered off and the solvent was then removed using a rotary evaporator under vacuum to afford dark brown oil. The crude product was purified by flash column chromatography (230-400 mesh silica, hexanes) to give 5-hexyldipyrromethane (**1**) (1.443 g, 44%) as a viscous brown liquid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.86 (3H, t, J = 6.7 Hz, $CHCH_2(CH_2)_4CH_3$), 1.16-1.38 (8H, m, $CHCH_2(CH_2)_4CH_3$), 1.91-1.97 (2H, m, $CHCH_2(CH_2)_4CH_3$), 3.98 (1H, t, J = 7.6 Hz, $CHCH_2(CH_2)_4CH_3$), 6.06 (2H, d, J = 0.7 Hz, pyrrole), 6.14 (2H, dd, J = 2.6, 5.3 Hz, pyrrole), 6.65 (2H, d, J = 1.4 Hz, pyrrole), 7.81 (2H, s, NH).

2.3.2 Synthesis of Dipyrromethane (2)

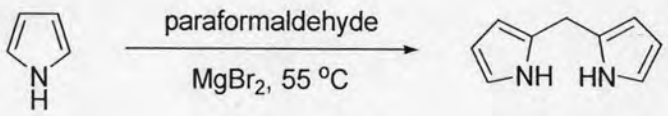
2.3.2.1 Synthesis of Dipyrromethane Using TFA as Catalyst [53]



2

A suspension of paraformaldehyde (0.436 g, 14.52 mmol) in pyrrole (25.0 mL, 361.12 mmol) was placed in a dried two-necked round-bottomed flask equipped with a water condenser in the reflux position. The reaction mixture was purged with a stream of N_2 for 10 min. The solution was heated to 55 °C for about 20 min under N_2, and then the heat source was removed. TFA (215 μL, 2.81 mmol) was added, and the mixture was stirred at room temperature for 10 min. The reaction was then quenched with triethylamine (0.35 mL) and stirred for 10 min. The mixture was filtered, and the filtrate was concentrated using a rotary evaporator under vacuum. Pyrrole was recovered as dark brown oil. The crude oil was purified by flash column chromatography (230-400 mesh silica, hexanes:CH_2Cl_2 = 9:1) to give dipyrromethane (**2**) (0.407 g, 19%) as a black solid and small colorless clear crystals.

2.3.2.2 Synthesis of Dipyrromethane Using $MgBr_2$ as Catalyst



2

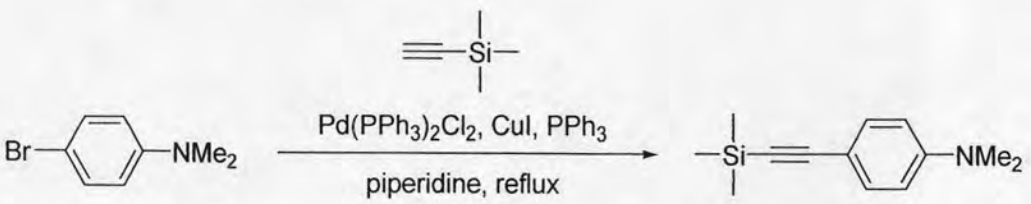
A suspension of paraformaldehyde (0.916 g, 30.50 mmol) in pyrrole (52.0 mL, 751.13 mmol) was placed in a dried two-necked round-bottomed flask equipped with a water condenser in the reflux position. The reaction mixture was purged with a

stream of N_2 for 10 min. The solution was heated to 55 °C for about 10 min under N_2. $MgBr_2$ (0.556 g, 3.02 mmol) was then added, and the mixture was stirred at 55 °C for 3 h. The heat source was removed, and K_2CO_3 (2.061 g, 14.91 mmol) was added to quench the reaction. The mixture was stirred for 1.5 h and then filtered. The filtrate was concentrated using a rotary evaporator under vacuum, and pyrrole was recovered. The crude viscous residue was left in the evaporation flask and was then triturated with hexanes to remove traces of pyrrole in the following manner three times: hexanes (20 mL) were added, and the volatile components were removed under vacuum. The crude product obtained after removing pyrrole was purified by flash column chromatography (230-400 mesh silica, hexanes:CH_2Cl_2:EtOAc = 7:2:1) to give dipyrromethane (**2**) (1.583 g, 36%) as a dark brown solid and small colorless crystals.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.95 (2H, s, C*H*$_2$), 6.06 (2H, s, pyrrole), 6.17 (2H, dd, *J* = 2.8, 5.7 Hz, pyrrole), 6.62 (2H, dd, *J* = 2.5, 4.0 Hz, pyrrole), 7.70 (2H, s, N*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 129.1, 117.3, 108.2, 106.4, 26.3; ESI-MS: *m/z* $[M]^+$ Calcd for $C_9H_{10}N_2$: 146.084, Found: 148.989.

2.4 Synthesis of Ethyne Derivatives

2.4.1 Synthesis of 1-(4-*N*,*N*-Dimethylaminophenyl)-2-trimethylsilylethyne (DMAP-TMSE, 3) [54]



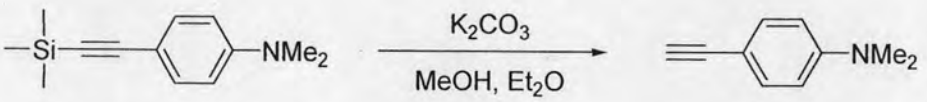
3

4-Bromo-*N*,*N*-dimethylaniline (1.407 g, 7.03 mmol), $Pd(PPh_3)_2Cl_2$ (0.028 g, 0.04 mmol), CuI (0.025 g, 0.13 mmol), PPh_3 (0.092 g, 0.35 mmol), and trimethylsilylacetylene (2.80 mL, 20.21 mmol) were dissolved in piperidine (25 mL). The reaction mixture was heated at reflux temperature (130-140 °C) under N_2 for 12 h, and then stirred overnight at room temperature. The mixture was concentrated under vacuum and saturated $NaHCO_3$ (20 mL) was added. The product was extracted with hexanes several times. The combined hexanes extracts were washed with water

and brine, then dried over anhydrous $MgSO_4$, and concentrated under vacuum. The desired product was isolated by column chromatography (70-230 mesh silica, hexanes) to give 1-(4-*N*,*N*-dimethylaminophenyl)-2-trimethylsilylethyne (**3**) (0.953 g, 62%) as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.25 (9H, s, Si(CH_3)$_3$), 2.97 (6H, s, N(CH_3)$_2$), 6.61 (2H, d, J = 8.6 Hz, Ar), 7.35 (2H, d, J = 8.9 Hz, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 0.2, 40.2, 91.2, 106.5, 109.9, 111.6, 133.1, 150.0.

2.4.2 Synthesis of 4-*N*,*N*-Dimethylaminophenylethyne (DMAPE, 4)

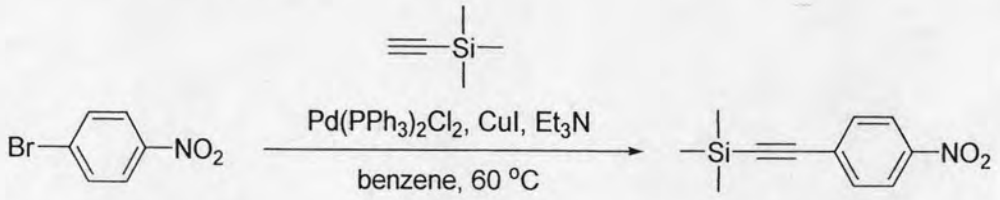


3 **4**

A mixture of 1-(4-*N*,*N*-dimethylaminophenyl)-2-trimethylsilylethyne (**3**) (0.436 g, 2.01 mmol) and K_2CO_3 (2.772 g, 20.06 mmol) in MeOH-diethyl ether (30 mL-25 mL) was stirred at room temperature for 5 h. After the reaction was complete, the reaction mixture was poured into water and extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum to give 4-*N*,*N*-dimethylaminophenylethyne (**4**) (0.250 g, 86%) as a brown solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.97 (7H, s, N(CH_3)$_2$ and C*H*), 6.62 (2H, d, J = 8.9 Hz, Ar), 7.37 (2H, d, J = 8.9 Hz, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 40.2, 74.8, 84.9, 108.7, 111.7, 133.2, 150.4.

2.4.3 Synthesis of 1-(4-Nitrophenyl)-2-trimethylsilylethyne (NP-TMSE, 5) [55]

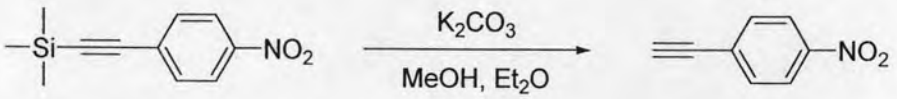


5

4-Bromonitrobenzene (1.010 g, 5.00 mmol), $Pd(PPh_3)_2Cl_2$ (0.135 g, 0.19 mmol), CuI (0.020 g, 0.11 mmol), and trimethylsilylacetylene (0.80 mL, 5.77 mmol) were dissolved in triethylamine-benzene (20 mL-20 mL). The reaction mixture was stirred at 60 °C under N_2 for 24 h. After the reaction was complete, the mixture was poured into water and extracted with diethyl ether. The organic layer was washed with brine, then dried over anhydrous $MgSO_4$, and concentrated under vacuum. The desired product was isolated by column chromatography (70-230 mesh silica, hexanes) to give 1-(4-nitrophenyl)-2-trimethylsilylethyne (**5**) (0.922 g, 84%) as a pale yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.27 (9H, s, Si(CH_3)$_3$), 7.59 (2H, d, J = 8.8 Hz, Ar), 8.17 (2H, d, J = 8.8 Hz, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ -0.3, 100.6, 102.7, 123.5, 130.0, 132.7, 147.1.

2.4.4 Synthesis of 4-Nitrophenylethyne (NPE, 6)

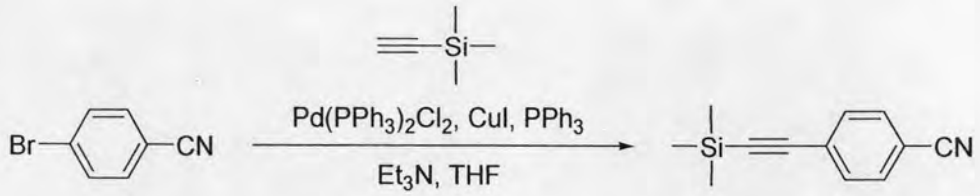


5 **6**

A mixture of 1-(4-nitrophenyl)-2-trimethylsilylethyne (**5**) (0.661 g, 3.01 mmol) and K_2CO_3 (2.096 g, 15.17 mmol) in MeOH-diethyl ether (30 mL-25 mL) was stirred at room temperature for 5 h. After the reaction was complete, the reaction mixture was poured into water and extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum to give 4-nitrophenylethyne (**6**) (0.414 g, 93%) as yellow crystals.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.36 (1H, s, C*H*), 7.64 (2H, d, J = 8.6 Hz, Ar), 8.20 (2H, d, J = 8.6 Hz, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 81.6, 82.3, 123.6, 128.9, 133.0.

2.4.5 Synthesis of 1-(4-Cyanophenyl)-2-trimethylsilylethyne (CP-TMSE, 7) [56]

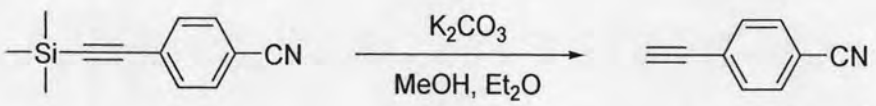


7

4-Bromobenzonitrile (0.920 g, 5.05 mmol), $Pd(PPh_3)_2Cl_2$ (0.163 g, 0.23 mmol), CuI (0.026 g, 0.14 mmol), PPh_3 (0.067 g, 0.26 mmol), triethylamine (1.00 mL, 7.17 mmol), and trimethylsilylacetylene (1.00 mL, 7.22 mmol) were dissolved in THF (15 mL). The reaction mixture was stirred at room temperature under N_2 for 19 h. After the reaction was complete, the mixture was concentrated under vacuum, and then hexanes were added. The mixture was filtered over Celite, and the filtrate was washed with water. The organic layer was dried over anhydrous $MgSO_4$, and concentrated under vacuum. The desired product was isolated by column chromatography (70-230 mesh silica, hexanes) to give 1-(4-cyanophenyl)-2-trimethylsilylethyne (**7**) (0.722 g, 72%) as a pale yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.26 (9H, s, $Si(CH_3)_3$), 7.53 (2H, d, J = 7.5 Hz, Ar), 7.59 (2H, d, J = 8.0 Hz, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ -0.3, 99.5, 102.9, 111.7, 118.4, 128.0, 131.9, 132.4.

2.4.6 Synthesis of 4-Cyanophenylethyne (CPE, 8)



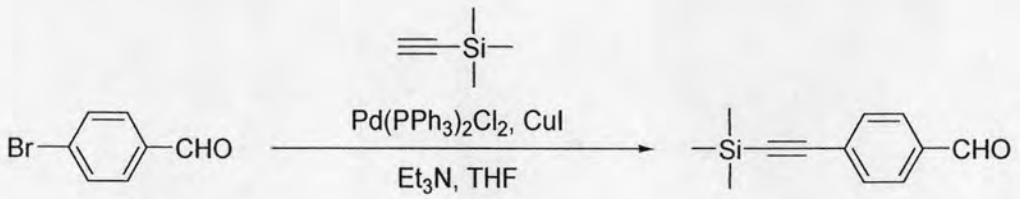
7 **8**

A mixture of 1-(4-cyanophenyl)-2-trimethylsilylethyne (**7**) (0.599 g, 3.01 mmol) and K_2CO_3 (2.093 g, 15.14 mmol) in MeOH-diethyl ether (30 mL-25 mL) was stirred at room temperature for 5 h. After the reaction was complete, the reaction mixture was poured into water and extracted with diethyl ether. The organic layer was

dried over anhydrous $MgSO_4$ and concentrated under vacuum to give 4-cyanophenylethyne (**8**) (0.379 g, 99%) as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.30 (1H, s, C*H*), 7.57 (2H, d, *J* = 8.2 Hz, Ar), 7.62 (2H, d, *J* = 7.9 Hz, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 79.3, 81.5, 112.3, 118.3, 126.7, 127.0, 132.0, 132.7.

2.4.7 Synthesis of 1-(4-Formylphenyl)-2-trimethylsilylethyne (FP-TMSE, 9)

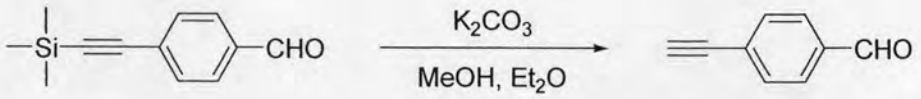


9

4-Bromobenzaldehyde (0.561 g, 3.03 mmol), $Pd(PPh_3)_2Cl_2$ (0.066 g, 0.09 mmol), CuI (0.010 g, 0.05 mmol), triethylamine (0.60 mL, 4.30 mmol), and trimethylsilylacetylene (0.60 mL, 4.33 mmol) were dissolved in THF (10 mL). The reaction mixture was stirred at room temperature under N_2 for 20 h. After the reaction was complete, the mixture was concentrated under vacuum, and then hexanes were added. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The desired product was isolated by column chromatography (70-230 mesh silica, hexanes:CH_2Cl_2 = 1:1) to give 1-(4-formylphenyl)-2-trimethylsilylethyne (**9**) (0.362 g, 59%) as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.30 (9H, s, Si(C*H*$_3$)$_3$), 7.64 (2H, d, *J* = 8.3 Hz, Ar), 7.85 (2H, d, *J* = 8.2 Hz, Ar), 10.03 (1H, s, C*H*O); ^{13}C NMR ($CDCl_3$, 100 MHz): δ -0.2, 99.0, 103.8, 129.4, 130.0, 132.0, 132.5, 191.5; ESI-MS: *m/z* $[M]^+$ Calcd for $C_{12}H_{14}OSi$: 202.081, Found: 203.126.

2.4.8 Synthesis of 4-Formylphenylethyne (FPE, 10)

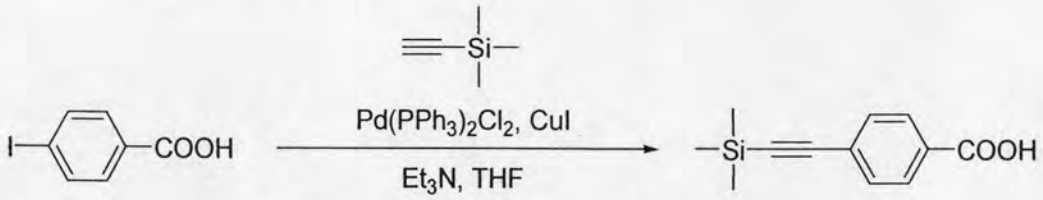


9 **10**

A mixture of 1-(4-formylphenyl)-2-trimethylsilylethyne (**9**) (0.304 g, 1.50 mmol) and K_2CO_3 (2.088 g, 15.11 mmol) in MeOH-diethyl ether (20 mL-15 mL) was stirred at room temperature for 5 h. After the reaction was complete, the reaction mixture was poured into water and extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum to give 4-formylphenylethyne (**10**) (0.074 g, 38%) as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.30 (1H, s, C*H*), 7.64 (2H, d, J = 8.2 Hz, Ar), 7.84 (2H, d, J = 8.3 Hz, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 81.1, 82.6, 128.3, 129.5, 132.7, 135.9, 191.4; ESI-MS: *m/z* $[M]^+$ Calcd for C_9H_6O: 130.042, Found: 130.019.

2.4.9 Synthesis of 1-(4-Carboxyphenyl)-2-trimethylsilylethyne (CarP-TMSE, 11)

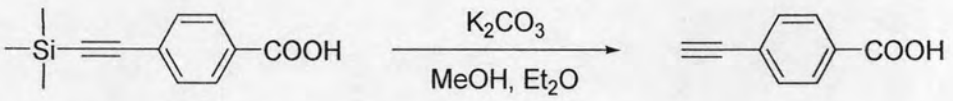


11

4-Iodobenzoic acid (1.004 g, 4.05 mmol), $Pd(PPh_3)_2Cl_2$ (0.103 g, 0.15 mmol), CuI (0.023 g, 0.12 mmol), triethylamine (1.60 mL, 11.48 mmol), and trimethylsilylacetylene (0.80 mL, 5.77 mmol) were dissolved in THF (10 mL). The reaction mixture was stirred at room temperature under N_2 for 22 h. After the reaction was complete, 10% HCl solution (10 mL) and ethyl acetate was added to extract the product. The organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The desired product was isolated by column chromatography (70-230 mesh silica, hexanes:EtOAc = 2:1) to give 1-(4-carboxyphenyl)-2-trimethylsilylethyne (**11**) (0.605 g, 69%) as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.27 (9H, s, Si(CH_3)$_3$), 7.55 (2H, d, J = 8.3 Hz, Ar), 8.05 (2H, d, J = 8.3 Hz, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ -0.2, 98.4, 103.9, 128.7, 130.0, 132.0, 171.5; ESI-MS: *m/z* $[M]^+$ Calcd for $C_{12}H_{14}O_2Si$: 218.076, Found: 217.144.

2.4.10 Synthesis of 4-Carboxyphenylethyne (CarPE, 12)



11 **12**

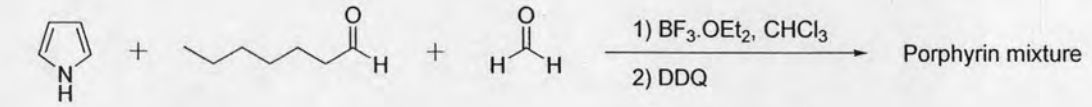
A mixture of 1-(4-carboxyphenyl)-2-trimethylsilylethyne (**11**) (0.442 g, 2.02 mmol) and K_2CO_3 (2.803 g, 20.28 mmol) in MeOH-diethyl ether (20 mL-15 mL) was stirred at room temperature for 5 h. After the reaction was complete, 10% HCl solution (30 mL) was added to the reaction mixture. The mixture was poured into water and extracted with diethyl ether. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum to give 4-carboxyphenylethyne (**12**) (0.246 g, 83%) as a brown solid.

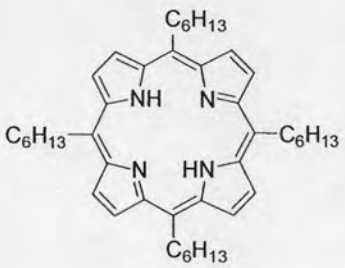
^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.26 (1H, s, C*H*), 7.59 (2H, d, J = 8.4 Hz, Ar), 8.06 (2H, d, J = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 80.5, 82.7, 130.0, 132.2; ESI-MS: *m/z* $[M]^+$ Calcd for $C_9H_6O_2$: 146.037, Found: 147.018.

2.5 Synthesis of *meso*-Dihexylporphyrin Derivatives

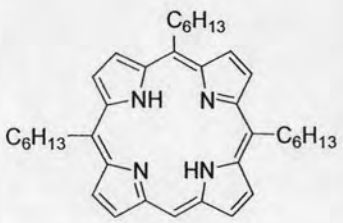
2.5.1 Synthesis of 5,15-Dihexylporphyrin (DHP, 13)

2.5.1.1 Attempts to synthesize DHP *via* Monopyrrole Tetramerization

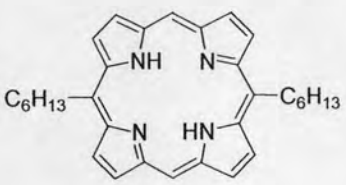




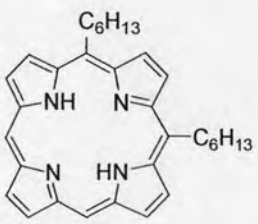
5,10,15,20-THP



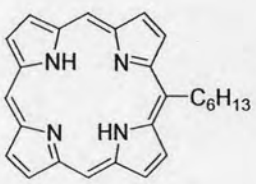
5,10,15-THP



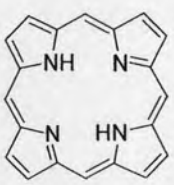
5,15-DHP



5,10-DHP



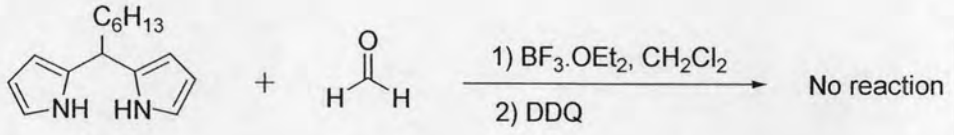
5-HP



Porphine

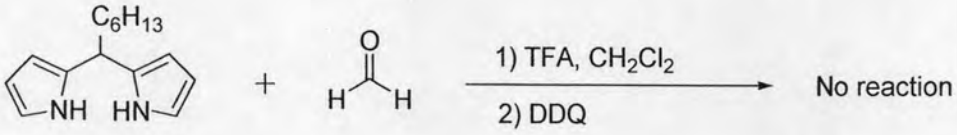
A solution of heptaldehyde (0.42 mL, 3.01 mmol), 37% formaldehyde (0.08 mL, 1.07 mmol), and pyrrole (25.0 mL, 4.04 mmol) in $CHCl_3$ (60 mL) was treated with $BF_3.OEt_2$ (0.13 mL, 1.03 mmol). The mixture was stirred at room temperature for 3 h. Subsequently, a solution of DDQ (0.454 g, 2.00 mmol) in THF (5 mL) was added, and stirred for 2 h. The mixture was concentrated under vacuum and passed over a short silica column using CH_2Cl_2 as eluent. Fractions containing porphyrins were concentrated and separated by flash column chromatography (230-400 mesh silica, hexanes). However, the desired product 5,15-dihexylporphyrin cannot be completely separated from other components of product mixture.

2.5.1.2 Attempts to synthesize DHP from 5-Hexyldipyrromethane



1

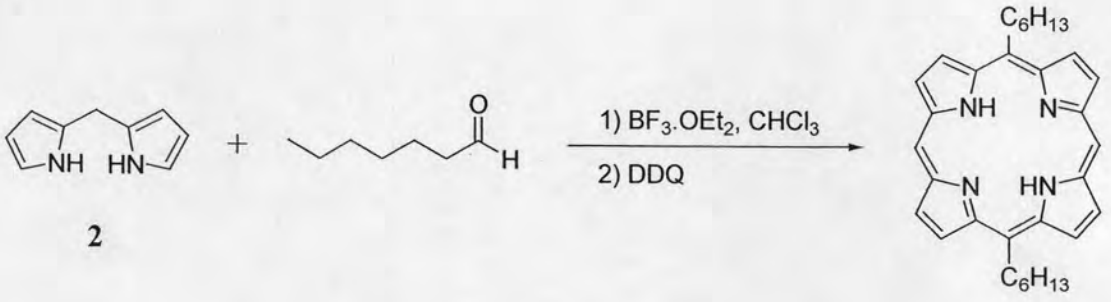
Method I : A solution of 5-hexyldipyrromethane (**1**) (0.464 g, 2.01 mmol), and formaldehyde 37% (0.20 mL, 2.67 mmol) in CH_2Cl_2 (80 mL) was treated with $BF_3.OEt_2$ (0.13 mL, 1.03 mmol). The mixture was stirred at room temperature for 2 h. Then, DDQ (0.488 g, 2.15 mmol) was added, and stirred for 1.5 h. The reaction was quenched by adding triethylamine (0.14 mL, 1.01 mmol) and stirred for 10 min. The mixture was concentrated under vacuum and passed over a short silica column using CH_2Cl_2 as eluent. After removal of solvent, the porphyrin product was not obtained.



1

Method II : A solution of 5-hexyldipyrromethane (**1**) (0.461 g, 2.00 mmol), and formaldehyde 37% (0.20 mL, 2.67 mmol) in CH_2Cl_2 (80 mL) was treated with TFA (0.31 mL, 4.05 mmol). The mixture was stirred at room temperature for 2 h. Then, DDQ (0.454 g, 2.00 mmol) was added, and stirred for 1.5 h. The reaction was quenched by adding triethylamine (0.14 mL, 3.02 mmol) and stirred for 20 min. The mixture was concentrated under vacuum and passed over a short silica column using CH_2Cl_2 as eluent. After removal of solvent, the porphyrin product was not obtained.

2.5.1.3 Synthesis of DHP from Dipyrromethane

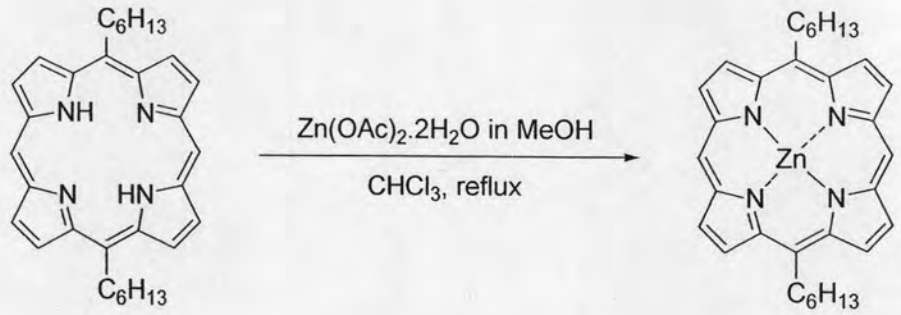


2 **13**

A solution of dipyrromethane (**2**) (0.296 g, 2.02 mmol), and heptaldehyde (0.28 mL, 2.01 mmol) in $CHCl_3$ (100 mL) was treated with $BF_3.OEt_2$ (0.13 mL, 1.03 mmol). The mixture was stirred at room temperature for 1 h. Then, DDQ (0.500 g, 2.19 mmol) was added, and stirred for 1 h. The reaction was quenched by adding triethylamine (0.14 mL, 3.02 mmol) and stirred for 10 min. The mixture was concentrated under vacuum and passed over a short silica column using CH_2Cl_2 as eluent. Fractions containing porphyrin were concentrated under vacuum to obtain 5,15-dihexylporphyrin (DHP, **13**) (0.112 g, 23%) as a dark purple solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ -2.94 (2H, s, NH), 0.93 (6H, t, J = 7.2 Hz, $(CH_2)_5CH_3$), 1.35-1.44 (4H, m, $(CH_2)_4CH_2CH_3$), 1.49-1.56 (4H, m, $(CH_2)_3CH_2$ CH_2CH_3), 1.78-1.85 (4H, m, $(CH_2)_2CH_2(CH_2)_2CH_3$), 2.51-2.58 (4H, m, CH_2CH_2 $(CH_2)_3CH_3$), 5.00 (4H, t, J = 7.9 Hz, $CH_2(CH_2)_4CH_3$), 9.40 (4H, d, J = 4.4 Hz, β-H), 9.57 (4H, d, J = 4.4 Hz, β-H), 10.16 (2H, s, *meso*-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{32}H_{38}N_4$: 478.310, Found: 479.400; UV-visible (THF, nm): λ_{max} (log ε) 402 (5.33), 502 (4.08), 533 (3.48), 578 (3.55), and 634 (3.04); Fluorescence (THF, nm): λ_{max} 637 and 704.

2.5.2 Synthesis of (5,15-Dihexylporphyrinato)zinc(II) (Zn-DHP, 14)

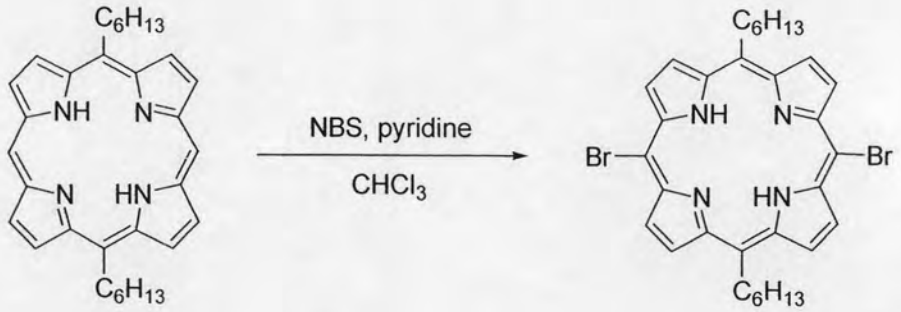


13 **14**

A saturated solution of $Zn(OAc)_2.2H_2O$ (0.089 g, 0.41 mmol) in MeOH (2 mL) was added to a boiling solution of 5,15-dihexylporphyrin (DHP, **13**) (0.048 g, 0.10 mmol) in $CHCl_3$ (20 mL). The reaction mixture was refluxed for 20 min, during which time the mixture became bright red. Then, the mixture was cooled down, and extracted three times with distilled water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum to obtain (5,15-dihexylporphyrinato)zinc(II) (Zn-DHP, **14**) (0.052 g, 96%) as a red solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.96 (6H, t, J = 7.3 Hz, $(CH_2)_5CH_3$), 1.36-1.48 (4H, m, $(CH_2)_4CH_2CH_3$), 1.52-1.58 (4H, m, $(CH_2)_3CH_2CH_2CH_3$), 1.84-1.91 (4H, m, $(CH_2)_2CH_2(CH_2)_2CH_3$), 2.54-2.62 (4H, m, $CH_2CH_2(CH_2)_3CH_3$), 5.03 (4H, t, J = 8.2 Hz, $CH_2(CH_2)_4CH_3$), 9.40 (4H, d, J = 4.5 Hz, β-H), 9.65 (4H, d, J = 4.5 Hz, β-H), 10.09 (2H, s, *meso*-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{32}H_{36}N_4Zn$: 540.223, Found: 540.359; UV-visible (THF, nm): λ_{max} (log ε) 410 (5.42), 546 (4.07), and 578 (3.20); Fluorescence (THF, nm): λ_{max} 591 and 638.

2.5.3 Synthesis of 5,15-Dibromo-10,20-dihexylporphyrin (Br_2DHP, 15)

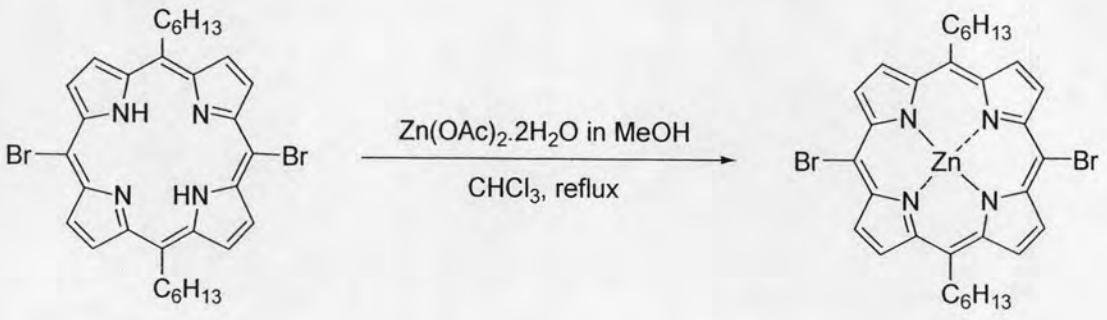


13 **15**

A solution of 5,15-dihexylporphyrin (DHP, **13**) (0.048 g, 0.10 mmol) in $CHCl_3$ (40 mL) was treated with NBS (0.036 g, 0.20 mmol) and pyridine (0.1 mL). The reaction mixture was stirred at room temperature for 15 min. The reaction was quenched by an addition of acetone (15 mL), stirred for 5 min and extracted three times with distilled water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum to obtain 5,15-dibromo-10,20-dihexylporphyrin (Br_2DHP, **15**) (0.050 g, 79%) as a purple solid.

^1H NMR ($CDCl_3$, 400 MHz): δ -2.67 (2H, s, NH), 0.93 (6H, t, J = 7.2 Hz, $(CH_2)_5CH_3$), 1.36-1.43 (4H, m, $(CH_2)_4CH_2CH_3$), 1.47-1.54 (4H, m, $(CH_2)_3CH_2$ CH_2CH_3), 1.74-1.82 (4H, m, $(CH_2)_2CH_2(CH_2)_2CH_3$), 2.43-2.51 (4H, m, CH_2CH_2 $(CH_2)_3CH_3$), 4.87 (4H, t, J = 8.2 Hz, $CH_2(CH_2)_4CH_3$), 9.42 (4H, d, J = 4.8 Hz, β-H), 9.68 (4H, d, J = 4.9 Hz, β-H); MALDI-TOF-MS (dithranol): m/z $[M]^+$ Calcd for $C_{32}H_{36}N_4Br_2$: 634.131, Found: 636.555; UV-visible (THF, nm): λ_{max} (log ε) 418 (5.44), 522 (4.16), 555 (4.11), 605 (3.62), and 665 (3.93); Fluorescence (THF, nm): no emission.

2.5.4 Synthesis of (5,15-Dibromo-10,20-dihexylporphyrinato)zinc(II) (Zn-Br_2DHP, 16)



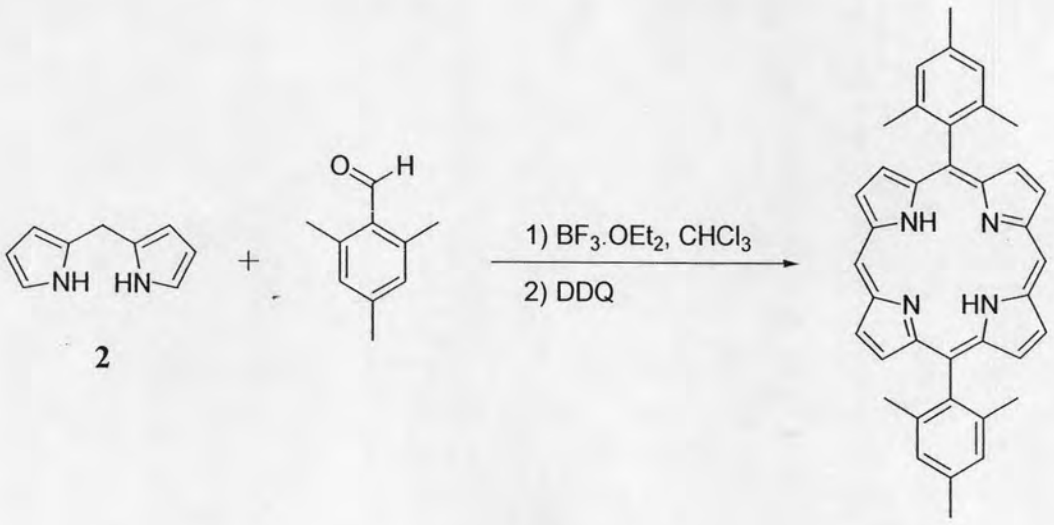
15 **16**

A saturated solution of $Zn(OAc)_2.2H_2O$ (0.031 g, 0.14 mmol) in MeOH (2 mL) was added to a boiling solution of 5,15-dibromo-10,20-dihexylporphyrin (Br_2DHP, **15**) (0.006 g, 0.01 mmol) in $CHCl_3$ (15 mL). The reaction mixture was refluxed for 1 h, during which time the mixture became bright green-blue. Then, the mixture was cooled down, and MeOH (20 mL) was added to precipitate the product. The amount of solvent was reduced under vacuum to a small volume and then the precipitate was filtered off. The solid was washed with MeOH to obtain (5,15-dibromo-10,20-dihexylporphyrinato)zinc(II) (Zn-Br_2DHP, **16**) (0.005 g, 71%) as a dark brown solid.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.89 (6H, t, J = 7.3 Hz, $(CH_2)_5CH_3$), 1.30-1.39 (4H, m, $(CH_2)_4CH_2CH_3$), 1.43-1.50 (4H, m, $(CH_2)_3CH_2CH_2CH_3$), 1.73-1.80 (4H, m, $(CH_2)_2CH_2(CH_2)_2CH_3$), 2.36-2.43 (4H, m, $CH_2CH_2(CH_2)_3CH_3$), 4.96 (4H, t, J = 8.0 Hz, $CH_2(CH_2)_4CH_3$), 9.64 (4H, d, J = 4.8 Hz, β-H), 9.67 (4H, d, J = 4.8 Hz, β-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{32}H_{34}N_4Br_2Zn$: 696.044, Found: 698.623; UV-visible (THF, nm): λ_{max} (log ε) 427 (5.40), 568 (3.94), and 614 (3.90); Fluorescence (THF, nm): no emission.

2.6 Synthesis of *meso*-Dimesitylporphyrin Derivatives

2.6.1 Synthesis of 5,15-Dimesitylporphyrin (DMP, 17)

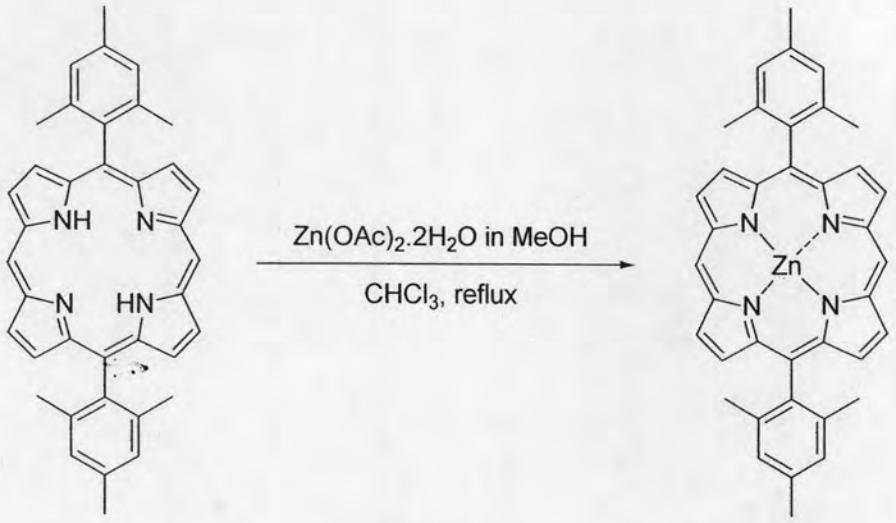


2 **17**

A solution of dipyrromethane (**2**) (0.177 g, 1.21 mmol), and mesitaldehyde (0.17 mL, 1.17 mmol) in $CHCl_3$ (40 mL) was treated with $BF_3.OEt_2$ (0.08 mL, 0.63 mmol). The mixture was stirred at room temperature for 1 h. Then, DDQ (0.342 g, 1.50 mmol) was added, and stirred for 45 min. The reaction was quenched by adding triethylamine (0.08 mL, 0.57 mmol) and stirred for 10 min. The mixture was filtered through silica using CH_2Cl_2 as eluent. Fractions containing porphyrin were concentrated under vacuum to give 5,15-dimesitylporphyrin (DMP, **17**) (0.127 g, 40%) as a dark purple solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ -3.06 (2H, s, NH), 1.85 (12H, s, Ar-CH_3), 2.67 (6H, s, Ar-CH_3), 7.33 (4H, s, Ar), 8.89 (4H, d, J = 4.5 Hz, β-H), 9.33 (4H, d, J = 4.5 Hz, β-H), 10.23 (2H, s, *meso*-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{38}H_{34}N_4$: 546.278, Found: 546.392; UV-visible (THF, nm): λ_{max} (log ε) 404 (5.41), 500 (4.20), 531 (3.62), 575 (3.72), and 630 (3.14); Fluorescence (THF, nm): λ_{max} 633 and 700.

2.6.2 Synthesis of (5,15-Dimesitylporphyrinato)zinc(II) (Zn-DMP, 18)

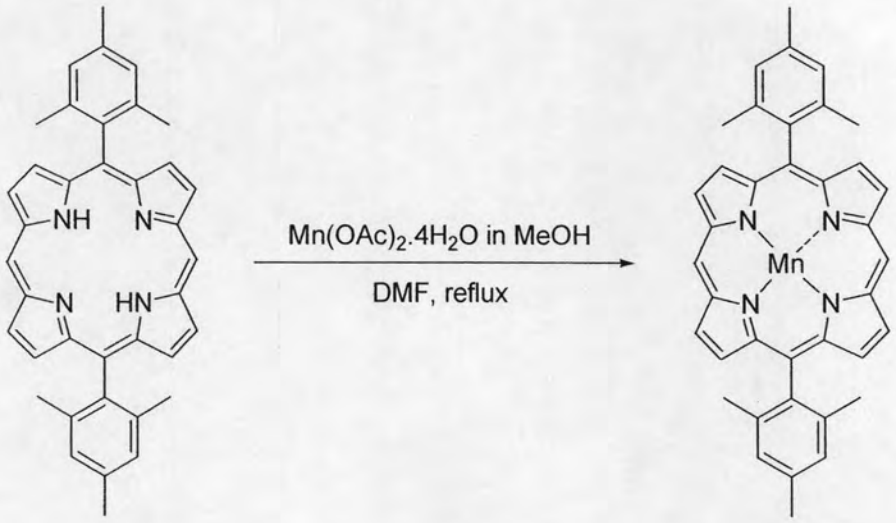


17 **18**

A saturated solution of $Zn(OAc)_2.2H_2O$ (0.225 g, 1.03 mmol) in MeOH (2 mL) was added to a boiling solution of 5,15-dimesitylporphyrin (DMP, **17**) (0.165 g, 0.30 mmol) in $CHCl_3$ (50 mL). The reaction mixture was refluxed for 1 h, during which time the mixture became bright red. Then, the mixture was cooled down, and extracted three times with distilled water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum to give (5,15-dimesitylporphyrinato)zinc(II) (Zn-DMP, **18**) (0.180 g, 98%) as a red solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.83 (12H, s, Ar-C*H*$_3$), 2.67 (6H, s, Ar-C*H*$_3$), 7.33 (4H, s, Ar), 8.97 (4H, d, J = 4.4 Hz, *β*-H), 9.39 (4H, d, J = 4.5 Hz, *β*-H), 10.25 (2H, s, *meso*-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{38}H_{32}N_4Zn$: 608.192, Found: 608.341; UV-visible (THF, nm): λ_{max} (log ε) 410 (5.43), 544 (4.29), and 578 (3.30); Fluorescence (THF, nm): λ_{max} 584 and 636.

2.6.3 Synthesis of (5,15-Dimesitylporphyrinato)manganese(II) (Mn-DMP, 19)

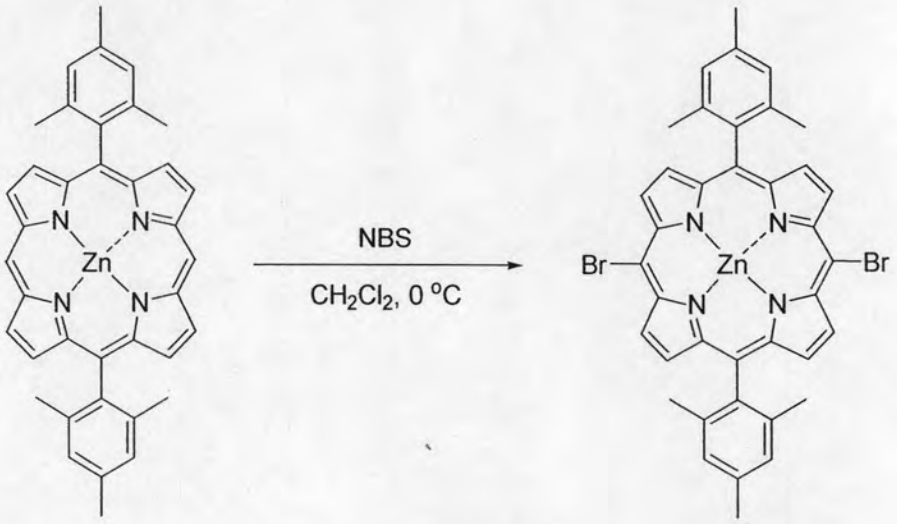


17 **19**

A saturated solution of $Mn(OAc)_2.4H_2O$ (0.297 g, 1.21 mmol) in MeOH (1 mL) was added to a boiling solution of 5,15-dimesitylporphyrin (DMP, **17**) (0.220 g, 0.40 mmol) in DMF (15 mL). The reaction mixture was refluxed for 2 h, during which time the mixture became brown. Then, the mixture was cooled down, $CHCl_3$ was added, and extracted three times with distilled water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum to give (5,15-dimesitylporphyrinato)manganese(II) (Mn-DMP, **19**) (0.210 g, 88%) as a dark brown solid.

MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{38}H_{32}N_4Mn$: 599.201, Found: 599.532; UV-visible (THF, nm): λ_{max} (log ε) 422 (4.73), 460 (4.79), and 561 (3.93); Fluorescence (THF, nm): no emission.

2.6.4 Synthesis of (5,15-Dibromo-10,20-dimesitylporphyrinato)zinc(II) (Zn-Br_2DMP, 20)

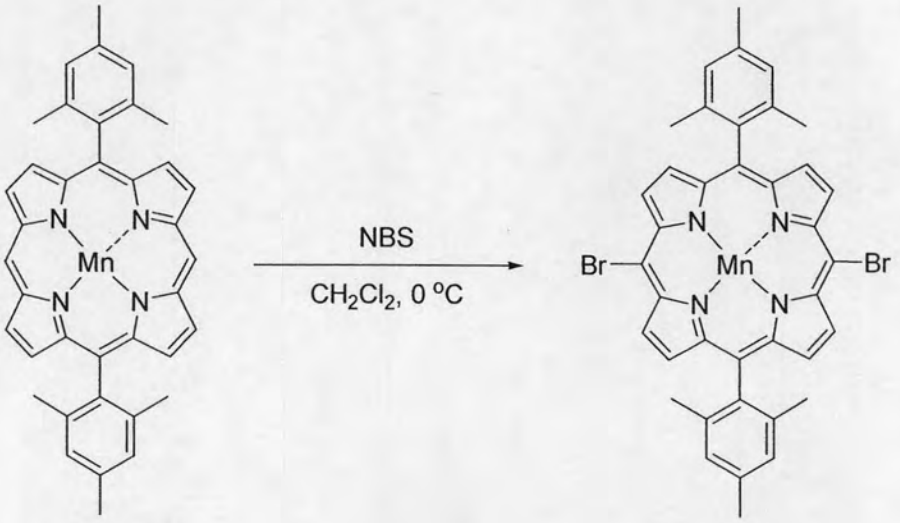


18 **20**

A solution of (5,15-dimesitylporphyrinato)zinc(II) (Zn-DMP, **18**) (0.275 g, 0.45 mmol) in CH_2Cl_2 (10 mL) was treated with NBS (0.167 g, 0.94 mmol). The reaction mixture was stirred at 0 °C for 10 min. The reaction was quenched by adding acetone (3 mL) and stirred for 10 min. MeOH was added and the solvent was reduced to a small volume. The solution was then filtered and the residue was washed with MeOH to give (5,15-dibromo-10,20-dimesitylporphyrinato)zinc(II) (Zn-Br_2DMP, **20**) (0.331 g, 96%) as a dark purple solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.81 (12H, s, Ar-CH_3), 2.65 (6H, s, Ar-CH_3), 7.29 (4H, s, Ar), 8.79 (4H, d, J = 4.7 Hz, β-H), 9.67 (4H, d, J = 4.7 Hz, β-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{38}H_{30}N_4Br_2Zn$: 764.013, Found: 766.601; UV-visible (THF, nm): λ_{max} (log ε) 427 (5.42), 566 (4.21), and 606 (3.91); Fluorescence (THF, nm): no emission.

2.6.5 Synthesis of (5,15-Dibromo-10,20-dimesitylporphyrinato)-manganese(II) (Mn-Br_2DMP, 21)



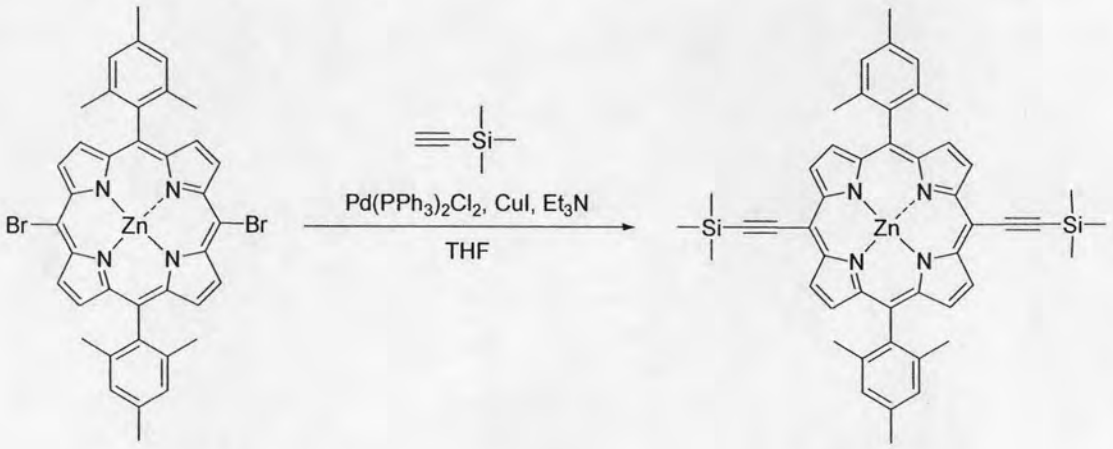
19 **21**

A solution of (5,15-dimesitylporphyrinato)manganese(II) (Mn-DMP, **19**) (0.150 g, 0.25 mmol) in CH_2Cl_2 (10 mL) was treated with NBS (0.223 g, 1.25 mmol). The reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched by adding acetone (6 mL), stirred for 10 min, and then extracted three times with distilled water. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum to give (5,15-dibromo-10,20-dimesitylporphyrinato)manganese(II) (Mn-Br_2DMP, **21**) (0.180 g, 95%) as a dark green solid.

MALDI-TOF-MS (dithranol): m/z $[M]^+$ Calcd for $C_{38}H_{30}N_4Br_2Mn$: 755.022, Found: 757.934; UV-visible (THF, nm): λ_{max} (log ε) 410 (4.46), 488 (4.49), and 647 (3.83); Fluorescence (THF, nm): no emission.

2.7 Synthesis of Alkyne-Linked Porphyrin Metal Complexes

2.7.1 Synthesis of [5,15-Bis(trimethylsilylethynyl)-10,20-dimesityl-porphyrinato]zinc(II) (Zn-(TMSE)$_2$DMP, 22)

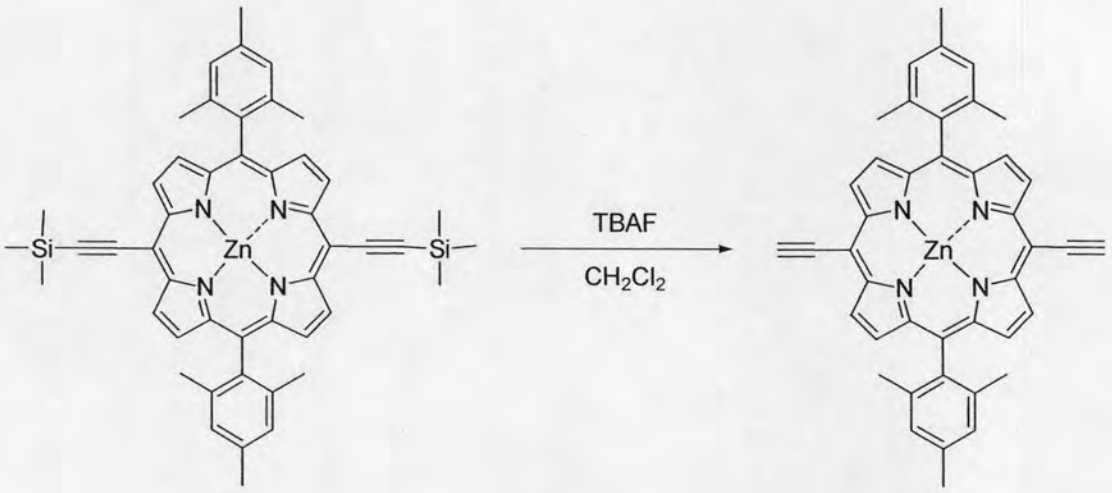


20 **22**

Trimethylsilylacetylene (0.22 mL, 1.59 mmol) and triethylamine (10 mL) were added by using syringe to a stirred solution of (5,15-dibromo-10,20-dimesitylporphyrinato)zinc(II) (Zn-Br$_2$DMP, **20**) (0.302 g, 0.39 mmol), $Pd(PPh_3)_2Cl_2$ (0.030 g, 0.04 mmol), CuI (0.045 g, 0.24 mmol) in THF (80 mL). The reaction mixture was stirred at room temperature under N_2 for 24 h. The mixture was concentrated under vacuum, and filtered through silica using THF as eluent. The solvent was removed under vacuum and the butadiynyl compound formed as a side product was removed by sublimation to afford [5,15-bis(trimethylsilylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(TMSE)$_2$DMP, **22**) (0.282 g, 88%) as a dark purple solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.58 (18H, s, Si(C*H*$_3$)$_3$), 1.81 (12H, s, Ar-C*H*$_3$), 2.64 (6H, s, Ar-C*H*$_3$), 7.29 (4H, s, Ar), 8.74 (4H, d, J = 4.6 Hz, β-H), 9.63 (4H, d, J = 4.6 Hz, β-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{48}H_{48}N_4Si_2Zn$: 800.271, Found: 801.062; UV-visible (THF, nm): λ_{max} (log ε) 438 (5.43), 446 (5.27), 582 (4.04), and 634 (4.45); Fluorescence (THF, nm): λ_{max} 642 and 702.

2.7.2 Synthesis of (5,15-Diethynyl-10,20-dimesitylporphyrinato)zinc(II) (Zn-E_2DMP, 23)

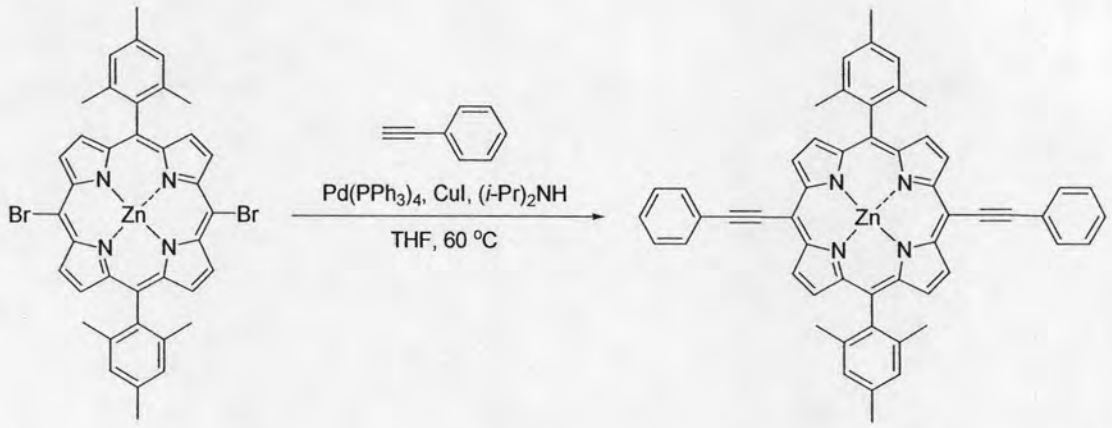


22 **23**

A solution of TBAF (30 μL, 1 M in THF) was added to a solution of [5,15-bis(trimethylsilylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(TMSE)$_2$DMP, **22**) (8.0 mg, 9.97 μmol) in CH_2Cl_2 (4 mL). The reaction mixture was stirred at room temperature for 30 min. After that, water (4 mL) was added to a mixture, and stirred at room temperature for an additional 30 min. The organic layer was separated, dried over anhydrous $MgSO_4$ and concentrated under vacuum to give (5,15-diethynyl-10,20-dimesitylporphyrinato)zinc(II) (Zn-E_2DMP, **23**) (4.1 mg, 62%) as a purple solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.82 (12H, s, Ar-C*H*$_3$), 2.65 (6H, s, Ar-C*H*$_3$), 4.14 (2H, s, C*H*), 7.30 (4H, s, Ar), 8.77 (4H, d, J = 4.4 Hz, β-H), 9.66 (4H, d, J = 4.3 Hz, β-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{42}H_{32}N_4Zn$: 656.192, Found: 656.919; UV-visible (THF, nm): λ_{max} (log ε) 432 (5.30), 441 (5.15), 573 (4.00), and 624 (4.09); Fluorescence (THF, nm): λ_{max} 630 and 687.

2.7.3 Synthesis of [5,15-Bis(phenylethynyl)-10,20-dimesitylporphyrinato]-zinc(II) (Zn-(PE)$_2$DMP, 24)

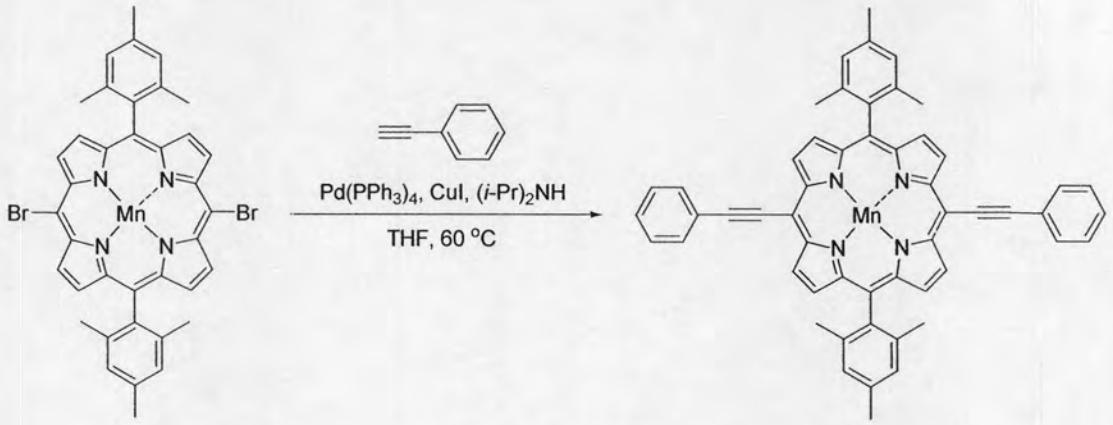


20 **24**

Diisopropylamine (3 mL) was added *via* syringe to a stirred solution of (5,15-dibromo-10,20-dimesitylporphyrinato)zinc(II) (Zn-Br$_2$DMP, **20**) (0.154 g, 0.20 mmol), phenylacetylene (0.10 mL, 0.91 mmol), $Pd(PPh_3)_4$ (0.036 g, 0.03 mmol), and CuI (0.167 g, 0.88 mmol) in THF (30 mL). The reaction mixture was stirred at 60 °C under N_2 for 24 h. The mixture was filtered to remove catalysts, concentrated under vacuum, and purified by flash column chromatography (230-400 mesh silica, hexanes:THF = 6:1). The green band was collected and evaporated to afford [5,15-bis(phenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(PE)$_2$DMP, **24**) (0.072 g, 44%) as a dark purple solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.85 (12H, s, Ar-CH_3), 2.66 (6H, s, Ar-CH_3), 7.31 (4H, s, Ar), 7.49 (2H, t, J = 7.3 Hz, *p*-phenyl), 7.56 (4H, t, J = 7.4 Hz, *m*-phenyl), 8.01 (4H, d, J = 7.3 Hz, *o*-phenyl), 8.76 (4H, d, J = 4.6 Hz, β-H), 9.71 (4H, d, J = 4.5 Hz, β-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{54}H_{40}N_4Zn$: 808.254, Found: 809.232; UV-visible (THF, nm): λ_{max} (log ε) 447 (5.41), 597 (3.87), and 651 (4.54); Fluorescence (THF, nm): λ_{max} 660 and 720.

2.7.4 Synthesis of [5,15-Bis(phenylethynyl)-10,20-dimesitylporphyrinato]-manganese(II) (Mn-(PE)$_2$DMP, 25)

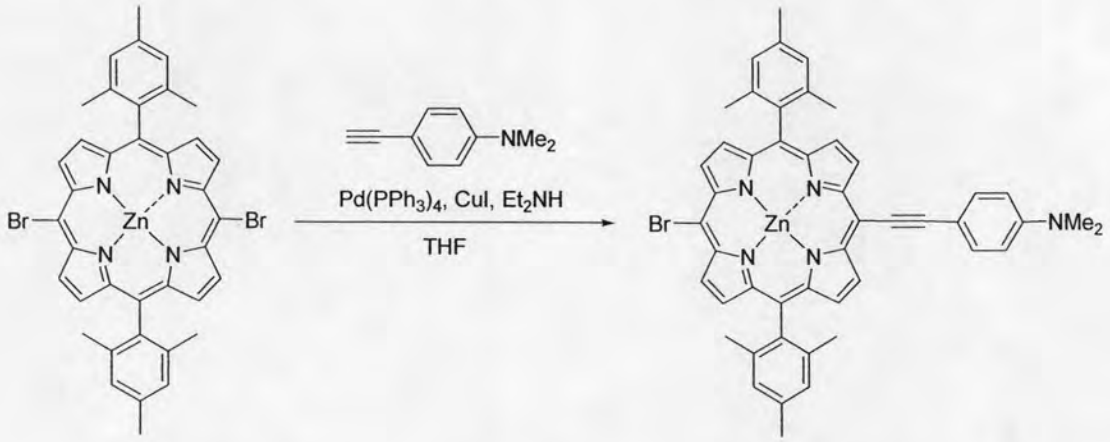


21 **25**

Diisopropylamine (2 mL) was added by using syringe to a stirred solution of (5,15-dibromo-10,20-dimesitylporphyrinato)manganese(II) (Mn-Br$_2$DMP, **21**) (0.076 g, 0.10 mmol), phenylacetylene (0.05 mL, 0.46 mmol), $Pd(PPh_3)_4$ (0.022 g, 0.02 mmol), and CuI (0.022 g, 0.12 mmol) in THF (20 mL). The reaction mixture was stirred at 60 °C under N_2 for 24 h. The mixture was filtered to remove catalysts and the filtrate was concentrated under vacuum to afford [5,15-bis(phenylethynyl)-10,20-dimesitylporphyrinato]manganese(II) (Mn-(PE)$_2$DMP, **25**) (0.040 g, 50%) as a dark green solid.

MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{54}H_{40}N_4Mn$: 799.263, Found: 799.896; UV-visible (THF, nm): λ_{max} (log ε) 445 (4.25), 489 (4.23), and 675 (3.76); Fluorescence (THF, nm): no emission.

2.7.5 Synthesis of [5-Bromo-15-(4′-*N*,*N*-dimethylaminophenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(DMAPE)(Br)DMP, 26)

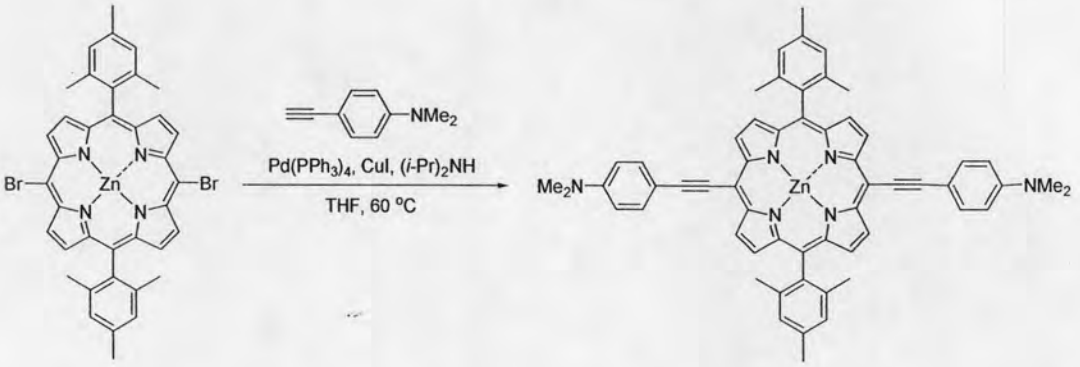


20 **26**

A solution of 4-*N*,*N*-dimethylaminophenylethyne (**4**) (0.066 g, 0.45 mmol) in THF (10 mL) was added slowly by using syringe to a stirred solution of (5,15-dibromo-10,20-dimesitylporphyrinato)zinc(II) (Zn-Br_2DMP, **20**) (0.232 g, 0.30 mmol), $Pd(PPh_3)_4$ (0.034 g, 0.03 mmol), CuI (0.017 g, 0.09 mmol), and diethylamine (5 mL) in THF (20 mL). The reaction mixture was stirred at room temperature under N_2 for 48 h. The mixture was filtered to remove catalysts, concentrated under vacuum, and purified by flash column chromatography (230-400 mesh silica, hexanes:THF = 9:1). The green band was collected and evaporated to afford [5-bromo-15-(4′-*N*,*N*-dimethylaminophenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(DMAPE)(Br)DMP, **26**) (0.064 g, 26%) as a dark green solid.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.70 (12H, s, Ar-CH_3), 2.52 (6H, s, Ar-CH_3), 2.97 (6H, s, N(CH_3)$_2$), 6.84 (2H, d, J = 8.3 Hz, Ar), 7.26 (4H, s, Ar), 7.80 (2H, d, J = 8.2 Hz, Ar), 8.43 (2H, d, J = 4.5 Hz, β-H), 8.48 (2H, d, J = 4.4 Hz, β-H), 9.39 (2H, d, J = 4.6 Hz, β-H), 9.53 (2H, d, J = 4.5 Hz, β-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{48}H_{40}N_5BrZn$: 829.176, Found: 832.157; UV-visible (THF, nm): λ_{max} (log ε) 452 (5.14), 585 (3.98), and 643 (4.53); Fluorescence (THF, nm): no emission.

2.7.6 Synthesis of [5,15-Bis(4′-*N*,*N*-dimethylaminophenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(DMAPE)$_2$DMP, 27)

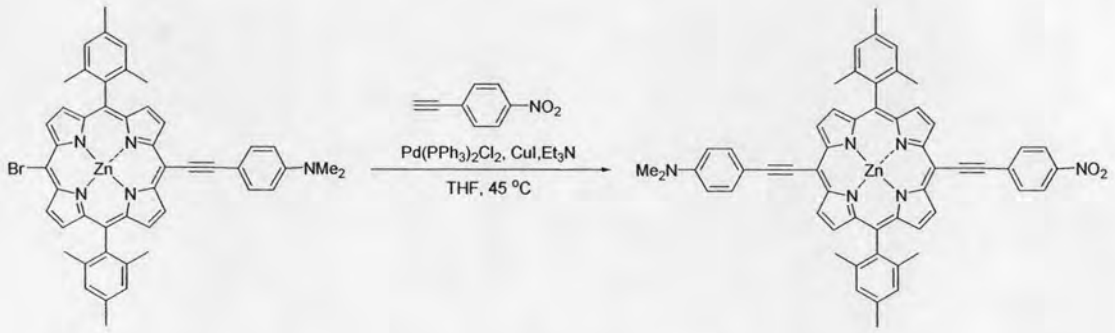


20 **27**

Diisopropylamine (1 mL) was added by using syringe to a stirred solution of (5,15-dibromo-10,20-dimesitylporphyrinato)zinc(II) (Zn-Br$_2$DMP, **20**) (0.038 g, 0.05 mmol), 4-*N*,*N*-dimethylaminophenylethyne (**4**) (0.023 g, 0.16 mmol), Pd(PPh$_3$)$_4$ (0.012 g, 0.01 mmol), and CuI (0.011 g, 0.06 mmol) in THF (20 mL). The reaction mixture was stirred at 60 °C under N_2 for 24 h. The mixture was filtered to remove catalysts, concentrated under vacuum, and purified by flash column chromatography (230-400 mesh silica, hexanes:THF = 5:1). The green band was collected and evaporated to afford [5,15-bis(4′-*N*,*N*-dimethylaminophenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(DMAPE)$_2$DMP, **27**) (0.019 g, 21%) as a dark green solid.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.81 (12H, s, Ar-CH_3), 2.61 (6H, s, Ar-CH_3), 3.06 (12H, s, N(CH_3)$_2$), 6.93 (4H, d, J = 8.4 Hz, Ar), 7.35 (4H, s, Ar), 7.87 (2H, d, J = 8.3 Hz, Ar), 8.50 (4H, d, J = 4.3 Hz, β-H), 9.55 (4H, d, J = 4.3 Hz, β-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{58}H_{50}N_6Zn$: 894.339, Found: 895.298; UV-visible (THF, nm): λ_{max} (log ε) 467 (5.20), and 676 (4.59); Fluorescence (THF, nm): λ_{max} 695.

2.7.7 Synthesis of [5-(4′-*N*,*N*-dimethylaminophenylethynyl)-15-(4′′-nitrophenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(DMAPE)(NPE)DMP, 28)

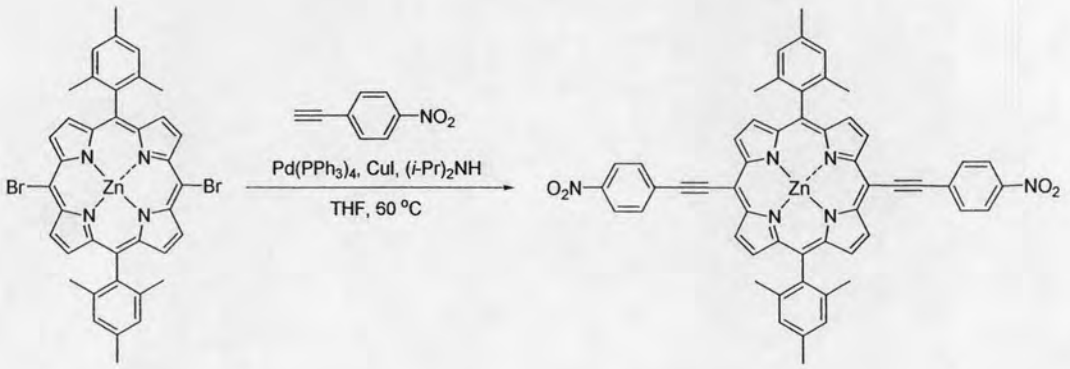


26 28

Triethylamine (3 mL) was added to a stirred solution of [5-bromo-15-(4′-*N*,*N*-dimethylaminophenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(DMAPE)(Br)DMP, **26**) (0.025 g, 0.03 mmol), 4-nitrophenylethyne (**6**) (0.014 g, 0.10 mmol), $Pd(PPh_3)_4$ (0.003 g, 0.004 mmol), and CuI (0.002 g, 0.01 mmol) in THF (20 mL). The reaction mixture was stirred at 40 °C under N_2 for 6 days. The mixture was filtered to remove catalysts, concentrated under vacuum, and purified by flash column chromatography (230-400 mesh silica, hexanes:$CHCl_3$ = 5:1). The green band was collected and evaporated to afford [5-(4′-*N*,*N*-dimethylaminophenylethynyl)-15-(4′′-nitrophenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(DMAPE)(NPE)DMP, **28**) (0.003 g, 11%) as a dark purple solid.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.82 (12H, s, Ar-CH_3), 2.62 (6H, s, Ar-CH_3), 3.07 (6H, s, N(CH_3)$_2$), 6.93 (2H, d, J = 8.6 Hz, Ar), 7.36 (4H, s, Ar), 7.90 (2H, d, J = 9.1 Hz, Ar), 8.36 (2H, d, J = 8.6 Hz, Ar), 8.47 (2H, d, J = 8.6 Hz, Ar), 8.52 (2H, d, J = 4.4 Hz, β-H), 8.57 (2H, d, J = 4.5 Hz, β-H), 9.60 (2H, d, J = 4.5 Hz, β-H), 9.64 (2H, d, J = 4.5 Hz, β-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{56}H_{44}N_6O_2Zn$: 896.282, Found: 897.084; UV-visible (THF, nm): λ_{max} (log ε) 456 (4.76), and 678 (4.17); Fluorescence (THF, nm): λ_{max} 705.

2.7.8 Synthesis of [5,15-Bis(4′-nitrophenylethynyl)-10,20-dimesityl-porphyrinato]zinc(II) (Zn-(NPE)$_2$DMP, 29)

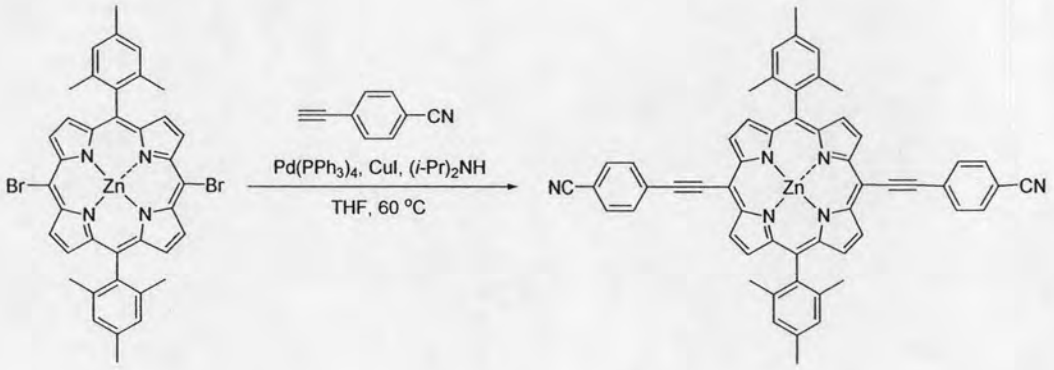


20 **29**

Diisopropylamine (3 mL) was added by using syringe to a stirred solution of (5,15-dibromo-10,20-dimesitylporphyrinato)zinc(II) (Zn-Br$_2$DMP, **20**) (0.115 g, 0.15 mmol), 4-nitrophenylethyne (**6**) (0.067 g, 0.46 mmol), Pd(PPh$_3$)$_4$ (0.023 g, 0.02 mmol), and CuI (0.030 g, 0.16 mmol) in THF (20 mL). The reaction mixture was stirred at 60 °C under N_2 for 24 h. The mixture was filtered to remove catalysts, concentrated under vacuum, and purified by flash column chromatography (230-400 mesh silica, hexanes:THF = 6:1). The green band was collected and evaporated to afford [5,15-bis(4′-nitrophenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(NPE)$_2$DMP, **29**) (0.067 g, 50%) as a dark purple solid.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.82 (12H, s, Ar-CH_3), 2.62 (6H, s, Ar-CH_3), 7.38 (4H, s, Ar), 8.36 (4H, d, J = 8.4 Hz, Ar), 8.46 (2H, d, J = 8.4 Hz, Ar), 8.61 (4H, d, J = 4.5 Hz, β-H), 9.71 (4H, d, J = 4.5 Hz, β-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{54}H_{38}N_6O_4Zn$: 898.225, Found: 899.349; UV-visible (THF, nm): λ_{max} (log ε) 461 (5.15), 579 (3.95), and 668 (4.50); Fluorescence (THF, nm): λ_{max} 687 and 751.

2.7.9 Synthesis of [5,15-Bis(4′-cyanophenylethynyl)-10,20-dimesityl-porphyrinato]zinc(II) (Zn-(CPE)$_2$DMP, 30)

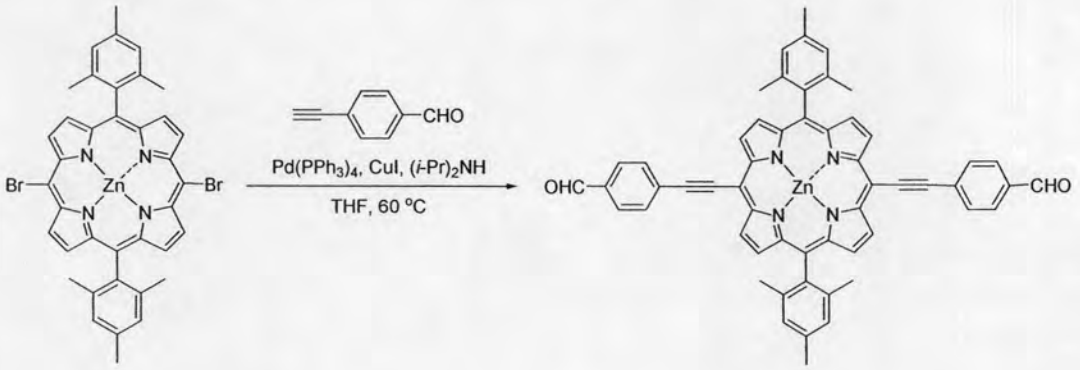


20 **30**

Diisopropylamine (3 mL) was added by using syringe to a stirred solution of (5,15-dibromo-10,20-dimesitylporphyrinato)zinc(II) (Zn-Br$_2$DMP, **20**) (0.116 g, 0.15 mmol), 4-cyanophenylethyne (**8**) (0.059 g, 0.46 mmol), Pd(PPh$_3$)$_4$ (0.024 g, 0.02 mmol), and CuI (0.022 g, 0.12 mmol) in THF (20 mL). The reaction mixture was stirred at 60 °C under N_2 for 24 h. The mixture was filtered to remove catalysts, concentrated under vacuum, and purified by flash column chromatography (230-400 mesh silica, hexanes:THF = 5:1). The green band was collected and evaporated to afford [5,15-bis(4′-cyanophenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(CPE)$_2$DMP, **30**) (0.051 g, 40%) as a dark purple solid.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.81 (12H, s, Ar-CH_3), 2.62 (6H, s, Ar-CH_3), 7.37 (4H, s, Ar), 8.11 (4H, d, J = 8.2 Hz, Ar), 8.31 (2H, d, J = 8.2 Hz, Ar), 8.59 (4H, d, J = 4.6 Hz, β-H), 9.69 (4H, d, J = 4.5 Hz, β-H); MALDI-TOF-MS (dithranol): m/z $[M]^+$ Calcd for $C_{56}H_{38}N_6Zn$: 858.245, Found: 859.070; UV-visible (THF, nm): λ_{max} (log ε) 453 (5.39), 583 (3.86), and 660 (4.56); Fluorescence (THF, nm): λ_{max} 673 and 733.

2.7.10 Synthesis of [5,15-Bis(4′-formylphenylethynyl)-10,20-dimesityl-porphyrinato]zinc(II) (Zn-(FPE)$_2$DMP, 31)

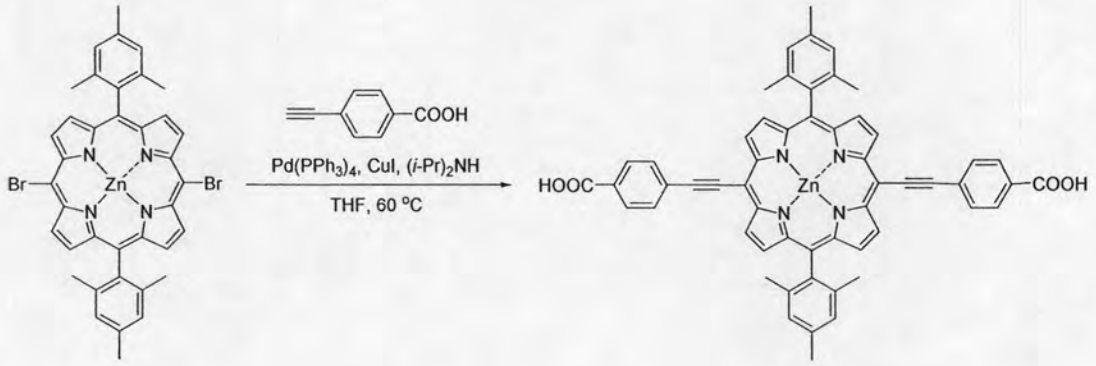


20 **31**

Diisopropylamine (3 mL) was added by using syringe to a stirred solution of (5,15-dibromo-10,20-dimesitylporphyrinato)zinc(II) (Zn-Br$_2$DMP, **20**) (0.118 g, 0.15 mmol), 4-formylphenylethyne (**10**) (0.058 g, 0.45 mmol), Pd(PPh$_3$)$_4$ (0.024 g, 0.02 mmol), and CuI (0.020 g, 0.11 mmol) in THF (20 mL). The reaction mixture was stirred at 60 °C under N_2 for 24 h. The mixture was filtered to remove catalysts, concentrated under vacuum, and purified by flash column chromatography (230-400 mesh silica, hexanes:THF = 5:1). The green band was collected and evaporated to afford [5,15-bis(4′-formylphenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(FPE)$_2$DMP, **31**) (0.038 g, 29%) as a dark purple solid.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.81 (12H, s, Ar-CH_3), 2.62 (6H, s, Ar-CH_3), 7.37 (4H, s, Ar), 8.10 (4H, d, J = 8.2 Hz, Ar), 8.31 (2H, d, J = 8.1 Hz, Ar), 8.59 (4H, d, J = 4.6 Hz, β-H), 9.69 (4H, d, J = 4.5 Hz, β-H); MALDI-TOF-MS (dithranol): m/z $[M]^+$ Calcd for $C_{56}H_{40}N_4O_2Zn$: 864.244, Found: 865.152; UV-visible (THF, nm): λ_{max} (log ε) 455 (5.46), 588 (3.85), and 663 (4.76); Fluorescence (THF, nm): λ_{max} 678 and 737.

2.7.11 Synthesis of [5,15-Bis(4′-carboxyphenylethynyl)-10,20-dimesityl-porphyrinato]zinc(II) (Zn-(CarPE)$_2$DMP, 32)



20 **32**

Diisopropylamine (5 mL) was added by using syringe to a stirred solution of (5,15-dibromo-10,20-dimesitylporphyrinato)zinc(II) (Zn-Br$_2$DMP, **20**) (0.115 g, 0.15 mmol), 4-carboxyphenylethyne (**12**) (0.066 g, 0.45 mmol), Pd(PPh$_3$)$_4$ (0.024 g, 0.02 mmol), and CuI (0.019 g, 0.10 mmol) in THF (20 mL). The reaction mixture was stirred at 60 °C under N_2 for 24 h. The mixture was filtered to remove catalysts, concentrated under vacuum to afford [5,15-bis(4′-carboxyphenylethynyl)-10,20-dimesitylporphyrinato]zinc(II) (Zn-(CarPE)$_2$DMP, **32**) (0.044 g, 33%) as a dark green solid.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.81 (12H, s, Ar-CH_3), 2.62 (6H, s, Ar-CH_3), 7.36 (4H, s, Ar), 8.12 (4H, br, Ar), 8.19 (2H, br, Ar), 8.57 (4H, br, β-H), 9.64 (4H, br, β-H); MALDI-TOF-MS (dithranol): *m/z* $[M]^+$ Calcd for $C_{56}H_{40}N_4O_4Zn$: 896.234, Found: 897.398; UV-visible (THF, nm): λ_{max} (log ε) 451 (5.08), 583 (3.74), and 658 (4.21); Fluorescence (THF, nm): λ_{max} 668 and 727.

2.8 Investigation of Photophysical Properties

The stock solutions of 1.0×10^{-4} M of all synthesized porphyrins in THF were prepared by adding dried THF (10 mL) to porphyrins (1.0×10^{-3} mmol) in 10 mL volumetric flasks. The amounts of each of the porphyrins which were used in the preparation of the stock solutions are presented in **Table 2.1**.

Table 2.1 The amounts of porphyrins used in the preparation of the stock solutions

porphyrins	MW	weight (mg)	amount (mmol)	concentration of porphyrins (mol/dm^3)
DHP, **13**	478.67	0.50	1.0×10^{-3}	1.0×10^{-4}
Zn-DHP, **14**	636.46	0.64	1.0×10^{-3}	1.0×10^{-4}
Br_2-DHP, **15**	542.05	0.56	1.0×10^{-3}	1.0×10^{-4}
Zn-Br_2DHP, **16**	699.84	0.71	1.0×10^{-3}	1.0×10^{-4}
DMP, **17**	546.70	0.57	1.0×10^{-3}	1.0×10^{-4}
Zn-DMP, **18**	610.08	0.64	1.0×10^{-3}	1.0×10^{-4}
Mn-DMP, **19**	599.63	0.62	1.0×10^{-3}	1.0×10^{-4}
Zn-Br_2DMP, **20**	767.87	0.78	1.0×10^{-3}	1.0×10^{-4}
Mn-Br_2DMP, **21**	755.42	0.76	1.0×10^{-3}	1.0×10^{-4}
Zn-$(TMSE)_2$DMP, **22**	802.48	0.80	1.0×10^{-3}	1.0×10^{-4}
Zn-E_2DMP, **23**	658.12	0.66	1.0×10^{-3}	1.0×10^{-4}
Zn-$(PE)_2$DMP, **24**	810.31	0.82	1.0×10^{-3}	1.0×10^{-4}
Mn-$(PE)_2$DMP, **25**	799.86	0.80	1.0×10^{-3}	1.0×10^{-4}
Zn-(DMAPE)(Br)DMP, **26**	832.16	0.83	1.0×10^{-3}	1.0×10^{-4}
Zn-$(DMAPE)_2$DMP, **27**	896.45	0.90	1.0×10^{-3}	1.0×10^{-4}
Zn-(DMAPE)(NPE)DMP, **28**	898.38	0.91	1.0×10^{-3}	1.0×10^{-4}
Zn-$(NPE)_2$DMP, **29**	900.31	0.92	1.0×10^{-3}	1.0×10^{-4}
Zn-$(CPE)_2$DMP, **30**	860.33	0.87	1.0×10^{-3}	1.0×10^{-4}
Zn-$(FPE)_2$DMP, **31**	866.33	0.88	1.0×10^{-3}	1.0×10^{-4}
Zn-$(CarPE)_2$DMP, **32**	898.33	0.90	1.0×10^{-3}	1.0×10^{-4}

2.8.1 UV-Visible Spectroscopy

A stock solution of porphyrins (0.1 mL) was added to a 1 cm quartz cuvette and THF (0.9 mL) was added to adjust the solution to 1 mL by using a micropipette. The UV-visible absorption spectra of all porphyrins were measured at 1.0×10^{-5} M in THF and recorded from 200 nm to 800 nm at ambient temperature.

2.8.2 Fluorescence Spectroscopy

A stock solution of porphyrins (0.2 mL) was added to a 1 cm quartz cuvette and then THF (1.8 mL) was added to adjust the solution to 2 mL by using a micropipette. The fluorescence emission spectra of all porphyrins were measured at 1.0×10^{-5} M in THF and recorded from 400 nm to 850 nm at ambient temperature.

2.9 Investigation of Coordination Properties

2.9.1 ^{1}H NMR Titration

Three porphyrin derivatives including DMP (**17**), Zn-DMP (**18**), and Zn-$(TMSE)_2$DMP (**22**) were chosen to investigate their coordination properties by ^{1}H NMR spectroscopy. Typically, a solution of 0.05 M of porphyrins (0.025 mmol) in $CDCl_3$ (0.5 mL) was prepared in an NMR tube. The amounts of each of the porphyrins which were used in this investigation are presented in **Table 2.2**. An initial ^{1}H NMR spectrum of the solution of porphyrins was recorded. Then, pyridine was added directly to the NMR tube by using a microsyringe. The ^{1}H NMR spectra were recorded after each addition. The amounts of added pyridine and ratio of pyridine:porphyrins are reported in **Table 2.3**.

Table 2.2 The amounts of porphyrins used in the ^{1}H NMR titration

porphyrins	MW	weight (mg)	amount (mmol)
DMP, **17**	546.70	13.8	0.025
Zn-DMP, **18**	610.08	15.2	0.025
Zn-$(TMSE)_2$DMP, **22**	802.48	20.0	0.025

Table 2.3 The amounts of added pyridine and ratio of pyridine:porphyrins in the ^{1}H NMR titration

entry	added pyridine (μL)	total pyridine (μL)	amount of pyridine (mmol)	mole ratio of pyridine:porphyrins
1	1	1	0.012	0.5 : 1
2	1	2	0.025	1 : 1
3	2	4	0.050	2 : 1
4	2	6	0.074	3 : 1
5	2	8	0.099	4 : 1
6	2	10	0.124	5 : 1
7	2	12	0.149	6 : 1
8	2	14	0.174	7 : 1
9	2	16	0.199	8 : 1
10	2	18	0.223	9 : 1
11	2	20	0.248	10 : 1
12	10	30	0.372	15 : 1
13	10	40	0.497	20 : 1

2.9.2 UV-Visible Titration

Six porphyrin derivatives including Zn-DMP (**18**), Mn-DMP (**19**), Zn-Br_2DMP (**20**), Zn-$(TMSE)_2$DMP (**22**), Zn-E_2DMP (**23**), and Zn-$(PE)_2$DMP (**24**) were chosen to investigate their coordination properties by UV-visible spectroscopy. Typically, a stock solution of porphyrins (0.2 mL) was added to a 1 cm quartz cuvette and then THF (1.8 mL) was added to adjust the solution to 2 mL by using a micropipette. An initial UV-visible absorption spectrum of the solution of porphyrins was measured at 1.0×10^{-5} M in THF and recorded from 200 nm to 800 nm at 25 °C. Subsequently, pyridine was added directly to the quartz cuvette by using a microsyringe. The UV-visible absorption spectra were recorded after each addition. The amounts of added pyridine and ratio of pyridine:porphyrins are reported in **Table 2.4**.

2.9.3 Fluorescence Titration

Three porphyrin derivatives including Zn-DMP (**18**), Zn-$(TMSE)_2$DMP (**22**), and Zn-$(PE)_2$DMP (**24**) were chosen to investigate their coordination properties by fluorescence spectroscopy. Typically, a stock solution of porphyrins (0.2 mL) was added to a 1 cm quartz cuvette and then THF (1.8 mL) was added to adjust the solution to 2 mL by using a micropipette. An initial fluorescence emission spectrum of the solution of porphyrins was measured at 1.0×10^{-5} M in THF and recorded from 400 nm to 850 nm at ambient temperature. Then, pyridine was added directly to the quartz cuvette by using a microsyringe. The fluorescence emission spectra were recorded after each addition. The amounts of added pyridine and ratio of pyridine:porphyrins are reported in **Table 2.4**.

Table 2.4 The amounts of added pyridine and ratio of pyridine:porphyrins in the UV-visible and florescence titration

entry	added pyridine (μL)	total pyridine (μL)	amount of pyridine (mmol)	mole ratio of pyridine:porphyrins
1	1	1	0.012	600 : 1
2	1	2	0.025	1250 : 1
3	2	4	0.050	2500 : 1
4	2	6	0.074	3700 : 1
5	2	8	0.099	4950 : 1
6	2	10	0.124	6200 : 1
7	5	15	0.186	9300 : 1
8	5	20	0.248	12400 : 1
9	5	25	0.310	15500 : 1
10	5	30	0.372	18600 : 1
11	5	35	0.434	21700 : 1
12	5	40	0.496	24800 : 1
13	10	50	0.619	30950 : 1
14	10	60	0.743	37150 : 1