Synthesis of *meso*-Substituted Porphyrin Metal Complexes Bearing Multiple Functional Groups

Lakshmi C. Kasi Viswanath

Department of Chemistry, Oklahoma State University, Stillwater, OK 74078

Suaad M. Abuskhuna

Department of Chemistry, Oklahoma State University, Stillwater, OK 74078

Laura D. Shirtcliff

Department of Chemistry, Oklahoma State University, Stillwater, OK 74078

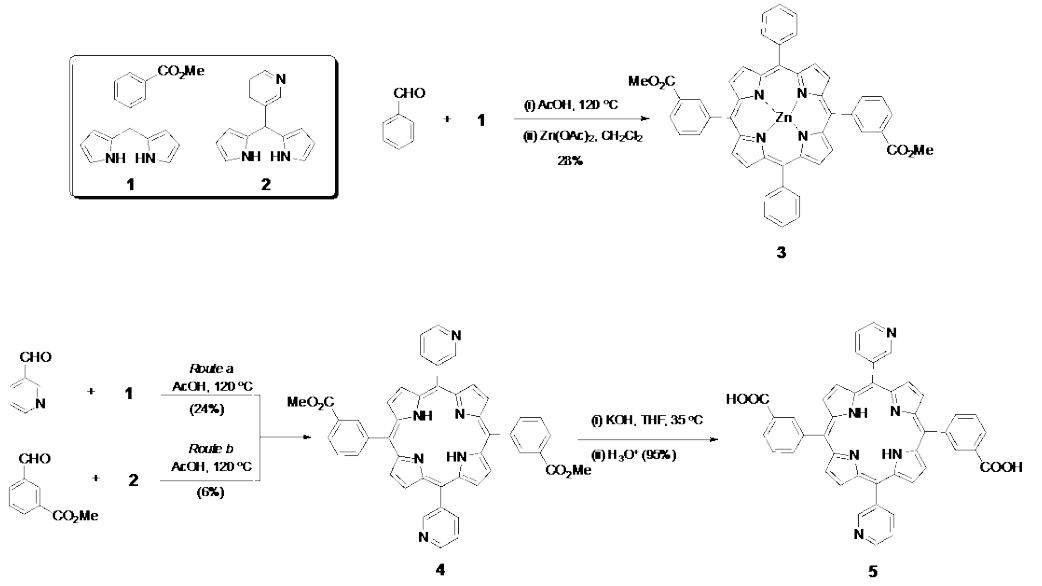
K. Darrell Berlin

Department of Chemistry, Oklahoma State University, Stillwater, OK 74078

Abstract: The acid-catalyzed porphyrin syntheses of a set of rare and novel *meso*-substituted porphyrins possessing substitution at the *meta* and *para* positions have been completed. Such porphyrins have been prepared which possess at least one of the following peripheral functional groups namely, a free amine, a carboxylic acid, an ester, or a terminal alkyne group. Functionalized dipyrromethanes at the 3-position were condensed with the corresponding aldehydes under acidic conditions (AcOH, TFA or BF_3 ethereate) to afford the *meso*-substituted porphyrins. Characterization of products was accomplished by NMR and MALDI-TOF analyses. *©2014 Oklahoma Academy of Science*

Introduction

Results have been reported on the synthesis of a few *meso*-substituted porphyrins (Kadish et al., 2000); Holten et al., 2001) which can be widely utilized in the establishment of bio-organic model systems and molecular devices (Mak et al, 1998, 1999; Li et al., 1999; Mongin et al, 1999; Nakano et al. 1998). The design and the synthesis of porphyrins containing specific patterns of functionality still remain challenging despite the variety of available procedures (Cammidge et al, 2001; Dogutan et al., 2008). The major issue in the porphyrin synthesis is the isolation of the target molecules in very low yields owing to the scrambling processes. While a number of sophisticated experiments are available for the synthesis of porphyrins with less or no scrambling (Cammidge et al, 2001; Dogutan et al., 2008), porphyrin derivatives with certain functional groups remain unavailable. In the present work, we have synthesized a series of *meso*-substituted porphyrin derivatives possessing at least one of the following functional groups namely, a free amine, a carboxylic acid, an ester, and/or a terminal alkyne group. Such functional groups offer a variety of derivatives for potential molecular devices.



Scheme 1. Synthesis of ester- and acid-substituted porphyrins.

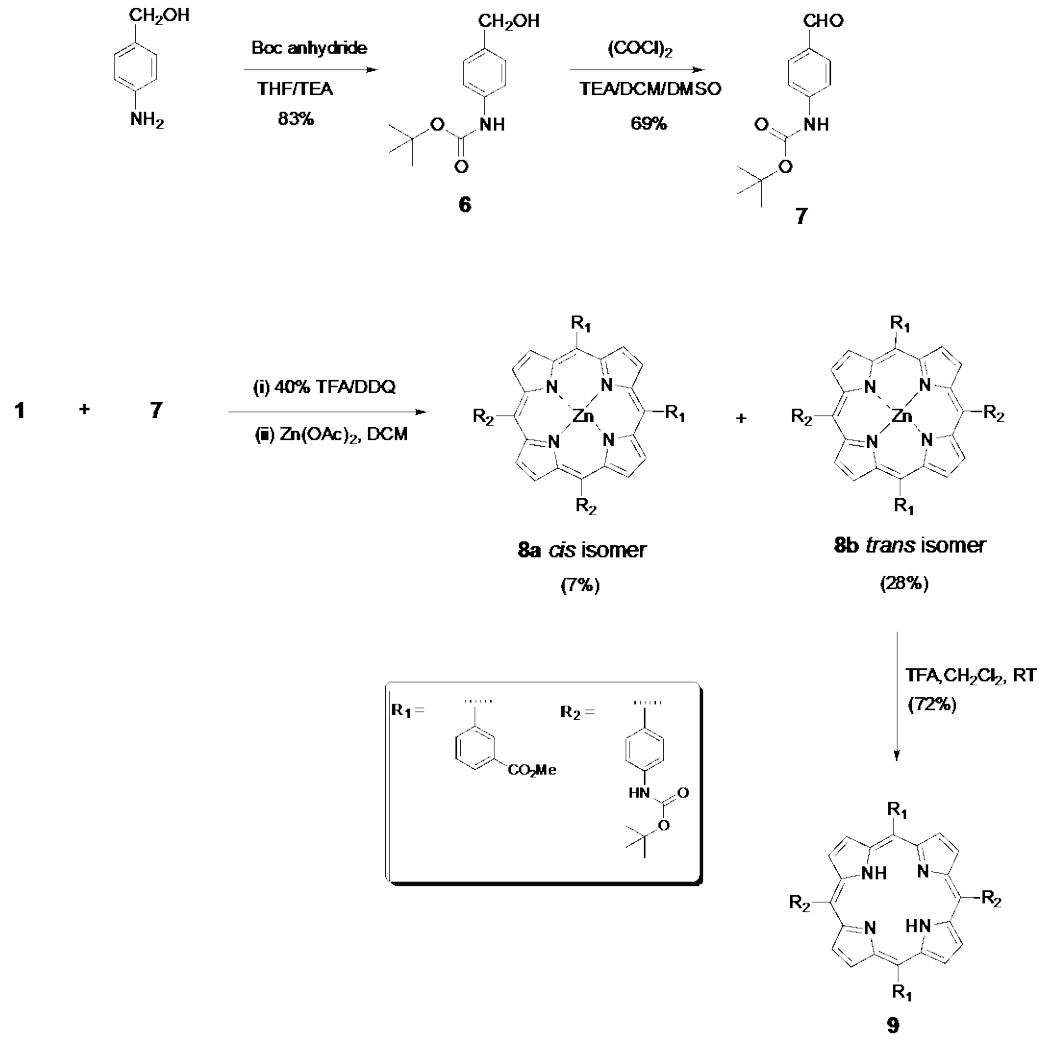
Results and Discussion

Synthesis

As a first step towards the synthesis of *meso*-substituted porphyrins, functionalized dipyrromethanes were prepared by the acid-catalyzed condensation of aldehydes with pyrrole. Dipyrromethanes **1** and **2** were obtained (Littler et al., 1999; Gryko et al., 2000), but the overall yields of the porphyrins are affected by a variety of factors, including the choice of acid catalyst and oxidant, the duration of the condensation period, the concentrations of acid, pyrrole, aldehyde, and the presence of water in the solvent. Dipyrromethanes **1** and **2** were reacted with the corresponding aldehydes in an acid to yield the target porphyrins. The synthesis of **3** was performed by reacting a mixture of dipyrromethane **1** and benzaldehyde in equimolar proportions with acetic acid (Scheme 1). For the synthesis of **4**, two different synthetic routes were investigated.

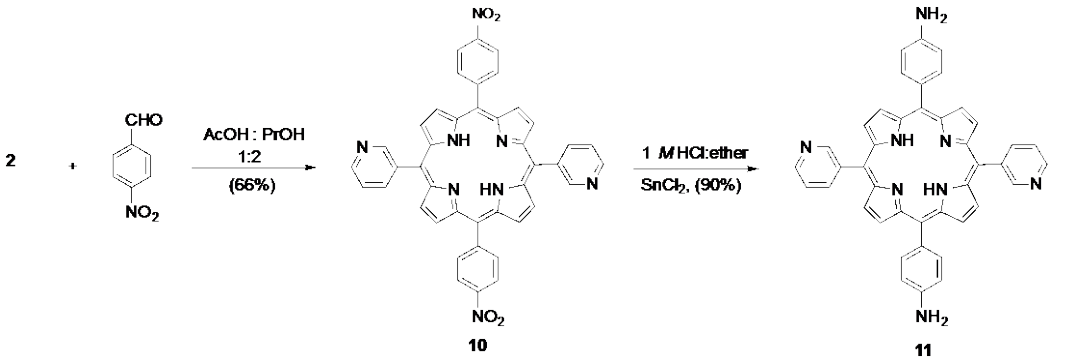
Reaction of a 1:1 mixture of nicotinaldehyde and dipyrromethane **1** with AcOH under reflux conditions afforded **4** (24%). In contrast, when dipyrromethane **1** was replaced by the pyridine-substituted dipyrromethane **2**, product **4** was achieved in relatively low yield (6%). Saponification (Muniappan et al., 2007) of **4** with 1 *M* KOH/methanol in THF at 35 ˚C, followed by acidification with 1 *M* HCl, led to the acid porphyrin **5** (95%)**.**

The synthesis (Scheme 2) of a diester-substituted porphyrin containing two free amine groups in a *trans*

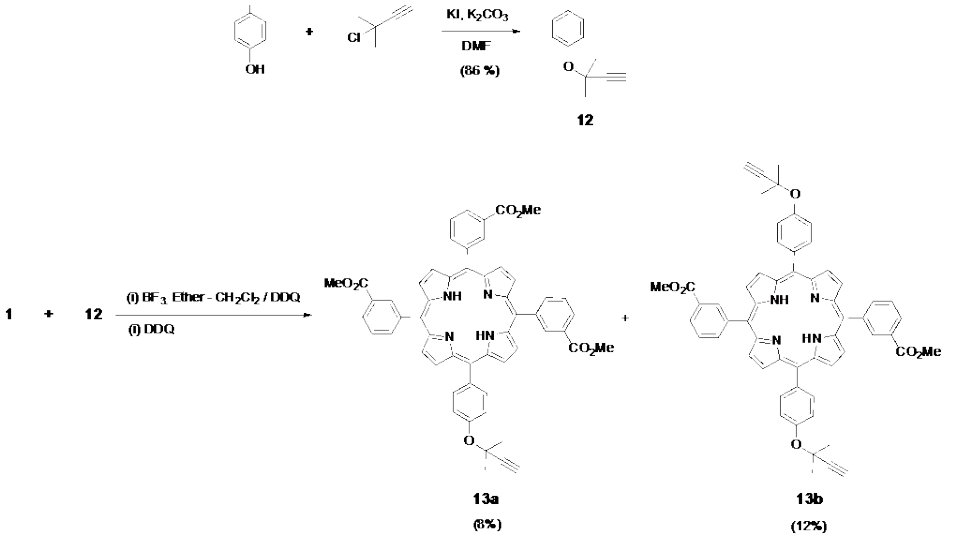


Scheme 2 Synthesis of diamineo diester porphyrins

arrangement is outlined in the scheme. Boc protection of *p*-aminobenzyl alcohol gave **6** (83%), and oxidation of compound **6** with oxalyl chloride, afforded aldehyde **7** (69%) (Rai et al., 1992). Acid-catalyzed condensation (Schmidt et al., 2006) of **7** with dipyrromethane **1**, using 40% TFA and DDQ as the oxidant and subsequent zinc metallation, gave a mixture of *cis*- and *trans*-substituted porphyrins **8a** and **8b** in the ratio 1:4. Isolation of the free *cis*- and *trans*-porphyrins did not prove feasible, and hence the compounds were converted to their zinc complexes which were separable by column chromatography. Reaction of **8b** with TFA resulted in removal of the Boc group and the metal to afford the diamino diester porphyrin **9**.



Scheme 3 Synthesis of diamino pyridyl substituted porphyrins.



Scheme 4. Synthesis of terminal alkyne substituted porphyrins.

Scheme 3 illustrates the synthesis of a *trans-meso*-diaminodipyridyl porphyrin. The starting material, *p*-nitrobenzaldehyde, was treated with dipyrromethane **1** in a 2:1 mixture of acetic acid and propionic acid and produced **10** (66%). Reduction of **10** with $SnCl_2.H_2O$ in a 1 *M* HCl/ether mixture at room temperaturn (Hatay et al., 2010) under dark conditions afforded **11** (90%)**.**

The aldehyde precursor **12**, required for the synthesis of the targeted terminal alkyne-substituted porphyrins, was prepared (Scheme 4) by O-alkylation of *p*-hydroxybenzaldehyde using 3-chloro-3-methylbutyne (Kyogoku et al., 1975). Condensation of **1** and **12** under mild conditions using BF_3 etherate in CH_2Cl_2 afforded a mixture of mono- and di-substituted porphyrins **13a** and **13b** which were separated by column chromatography.

In summary, by employing a variety of reaction conditions, convenient procedures were developed for the synthesis of several rare *meso*-substituted porphyrins containing specific functional groups. The compounds were characterized by ^{1}H NMR and MALDI-TOF spectroscopy. Such structures are potential candidates for light harvesting systems and energy storage via electron

transfer in molecular devices (Kadish et al., 2000).

Methods

General

Melting points (mp) were determined using a Stuart SMP10 instrument. ^{1}H NMR spectra were acquired in $DCCl_3$ or DMSO-d_6 using a Varian 400 MHz or a Gemini 300 MHz spectrometer. Chemical shifts (δ) are expressed in ppm relative to residual chloroform (^{1}H: 7.26 ppm) or to DMSO (^{1}H: 2.49 ppm). Column chromatography occurred on silica gel (Sorbent Technologies, 230-400 mesh), and TLC was performed with polyester sheets precoated with silica gel (Sorbent Technologies). MALDI-TOF experiments were performed on a Voyager Spec instrument. Methyl 3-formylbenzoate, nicotinaldehyde, benzaldehyde, *p*-nitrobenzaldehyde, *p*-aminobenzyl alcohol, 3-chloro-3-methyl-1-butyne (Sigma-Aldrich), trifluoroacetic acid (Alfa Aesar), DDQ, oxalyl chloride, Boc anhydride, and *p*-hydroxybenzaldehyde (Alfa Aesar) were used as received unless otherwise indicated. All final products showed one spot on TLC analysis.

General Procedure for the Synthesis of Porphyrins using Acetic acid

In a single-necked, round-bottomed flask fitted with a condenser and magnetic stirrer were placed dipyrromethane **1** (1.0 equiv) and the corresponding aldehyde (1.0 equiv). Acetic acid (100 volumes w.r.t dipyrromethane) was added to the solution which was refluxed with stirring at 120 ˚C for 4-5 h. The reaction contents became a thick, black solution which was allowed to cool to room temperature. The solvent was evaporated, and the residue was dissolved in ethyl acetate (20 mL). The ethyl acetate solution was treated with 1 *M* NaOH, followed by brine. The organic layer was separated, dried (Na_2SO_4) and evaporated to dryness to yield a black solid. The product was redissolved in CH_2Cl_2 (20 mL), and the solution was passed through a pad of silica to remove most of the impurities. Evaporation of the solvent under vacuum afforded the base porphyrin.

5,15-Bis(3-Methoxycarbonylphenyl)-10,20-bis(4-phenyl)porphinato-Zinc(II) (3).

Compound **1** (0.1 g, 0.35 mol) and benzaldehyde (0.037 g, 0.35 mmol) were treated with acetic acid (20 mL) according to the general procedure. Metallation of the porphyrin occurred when a solution of the product in CH_2Cl_2:MeOH mixture (1:1, 4 mL) was stirred with $Zn(OAc)_2{\cdot}2H_2O$ (0.1 g, 0.45 mol) for 12 h at room temperature. The solvent was evaporated, and the residue was extracted (ethyl acetate, 2 x 20 mL). The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated to a dark purple solid which was then flash chromatographed using ethyl acetate:hexane (1:3) to afford the zinc porphyrin **3**, (79 mg , 28%); mp >300 ˚C. ^{1}H NMR (300 MHz $DCCl_3$): δ 8.96 (d, 4H, J = 4.8 Hz, pyrrole), 8.89 (s, 2H, Ar-CO_2Me), 8.86 (d, 4H, J = 4.8 Hz, pyrrole), 8.49 (d, 2H, J = 7.5 Hz, Ar-CO_2Me), 8.42 (d, 2H, J = 7.5 Hz, Ar-CO_2Me), 8.21 (d, 4H, J = 5.7 Hz, *o*-phenyl), 7.84 (t, 2H, J = 7.5 Hz, Ar-CO_2Me), 7.75 (m, 6H, *m,p*-phenyl), 3.96 (s, 12H, -OCH_3-ester). MALDI-TOF ($C_{48}H_{32}N_4O_4Zn$): Calculated: 792.17. Found: 792.16.

5, 10-Bis(3-Pyridyl)-15, 20-bis(3-methylcarboxyphenyl)porphyrin (4).

Compound **1** (0.8 g, 2.8 mmol) and nicotinaldehyde (0.31 g, 2.8 mmol) were refluxed in acetic acid (350 mL) for 5 h via the general procedure to give **4** as a purple solid (0.51 g, 24%). Reaction of a 1:1 ratio of dipyromethane **2** and methyl 3-formylbenzoate using the same procedure (Scheme 1) gave a low yield of **4** (6%); mp >300 ˚C. ^{1}H NMR (300 MHz, $DCCl_3$): δ 9.46 (d, J = 1.5 Hz, 2H, 2-py), 9.06 (dd, 2H, *J* = 5.2 Hz, J = 1.5 Hz, 6-py), 8.89-8.81 (m, 10H, 8H-pyrrole, 2H-Ar-CO_2Me), 8.53-8.49 (m, 2H, 4 py), 8.41 (d, 2H, *J* = 7.5 Hz, Ar-CO_2Me), 7.86 (t, 2H, *J* = 7.8 Hz, Ar-CO_2Me), 7.76 (td, 2H, *J* = 5.1 Hz, J = 2.4 Hz, 5-py), 3.96 (s, 6H, OCH_3-Ar-CO_2Me), -2.82 (s, 2H, -NH-Porph). MALDI-TOF ($C_{46}H_{32}N_6O_4$): Calcd. 732.24. Found: 732.18.

5, 10-Bis(3-Pyridyl)-15, 20-bis(3-carboxyphenyl)porphyrin (5).

To a stirred solution of porphyrin **4** (0.35 g, 0.47 mmol) in THF (10 mL) was added KOH (4 mL, 1 *M*/methanol). The resulting mixture was stirred at 35 ºC for 6 h. After evaporation of the solvent, water (75 mL) was added, and the reaction mixture was acidified with 1 *M* HCl to pH 4-6. The solution was extracted (ethyl acetate, 3 x 100 mL) and the combined extracts were evaporated to dryness to afford porphyrin **5** (0.32 g, 95%) as a purple solid; mp: >300 ˚C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 13.28 (s, 2H), 9.36 (d, 2H, J = 1.5 Hz, 2-py), 9.03 (dd, 2H, *J* = 5.2 Hz, 1.5 Hz, 6-py), 8.83 (m, 10H, 8H-pyrrole, 2H-Ar-CO_2Me), 8.67 (m, 2H, 4 py), 8.39 (d, 4H, *J* = 7.5 Hz, Ar-CO_2Me), 7.95 (t, 2H, *J* = 7.8 Hz, Ar-CO_2Me), 7.88 (td, 2H, *J* = 5.1 Hz, J = 2.4 Hz, 5-py), -2.82 (s, 2H, -NH-Porph). MALDI-TOF ($C_{44}H_{28}N_6O_4$): Calculated: 704.21. Found: 704.26.

Synthesis of 4-[N-(tert-Butyloxycarbonyl)amino]benzyl Alcohol (6).

Although **6** was reported (Rai et al., 1992), the following procedure is much easier to perform, A solution of *p*-aminobenzyl alcohol (3.0 g, 0.024 mol) in THF (50 mL) was taken in a two-necked, 100-mL, round-bottomed flask fitted with a magnetic stirrer and was stirred for 5 min. To the solution was added triethylamine (6.7 mL, 0.0487 mol) and Boc anhydride (7.97 g, 0.0365 mol). The resulting solution was stirred at room temperature for 24 h while reaction progress was monitored by TLC. After disappearance of the starting materials via TLC analysis, water (35 mL) was added to the mixture, and the product was extracted (ethyl acetate, 2 x 30 mL). The extracts were washed with brine, were separated, dried (Na_2SO_4), filtered, and evaporated to give **6** as a pale yellow liquid (4.5 g, 83%). The ^{1}H NMR spectrum was identical to the reported (Rai et al., 1992).

Synthesis of 4-[N-(tert-Butyloxycarbonyl)amino]benzaldehyde (7)

Although reported (Rai et al., 1992), **7** was obtained by a more facile procedure. In a 100-mL, two-necked, round-bottomed flask fitted with a rubber septum and an addition funnel was placed a mixture of CH_2Cl_2 (1.15 mL) and DMSO (0.54 mL, 7.73 mmol). The solution was cooled to –78 ˚C (dry ice-acetone bath). Oxalyl chloride (0.71 mL, 8.2 mmol) was added dropwise, and the solution was stirred (30 min), maintaining the temperature at -78 ˚C. Compound **6** (1.15 g, 5.1 mmol) dissolved in CH_2Cl_2 (3 mL) was added dropwise to the reaction mixture which was stirred at -78 ˚C (30 min). TEA (3.59 mL, 25.7 mmol) was then added, and the pale yellow solution generated was stirred for 15 min. The product was extracted (ethyl acetate, 2 x 10 mL), and the combined extracts were washed with brine, dried (Na_2SO_4), filtered and evaporated under reduced pressure to give **7** as a white solid (0.98 g, 87%); mp 136-138 ˚C. (lit[6] mp 138 ˚C). The ^{1}H NMR spectrum was identical to that reported (Rai et al., 1992).

cis- and trans-5,15-Bis[(4-tert-Butoxycarbonylamino)phenyl]-10,20-bis(3-methoxycarbonyl-phenyl)porphinato-Zinc(II) (8a, 8b).

A sample of **1** (0.5 g, 1.7 mmol) and aldehyde **7** (0.39 g, 1.78 mmol) were dissolved in CH_2Cl_2 (190 mL) in a 100-mL, single-necked, round-bottomed flask fitted with a magnetic stirrer. Then TFA (0.243 mL, 3.18 mmol) was added, and the reaction mixture was stirred at room temperature (30 min). Then dichlorodicyanobenzoquinone (DDQ, 0.606 g, 0.00267 mol) was added, and the reaction mixture was stirred at room temperature for 2 h. After completion of the reaction, as judged by TLC analysis, the mixture was neutralized with TEA (3.0 mL). Filtration of the crude mixture through a pad of silica was followed by washing of the pad with CH_2Cl_2. The liquid filtrate was evaporated to dryness to give a dark purple solid. A mixture of methanol and CH_2Cl_2 (10 mL, 1:1) and $Zn(OAc)_2.2H_2O$ (0.5 g, 0.0022 mol) was added to the purple solid, and the resulting solution was stirred overnight at room temperature. Evaporation of the solvent

gave the crude solid which was extracted (CH_2Cl_2 (30 mL). The extract was washed with brine, dried (Na_2SO_4), filtered and evaporated under reduced pressure. Column chromatography of the metallated porphyrin mixture using ethyl acetate:hexane (1:8) afforded a purple solid mixture of *cis*- and *trans*-substituted porphyrins. The isomers were further separated by column chromatography using toluene:methanol (20:1). The *cis*-isomer eluted from the column first. *cis*-**8a:** yield: 0.12 g (7%); mp >300˚C. ^{1}H NMR (400 MHz, $DCCl_3$): δ 8.95 (m, 6H, 4H-pyrrole), 8.85 (s, 2H, Ar-CO_2Me), 8.85 (m, 4H, pyrrole), 8.48 (d, 2H, J = 8 Hz, Ar-CO_2Me), 8.42 (d, 2H, J = 8 Hz, Ar-CO_2Me), 8.13 (d, 4H, J = 8.4 Hz, Ar-NHBoc), 7.84 (t,2H, J = 7.6 Hz, Ar-CO_2Me), 7.72 (d, 4H, J = 8.4 Hz, Ar-NHBoc), 3.96 (s, 6H, -OCH_3-ester), 1.63 (s, 18H, -CH_3-Boc). MALDI-TOF ($C_{58}H_{50}N_6O_8Zn$): Calculated: 1022.29. Found: 1022.24. *trans*-**8b:** yield: 0.5 g (28%); mp: >300 ˚C. ^{1}H NMR (400 MHz, $DCCl_3$): δ 8.96 (d, 4H, J = 4.8, pyrrole), 8.86 (s, 2H, Ar-CO_2Me), 8.85 (d, 4H, J = 4.8, pyrrole), 8.45 (d, 2H, J = 8 Hz, Ar-CO_2Me), 8.42 (d, 2H, J = 8 Hz, Ar-CO_2Me), 8.12 (d, 4H, J = 8.4 Hz, Ar-NHBoc), 7.82 (t, 2H, J = 8 Hz, Ar-CO_2Me), 7.72 (d,4H, J = 8.4 Hz, Ar-NHBoc), 1.65 (s, 18H, -CH_3-Boc), 3.92 (s, 6H, -OCH_3-ester). MALDI-TOF ($C_{58}H_{50}N_6O_8Zn$): Calculated: 1022.29. Found: 1022.25.

5,15-Bis[(4-Amino)phenyl]-10,20-bis(3-methoxycarbonylphenyl)porphine (9).

For deprotection of **8b**, a solution of **8b** (0.1 g, 0.097 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 ˚C in a 100-mL, single-necked, round-bottomed flask fitted with a magnetic stirrer. Then TFA (0.021 mL) was added dropwise. The solution changed from purple to a green color. While stirring the mixure for 2 h at room temperature, the process was monitored by TLC analysis via following a polar spot corresponding to the amine. The reaction mixture was neutralized with 0.1 *M* NaOH (3 mL) and was then extracted (ethyl acetate, 2 x 10 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and evaporated to dryness to afford the di-amino,di-ester porphyrin **9** (0.05 g, 72%) as a purple solid; mp >300 ˚C. ^{1}H NMR (400 MHz, $DCCl_3$): δ 8.94 (d, 4H, J = 4.8 Hz, pyrrole), 8.89 (s, 2H, Ar-CO_2Me), 8.74 (d, 4H, J = 4.8 Hz, pyrrole), 8.46 (d, 2H, J = 8 Hz, Ar-CO_2Me), 8.38 (d, 2H, J = 8 Hz, Ar-CO_2Me), 7.97 (d, 4H, J = 8 Hz, Ar-NH_2), 7.82 (t, 2H, J = 7.6 Hz, Ar-CO_2Me), 7.06 (d, 4H, J = 8 Hz, Ar-NH_2), 3.92 (s, 6H, -OCH_3-ester), -2.78 (s, 2H, NH- Porph). MALDI-TOF ($C_{48}H_{36}N_6O_4$): Calculated: 760.28. Found: 760.24.

5, 10-Bis(3-Pyridyl)-15, 20-bis(4-nitrophenyl)porphyrin (10).

The starting materials, dipyrromethane **2** (0.2 g, 0.89 mmol) and *p*-nitrobenzaldehyde (0.13 g, 0.89 mmol), were placed in a 100-mL, single necked, round bottomed flask fitted with a condenser. A mixture of acetic acid and propionic acid (50 mL, 1:0.5) was added, and the resulting pale yellow solution was refluxed for 4 h. After the reaction mixture was cooled to room temperature, evaporation of the solvent under reduced pressure gave a crude solid. Column chromatography of this crude solid using ethyl acetate:hexane (3:1) afforded the target porphyrin **10** as a purple solid (0.39 g, 61%); mp >300 ˚C. ^{1}H-NMR (300 MHz, $DCCl_3$): δ 9.43 (d, 2H, J = 1.5 Hz, 2-py), 9.07 (dd, 2H, *J* = 5.1, 1.5 Hz, 6-py), 8.85 (d, 4H, J = 4.8 Hz, pyrrole), 8.80 (d, 4H, J = 4.8 Hz, pyrrole), 8.64 (d, 4H, *J* = 7.8 Hz, Ar-NO_2), 8.53 (d, 2H, *J* = 7.5 Hz, 4-py), 8.38 (d, 4H, *J* = 7.8 Hz, Ar-NO_2), 7.78 (td, 2H, *J* = 5.1 Hz, 2.4 Hz, 5-py), -2.84 (s, 2H, -NH). MALDI-TOF ($C_{42}H_{26}N_8O_4Zn$): Calculated: 706.21. Found: 706.23.

5, 10-Bis(3-Pyridyl)-15, 20-bis(4-aminophenyl)porphyrin (11).

To the stirred mixture of HCl/ether (20 mL, 1 *M*) in a 50-mL, round-bottomed flask was added $SnCl_2.H_2O$ (1.5 g). Compound **10** (0.1 g, 0.14 mmol) dissolved in $CHCl_3$ (10 mL) was added to the above mixture which was then stirred at room temperature for 8 h. After completion of the reaction, the crude, thick mass obtained was poured onto crushed ice. When the ice melted, $HCCl_3$ (50 mL) was added. The resulting organic layer was separated, washed with water (20 mL),

washed with 1 *M* NaOH (20 mL), washed with brine, dried (Na_2SO_4), filtered, and concentrated to afford porphyrin **11** (0.083 g, 90%) as a purple solid. mp >300 ˚C. ^{1}H-NMR (300 MHz, $DCCl_3$): δ 9.44 (d, 2H, J = 1.5 Hz 2-py), 9.03 (dd, 2H, *J* = 5.1 Hz, 1.5 Hz 6-py), 8.97 (d, 4H, *J* = 4.8 Hz, pyrrole), 8.77 (d, 4H, *J* = 4.8 Hz, pyrrole), 8.50 (d, 2H, *J* = 7.5 Hz, 4-py), 7.97 (d, 4H, *J* = 7.8 Hz, Ar-NO_2), 7.74 (td, 2H, *J* = 5.1 Hz, 2.4 Hz, 5-py), 7.08 (d, 4H, *J* = 7.8 Hz, Ar-NO_2), -2.78 (s, 2H, NH). MALDI-TOF ($C_{42}H_{30}N_8$): Calculated: 646.25. Found: 646.18.

4-[(2-Methylbut-3-yn-2-yl)oxy]benzaldehyde (12).

A mixture of *p*-hydroxybenzaldehyde (1.0 g, 0.0081 mol) and 3-chloro-3-methyl-1-butyne (12.34 g, 0.1210 mol) was placed in a 100-mL, two-necked, round-bottomed flask fitted with a condenser and a magnetic stirrer. Dry DMF (40 mL) was added, and the system was purged with Ar for 15 min. Anhydrous K_2CO_3 (2.0 g, 0.014 mol) and KI (2.28 g, 0.0137 mol) were added, and the reaction mixture was stirred at 65 ˚C for 24 h under Ar. The heterogenous mixture and the combined extracts were allowed to cool to RT and were then filtered. The filtrate was extracted (ethyl acetate, 2 x 20 mL), and the combined extracts were washed with brine, dried (Na_2SO_4), filtered, and evaporated under vacuum to give the crude material. Further purification was achieved by flash chromatography using ethyl acetate:hexane (1:4) to give **12** as an yellow oil (1.31 g 86%). The material was used immediatelly in the next step.

5-(4-[(2-Methylbut-3-yn-2-yl)oxy])phenyl-10,15,20-tris(3-methoxycarbonylphenyl)porp-hyrin (13a), 5,15-(4-[(2-Methylbut-3-yn-2-yl)oxy])phenyl-10,20-tris(3-methoxycarbonyl-phenyl)porphyrin (13b).

To a 100-mL, single-necked, round-bottomed flask fitted with a gas bubbler and a magnetic stirrer was added a solution of **12** (0.067 g, 0.35 mmol) and dipyrromethane **1** (0.1 g, 0.35 mmol) dissolved in dry CH_2Cl_2 (50 mL). The system was degassed for about 15 min with Ar. Then BF_3 ethereate (0.09 mL, 0.7 mmol) was added slowly to the reaction mixture which was stirred at RT for 12 h. A change in color was observed from pale yellow to a dark brown solution. The flask was covered with aluminium foil, and the system was stirred at RT for 1 h during which time a color change occurred from a dark brown to a purple solution. Then DDQ (0.12 g, 0.53 mmol) was added to the reaction, and the solution was purged with Ar with continuous stirring for 1.3 h. The solvent was evaporated, and the crude solid was placed on a pad of silica–celite and was washed with CH_2Cl_2:ethyl acetate (3:1, 450 mL). The liquid filtrate was evaporated to dryness, and the product was further purified by column chromatography using ethyl acetate:hexane (1:5) to give two fractions from which porphyrins **13a** and **13b** were isolated as purple solids. Compound **13a** eluted first from the column. **13a**: yield: (0.024 g, 8%); mp >300 ˚C. ^{1}H NMR (300 MHz, $DCCl_3$): δ 8.92 (d, 2H, J = 4.8 Hz, pyrrole), 8.90 (s, 2H, Ar-CO_2Me), 8.79 (s, 6H, pyrrole), 8.48 (d, 3H, J = 7.8, Ar-CO_2Me), 8.39 (d, 3H, J = 7.8 Hz, Ar-CO_2Me), 8.10 (d, 2H, J = 8.4 Hz, Ar-Alkyne), 7.83 (t, 3H, J = 7.8 Hz, Ar-CO_2Me), 7.60 (d, 2H, J = 8.4 Hz, Ar-Alkyne), 3.99 (s, 9H, -OCH_3-ester), 2.76 (s, 1H, -CH-Alkyne), 1.88 (s, 6H, -CH_3-Alkyne), -2.78 (s, 2H, NH-Porph). MALDI-TOF ($C_{55}H_{42}N_4O_7$): Calculated: 870.30. Found: 870.31. **13b**: yield: 0.038 g (12%); mp: >300 ˚C. ^{1}H NMR (400 MHz, $DCCl_3$): δ 8.90 (bs, 6H, 4H-pyrrole, 2H- Ar-CO_2Me), 8.77 (d, 4H, J = 4.8 Hz, pyrrole), 8.47 (d, 2H, J = 8.1 Hz, Ar-CO_2Me), 8.39 (d, 2H, J = 8.1 Hz, Ar-CO_2Me), 8.10 (d, 4H, J = 8.4 Hz, Ar-Alkyne), 7.83 (t, 2H, J = 8.1 Hz, Ar-CO_2Me), 7.60 (d, 4H, J = 8.4 Hz, Ar-Alkyne), 3.99 (s, 6H, -OCH_3-ester), 2.76 (s, 2H, -CH-Alkyne), 1.88 (s, 12H, -CH_3-Alkyne), -2.78 (s, 2H, NH-Porph). MALDI-TOF ($C_{55}H_{42}N_4O_7$): Calculated: 894.3417. Found: 894.3512.

Conclusions

We have developed procedures to obtain 10 different *meso*-substituted porphyrins containing peripheral functional groups. The structures of all synthesized compounds were characterized by ^{1}H NMR and MALDI–TOF

spectrosocopy. The new porphyrins may find use as building blocks for the construction of novel supramolecular assemblies which can potentially be applied in various bioorganic model systems and molecular devices.

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Received August 27, 2014 Accepted November 5, 2014