Articles

Synthesis of β-Mono-, Tetra-, and Octasubstituted Sterically Bulky Porphyrins via Suzuki Cross Coupling

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β-Mono-, tetra-, and octasubstituted tetramesitylporphyrins were prepared in good yields by Suzuki cross-coupling reactions of β-bromotetramesitylporphyrins with aryl- and alkylboronic acids.

Introduction

The continuing interests in porphyrins and metalloporphyrins have encompassed areas in organometallic chemistry,[1] biomimetic oxidation catalysis,[2] photodynamic therapy,[3] and material sciences.[4] Sterically-encumbered porphyrins have been widely used as biomimetic models.[5] Tetramesitylporphyrin[6] (H_2TMP) is one of the most accessible sterically hindered tetraarylporphyrin ligands which have been used in metalloporphyrin-catalyzed oxygenation reactions. Substituents on β-positions of porphyrins seem to confer some unusual optical properties, enhanced electrochemical redox stability,[7,8] and increased catalytic efficiency to the metal complexes.[8] Until now, the synthesis of β-substituted porphyrins, especially for sterically hindered porphyrins, has been plagued by the relative inaccessibility of 3-, and 3,4-substituted pyrroles, low yields, and tedious chromatographic separation and purification of products.[10]

The synthesis of 3- and 3,4-substituted pyrroles has been improved recently by at least two routes. Employing the blocking group approach, the regioselective bromination−lithiation−alkylation of *N*-(triisopropylsilyl)-pyrrole followed by deprotection produces 3-, or 3,4-substituted pyrroles.[9a−c] Alternatively, the procedures by Barton and Zard, Lash, and Burns using nitroalkenes and isocyanoacetates are versatile entries.[9d−f] Although these are all facile synthetic methods, an alternative approach for the synthesis of β-porphyrins bypassing the need of preparing these pyrroles could be empolyed through the functional group manipulation of β-bromoporphyrins.

One classical and frequently employed porphyrin synthesis involves the tetramerization of pyrroles and aldehydes under either protic or Lewis acid catalyzed conditions.[11,12] Limitation exists for the preparation of sterically hindered porphyrins for the one-pot condensation in refluxing propionic acid as a metal-templated method is necessary.[13] Lindsey has improved the synthesis of sterically hindered porphyrin by employing $BF_3{\cdot}Et_2O$ as the Lewis acid with subsequent oxidation by DDQ.[12] We have recently demonstrated a facile method in synthesizing β-aryl-substituted tetraphenylporphyrins via the Suzuki cross-coupling[14] reactions of the corresponding bromoporphyrins with arylboronic acids.[15] We now further utilize this cross-coupling route for the preparation of sterically hindered β-mono-, tetra-, and octasubstituted tetramesitylporphyrins [H_2TMP(R)$_n$] (n = 1, 4, 8; R = Me, Ar) from their corresponding bromoporphryins.[16]

Results and Discussion

Bromoporphyrins H_2TMP(Br) (**2**), H_2TMP(Br)$_4$ (**3**),[17] and H_2TMP(Br)$_8$ (**4**)[18] were conveniently prepared via the controlled bromination of H_2TMP (**1**) with either NBS via

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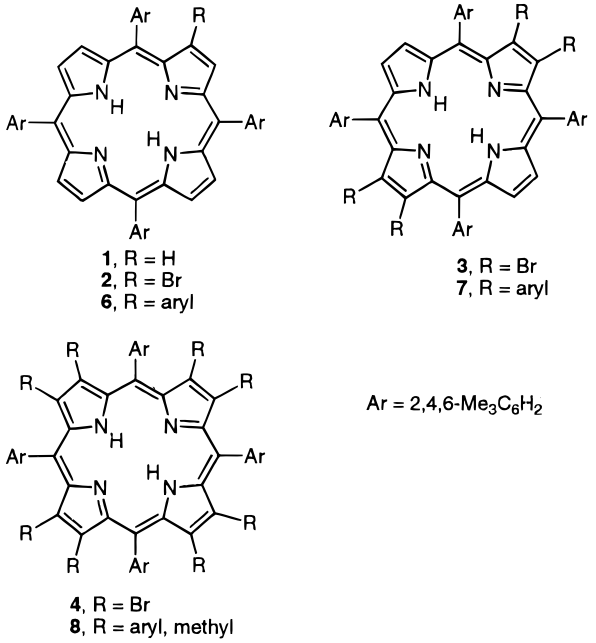
Scheme 1



the free porphyrin or with Br_2 via the zinc porphyrin complex (ZnTMP)[18] according to the literature procedure-(eqs 1−3). H_2TMP(Br) (**2**) was isolated by chromatography in 36% yield when H_2TMP was reacted with 1.6 equiv of NBS. H_2TMP$(Br)_4$ (**3**) was in contrast obtained in a much higher yield of 52% when **1** reacted with 6.7 equiv of NBS. Presumably it is more difficult to further introduce more than four bromine atoms into **1** under these reaction conditions. The structure of the tetrabromoporphyrin **3** has been determined previously[17] with the bromines in the antipodal positions and is consistent with that of the tetraphenylporphyrin derivative.[15]

H_2TMP (**1**) —NBS, 1.7 equiv→ H_2TMP(Br) (**2**, 36%) (1)

H_2TMP (**1**) —NBS, 6.7 equiv→ H_2TMP$(Br)_4$ (**3**, 52%) (2)

ZnTMP —NBS→ ZnTMP$(Br)_8$ (58%) —TFA→ H_2TMP$(Br)_8$ (**4**, 95%) (3)

All the bromoporphyrins, H_2TMP$(Br)_n$ (n = 1, 4, 8), underwent smooth Suzuki cross-coupling reactions with aryl- and methylboronic acids (**5a**−**g**, 16 equiv) using a catalytic amount of $Pd(PPh_3)_4$ (10 −15 mol %) and anhydrous K_2CO_3 (32 equiv) (Scheme 1) in toluene or toluene/THF at 90−100 °C. The β-aryl- or β-methylprophyins were isolated in 45−90% yields (Table 1). While monoarylation took only 1 d to complete, the longer reaction time of 2−4 d and 7 d was necessary for tetra- and octaarylation to complete, respectively. All the *para*-substituted phenylboronic acids successfully reacted. For arylboronic acids, the solvent used was toluene while for methylboronic acid a solvent mixture of THF−toluene was employed to enhance the solubility of methylboronic acid. When compared to the influence of the *meso*-phenyl group in tetraphenylporphyrin, the sterically more bulky and electronically more rich mesityl group did not seem to prolong the reaction time likely due to the enhanced solubility in counter balancing off the increase in steric hindrance. No protection of the porphyrins as zinc complexes is necessary.[19]

Table 1. Suzuki Cross Coupling of H_2TPP$(Br)_n$ with $RB(OH)_2$ (eqs 4−6)

H_2TMP(Br) (**2**) + $RB(OH)_2$ (**5**) —$Pd(PPh_3)_4$, K_2CO_3, 90-100°C, 1-2days, toluene→ H_2TMP(R) (**6**) (4)

H_2TMP$(Br)_4$ (**3**) + $4RB(OH)_2$ (**5**) —$Pd(PPh_3)_4$, K_2CO_3, 90-100°C, 2-4days, toluene→ H_2TMP$(R)_4$ (**7**) (5)

H_2TMP$(Br)_8$ (**4**) + $8RB(OH)_2$ (**5**) —$Pd(PPh_3)_4$, K_2CO_3, 90-100°C, 7days, toluene or toluene-THF→ H_2TMP$(R)_8$ (**8**) (6)

		% yield of H_2TMP$(R)_n$ at various reaction times		
R =		H_2TMP(R) 1 −2 d	H_2TMP$(R)_4$ 2−4 d	H_2TMP$(R)_8$ 7 d
Ph	**5a**	74 **6a**	71 **7a**	53 **8a**
p-MePh	**5b**	90 **6b**	84 **7b**	56 **8b**
p-CF_3Ph	**5c**		75 **7c**	78 **8c**
p-MeOPh	**5d**	78 **6d**		50 **8d**
p-ClPh	**5e**	79 **6e**		88 **8e**
p-^{t}BuPh	**5f**			45 **8f**
Me	**5g**			74 **8g**

This synthetic approach to β-phenylporphyrins is a unique entry. The synthesis of β-phenylporphyrins, such as dodecaphenylporphyrin, employed the reaction of 3,4-diphenylpyrrole with benzaldehyde to give the product in high yield (47%).[7,20] Yet, the less readily accessible 3,4-diarylpyrroles, in contrast with the more readily available arylboronic acids,[15b] limit the synthesis. Furthermore, the condensation of 3,4-diphenylpyrrole with sterically hindered aryl aldehydes was not always successful. While 2,6-dichlorobenzaldehyde gave only a small amount of the corresponding porphyrin (<2%),[21] in a preliminary run, mesityl aldehyde did not yield any porphyrin **8a** at all. Presumably the reduced nucleophilic and sterically more hindered 3,4-diphenylpyrrole compared to pyrrole decreases in reactivity.[22]

The product **8g** has been structurally characterized. It showed a tetrahedral and nonplanar saddled structure[16] and is typical of β-octasubstituted porphyrins.[7]

Experimental Section

^{1}H NMR spectra were measured at 250 and 270 MHz. In all ^{1}H NMR measurements, chemical shifts were referenced with tetramethylsilane δ = 0.00 ppm. Mass spectra were obtained either in EI mode at 70 eV or in FAB mode using NBA as the matrix. Elemental analyses were performed by the Medac Ltd. Department of Chemistry, Brunel University, U.K. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification.

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All the arylboronic acid were prepared according to the literature method.[15] Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and toluene was distilled from sodium immediately prior to use. All cross-coupling reactions were run with the reaction mixture deoxygenated by the freeze−pump−thaw method (−195 to 25 °C, three cycles). Flash chromatography was performed with silica gel (70−230 or 230−400 mesh).

Synthesis of 2-Bromo-5,10,15,20-tetramesitylporphyrin, H_2TMP(Br) (2). H_2TMP (110 mg, 0.14 mmol) and *N*-bromosuccinimide (43 mg, 0.24 mmol) were refluxed in boiling chloroform for 45 min. The crude product was chromatographed on silica gel using CH_2Cl_2:hexane = 1:3 as the eluent, yielding H_2TMP(Br) (43 mg, 36%): R_f = 0.16 (CH_2Cl_2:hexane = 1:3); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.62 (bs, 2 H), 1.22 (q, 6 H, J = 7.1 Hz), 1.78−1.81 (ms, 24 H), 2.60 (s, 12 H), 3.71 (t, 4 H, J = 7.0 Hz), 7.24−7.25 (m, 8 H), 8.54 (s, 2 H), 8.63−8.66 (m, 4 H), 8.73 (s, 1H); FABMS m/z 861.4, 863.4 [M(^{79}Br^{81}Br) + H]$^+$; HRMS (matrix, NBA) calcd for $C_{56}H_{53}N_4Br{\cdot}H^+$ 861.3532, found 861.3378; λ_{max} (CH_2Cl_2, nm, log ϵ) 421 (5.58), 517 (4.30), 549 (3.65), 593 (3.76), 649 (3.67). Anal. Calcd for $C_{56}H_{53}N_4Br{\cdot}2C_2H_5OH$: C, 75.53; H, 6.87; N, 5.87. Found: C, 75.79; H, 7.27; N, 5.16.

Synthesis of 2,3,12,13-Tetrabromo-5,10,15,20-tetramesitylporphyrin, H_2TMP(Br)$_4$ (3).[17] H_2TMP (200 mg, 0.26 mmol) and *N*-bromosuccinimide (309 mg, 1.74 mmol, 6.7 equiv) were refluxed in boiling chloroform for 3 h until the Soret band had shifted to 430 nm. The product was purified by column chromatography on silica gel using CH_2Cl_2:hexane = 1:5 as eluent. The violet solid obtained was recrystallized from CH_2Cl_2/MeOH to yield pure violet crystals of H_2TMP(Br)$_4$ (147 mg, 52%): R_f = 0.20 (CH_2Cl_2:hexane = 1:5); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −3.00 (bs, 2 H), 1.75 (s, 24 H), 2.59 (s, 12 H), 7.22 (s, 8 H), 8.58 (s, 4 H); λ_{max} (CH_2Cl_2, nm, log ϵ) 431 (5.48), 525 (4.32), 605 (3.71), 660 (3.94). L-SIMS m/z 1095.1 [M(^{79}Br) + H]$^+$, 1097.1 [M(^{79}Br$_3^{81}$Br) + H]$^+$, 1099.1 [M(^{79}Br$_2^{81}$Br$_2$) + H]$^+$, 1101.1 [M(^{79}Br^{81}Br$_3$) + H]$^+$, 1103.1 [M(^{81}Br$_4$) + H]$^+$.

Synthesis of 2-(4′-Toluyl)-5,10,15,20-tetramesitylporphyrin, H_2TMP(*p*-MePh) (6b). A Teflon-stoppered flask (50 mL) was charged with H_2TMP(Br) (40 mg, 0.046 mmol), Pd(PPh_3)$_4$ (5 mg, 10 mol %), toluene (15 mL), anhydrous K_2CO_3 (51 mg, 0.37 mmol), and 4-toluylboronic acid (20 mg, 0.19 mmol). The brown suspension was degassed by the freeze−pump−thaw method (three cycles) and then was heated at 90−100 °C under N_2 for 2 days. Solvent was evaporated off, and the crude product was purified by column chromatography on silica gel using CH_2Cl_2:hexane = 1:3 as the eluent. The brown solution obtained was evaporated to give a violet solid which was recrystallized from CH_2Cl_2/MeOH to yield pure 2-(4′-toluyl)-5,10,15,20-tetramesitylporphyrin (90%): R_f = 0.06 (CH_2Cl_2:hexane = 1:3); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.44 (bs, 2 H), 1.74 (s, 6 H), 1.83−1.85 (ms, 18 H), 2.33 (s, 3 H), 2.38 (s, 3 H), 2.55 (s, 3H), 2.60 (s, 6H), 6.74 (s, 2 H), 6.95 (d, 2 H, J = 7.9 Hz), 7.14−7.26 (m, 8 H), 8.51−8.61 (ms, 7 H); λ_{max} (CH_2Cl_2, nm, log ϵ) 424 (5.42), 520 (4.19), 553 (3.67), 594 (3.66), 650 (3.25); FABMS m/z 872 (M$^+$). Anal. Calcd for $C_{63}H_{60}N_4{\cdot}0.5H_2O$: C, 85.77; H, 6.97; N, 6.35. Found: C, 86.04; H, 6.84; N, 5.70.

2-Phenyl-5,10,15,20-tetramesitylporphyrin, H_2TMP(Ph) (6a) (74%): R_f = 0.76 (CH_2Cl_2:hexane =1:2); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.50 (s, 2 H), 1.68 (s, 6 H), 1.78−1.80 (ms, 18 H), 2.24 (s, 3 H), 2.50 (s, 3H), 2.55 (s, 6H), 6.65 (s, 2 H), 7.05−7.22 (m, 11 H), 8.45−8.55 (ms, 7 H); λ_{max} (CH_2Cl_2, nm, log ϵ) 424 (5.39), 519 (4.23), 552 (3.88), 594 (3.85), 651 (3.66); FABMS m/z 859 (M$^+$). Anal. Calcd for $C_{62}H_{58}N_4$: C, 86.67; H, 6.80; N, 6.52. Found: C, 86.57; H, 6.76; N, 5.88.

2-(4′-Methoxyphenyl)-5,10,15,20-tetramesitylporphyrin, H_2TMP(*p*-MeOPh) (6d) (78%): R_f = 0.52 (CH_2Cl_2:hexane = 1:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.49 (s, 2 H), 1.68 (s, 6 H), 1.77−1.80 (ms, 18 H), 2.29 (s, 3 H), 2.54 (s, 3H), 2.55 (s, 6H), 3.79 (s, 3 H), 6.63 (d, 2 H, J = 8.6 Hz), 6.71 (s, 2 H), 7.13−7.26 (m, 8 H), 8.51−8.61 (ms, 7 H); λ_{max} (CH_2Cl_2, nm, log ϵ) 421(5.43), 517 (4.25), 550 (3.83), 592 (3.85), 648 (3.67); FABMS m/z 889 (M$^+$). Anal. Calcd for $C_{63}H_{60}N_4{\cdot}2H_2O$: C, 81.79; H, 6.97; N, 6.06. Found: C, 82.07; H, 6.82; N, 5.60.

2-(4′-Chlorophenyl)-5,10,15,20-tetramesitylporphyrin, H_2TMP(*p*-ClPh) (6e) (79%): R_f = 0.52 (CH_2Cl_2:hexane = 1:2); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.46 (s, 2 H), 1.72−1.73 (ms, 8 H), 1.82−1.85 (ms, 16 H), 2.39 (s, 4 H), 2.55 (s, 4H), 2.60 (s, 4H), 6.79 (s, 3 H), 7.09−7.24 (m, 9 H), 8.52−8.60 (ms, 7 H); λ_{max} (CH_2Cl_2, nm, log ϵ) 421 (5.31), 517 (4.56), 550 (4.27), 593 (4.26), 650 (4.15); FABMS m/z 893 (M$^+$). Anal. Calcd for $C_{62}H_{57}N_4Cl{\cdot}H_2O$: C, 81.68; H, 6.52; N, 6.14. Found: C, 81.83; H, 6.32; 5.86.

Synthesis of H_2TMP(Ar)$_4$. A typical procedure is shown for **7b**. A Teflon-stoppered flask (50 mL) was charged with H_2TMP(Br)$_4$ (50 mg, 0.046 mmol), Pd(PPh_3)$_4$ (5 mg, 10 mol %), toluene (15 mL), anhydrous K_2CO_3 (201 mg, 1.46 mmol), and 4-toluylboronic acid (80 mg, 0.73 mmol). The brown suspension was degassed by the freeze−pump−thaw method (three cycles), and then was heated at 90−100 °C under N_2 for 2 days. Solvent was evaporated to obtain the crude product which was purified by column chromatography on silica gel using CH_2Cl_2:hexane = 2:1 as the eluent. The brown solution obtained was evaporated to give a violet solid which was recrystallized from CH_2Cl_2/MeOH to yield pure **7b** (84%): R_f = 0.24 (CH_2Cl_2:hexane = 2:1); ^{1}H NMR (250 MHz, $CDCl_3$) δ −2.09 (bs, 2 H), 1.78 (s, 24 H), 2.28 (s, 12 H), 2.34 (s, 12 H), 6.65 (s, 8 H), 6.67 (d, 8 H, J = 7.9 Hz), 6.86 (d, 8 H, J = 7.9 Hz), 8.22 (s, 4 H); λ_{max} (CH_2Cl_2, nm, log ϵ) 431.0 (5.28), 525.0 (4.07), 559.0 (3.66), 601.0 (3.58), 661 (3.10); FABMS m/z 1142 (M$^+$). Anal. Calcd for $C_{84}H_{78}N_4{\cdot}3H_2O$: C, 84.24; H, 7.07; N, 4.68. Found: C, 84.51; H, 6.83; N, 4.51.

2,3,12,13-Tetraphenyl-5,10,15,20-tetramesitylporphyrin, H_2TMP(Ph)$_4$ (7a) (71%): R_f = 0.62 (CH_2Cl_2:hexane =1:1.6); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.06 (s, 2 H), 1.80 (s, 24 H), 2.24 (s, 12 H), 6.62 (s, 8 H), 6.80−6.97 (m, 20 H), 8.28 (s, 4 H); λ_{max} (CH_2Cl_2, nm, log ϵ) 431 (5.37), 525 (4.23), 558 (3.83), 598 (3.82), 659 (3.59); FABMS m/z 1087 (M$^+$). Anal. Calcd for $C_{80}H_{70}N_4$: C, 88.34; H, 6.49; N, 5.15. Found: C, 88.01; H, 6.91; N, 4.89.

2,3,12,13-Tetrakis-(4′-(trifluoromethylphenyl)-5,10,15,-20-tetramesitylporphyrin, H_2TMP(*p*-CF_3Ph)$_4$ (7c) (75%): R_f = 0.80 (CH_2Cl_2:hexane = 1:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.25 (s, 2H), 1.87 (s, 24 H), 2.25 (s, 12 H), 6.67 (s, 8 H), 7.05−7.16 (m, 16 H), 8.35 (s, 4 H); λ_{max} (CH_2Cl_2, nm, log ϵ) 430 (5.47), 525 (4.49), 562 (4.33), 600 (4.32), 666 (4.28); FABMS m/z 1058 (M$^+$ − 1). Anal. Calcd for $C_{84}H_{66}N_4F_{12}{\cdot}H_2O$: C, 73.25; H, 4.98; N, 4.06. Found: C, 72.98; H, 5.01; N, 3.95.

A Typical Procedure for the Synthesis of H_2TMP(Ar)$_8$. A 50 mL Telfon-stoppered flask was charged with the H_2TMP(Br)$_8$ (**4**) (1 equiv), Pd(PPh_3)$_4$ (15 mol %), toluene (25−30 mL, 40% THF for porphyrin **8g**), anhydrous potassium carbonate (40 equiv), and an arylboronic acid (20 equiv). The green suspension was degassed by the freeze−pump−thaw method (three cycles), and then the mixture was heated between 90 and 100 °C under N_2 for 7 days. The reaction mixture was worked up by adding an equal volume of CH_2Cl_2 and washed with $NaHCO_3$ (40 mL), water (2 × 40 mL), and NaCl (satd). The organic layer was dried with anhydrous $MgSO_4$. After rotary evaporation, the crude product was purified by column chromatography on silica gel using a solvent mixture of $CHCl_3$, CH_2Cl_2, and hexane as the eluent. The last slow-moving green band was collected and evaporated to dryness to give a green solid, recrystallized by using a solvent mixture of CH_2Cl_2/EtOH to give the pure green crystal of H_2TMP(Ar)$_8$.

2,3,7,8,12,13,17,18-Octaphenyl-5,10,15,20-tetramesitylporphyrin, H_2TMP(Ph)$_8$ (8a) (53%): R_f = 0.30 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −0.93 (s, 2 H), 1.85−1.95 (ms, 24 H), 2.01 (s, 12 H), 6.11 (s, 8 H), 6.63−6.70 (m, 40 H); UV/vis λ_{max} (CH_2Cl_2, nm, log ϵ) 461.0 (5.65), 557.5 (4.40), 601.0 (4.27), 703.5 (4.36); FABMS m/z 1392 (M$^+$). Anal. Calcd for $C_{104}H_{86}N_4{\cdot}2H_2O$: C, 87.48; H, 6.35; N, 3.92. Found: C, 87.92; H, 6.13; N, 4.00.

2,3,7,8,12,13,17,18-Octa-4′-toluyl-5,10,15,20-tetramesitylporphyrin, H_2TMP(*p*-MePh)$_8$ (8b) (56%): R_f = 0.16 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −0.95 (s, 2 H), 1.79−2.30 (ms, 60 H), 6.14−6.91 (m, 40 H); UV/vis λ_{max} (CH_2Cl_2, nm, log ϵ) 457.0 (5.68), 551.0 (4.48), 635.0 (4.30), 696.5 (4.60). FABMS m/z 1504 (M$^+$). Anal. Calcd for $C_{112}H_{102}N_4{\cdot}4H_2O$: C, 85.40; H, 7.03; N, 3.57. Found: C, 85.23; H, 6.84; N, 3.73.

2,3,7,8,12,13,17,18-Octakis(4′-(trifluoromethyl)phenyl)-5,10,15,20-tetramesitylporphyrin, H_2TMP(*p*-CF_3Ph)$_8$ (8c) (78%): R_f = 0.78 (CH_2Cl_2:hexane = 1:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −0.94 (s, 2 H), 1.88 (s, 24 H), 2.07 (s, 12 H), 6.18 (s, 8 H), 6.76−6.78 (m, 16 H), 6.96 (d, 16 H, J = 8.1 Hz); λ_{max} (CH_2Cl_2, nm, log ϵ) 458 (5.60), 556 (4.78), 598 (4.76), 720 (4.74); FABMS m/z 1934 (M^+ − 1). Anal. Calcd for $C_{112}H_{78}N_4F_{24}\cdot H_2O$: C, 68.85; H, 4.13; N, 2.87. Found: 68.45; H, 4.25; N, 2.77.

2,3,7,8,17,18-Octakis(4′-methoxyphenyl)-5,10,15,20-tetramesitylporphyrin, H_2TMP(*p*-MeOPh)$_8$ (8d) (50%): R_f = 0.16 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −0.94 (s, 2 H), 1.89 (s, 24 H), 2.02 (s, 12 H), 3.55−3.71 (ms, 24 H), 6.17−6.20 (m, 25 H), 6.48 (ms, 15 H); UV/vis λ_{max} (CH_2Cl_2, nm, log ϵ) 457.0 (5.36), 551.0 (4.18), 635.0 (3.99), 696.5 (4.28); FABMS m/z 1840 (M^+). Anal. Calcd for $C_{112}H_{102}N_4O_8\cdot 2H_2O$: C, 80.64; H, 6.41; N, 3.36. Found: C, 80.90; H, 6.42; N, 4.00.

2,3,7,8,12,13,17,18-Octakis(4′-chlorophenyl)-5,10,15,20-tetramesitylporphyrin, H_2TMP(*p*-ClPh)$_8$ (8e) (88%): R_f = 0.86 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −1.04 (s, 2 H), 1.85 (s, 24 H), 2.11 (s, 12 H), 6.28 (s, 8 H), 6.53−6.68 (m, 32 H); UV/vis λ_{max} (CH_2Cl_2, nm, log ϵ) 460.0 (5.82), 555.5 (4.58), 600.5 (4.40); FABMS m/z 1668 (M^+). Anal. Calcd for $C_{104}H_{78}N_4Cl_8\cdot H_2O$: C, 74.09; H, 4.78; N, 3.32. Found: C, 73.62; H, 4.70; N, 3.43.

2,3,7,8,12,13,17,18-Octakis(4′-*tert*-butylphenyl)-5,10,15,-20-tetramesitylporphyrin, H_2TMP(*p*-^{t}BuPh)$_8$ (8f) (45%): R_f = 0.25 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ −0.96 (brs, 2 H), 0.96−1.09 (m, 54 H), 1.19−1.23 (ms, 18 H), 1.73−1.97 (ms, 33 H), 2.19 (s, 3 H), 6.10−6.16 (ms, 6 H), 6.33−6.76 (m, 31 H), 6.89 (s, 3 H); UV/vis λ_{max} (CH_2Cl_2, nm, log ϵ) 464.0 (5.37), 558.5 (4.18), 706.5 (3.78); FABMS m/z 1840 (M^+). Anal. Calcd for $C_{136}H_{150}N_4\cdot 3H_2O$: C, 86.25; H, 8.31; N, 2.96. Found: C, 86.19; H, 8.01; N, 3.18.

2,3,7,8,12,13,17,18-Octamethyl-5,10,15,20-tetramesitylporphyrin, H_2TMP(Me)$_8$ (8g) (74%): R_f = 0.11 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.90 (s, 24 H), 2.18 (s, 24 H), 2.55 (s, 12 H), 7.24 (s, 8 H); UV/vis λ_{max} (CH_2Cl_2, nm, log ϵ) 458.5 (5.17), 614.5 (4.11), 666.0 (4.09); FABMS m/z 896 (M^+). Anal. Calcd for $C_{64}H_{70}N_4\cdot 4H_2O$: C, 79.49; H, 8.13; N, 5.79; Found: C, 79.13; H, 7.98; N, 5.79.

Conclusion

In conclusion, we have developed a facile synthesis of β-mono-, tetra-, and octasubstituted tetramesitylporphyrins by Suzuki cross-coupling reactions of β-octabromotetramesitylporphyrin with aryl- and alkylboronic acids. Further applications of these ligands in metalloporphyrin chemistry are underway.

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