Synthesis of β-Linked Diporphyrins and Their Homo- and Hetero-Bimetallic Complexes

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β-Meta- and -para-linked diporphyrins have been synthesized from two complementary routes using Suzuki cross-coupling and Adler condensation. Porphyrin boronate **6** cross couples with β-monobromoporphyrin **2** to give unsymmetrically substituted porphyrin dimer **7c** in high yield, and Adler condensation of β-formylphenyltetraphenylporphyrins **9b,c** with aryl aldehydes yields electronically tunable diporphyrins **7a**−**e**. The homo- and hetero-bimetallic complexes **11a**−**c** have been synthesized. Selective mono-metalation with zinc acetate at the β-substituted site has been found for **7a**. The Zn−Co diporphyrin complex **11c** undergoes strong emission quenching compared to that of the diporphyrin **11a** and dizinc diporphyrin **11b**.

Introduction

Porphyrin arrays and their metal complexes with different geometries and separation distances bear structural and light-absorbing similarities with the chlorophyll and have been utilized as synthetic models for biochemical and photochemical processes[1−3] as well as electrochemical catalysts. Porphyrin arrays with electron donor, electron relays, and electron acceptors serve as biomimics for the understanding of the energy utilization in the dimeric porphyrin-like nature of electron donor in photosynthetic system I.[1] Dimanganese diporphyrins have also been used to model successfully the oxidation of water to oxygen catalyzed by the maganese clusters in the active sites of photosynthetic system II.[2] Cofacially-bridged dimeric porphyrin cobalt complexes have exhibited enhanced efficiency as catalysts for the electrochemical reduction of O_2 to water via a four-electron process with reduced overvoltage as a result of bimetallic cooperativity.[3]

Most of the reported porphyrin dimers can be broadly classified into two categories: (1) linear stacked dimers either covalently[4] linked or hydrogen bonded;[5] (2) cofacial dimers linked by linear spacers to achieve parallel configuration.[6]

All the reported dimers are mainly *meso*-aryl-linked[4−6] though some recent ones are beta-[7] and *meso*-alkyne-linked.[8] They are prepared through lengthly routes such as the classic [2 + 2] condensation of valuable dipyrrolmethanes and dialdehydes.[9] The improved preparation of porphyrin dimers would facilitate the biomimetic and catalytic studies. We report herein our results of the facile synthesis of porphyrin dimers linked between *meso*-

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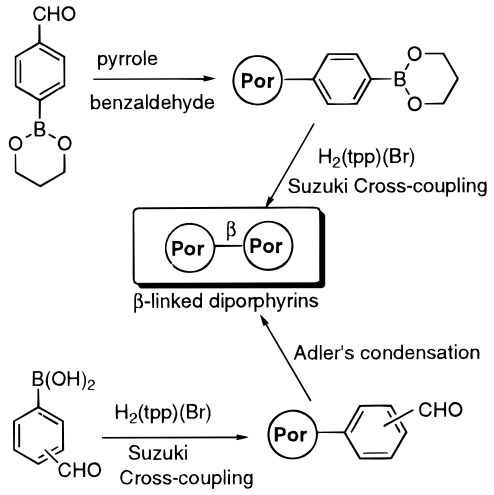
Scheme 1. Synthetic Strategy for Diporphyrins



position and β-position by phenyl groups through key Suzuki cross-coupling[10] in two complementary routes.[11,12] Furthermore, we have prepared new homo- and hetero-metallodiporphyrins selectively and studied their emission properties.

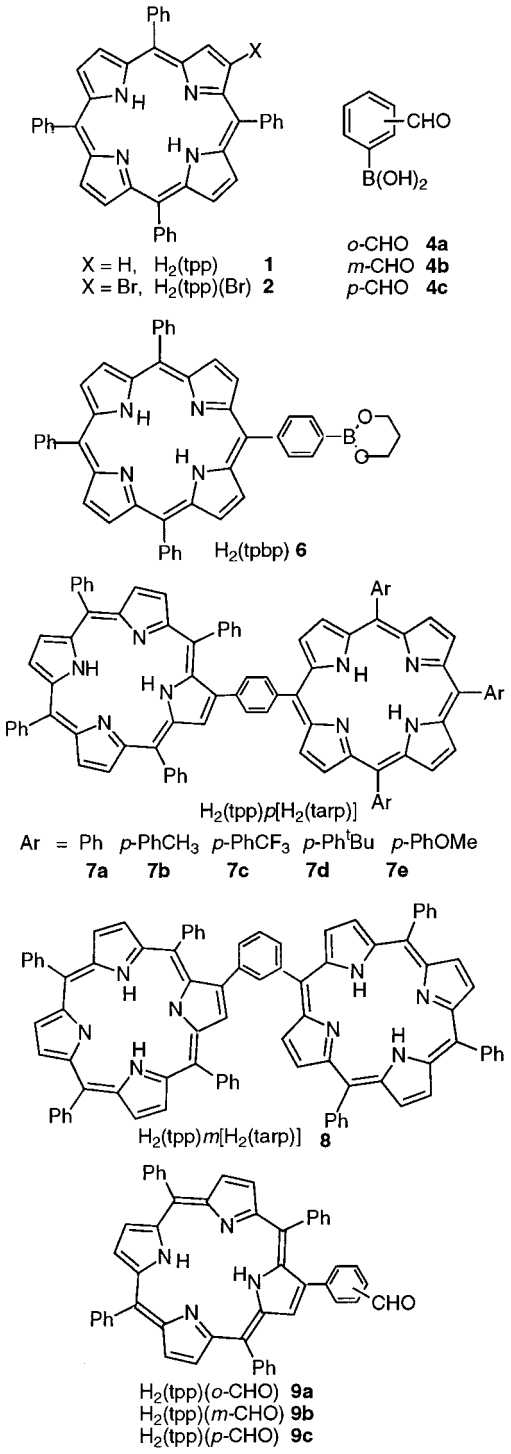
Result and Discussion

Inspired by our success in synthesizing β-substituted porphyrins by Suzuki cross-coupling with aryl and alkyl boronic acids,[11] we envisaged that a diporphyrin would be easily obtained from two complementary procedures: (A) mixed Adler[13] condensation of a boronated aldehyde with aldehyde and pyrrole—Suzuki cross-coupling with β-bromo porphyrin; (B) Suzuki cross-coupling of a β-bromo porphyrin with a boronic acid aldehyde—mixed Adler condensation of porphyrin aldehydes with aryl aldehydes and pyrrole (Scheme 1). These new, unsymmetrical diporphyrins would provide possibilities for the preparation of both homo- and hetero-metalloporphyrins. Subsequently, the interaction of porphyrin and metallo dimers with a β-aryl linkage could be probed.

(A). Synthesis of Diporphyrins via Condensation. Suzuki Cross-Coupling. This method involved the preparation of porphyrin boronate [H_2(tpbp)] **6** and its subsequent condensation with β-monobromoporphyrin [H_2(tpp)(Br)] **2** via Suzuki cross-coupling reaction to form diporphyrin **7a** (Scheme 2). *p*-Tolylboronic acid (**3c**) was oxidized to the aldehyde boronic acid **4c** by NBS after hydrolysis (eq 1). Subsequent protection of the boronic acid with 1,3-propanediol to avoid undesired reaction at the electrophilic boron atom yielded *p*-(1,3-dioxaboryl)-benzaldehyde (**5c**) in 33% yield (eq 2).[14] The porphyrin boronate **6** was prepared in 33% yield from the mixed Adler condensation **5c** (1 equiv) and benzaldehyde (3 equiv) with pyrrole (4 equiv) in $CHCl_3$ at room temperature for 24 h under N_2 with a catalytic amount of TsOH[14] after oxidation by *p*-chloranil (eq 3).

Porphyrin **6** (4 equiv) underwent a smooth Suzuki cross-coupling reaction with H_2(tpp)(Br) **2** (1 equiv),

Scheme 2. Structures of Porphyrins



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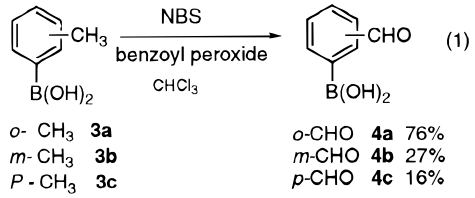
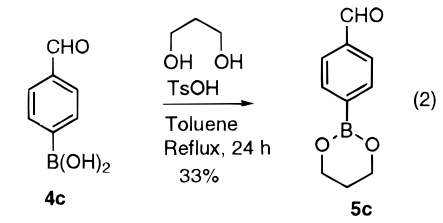
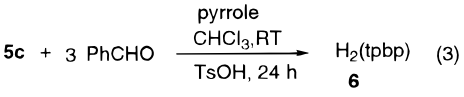
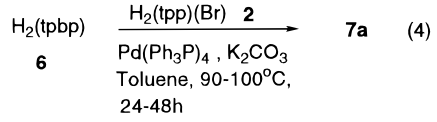






prepared from monobromination with NBS from H_2(tpp)-(Br) **1**, with 8 equiv of potassium carbonate and 10 mol % of $(Ph_3P)_4Pd$ in toluene at 100 °C for 48 h to give 88% yield of unsymmetrically substituted porphyrin dimer **7a** (eq 4). In principle, this approach should be applicable for other monobromoporphyrins and porphyrin boronates.



(B) Synthesis of Diporphyrins via Suzuki Cross-Coupling Condensation. Alternatively, diporphyrins **7** and **8** with both electron-withdrawing and electron-donating groups at the aryl rings were prepared via mixed condensation of β-arylporphyrin aldehydes **9b,c** with aryl aldehydes. β-Substituted porphyrin aldehydes **9a**−**c** were prepared from the Suzuki reaction of H_2(tpp)-(Br) **2** with boronated aldehydes **4a**−**c** in 62%, 86%, and 75% yields, respectively (eq 5). **9b** and **9c** (1 equiv) were reacted with aryl aldehydes **10a**−**e** (28 equiv) and pyrrole (29 equiv) in refluxing propionic acid to give diporphyrins **7a**−**e** and **8** in 17−23% yields in a procedure similar to that reported by Sauvage.[15] The sequence of adding reactants was very important for the condensation. Aryl aldehydes were first dissolved in propionic acid and heated up to reflux for 1−5 min. **9b** or **9c** was added then in one portion, and the mixture was refluxed for several minutes. Subsequently, pyrrole was added into the mixture. If pyrrole, aryl aldehyde, and **9b** or **9c** were added in one portion, no desired diporphyrins were obtained.

The azeotropic removal of propionic acid from the reaction mixture was crucial. If propionic acid was distilled out at atmospheric pressure, diporphyrin decomposition occurred. It was gratifying that propionic acid forms an azeotropic mixture with toluene. After the reflux, the reaction mixture was first cooled down, and the solution was rotary evaporated off with successive portions of toluene (binary system at 80 °C). Further chromatography of diporphyrins yielded pure products.

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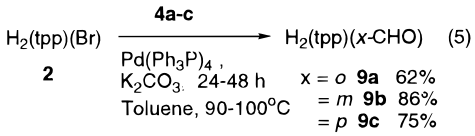
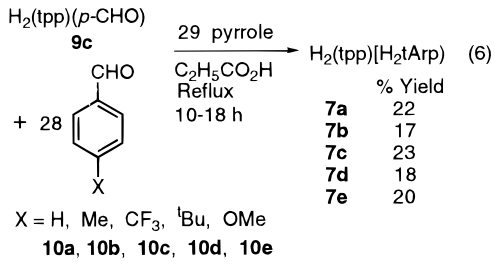
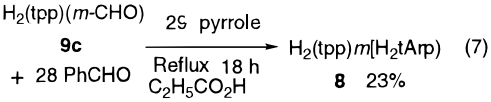
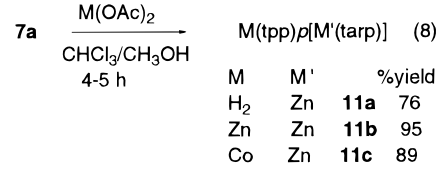




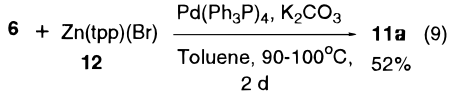


The ortho-substituted porphyrin aldehyde **9a** did not give any diporphyrin presumably due to the steric hindrance. The advantages of this method are (1) synthesis of β-substituted benzaldehyde porphyrins *via* Suzuki cross-coupling do not require any protection of aldehyde or boronic oxide, (2) β-substituted benzaldehyde porphyrins can be synthesized in one step, (3) electron-withdrawing or electron-donating groups can be easily introduced in the Adler condensation.

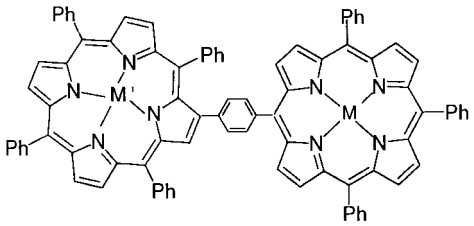
Metalation of Diporphyrins. A homodizinc complex of **11b** was prepared in high yield by stirring **7a** in $CHCl_3$ with a solution of zinc acetate in MeOH at rt (Scheme 3 and eq 8). Diporphyrin **7a** was found to undergo selective monometalation with zinc acetate at the β-substituted porphyrin core. When 1 equiv of $Zn(OAc)_2 \cdot 2H_2O$ in methanol was slowly added to **7a** in $CHCl_3$ at rt at a rate of 1 drop every 5 min, the major product was found to be **11a** in 76% yield based on consumed **7a**. If the rate of addition was too fast or more than 1 equiv of $Zn(OAc)_2$ was used, nonselective metalation was observed.



The structure of **11a** was ascertained by an independent synthesis through the cross-coupling of H_2(tpbp) **6** with Zn(tpp)(Br) **12** in which **11a** was obtained in 52% yield (eq 9). Both products from the selective metalation and coupling reaction exhibited identical R_f values in TLC and ^{1}H NMR spectra. The NH resonance of **11a** synthesized from the coupling of **6** with Zn(tpp)(Br) **12** exhibited an identical NH chemical shift at δ −2.73 ppm while the diporphyrin **7a** showed two internal pyrrole resonance at δ −2.49 and −2.73 ppm, respectively, due to two different porphyrinic NH protons.



Scheme 3. Structures of Metallodiporphyrins



M (tpp)*p*[M'(tarp)]

M	M'	
H_2	Zn	**11a**
Zn	Zn	**11b**
Co	Zn	**11c**

Selective metalation at the β-substituted ring may be due to its possible nonplanar conformation. Takeda reported[16] that the nonplanar porphyrin dodecaphenyl porphyrin [H_2(tpp)] reacted with Cu(II) 6×10^5 faster than the planar porphyrin H_2(tpp) due to the lower entropy of activation. A recent structure of β-monosubstituted porphyrin has revealed the nonplanar gometry and is supportive of this geometric influence in accelerating metalation.[7b]

The position, the shape, and the width of the Soret bands in diporphyrins have been used as probes for estimating the size of coupling interaction between the two chromophores.[17] The visible absorption spectra of the diporphyrins displayed two well-resolved peaks at 416, 426 (**7a**); 420, 426 (**7b**); 419, 427 (**7c**); 421, 428 (**7d**); 420, 427 (**7e**); and 417, 427 (**8**) nm whereas H_2(tpp) and [H_2(tpp)(Ph)][11a] exhibited only a sharp single Soret band at 419 nm. The splittings of Soret bands also depend on the spatial arrangement of the two porphyrin rings.[18] The difference of red shift of **7a** (8 nm) and **8** (9 nm) is just 1 nm; it is likely the difference of porphyrin interaction between **7a** and **8** is small. The visible absorption spectra of zinc−cobalt complex **11c** showed no split Soret bands, but only a broad peak compared with that of H_2(tpp). The broadened Soret band is likely due to the expansion of porphyrin ring π-system through excitonic interaction.

Excitation and Emission Spectroscopy. The early study[19] of light-induced energy transfer between the chlorophylls of antenna pigments and electron transfer between the (bacterio−)chlorophylls of photosynthetic reaction centers are crucial initial steps in understanding natural photosynthesis. Porphyrin dimers[1,7,8] appear to be useful models for understanding the photophysical characteristics of such natural hydroporphyrin assembles. In order to gain further insight into the understanding the electron transfer of porphyrin chromophores, excitation and emission studies were carried out for the free base diporphyrin and their metal complexes.

The emission spectra of **7a**, **11b**, and **11c** in $CHCl_3$ at room temperature were shown in Figure 1. The Zn_2 diporphyrin **11b** exhibited an unsymmetrical emission band and showed little fluorescence quenching compared with that of diporphyrin **7a**. Zn−Co diporphyrin **11c** however showed strong quenching compared with that of diporphyrin **7a** and **11b**.

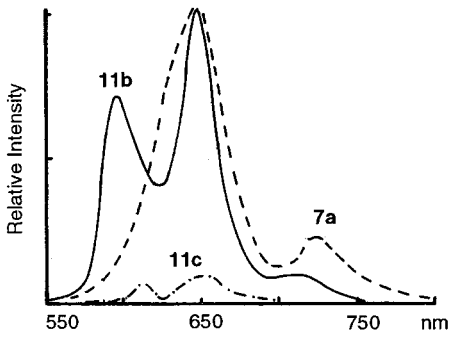


Figure 1. Room-temperature excitation and emission spectra of molecules **7a**, **11b,c**. Fluorescence excitation was monitored at 651 nm; λ_{ex}(emission) = 420 nm; $CHCl_3$ solvent.

The strong quenching may be attributed to intramolecular electron transfer. The difference in emission quenching between **7a**, **11b**, and **11c** may be rationalized by the redox potentials of metalloporphyrins. Co(tpp) possesses the least negative reduction potential (i.e. the easiest to be reduced (−0.82 V vs SCE) compared with those of H_2(tpp) (−1.05 V vs SCE) and Zn(tpp) (−1.35 V vs SCE).[20] Therefore, Co(TPP) accepts an electron from the excited zinc porphyrin easier than Zn(tpp) and H_2-(TPP). Consequently, the intramolecular (or intermolecular) electron-transfer pathway contributes significantly to the emission quenching.

Conclusion

meso-Aryl, β-linked diporphyrins have been prepared by two complementary routes using key Suzuki cross-coupling reaction and Adler condensation. Homo- and hetero-metal complexes of the diporphyrins have also been prepared. Selective mono-metalation of Zn has been found to occur at the β-substituted porphyrin core for diporphyrin **7a**. The Co−Zn diporphyrin complex **11c** shows strong emission quenching compared to the free base likely due to the intrmolecular (intermolecular) electron transfer.

Experimental Section

^{1}H NMR spectra were recorded at 250 or 500 MHz, respectively. Chemical shifts were internally referenced to the residual proton resonance in $CDCl_3$ (δ 7.24), or with tetramethylsilane as an internal standard. Coupling constants (J) were reported in hertz (Hz). Mass spectra were obtained on electron ionization or in FAB mode. Elemental analyses were carried out at the MEDAC Ltd., Department of Chemistry, Brunnel University, Uxbridge, Middlesex UB8 3PH, U.K. UV−vis spectra were recorded on a Hitachi UV-3000 spectrophotometer. Toluene and THF were freshly distilled from sodium−benzophenone ketyl and sodium under nitrogen and degassed by the freeze−thaw−pump method (−196 to 25 °C, three cycles). Column chromatography was carried out in air using silica gel (70−230 mesh or 230−400 mesh). All reaction were monitored by thin-layer chromatography. All materials were obtained from commercial suppliers and used without further purification.

2-Tolylboronic acid (**3a**),[21] 3-tolylboronic acid (**3b**),[22] 4-tolylboronic acid (**3c**),[22] 2-formylphenylboronic acid (**4a**),[23] 3-formylbenzeneboronic acid (**4a**),[24] 4-formylphenylboronic acid (**4c**),[24] and H_2(tpp)(Br) (**2**)[11a,25] were prepared according to the literature method.

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Preparation of Protected *p*-Formylphenyl Boronate (5c). **4c** (1.0 g, 6.67 mmol) and propane-1,3-diol (0.51 g, 6.67 mmol) were added to toluene (20 mL). The solution was refluxed for 2 h and then cooled to rt. A precipitate formed and was washed with cold toluene three times (3 × 10 mL) to give a white filter of *p*-formylphenyl boronate (**5c**) (320 mg, 23% yield): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.06 (m, 2 H), 4.16 (t, 4 H, J = 5.3 Hz), 7.79−7.91 (m, 4 H), 10.00 (s, 1 H); MS *m/e* 190 (M^+). Anal. Calcd for $C_{10}H_{11}BO_3$: C, 63.21; H, 5.83. Found: 62.68; H, 5.73.

5 (4′-Boronate-),10,15,20-tetraphenylporphyrin 6. Pyrrole (120.8 mg, 1.80 mmol), benzaldehyde (143.3 mg, 1.35 mmol), and **5c** (85.5 mg, 0.45 mmol) were added to $CHCl_3$ (150 mL, distilled from $CaCl_2$). The solution mixture was purged with nitrogen for 5 min. $BF_3{\cdot}Et_2O$ (0.2 mL, 1.60 mmol) was added, and the mixture was stirred at rt for 1.5 h. Chloranil (435 mg, 1.80 mmol) was added, and stirring was maintained for 30 min. The solvent was evaporated off. The crude product was chromatographed with $CHCl_3$ as the eluent to give porphyrin **6** (48 mg, 33% yield): R_f = 0.11 ($CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ −2.81 (s, 2 H), 2.17−2.22 (m, 2 H), 4.31 (t, 4 H, J = 5.0 Hz), 7.70−7.80 (m, 9 H), 8.15−8.24 (m, 10 H), 8.82 (s, 8 H). Anal. Calcd for $C_{47}H_{35}N_4BO_2{\cdot}H_2O$: C, 78.77; H, 5.20; N, 7.82. Found: C, 78.80; H, 4.99; N, 7.62. FABMS *m/e*: 698 (M^+). UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 417 (5.63), 514 (4.45), 549 (4.12), 590 (3.95), 646 (3.91).

4′-, 3′-, or 2′-Formylphenyl Porphyrin 9a, 9b, and 9c. A 50 mL Teflon-stoppered flask was charged with H_2(tpp)(Br) **2** (1 equiv), formylphenyl boronic acid (**4a**, **4b**, or **4c**) (4 equiv), $Pd(Ph_3P)_4$ (10 mol %), anhydrous toluene (25−30 mL), and anhydrous potassium carbonate (8 equiv). The purple suspension was degassed by the freeze−pump−thaw method (three cycles) and was then heated between 90 and 100 °C under N_2 for 48 h. The reaction mixture was worked up by adding an equal volume of CH_2Cl_2 and washed with Na_2CO_3 (saturated 40 mL), water (2 × 40 mL), and brine (40 mL). The organic layer was dried ($MgSO_4$) and rotary evaporated to dryness. The crude product was purified by column chromatography on silica gel using a solvent mixture of CH_2Cl_2/hexane (2:1) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid which was recrystallized from CH_2Cl_2−methanol.

2-(2′-Formylphenyl)-5,10,15,20-tetraphenylporphyrin (9a) (75% yield): R_f = 0.15 (CH_2Cl_2:hexane = 2:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.65 (s, 2 H), 7.22−7.30 (m, 2 H), 7.40−7.45 (m, 2 H), 7.69−7.76 (m, 13 H), 8.21 (bs, 6 H), 8.62 (d, 1 H, J = 5.0 Hz), 8.61−8.86 (ms, 7 H), 9.88 (s, 1 H). Anal. Calcd for $C_{51}H_{34}N_4O{\cdot}2H_2O$: C, 81.15; H, 5.05; N, 7.43. Found: C, 80.84; H, 4.59; N, 7.35. FABMS *m/e*: 718 (M^+). UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 422 (5.59), 518 (4.15), 551 (4.11), 594 (4.08), 650 (4.03).

2-(3′-Formylphenyl)-5,10,15,20-tetraphenylporphyrin (9b) (86% yield): R_f = 0.20 (CH_2Cl_2:hexane = 2:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.64 (s, 2 H), 7.20−7.23 (m, 3 H), 7.71−7.76 (m, 13 H), 7.89 (s, 2 H), 8.19−8.23 (m, 6 H), 8.75−8.84 (ms, 7 H), 9.90 (s, 1 H). Anal. Calcd for $C_{51}H_{34}N_4O{\cdot}2.5H_2O$: C, 80.19; H, 5.15; N, 7.33. Found: C, 80.24; H, 4.56; N, 7.29. FABMS *m/e*: 718 (M^+). UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 421 (5.65), 518 (4.55), 5.94 (4.28), 650 (4.23).

2-(4′-Formylphenyl)-5,10,15,20-tetraphenylporphyrin (9c) (62% yield): R_f = 0.21 (CH_2Cl_2:hexane = 2:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.63 (s, 2 H), 7.22 (m, 2 H), 7.48 (d, 2 H, J = 8.1 Hz), 7.73−7.77 (m, 12 H), 7.91 (d, 2 H, J = 8.1 Hz), 8.18−8.23 (m, 6 H), 8.73−8.84 (ms, 7 H), 9.98 (s, 1 H). Anal. Calcd for $C_{51}H_{34}N_4O{\cdot}2H_2O$: C, 81.15; H, 5.05; N, 7.43. Found: C, 80.87; H, 4.59; N, 7.37. FABMS *m/e*: 718 (M^+). UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 421 (5.71), 518 (4.51), 554 (4.22), 594 (4.15), 651 (4.06).

1-[2-(5,10,15,20-Tetraphenylporphyl)]-4-(5,10,15,20-tetraphenylporphyl)benzene (7a). A 50 mL Teflon-stoppered flask was charged with H_2(tpp)(Br) (24.1 mg, 0.035 mmol), porphyrin boronate **6** (80 mg, 0.121 mmol), $Pd(Ph_3P)_4$ (10 mol%), toluene (25−30 mL), and anhydrous potassium carbonate (41.8 mg, 0.30 mmol). The purple suspension was degassed by the freeze−pump−thaw method (three cycles), and the mixture was then heated between 90 and 100 °C under N_2 for 48 h. The reaction mixture was worked up by adding an equal volume of CH_2Cl_2 and washed with Na_2CO_3 (saturated, 40 mL), water (2 × 40 mL), and brine (40 mL). The organic layer was dried ($MgSO_4$). The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using a solvent mixture of CH_2Cl_2/hexane (1:1) as the eluent. The purple red band was collected and evaporated to dryness to give a purple red solid which was further recrystallized from CH_2Cl_2−methanol (88% yield): R_f = 0.18 ($CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.74 (s, 2 H), −2.49 (s, 2 H), 7.24 (dd, 2 H, J = 7.4, 7.7 Hz), 7.61−7.83 (m, 21 H), 8.00 (d, 2 H, J = 9.0 Hz), 8.24−8.29 (m, 14 H), 8.81−9.06 (m, 15 H). Anal. Calcd for $C_{88}H_{58}N_8{\cdot}H_2O$: C, 84.85; H, 4.85; N, 9.00. Found: C, 85.00; H, 4.80; N, 8.85. UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 418 (5.38), 426 (5.39), 592 (3.76), 648 (3.70). FABMS *m/e*: 1227 (M^+ − 1).

Adler's Procedure for Preparation of Diporphyrins 7a−e and 8. An aryl aldehyde (9.74 mmol) was added to propionic acid (110 mL) in a 250 mL round bottom flask. As soon as the solution started refluxing, formylphenyl porphyrin **9b** or **9c** (0.25 g, 0.35 mmol) was added and stirred for several minutes with the color of the solution changing from green to red. Then pyrrole (0.67 g, 10.07 mmol) was added immediately. The mixture was refluxed for 18 h. The crude mixture was rotary evaporated off the solvent with an added equal volume toluene in an azeotropic manner and the procedure was repeated three times until the solvent was evaporated thoroughly. The crude dry product was chromatographed on silica gel using a mixture of CH_2Cl_2/hexane (2:1) as the eluent.

1-(5,10,15,20-Tetraphenylporphyl)-4-[2-(5-phenyl,10,-15,20-tritolylporphyl)benzene (7b) (22% yield): R_f = 0.12 (CH_2Cl_2:hexane = 1:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.73 (s, 2 H), −2.50 (s, 2 H), 2.70 (s, 3 H), 2.73 (s, 6 H), 7.61 (m, 7 H), 7.73−7.82 (m, 13 H), 8.15 (d, 2 H, J = 8.1 Hz), 8.16−8.27 (m, 14 H), 8.80−9.06 (m, 15 H); ^{13}C NMR (62.9 Hz, $CDCl_3$) δ 22.14, 120.79, 121.15, 122.03, 127.15, 127.41, 128.09, 128.39, 129.32, 131.75, 134.38, 135.22, 135.29, 137.18, 137.99, 140.14, 140.61, 142.62, 143.06, 147.48, 152.56, 157.17. Anal. Calcd for $C_{91}H_{64}N_8{\cdot}1.5H_2O$: C, 84.30; H, 5.21; N, 8.64. Found: C, 84.24; H, 5.12; N, 8.54. L-SIMS *m/e*: 1269.45 (M^+). UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 420 (5.83), 426 (5.87), 518 (4.84), 553 (4.64), 592 (4.53), 648 (4.48).

1-(5,10,15,20-Tetraphenylporphyl)-4-[2-[5-phenyl-10,-15,20-tris(4′-(α,α,α-trifloromethyl)phenyl)porphyl]]-benzene (7c) (23% yield): R_f = 0.39 (CH_2Cl_2:hexane = 2:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.77 (s, 2 H), −2.49 (s, 2 H), 7.58 (dd, 2 H, J = 7.5, 7.5 Hz), 7.72−7.84 (m, 12 H), 7.95 (d, 2 H, J = 7.9 Hz), 7.93−8.09 (m, 6 H), 8.23−8.26 (m, 6 H), 8.37−8.40 (m, 8 H), 8.81−9.05 (m, 15 H). Anal. Calcd for $C_{91}H_{55}N_8F_9{\cdot}1.5C_2H_5OH$: C, 75.24; H, 4.30; N, 7.47. Found: C, 75.65; H, 4.54; N, 6.89. L-SIMS (matrix: NBA) *m/e*: 1431.5 (M^+). UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 419 (5.92), 427 (5.96), 517 (4.92), 551 (4.64), 592 (4.53), 648 (4.42).

1-(5,10,15,20-Tetraphenylporphyl)-4-[2-[5-phenyl-10,-15,20-tris(4′-*tert*-butylyphenyl)porphyl]]benzene (7d) (20% yield): R_f = 0.71 (CH_2Cl_2:hexane = 2:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.69 (s, 2 H), −2.48 (s, 2 H), 1.54−1.64 (m, 27 H), 7.58 (dd, 2 H, J = 7.5, 7.6 Hz), 7.71−7.84 (m, 18 H), 7.97 (d, 2 H, J = 7.9 Hz), 8.18−8.28 (m, 14 H), 8.82−9.06 (ms, 15 H); ^{13}C NMR (62.9 Hz, $CDCl_3$) δ 32.37, 35.58, 120.55, 120.85, 124.25, 127.41, 128.40, 129.29, 131.74, 132.42, 134.46, 135.16, 137.15, 137.99, 140.03, 140.61, 142.18, 143.05, 143.38, 151.23. L-SIMS *m/e*: 1395.7 (M^+). HRMS calcd for $C_{100}H_{82}N_8{\cdot}H^+$ 1395.6741, found 1395.6963. UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 420.0 (5.71), 427.0 (5.75), 518.1 (4.71), 554.2 (4.53), 593.0 (4.38), 649.0 (4.36).

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1-(5,10,15,20-Tetraphenylporphyl)-4-[2-[5-phenyl-10,-15,20-tris(4′-methoxyphenyl)porphyl]]benzene (7e) (18% yield): R_f = 0.42 (CH_2Cl_2:hexane = 30:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.72 (s, 2 H), −2.50 (s, 2 H), 4.10 (s, 9 H), 7.24−7.33 (m, 6 H), 7.61 (dd, 2 H, J = 7.3, 8.2 Hz), 7.76 (m, 12 H), 7.97 (d, 2 H, J = 7.2 Hz), 8.12−8.36 (m, 14 H), 8.80−9.05 (ms, 15 H). Anal. Calcd for $C_{91}H_{64}N_8O_3 \cdot 2.5H_2O$: C, 80.21; H, 5.10; N, 8.22. Found: C, 79.94; H, 4.92; N, 7.89. FABMS *m/e*: 1317.6 (M^+). UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 421.0 (5.85), 428.0 (5.89), 518.0 (4.84), 554.0 (4.66), 593.0 (4.51), 650.0 (4.51).

1-(5,10,15,20-tetraphenylporphyl)-3-[2-(5,10,15,20-tetraphenylporphyl)]benzene (8) was obtained in 23% yield: R_f = 0.61 (CH_2Cl_2:hexane = 2:1); ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.71 (s, 2 H), −2.53 (s, 2 H), 7.47 (t, 2 H, J = 7.4 Hz), 7.58 (d, 1 H), 7.69−7.93 (m, 21 H), 8.08 (d, 2 H, J = 7.4 Hz), 8.26 (bs, 14 H), 8.54 (s, 1H), 8.77−9.13 (ms, 15 H); ^{13}C NMR ($CDCl_3$, 62.9 Hz) δ 120.84, 121.19, 121.96, 126.47, 127.38, 128.43, 131.01, 131.72, 132.39, 133.65, 134.63, 135.32, 136.93, 137.40, 137.84, 141.90, 142.22, 142.69, 143.13, 143.27, 146.03, 147.81. Anal. Calcd for $C_{88}H_{58}N_8 \cdot H_2O$: C, 84.85; H, 4.85; N, 9.00. Found: C, 84.38; H, 4.67; N, 8.85. FABMS *m/e*: 1228 (M^+). UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 417 (5.66), 427 (5.65), 517 (4.76), 551 (4.60), 593 (4.57), 650 (4.58).

1-[2-(5,10,15,20-Tetraphenylzincioporphyl)]-4-(5,10,15,-20-tetraphenylporphyl)benzene (11a). 7a (10 mg, 0.0082 mmol) was dissolved in $CHCl_3$ (30 mL) in a 50-mL round-bottomed flask equipped with a magnetic stirring bar. Zinc acetate (1.8 mg, 82 μmmol) in methanol (5 mL) was added via an additional funnel. The course of the reaction was monitored by TLC (silica gel) after each addition (1 drop/5 min). TLC analysis indicated the presence of two new spots. The faster moving one (R_f = 0.36, $CHCl_3$:hexane = 2:1) corresponded to **11a**; the other was **11b** (R_f = 0.11, $CHCl_3$:hexane = 2:1). After repeated chromatography and recrystallization with ethanol−CH_2Cl_2, **11a** was obtained (6.1 mg, 76% yield).

Suzuki Cross-Coupling Method. A 50-mL Teflon-stoppered flask was charged with Zn(tpp)(Br) (20 mg, 0.027 mmol), porphyrin boronate **6** (65 mg, 0.093 mmol), $Pd(Ph_3P)_4$ (10 mmol%), toluene (25−30 mL), and anhydrous potassium carbonate (32.1 mg, 0.23 mmol). The purple suspension was degassed by the freeze−pump−thaw method (three cycles), and the mixture was then heated between 90 and 100 °C under N_2 for 48 h. The reaction mixture was worked up by adding an equal volume of CH_2Cl_2 and washed with Na_2CO_3 (saturated, 40 mL), water (2 × 40 mL), and brine (40 mL). The organic layer was dried ($MgSO_4$), and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using a solvent mixture of $CHCl_3$/hexane (2:1) as the eluent. The purple red band was collected and evaporated to dryness to give a purple red solid which was further recrystallized from CH_2Cl_2−methanol to obtain diporphyrin **11a** (18 mg, 52% yield): ^{1}H NMR ($CDCl_3$, 250 MHz) δ −2.74 (s, 2 H), 7.24 (dd, 2 H, J = 7.4, 7.7 Hz), 7.59−7.81 (m, 21 H), 8.00 (d, 2 H, J = 9.0 Hz), 8.21−8.36 (m, 14 H), 8.86−9.16 (m, 15 H). Anal. Calcd for $ZnC_{88}H_{56}N_8 \cdot 2C_2H_5OH$: C, 79.90; H, 4.96; N, 8.10. Found: C, 79.58; H, 4.99; N, 7.67. FABMS *m/e*: 1289 ($M^+ - 1$). HRMS (matrix, NBA): calcd for $C_{88}H_{56}N_8Zn \cdot H^+$ 1289.3997, found 1289.3462. UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 416 (4.73), 426 (5.79), 514 (4.34), 550 (4.52), 588 (3.96), 646 (3.67).

Diporphyrin Complex 11b. Diporphyrin **7a** (16 μmol) solution in $CHCl_3$ (15 mL) was added with 5 equiv of zinc acetate solution in methanol (5 mL). The solution was stirred for about 4−5 h at rt. After rotary evaporation, the crude product was chromatographed on silica gel with CH_2Cl_2 as the eluent, R_f = 0.90 ($CHCl_3$), and was further recrystallized from CH_2Cl_2−ethanol to give **11b** as a red solid in 95% yield: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.24 (dd, 2 H, J = 7.4, 7.7 Hz), 7.61−7.83 (m, 21 H), 8.00 (d, 2 H, J = 9.0 Hz), 8.22−8.37 (m, 14 H), 8.93−9.19 (ms, 15 H). Anal. Calcd for $C_{88}H_{54}N_8Zn_2 \cdot 2.5C_2H_5OH$: C, 76.79; H, 4.46; N, 7.87. Found: C, 77.02; H, 4.94; N, 7.26. FABMS *m/e*: 1354 (M^+). HRMS (matrix, NBA): calcd for $C_{88}H_{54}N_8Zn_2 \cdot H^+$ 1351.3132, found 1351.3010. UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 415.0 (5.27), 429.0 (5.77), 550.0 (4.64), 654.0 (2.89).

Complex 11c. A solution **11a** in $CHCl_3$ (15 mL) was added with 5 equiv of a cobalt acetate solution in methanol (5 mL). The solution was stirred for about 4−5 h at rt. After rotary evaporation, the crude product was chromatographed on silica gel with CH_2Cl_2 as the eluent, R_f = 0.92 ($CHCl_3$), and was further recrystallized from CH_2Cl_2−methanol to give **11c** as a red solid in 89% yield. FABMS *m/e*: 1347 (M^+). Anal. Calcd for $C_{88}H_{54}N_8CoZn \cdot 2.5CH_3OH$: C, 76.15; H, 4.50; N, 7.85. Found: C, 75.75; H, 4.85; N, 7.35. UV−vis λ_{max} (CH_2Cl_2, nm, log ϵ): 423.0 (5.20), 550.0 (4.67).

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