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# Regioselective Borylation of Porphyrins by C–H Bond Activation under Iridium Catalysis to Afford Useful Building Blocks for Porphyrin Assemblies

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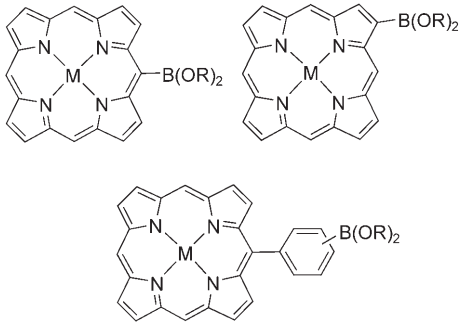
**Abstract:** Highly regioselective and efficient borylation of a variety of porphyrins has been achieved by reaction with bis(pinacolato)diboron through C–H bond activation under iridium catalysis on the basis of the synthetic protocol developed by Miyaura, Hartwig, and Smith. A boryl group can be selectively introduced at sterically uncongested positions in the peripheral aryl groups of porphyrin substrates whose peripheral β-positions are sterically hindered. Curiously, β substituents adjacent to the aryl group to be borylated have unexpectedly large effects on the regioselectivity, because the iridium catalyst can discriminate between subtle steric differences. Chemoselective borylation was also achieved for several functionalized porphyrins. This borylation protocol can be applied to various monomeric and oligomeric functional porphyrins, hence offering an efficient route to elaborate multiporphyrin-based molecular constructs.

**Keywords:** boron · C–C coupling · C–H activation · iridium · porphyrins

## Introduction

Multiporphyrin arrays[1] have attracted much attention because of their potential in a wide range of applications that include artificial photosynthetic antennae,[2] dye-sensitized solar cells,[3] conductive organic materials,[4] near-infrared dyes,[5] nonlinear optical (NLO) materials,[6] molecular wires,[7] and building blocks for supramolecular structures.[8] Among various linkages that have been used to connect porphyrins, aromatic spacers have a distinct advantage for restricting the conformations of porphyrin arrays because of the well-defined sizes of the aromatic segments and the somewhat predictable orientations of the aromatic spacer toward a porphyrin segment.[9] Diphenylethynyl and related spacers have also been extensively used for the construction of multiporphyrin arrays, which serve to enhance the electronic interaction between the linked porphyrins.[10,11] Most of these synthetic strategies employ dipyrromethanes that bear preinstalled suitable handles (aldehyde equivalents, halogens, and protected ethynyl groups) for the later porphyrin synthesis via acid-catalyzed condensation and oxidation. As a different approach, directly linked porphyrins have been synthesized through chemical or electrochemical oxidation.[12] However, these acidic and oxidative conditions restrict the functionalities that can be introduced onto porphyrins.

One promising candidate is the Suzuki–Miyaura coupling reaction,[13,14] which allows carbon–carbon bond formation with high compatibility toward a variety of functionalities under very mild conditions. This strategy achieves the efficient construction of well-designed molecular structures with borylated porphyrins as key building blocks.[15] Moreover, borylated porphyrins also exert an important function:

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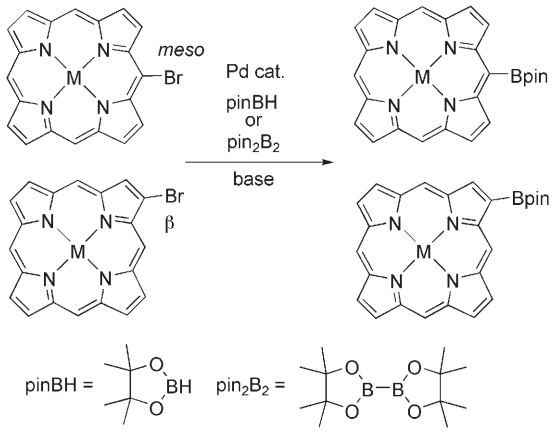
they serve as sensing agents for sugars and anions owing to the Lewis acidity of the boron center.[16,17] Shinkai and coworkers have used borylated porphyrins extensively for the precise recognition of sugars.

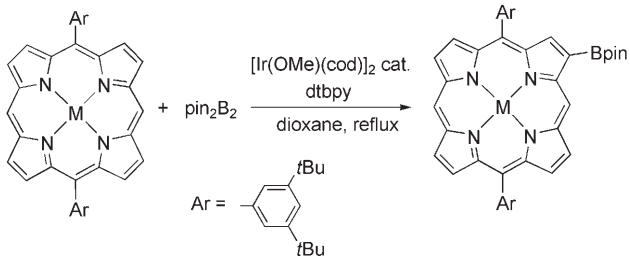
Porphyrins with borylated aromatic substituents have been synthesized in low yields through conventional porphyrin synthesis by using borylbenzaldehyde.[19] A new methodology for accessing this important class of compounds is highly desirable for the facile installation of boryl substituents into porphyrins after porphyrin synthesis.

The introduction of the boryl group onto the peripheral positions of porphyrins was pioneered by Therien and coworkers.[15c] *meso*-Boryl porphyrins constitute a good platform for the synthesis of *meso*-functionalized porphyrin derivatives. β-Borylporphyrin was prepared by Nocera and coworkers for the synthesis of β,β-linked diporphyrin.[15d] These peripherally borylated porphyrins were obtained by palladium-catalyzed coupling of *meso*- or β-bromoporphyrins with pinacolborane (pinBH) or bis(pinacolato)diboron ($pin_2B_2$) as the boron source (Scheme 1). Consequently, the regiochemistry is predetermined by the position of the bromide. Although *meso*-bromoporphyrins can be readily obtained by regioselective bromination of *meso*-unsubstituted porphyrins, selective β bromination by conventional methods is possible only with 5,10,15,20-tetrasubstituted porphyrins.[18] In this sense, β-selective functionalization of 5,15-disubstituted and 5,10,15-trisubstituted porphyrins is a rather difficult task. Accordingly, the design and synthesis of porphyrin-based molecules often rely on *meso*-functionalization. However, if a reaction that enables selective β functionalization of porphyrins is available, one can design and prepare new types of porphyrin assemblies with specific properties.

Recently, iridium-catalyzed direct borylation of aromatic compounds by C–H bond activation[20] has emerged as an efficient route to organoboron compounds.[21–23] Dioxaborolanyl groups can be efficiently introduced to aromatic and heteroaromatic compounds under mild reaction conditions, thus providing organoboranes that are otherwise often difficult to prepare by conventional methods. We envisioned the possibility of direct borylation for the synthesis of various borylated porphyrins and developed a new method of regioselective modification of porphyrins, which can be accomplished through direct borylation of various porphyrins under iridium catalysis (Scheme 2).[24]




Scheme 1. Synthesis of borylporphyrins from bromoporphyrins.




Scheme 2. Ir-catalyzed direct borylation of porphyrin by C–H activation. cod = 1,5-cyclooctadiene, dtbpy = 4,4′-di-*tert*-butyl-2,2′-dipyridyl.

Herein, we disclose the further application of the selective borylation strategy to a variety of substrates, including functionalized porphyrins and porphyrin oligomers, thus demonstrating the usefulness of this protocol in the synthesis of porphyrin-based molecular architectures.

**Abstract in Japanese:**
イリジウム触媒とビスピナコラートジボロンを用いた芳香族化合物の直接ホウ素化反応を様々なポルフィリン系化合物に適用した。全てのメゾ位に置換基をもつポルフィリンでは、芳香族置換基の立体障害の少ない位置に高選択的にホウ素を導入できる。この際、β位のアルキル基が大きく選択性に影響することが明らかとなった。一方、メゾ位に置換基を持たない場合には、*β*位でのホウ素化が優先的に起こる。本手法はポルフィリンオリゴマーや様々に官能基化されたポルフィリン誘導体の位置選択的な修飾反応として利用可能であり、ポルフィリンを基盤とする機能分子の合成に有効である。

## Results and Discussion

### Selective Borylation on *meso*-Aryl Groups of Porphyrins

As reported previously,[24a] the reactivity and selectivity in iridium-catalyzed borylation are heavily affected by the steric constraints of the substrates. For instance, tetrakis(3,5-di-*tert*-butylphenyl)porphyrin, which has only congested β-pyrrolic protons, was recovered unchanged even with excess diboron after a prolonged reaction time (Scheme 3). We then anticipated that the peripheral aromatic substituents could be selectively borylated instead of the porphyrin core by careful design of the substitution pattern of the porphyrin substrates.

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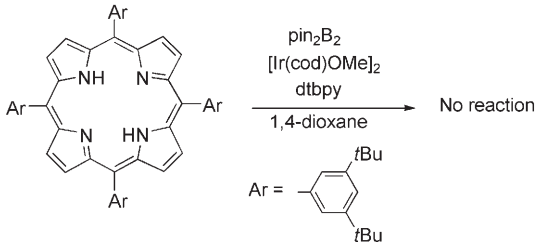
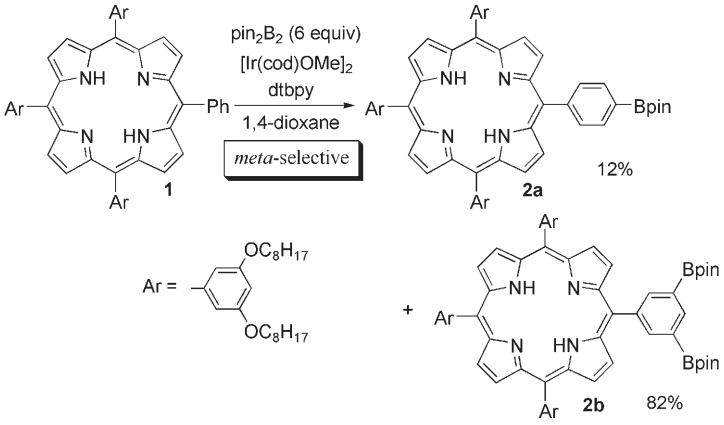
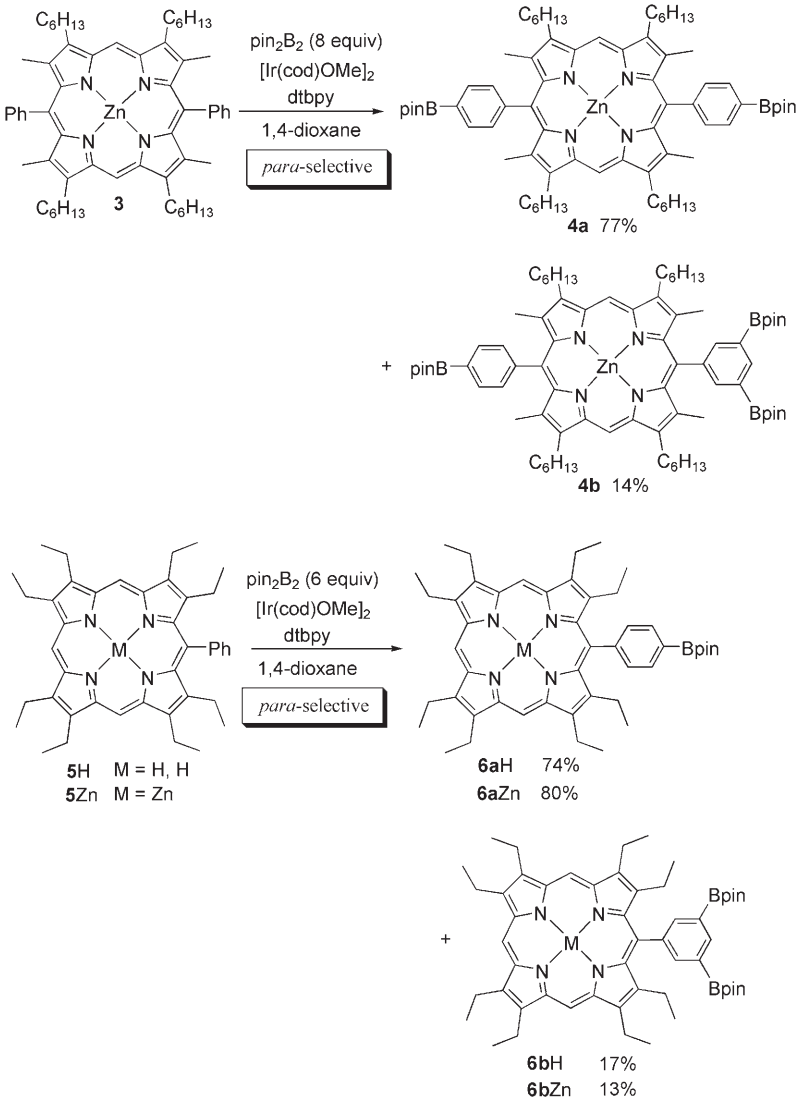



Scheme 3. The unreactivity of a 5,10,15,20-tetrasubstituted porphyrin.




Scheme 4. *meta*-Selective borylation.

Treatment of 5,10,15-tris(3,5-dioctyloxyphenyl)-20-phenylporphyin (**1**) with bis(pinacolato)diboron under iridium catalysis provided borylated porphyrins **2** (Scheme 4).[25] No borylation of the porphyrin core occurred. The reaction exhibited considerable *meta*-selectivity, and *meta*,*meta*-bisborylphenylporphyrin **2b** was selectively obtained in excellent yield with 6.0 equivalents of diboron reagent. Although borylation of simple monosubstituted benzenes often exhibits a statistical distribution of *meta*- and *para*-borylated products in a ratio of around 2:1, the selectivity in this case is much higher.[26] Interestingly, the regioselectivity was switched to *para*-selectivity in the case of β-alkylated porphyrins (Scheme 5): borylation of **3** provided predominantly di(*para*-boryl)phenylporphyrin **4a**. Such a dramatic change in regioselectivity due to the indirect spatial steric interaction is seldom observed in borylation of simple aromatic compounds. Borylation of **5** also exhibited *para*-selectivity, and the selectivity was slightly enhanced by zinc metallation.




Scheme 5. *para*-Selective borylation.

Recent theoretical calculations by DFT revealed that iridium-catalyzed borylation involves formation of an iridium–benzene π complex prior to the transition state of the oxidative addition of the active trisboryliridium complex [Ir(dtbpy)(Bpin)$_3$][27] to the C–H bond to yield the phenyliridium species.[28] In this situation, β-alkyl substituents are likely to interfere with the sterically demanding trisboryliridium species, which lies perpendicular to the phenyl ring, more severely at the *meta* than at the *para* position. The *meta* position is clearly closer to the β-alkyl substituents than the

*para*: the shortest distance between the β-methyl H and *meta*-phenyl C atoms is 3.13 Å, whereas that between the β-methyl H and *para*-phenyl C atoms is 3.64 Å in the optimized structure at the B3LYP/6-31G* level (Figure 1).

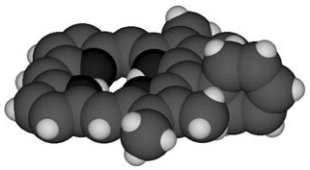
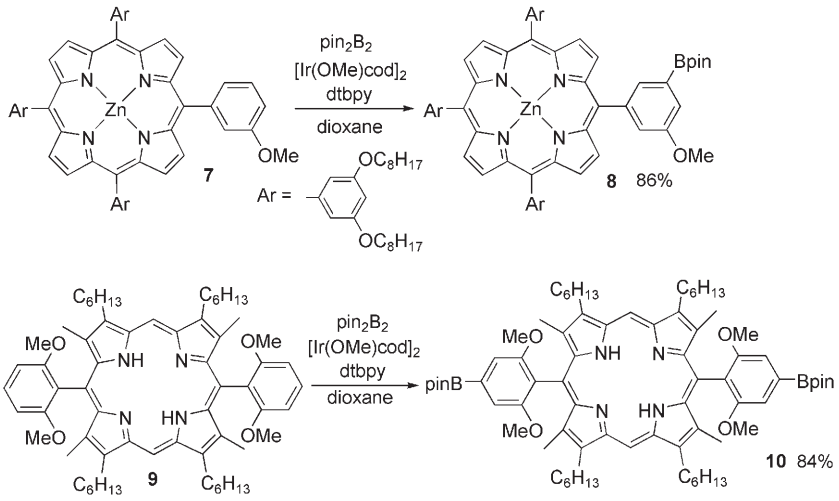


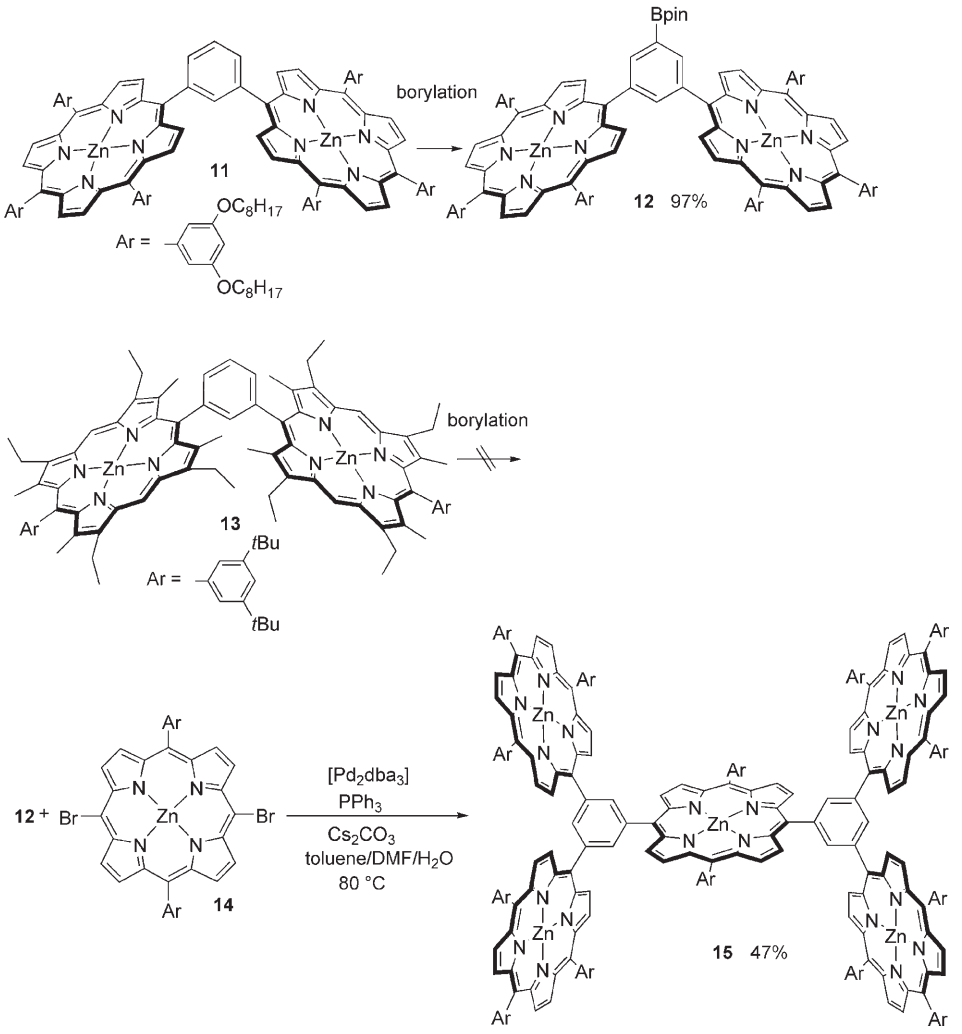
Figure 1. Optimized structure of a β-methyl porphyrin by the DFT method.




Scheme 6. Highly selective borylation of 3-methoxy- and 2,6-dimethoxyphenyl groups.

The borylation can be perfectly regioselective by the proper choice of the peripheral aromatic substituents to be borylated (Scheme 6). The reaction of porphyrin **7** with a 3-methoxyphenyl group furnished only *meta*-borylation product **8** in 86% yield, whereas the reaction of porphyrin **9** proceeded well with perfect *para*-selectivity.

This regioselective functionalization is quite powerful for the synthesis of multiporphyrinic architectures. Borylation of *meta*-phenylene-bridged diporphyrin **11** afforded monoborylated dimer **12** quantitatively (Scheme 7). Again, β-alkyl substituents have a crucial effect on the reaction, as borylation did not proceed with β-methyl porphyrin dimer **13**. Borylated *meta*-phenylene-bridged diporphyrin **12** enabled the rapid synthesis of porphyrin pentamer **15** over two steps from **11** through direct borylation and Suzuki–Miyaura coupling with *meso*-dibromoporphyrin **14**. Furthermore, we successfully demonstrated a terminal-selective functionalization of *meso*,*meso*-linked porphyrin tetramer **16** in an efficient manner, by taking advantage of the high regioselectivity in borylation with 3-methoxy substituents (Scheme 8). *meso*,*meso*-Linked porphyrin oligomers are expected to act as photonic wires that convey light energy




Scheme 7. Selective borylation of a porphyrin dimer and cross-coupling to a porphyrin pentamer. dba = dibenzylideneacetone, DMF = *N*,*N*-dimethylformamide.

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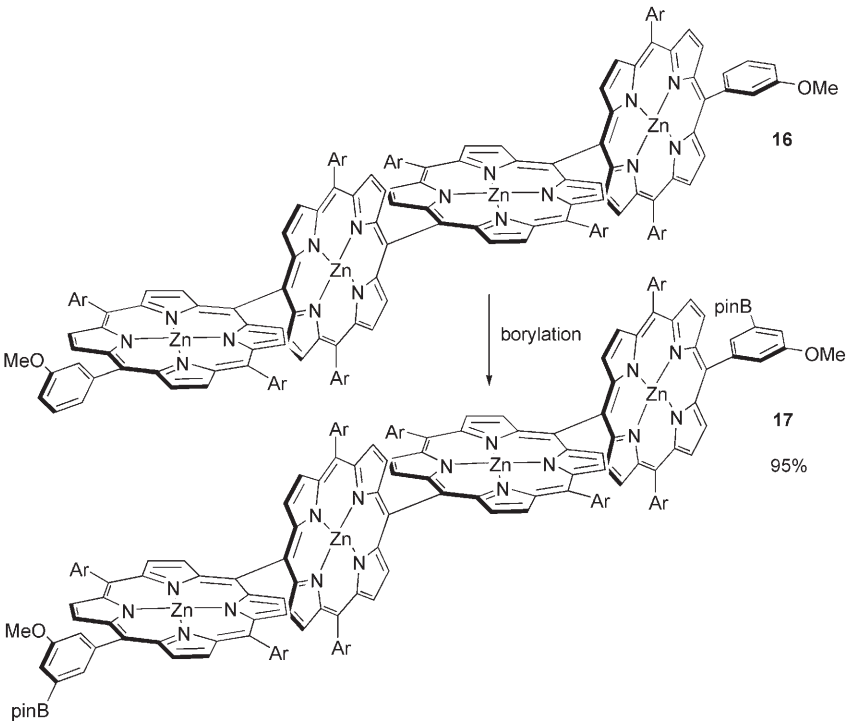



Scheme 8. Terminal-selective borylation of a porphyrin tetramer.

owing to the strong excitonic coupling between the adjacent porphyrin motifs.[12] In this sense, a terminal-selective reaction of molecular wires is important for the efficient synthesis of functional materials based on *meso*,*meso*-linked porphyrin oligomers.

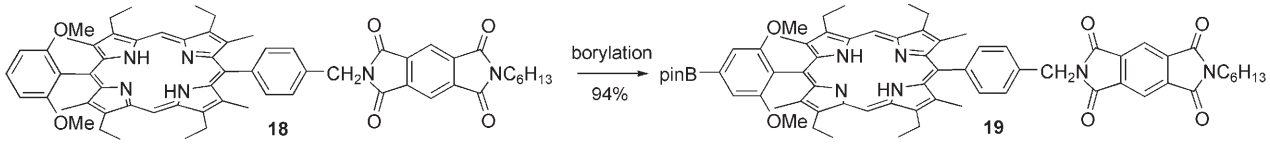
Iridium-catalyzed direct borylation exhibits a wide range of functional tolerance. We attempted the functionalization of porphyrin **18**, which bears a pyromellitimide as an electron acceptor (Scheme 9). To our delight, the reaction worked very well to provide borylated product **19** in 94% yield without affecting the imide functionalities. As subsequent Suzuki–Miyaura coupling would install further donor moieties onto **19**, the present direct-borylation procedure enables straightforward access to sophisticated molecules, which are useful in the study of photoinduced electron transfer.

It is important to compare the reactivity of the β-C–H bond of the porphyrin core with the aromatic C–H bond of the substituent. For this purpose, we designed porphyrin **20**, which bears both types of C–H bonds (Scheme 10). The 3,5-dioctyloxyphenyl groups enabled the reaction in hexane at lower temperatures. The reaction of **20** at 50 °C provided β-borylated porphyrins **21a** as a major product, clearly elucidating the higher reactivity at the β-positions in the borylation reaction of porphyrins.

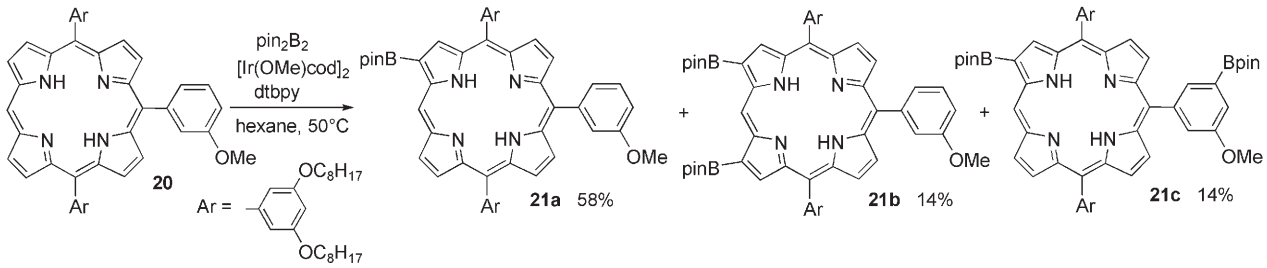
### Selective β Borylation of Porphyrin Core

In the preliminary communication, we reported β borylation of a limited number of substrates.[24a] We then applied this protocol further to various substrates, including functionalized ones, to elucidate the scope and limitations of this reaction.

We generally used 1,4-dioxane as the reaction solvent, but we encountered difficulty in carrying out the reaction with substrates that have low solubility in dioxane. In these cases,



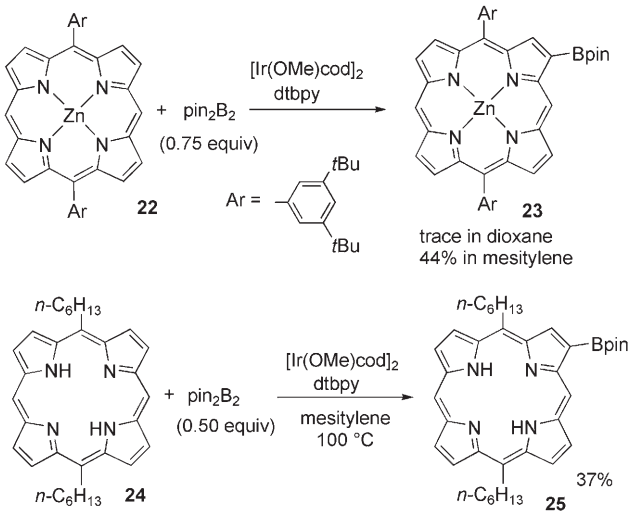

Scheme 9. Chemoselective borylation of a porphyrin bearing an electron acceptor.




Scheme 10. Comparison of the reactivity of C–H bonds at the β-position versus that of the aromatic substituent.

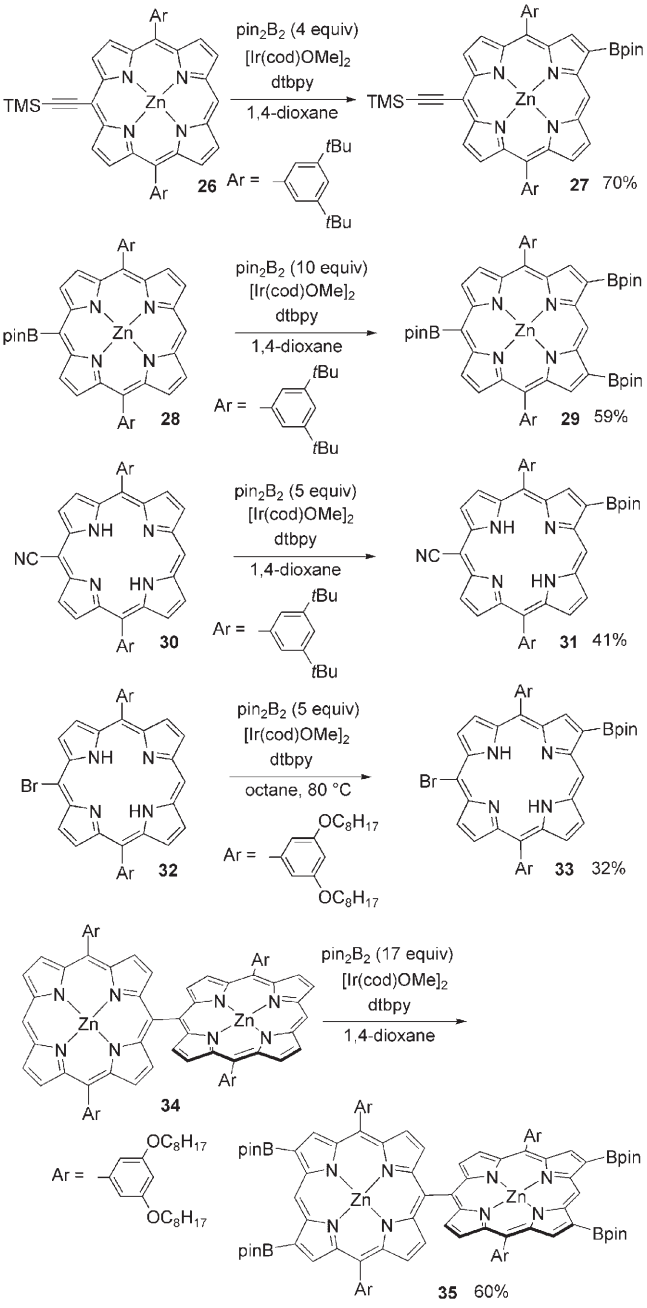
  

mesitylene can be used as an alternative solvent. For example, borylation of zinc porphyrin **22** in dioxane provided a trace of borylation products (Scheme 11). However, the use of mesitylene instead of dioxane allowed the reaction to proceed and afforded the desired porphyrin **23** in 44% yield. The reaction of *meso*-alkylporphyrin **24** was also sluggish in dioxane, but gave the desired product **25** in 37% yield in mesitylene, along with recovery of the starting material 2**4** (46%).




Scheme 11. Borylation of porphyrins in mesitylene.

Although the functional tolerance of the iridium-catalyzed borylation of aromatics has been documented, the present conditions require higher temperatures than the original Miyaura protocol. Hence, the compatibility of functionalized porphyrins in direct borylation was examined (Scheme 12). Borylation of alkynylporphyrin **26** proceeded nicely to furnish **27** without affecting the alkynyl moiety. This feature is worthy of note in view of the derivatization of alkynylporphyrins, which often exhibit fascinating electrooptical and NLO properties. *meso*,β,β′-Triborylporphyin **29** was obtained in reasonable yield under the same reaction conditions, but the reaction was complicated owing to the partial removal of the *meso*-boryl group. The reaction also tolerated the presence of a cyano group at the *meso* position to provide *meso*-cyano-β-borylporphyrin **31**. Unfortunately, the reaction of *meso*-bromoporphyrin with 3,5-di(*tert*-butyl)phenyl groups was sluggish, and debromination took place extensively under the standard conditions in refluxing dioxane. The use of octane as a solvent for bromoporphyrin **32**, whose long alkyl chains on the aromatic substituents make it soluble, allowed the borylation reaction to proceed at 80 °C to provide monoborylated bromoporphyrin **33** in 32% yield. However, even the modified conditions at lower temperature could not inhibit debromination perfectly. *meso*,*meso*-Linked porphyrin dimer **34** was efficiently borylated to provide tetraboryldiporphyrin **35** in 60% yield.




Scheme 12. Borylation of functionalized porphyrins. TMS = trimethylsilyl.

## Conclusions

We have achieved regioselective direct borylation of the porphyrin core and the aromatic substituents of a variety of porphyrins by the proper design of porphyrin substrates. Steric effect plays an essential role in determining the regioselectivity of borylation. β-Substituents, in particular, have a significant effect on the regioselectivity of borylation of the aromatic substituents through indirect steric interactions. Borylated porphyrins thus prepared would be useful platforms for constructing porphyrin-containing architectures by

Suzuki–Miyaura cross-coupling and as sensor molecules based on the properties of boronic acid moieties. The present protocol should allow for the selective borylation of other more-sophisticated functional segments, which would be a challenging subject worthy of further investigation.

## Experimental Section

*General*

$^1$H NMR (600 MHz) spectra were recorded on a JEOL ECA-600 spectrometer. Chemical shifts are reported in ppm relative to $CHCl_3$ and 1,1,2,2-tetrachloroethane as internal references ($\delta = 7.26$ and 5.91 ppm, respectively). UV/Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. MALDI-TOF mass spectra were obtained with a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer by using positive-MALDI ionization without matrix. High-resolution ESI-TOF mass spectra were recorded on a Bruker microTOF spectrometer. Recycling preparative GPC–HPLC was carried out on a JAI LC-908 chromatograph with preparative JAIGEL-2H, -2.5H, and -3H, or -2.5H, -3H, and -4H. 1,4-Dioxane and mesitylene were distilled from calcium hydride and stocked under argon with dried 4-Å molecular sieves. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Theoretical calculations were carried out by the DFT method with the Gaussian 03 package.[29]

*Procedure for Borylation of Porphyrins*

Borylation of 5,10,15-tris(3,5-dioctyloxyphenyl)-20-phenylporphyin (**1**): A flask containing $[Ir(OMe)(cod)]_2$ (4.0 mg, 6.0 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (3.2 mg, 12 μmol), bis(pinacolato)diboron (152.4 mg, 0.60 mmol), and **1** (138.4 mg, 0.10 mmol) was flushed with argon and then charged with 1,4-dioxane (1.5 mL). The mixture was stirred at reflux for 48 h. After cooling, the reaction mixture was passed through a short pad of silica gel with dichloromethane. Concentration and purification by recycling preparative GPC–HPLC gave the products **2a** (18.1 mg, 12%) and **2b** (133.8 mg, 82%). **2a**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 645 (7100), 590 (10000), 550 (11000), 515 (27000), 421 nm (531000 $M^{-1}cm^{-1}$); $^1$H NMR ($CDCl_3$): $\delta = 8.94$ (s, 4H, β-pyrrole), 8.94 (d, $J = 4.6$ Hz, 2H, β-pyrrole), 8.81 (d, $J = 4.6$ Hz, 2H, β-pyrrole), 8.23 (d, $J = 8.0$ Hz, 2H, *ortho*-phenyl), 8.20 (d, $J = 8.0$ Hz, 2H, *meta*-phenyl), 7.38–7.36 (m, 6H, *ortho*-dioctyloxyphenyl), 6.90–6.87 (m, 3H, *para*-dioctyloxyphenyl), 4.11 (t, $J = 6.4$ Hz, 12H, $OCH_2$), 1.90–1.83 (m, 12H, $CH_2$), 1.51 (s, 12H, pinacol), 1.51–1.46 (m, 12H, $CH_2$), 1.39–1.33 (m, 12H, $CH_2$), 1.33–1.24 (m, 36H, $CH_2$), 0.86 (t, $J = 6.9$ Hz, 18H, $CH_3$), −2.82 ppm (s, 2H, NH); HRMS (ESI): *m/z* calcd for $C_{98}H_{138}BN_4O_8$: 1510.0617 $[M+H]^+$; found: 1510.0567. **2b**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 646 (5600), 590 (7900), 550 (8900), 516 (23000), 422 nm (486000 $M^{-1}cm^{-1}$); $^1$H NMR ($CDCl_3$): $\delta = 8.98$ (s, 4H, β-pyrrole), 8.95 (d, $J = 3.7$ Hz, 2H, β-pyrrole), 8.79 (d, $J = 3.7$ Hz, 2H, β-pyrrole), 8.73 (d, $J = 1.4$ Hz, 2H, *ortho*-phenyl), 8.71 (d, $J = 1.4$ Hz, 1H, *para*-phenyl), 7.41–7.39 (m, 6H, *ortho*-dioctyloxyphenyl), 6.92–6.89 (m, 3H, *para*-dioctyloxyphenyl), 4.14 (t, $J = 6.6$ Hz, 12H, $OCH_2$), 1.91–1.86 (m, 12H, $CH_2$), 1.55–1.49 (m, 12H, $CH_2$), 1.40 (s, 24H, pinacol), 1.40–1.24 (m, 48H, $CH_2$), 0.89–0.85 (m, 18H, $CH_3$), −2.80 ppm (s, 2H, NH); HRMS (ESI): *m/z* calcd for $C_{104}H_{149}B_2N_4O_{10}$: 1636.1483 $[M+H]^+$; found: 1636.1430.

Borylation of 5,15-diphenyl-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrinatozinc(II) (**3**): The reaction of **3** (46.0 mg, 50 μmol) with $[Ir(OMe)(cod)]_2$ (3.3 mg, 5.0 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (2.7 mg, 10 μmol), and bis(pinacolato)diboron (102.4 mg, 0.40 mmol) in 1,4-dioxane (1.0 mL) gave **4a** (39.3 mg, 77%) and **4b** (7.4 mg, 14%). **4a**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 573 (0.031), 539 (0.053), 411 nm (1); $^1$H NMR ($CDCl_3$): $\delta = 10.08$ (s, 2H, *meso*), 8.18 (d, $J = 7.3$ Hz, 4H, *ortho*-phenyl), 8.10 (d, $J = 7.3$ Hz, 4H, *meta*-phenyl), 3.89 (t, $J = 7.8$ Hz, 8H, β-$CH_2$), 2.43 (s, 12H, β-$CH_3$), 2.17 (tt, $J = 7.8$, 7.5 Hz, 8H, $CH_2$), 1.75 (tt, $J = 7.5$, 7.5 Hz, 8H, $CH_2$), 1.56 (s, 24H, pinacol), 1.51 (tt, $J = 7.5$, 7.5 Hz, 8H, $CH_2$), 1.40 (qt, $J = 7.5$, 7.5 Hz, 8H, $CH_2$), 0.94 ppm (t, $J = 7.5$ Hz, 12H, $CH_3$); HRMS (ESI): *m/z* calcd for $C_{72}H_{99}B_2N_4O_4Zn$: 1169.7160 $[M+H]^+$; found: 1169.7165. **4b**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 574 (0.03), 539 (0.051), 412 nm (1); $^1$H NMR ($CDCl_3$): $\delta = 10.16$ (s, 2H, *meso*), 8.70 (s, 1H, *para*-phenyl), 8.62 (s, 2H, *ortho*-phenyl), 8.16 (d, $J = 7.8$ Hz, 2H, *ortho*-phenyl), 8.10 (d, $J = 7.8$ Hz, 2H, *meta*-phenyl), 3.96 (t, $J = 8.7$ Hz, 4H, β-$CH_2$), 3.95 (t, $J = 8.7$ Hz, 4H, β-$CH_2$), 2.45 (s, 6H, β-$CH_3$), 2.39 (s, 6H, β-$CH_3$), 2.20–2.15 (m, 8H, $CH_2$), 1.78–1.70 (m, 8H, $CH_2$), 1.54 (s, 12H, pinacol), 1.52–1.45 (m, 8H, $CH_2$), 1.42–1.32 (m, 8H, $CH_2$), 1.38 (s, 24H, pinacol), 0.94–0.89 ppm (m, 12H, $CH_3$); HRMS (ESI): *m/z* calcd for $C_{78}H_{110}B_3N_4O_6Zn$: 1295.8024 $[M+H]^+$; found: 1295.8007.

Borylation of 2,3,7,8,12,13,17,18-octaethyl-5-phenylporphyrin (**5**H): The reaction of **5**H (45.8 mg, 75 μmol) with $[Ir(OMe)(cod)]_2$ (3.0 mg, 4.5 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (2.4 mg, 9.0 μmol), and bis(pinacolato)diboron (114.3 mg, 0.45 mmol) in 1,4-dioxane (1.0 mL) gave **6a**H (41.5 mg, 74%) and **6b**H (12.0 mg, 17%). **6a**H: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 406 (1), 505 (0.085), 539 (0.042), 573 (0.039), 625 nm (0.016); $^1$H NMR ($CDCl_3$): $\delta = 10.22$ (s, 2H, *meso*), 9.98 (s, 1H, *meso*), 8.29 (dd, $J = 1.4$, 7.5 Hz, 2H, *ortho*-phenyl), 8.15 (dd, $J = 1.4$, 7.5 Hz, 2H, *meta*-phenyl), 4.15 (q, $J = 7.8$ Hz, 4H, β-$CH_2$), 4.12 (q, $J = 7.8$ Hz, 4H, β-$CH_2$), 4.07 (q, $J = 7.8$ Hz, 4H, β-$CH_2$), 2.81 (q, $J = 7.4$ Hz, 4H, β-$CH_2$), 1.97 (t, $J = 7.8$ Hz, 12H, β-$CH_3$), 1.91 (t, $J = 7.8$ Hz, 6H, β-$CH_3$), 1.56 (s, 12H, pinacol), 1.20 (t, $J = 7.4$ Hz, 6H, β-$CH_3$), −2.94 (s, 1H, NH), −3.08 ppm (s, 1H, NH); HRMS (ESI): *m/z* calcd for $C_{48}H_{62}BN_4O_2$: 737.4968 $[M+H]^+$; found: 737.4942. **6b**H: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 406 (1), 504 (0.084), 539 (0.041), 573 (0.038), 625 nm (0.015); $^1$H NMR ($CDCl_3$): $\delta =$ 10.17 (s, 2H, *meso*), 9.93 (s, 1H, *meso*), 8.75 (s, 2H, *ortho*-phenyl), 8.71 (s, 1H, *para*-phenyl), 4.11 (q, $J = 7.8$ Hz, 4H, β-$CH_2$), 4.08 (q, $J = 7.8$ Hz, 4H, β-$CH_2$), 4.01 (q, $J = 7.8$ Hz, 4H, β-$CH_2$), 2.67 (q, $J = 7.8$ Hz, 4H, β-$CH_2$), 1.93 (t, $J = 7.8$ Hz, 6H, β-$CH_3$), 1.92 (t, $J = 7.8$ Hz, 6H, β-$CH_3$), 1.87 (t, $J = 7.8$ Hz, 6H, β-$CH_3$), 1.36 (s, 24H, pinacol), 1.19 (t, $J = 7.8$ Hz, 6H, β-$CH_3$), −2.99 (s, 1H, NH), −3.17 ppm (s, 1H, NH); HRMS (ESI): *m/z* calcd for $C_{54}H_{73}B_2N_4O_4$: 863.5829 $[M+H]^+$; found: 863.5833.

Borylation of 2,3,7,8,12,13,17,18-octaethyl-5-phenylporphyrinatozinc(II) (**5**Zn): The reaction of **5**Zn (50.6 mg, 75 μmol) with $[Ir(OMe)(cod)]_2$ (3.0 mg, 4.5 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (2.4 mg, 9.0 μmol), and bis(pinacolato)diboron (114.3 mg, 0.45 mmol) in 1,4-dioxane (1.0 mL) gave **6a**Zn (48.0 mg, 80%) and **6b**Zn (8.9 mg, 13%). **6a**Zn: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 406 (1), 536 (0.058), 572 nm (0.054); $^1$H NMR ($CDCl_3$): $\delta = 10.14$ (s, 2H, *meso*), 9.95 (s, 1H, *meso*), 8.28 (d, $J = 7.5$ Hz, 2H, *ortho*-phenyl), 8.12 (d, $J = 7.5$ Hz, 2H, *meta*-phenyl), 4.06 (q, $J =$ 7.5 Hz, 8H, β-$CH_2$), 4.03 (q, $J = 7.5$ Hz, 4H, β-$CH_2$), 2.74 (q, $J = 7.5$ Hz, 4H, β-$CH_2$), 1.93 (t, $J = 7.5$ Hz, 6H, β-$CH_3$), 1.92 (t, $J = 7.5$ Hz, 6H, β-$CH_3$), 1.90 (t, $J = 7.5$ Hz, 6H, β-$CH_3$), 1.56 (s, 12H, pinacol), 1.19 (t, $J =$ 7.5 Hz, 6H, β-$CH_3$); HRMS (ESI): *m/z* calcd for $C_{48}H_{59}BN_4O_2Zn$: 798.4025 $[M]^+$; found: 798.4011. **6b**Zn: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 408 (1), 537 (0.049), 573 nm (0.046); $^1$H NMR ($CDCl_3$): $\delta = 10.17$ (s, 2H, *meso*), 10.07 (s, 1H, *meso*), 8.76 (s, 2H, *ortho*-phenyl), 8.70 (s, 1H, *para*-phenyl), 4.11 (q, $J = 7.8$ Hz, 8H, β-$CH_2$), 4.02 (q, $J = 7.8$ Hz, 4H, β-$CH_2$), 2.63 (q, $J = 7.5$ Hz, 4H, β-$CH_2$), 1.94 (t, $J = 7.8$ Hz, 6H, β-$CH_3$), 1.93 (t, $J = 7.8$ Hz, 6H, β-$CH_3$), 1.88 (t, $J = 7.8$ Hz, 6H, β-$CH_3$), 1.35 (s, 24H, pinacol), 1.20 ppm (t, $J = 7.5$ Hz, 6H, β-$CH_3$); HRMS (ESI): *m/z* calcd for $C_{54}H_{70}B_2N_4O_4Zn$: 924.4887 $[M]^+$; found: 924.4910.

Borylation of 5,10,15-tris(3,5-dioctyloxyphenyl)-20-(3-methoxyphenyl)-porphyrinatozinc(II) (**7**): The reaction of **7** (73.7 mg, 50 μmol) with $[Ir(OMe)(cod)]_2$ (1.7 mg, 2.5 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (1.3 mg, 5.0 μmol), and bis(pinacolato)diboron (63.5 mg, 0.25 mmol) in 1,4-dioxane (0.75 mL) gave **8** (43.2 mg, 86%) along with the starting porphyrin **7** (4.2 mg, 8%). **8**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 422 (1), 549 (0.044), 574 nm (0.009); $^1$H NMR ($CDCl_3$): $\delta = 9.06$ (s, 4H, β-pyrrole), 9.05 (d, $J = 4.6$ Hz, 2H, β-pyrrole), 8.96 (d, $J = 4.6$ Hz, 2H, β-pyrrole), 8.28 (s, 1H, *ortho*-phenyl), 7.90 (s, 1H, *ortho*-phenyl), 7.77 (s, 1H, *para*-phenyl), 7.41 (s, 6H, *ortho*-dioctyloxyphenyl), 6.90 (s, 3H, *para*-dioctyloxyphenyl), 4.16–4.11 (m, 12H, $OCH_2$), 4.04 (s, 3H, $OCH_3$), 1.91–1.86 (m, 12H, $CH_2$), 1.55–1.48 (m, 12H, $CH_2$), 1.41 (s, 12H, pinacol), 1.41–1.35 (m, 12H, $CH_2$), 1.35–1.26 (m, 36H, $CH_2$), 0.89 ppm (t, $J = 6.4$ Hz, 18H, $CH_3$); HRMS (ESI): *m/z* calcd for $C_{99}H_{138}BN_4O_9Zn$: 1601.9858 $[M+H]^+$; found: 1601.9912.

Borylation of 5,15-bis(2,6-dimethoxyphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrin (**9**): The reaction of **9** (76.9 mg, 80 μmol)

with $[Ir(OMe)(cod)]_2$ (3.2 mg, 4.8 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (2.6 mg, 9.6 μmol), and bis(pinacolato)diboron (121.9 mg, 0.48 mmol) in 1,4-dioxane (2.0 mL) afforded **10** (82.2 mg, 84%) after purification by recrystallization from dichloromethane/methanol. **10**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 411 (1), 508 (0.074), 543 (0.025), 576 (0.031), 628 nm (0.009); $^1$H NMR ($CDCl_3$): $\delta$ = 10.20 (s, 2H, *meso*), 7.49 (s, 4H, *meta*-phenyl), 4.05 (t, $J$ = 7.1 Hz, 8H, β-$CH_2$), 3.67 (s, 12H, $OCH_3$), 2.67 (s, 12H, β-$CH_3$), 2.26 (tt, $J$ = 7.1, 7.1 Hz, 8H, $CH_2$), 1.78 (tt, $J$ = 7.1, 7.1 Hz, 8H, $CH_2$), 1.57 (s, 24H, pinacol), 1.53 (tt, $J$ = 7.1, 7.1 Hz, 8H, $CH_2$), 1.43 (tq, $J$ = 7.1, 7.3 Hz, 8H, $CH_2$), 0.97 (t, $J$ = 7.3 Hz, 12H, $CH_3$), −2.11 ppm (s, 2H, NH); HRMS (ESI): *m/z* calcd for $C_{76}H_{109}B_2N_4O_8$: 1227.8449 $[M+H]^+$; found: 1227.8478.

Borylation of 1,3-bis[10,15,20-tris(3,5-dioctyloxyphenyl)porphyrinato-(zinc)-5-yl]benzene (**11**): The reaction of **11** (281.7 mg, 0.10 mmol) with $[Ir(OMe)(cod)]_2$ (4.0 mg, 6.0 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (3.2 mg, 12 μmol), and bis(pinacolato)diboron (152.4 mg, 0.60 mmol) in 1,4-dioxane (1.2 mL) afforded **12** (285.7 mg, 97%) after purification by recrystallization from dichloromethane/methanol. **12**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 419 (1), 432 (0.835), 549 (0.079), 587 nm (0.016); $^1$H NMR ($CDCl_3$): $\delta$ = 9.41 (d, $J$ = 4.6 Hz, 4H, β-pyrrole), 9.22 (dd, $J$ = 1.8, 1.8 Hz, 1H, *para*-phenyl), 9.18 (d, $J$ = 4.6 Hz, 4H, β-pyrrole), 9.05 (d, $J$ = 4.5 Hz, 4H, β-pyrrole), 9.04 (dd, $J$ = 1.8, 1.8 Hz, 2H, *ortho*-phenyl), 9.03 (d, $J$ = 4.5 Hz, 4H, β-pyrrole), 7.44 (s, 4H, *ortho*-dioctyloxyphenyl), 7.38 (s, 2H, *ortho*-dioctyloxyphenyl), 7.35 (s, 2H, *ortho*-dioctyloxyphenyl), 7.32 (s, 4H, *ortho*-dioctyloxyphenyl), 6.88 (s, 4H, *para*-dioctyloxyphenyl), 6.87 (s, 2H, *para*-dioctyloxyphenyl), 4.18–4.13 (m, 8H, $OCH_2$), 4.11 (t, $J$ = 6.4 Hz, 4H, $OCH_2$), 4.07 (t, $J$ = 6.7 Hz, 4H, $OCH_2$), 4.03 (t, $J$ = 6.4 Hz, 8H, $OCH_2$), 1.92–1.74 (m, 24H, $CH_2$), 1.56–1.45 (m, 24H, $CH_2$), 1.45–1.16 (m, 96H, $CH_2$), 1.41 (s, 12H, pinacol), 0.88 (t, $J$ = 6.7 Hz, 12H, $CH_3$), 0.86 (t, $J$ = 6.7 Hz, 6H, $CH_3$), 0.82 (t, $J$ = 6.7 Hz, 6H, $CH_3$), 0.78 (t, $J$ = 6.7 Hz, 12H, $CH_3$); HRMS (ESI): *m/z* calcd for $C_{184}H_{254}BN_8O_{14}Zn_2$: 2938.8103 $[M+H]^+$; found: 2938.8213.

Suzuki–Miyaura cross-coupling of **12** with **14**: Phenylene-bridged dimer **12** (29.4 mg, 10 μmol), **14** (4.8 mg, 4.0 μmol), $Cs_2CO_3$ (4.9 mg, 15 μmol), $[Pd_2(dba)_3]$ (0.5 mg, 0.50 μmol), and triphenylphosphine (0.5 mg, 2.0 μmol) were dissolved in a mixture of toluene (1.0 mL), DMF (0.50 mL), and water (0.10 mL). The solution was deoxygenated by applying a freeze–pump–thaw degas cycle three times, and the resulting mixture was stirred at 80°C under argon atmosphere. After 8 h, the reaction was quenched with water, and the mixture was extracted with diethyl ether. The organic layer was washed with water, dried over anhydrous $Na_2SO_4$, and evaporated. Purification by recycling preparative GPC–HPLC gave the coupling product **15** (12.5 mg, 47%). **15**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 593 (31000), 554 (125000), 433 (1180000), 416 (899000), 310 nm (95000 $M^{-1}cm^{-1}$); $^1$H NMR ([$D_2$]1,1,2,2-tetrachloroethane, 50°C): $\delta$ = 9.82 (d, $J$ = 4.6 Hz, 4H, β-pyrrole), 9.80 (d, $J$ = 4.6 Hz, 8H, β-pyrrole), 9.46 (s, 4H, *ortho*-phenyl), 9.45 (s, 2H, *para*-phenyl), 9.29(d, $J$=4.6 Hz 4H, β-pyrrole), 9.27 (d, $J$ = 4.6 Hz, 8H, β-pyrrole), 8.96 (d, $J$ = 4.6 Hz, 8H, β-pyrrole), 8.94 (d, $J$ = 4.6 Hz, 8H, β-pyrrole), 7.32 (s, 4H, *ortho*-dioctyloxyphenyl), 7.29 (s, 16H, *ortho*-dioctyloxyphenyl), 7.27 (s, 4H, *ortho*-dioctyloxyphenyl), 7.26 (s, 4H, *ortho*-dioctyloxyphenyl), 6.87 (s, 2H, *para*-dioctyloxyphenyl), 6.82 (s, 8H, *para*-dioctyloxyphenyl), 6.79 (s, 4H, *para*-dioctyloxyphenyl), 4.09–3.99 (m, 56H, $OCH_2$), 1.79–1.70 (m, 56H, $CH_2$), 1.41–1.33 (m, 56H, $CH_2$), 1.30–1.10 (m, 224H, $CH_2$), 0.77–0.68 ppm (m, 84H, $CH_3$); MS (MALDI-TOF): *m/z* calcd for $C_{420}H_{564}N_{20}O_{28}Zn_5$: 6655.98 $[M]^+$; found: 6660.07.

Borylation of *meso*,*meso*-di-(3-methoxyphenyl)-*meso*,*meso*-linked porphyrin tetramer **16**: The reaction of **16** (43.6 mg, 10 μmol) with $[Ir(OMe)(cod)]_2$ (2.7 mg, 4.0 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (2.1 mg, 8.0 μmol), and bis(pinacolato)diboron (101.6 mg, 0.40 mmol) in 1,4-dioxane (1.0 mL) afforded **17** (44.0 mg, 95%) after purification by recrystallization from dichloromethane/methanol. **17**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 571 (168000), 486 (386000), 417 (446000), 309 nm (67000 $M^{-1}cm^{-1}$); $^1$H NMR ($CDCl_3$): $\delta$ = 9.13 (d, $J$ = 4.6 Hz, 4H, β-pyrrole), 9.06 (d, $J$ = 4.6 Hz, 4H, β-pyrrole), 8.90 (d, $J$ = 4.6 Hz, 4H, β-pyrrole), 8.87 (d, $J$ = 4.6 Hz, 4H, β-pyrrole), 8.86 (d, $J$ = 4.6 Hz, 2H, β-pyrrole), 8.85 (d, $J$ = 4.6 Hz, 2H, β-pyrrole), 8.37 (s, 2H, *ortho*-phenyl), 8.30 (d, $J$ = 4.6 Hz, 4H, β-pyrrole), 8.24 (d, $J$ = 4.6 Hz, 4H, β-pyrrole), 8.24 (d, $J$ = 4.6 Hz, 2H, β-pyrrole), 8.17 (d, $J$ = 4.6 Hz, 2H, β-pyrrole), 7.98 (s, 2H, *ortho*-phenyl), 7.81 (s, 2H, *para*-phenyl), 7.44 (s, 16H, *ortho*-dioctyloxyphenyl), 6.82 (s, 4H, *para*-dioctyloxyphenyl), 6.71 (s, 4H, *para*-dioctyloxyphenyl), 4.10 (s, 6H, $OCH_3$), 4.08 (t, $J$ = 6.6 Hz, 16H, $OCH_2$), 4.10 (t, $J$ = 6.6 Hz, 16H, $OCH_2$), 1.81 (tt, $J$ = 6.6, 6.6 Hz, 16H, $CH_2$), 1.73 (tt, $J$ = 6.6, 6.6 Hz, 16H, $CH_2$), 1.44 (tt, $J$ = 6.6, 6.6 Hz, 16H, $CH_2$), 1.44 (s, 24H, pinacol), 1.38 (tt, $J$ = 6.6, 6.6 Hz, 16H, $CH_2$), 1.34–1.12 (m, 128H, $CH_2$), 0.81 (t, $J$ = 6.6 Hz, 24H, $CH_3$), 0.75 (s, $J$ = 6.6 Hz, 24H, $CH_3$); MS (MALDI-TOF): *m/z* calcd for $C_{282}H_{364}N_{16}O_{22}Zn_4$: 4604.52 $[M]^+$; found. 4607.10.

Borylation of phenylene-linked porphyrin pyromellitimide diad **18**: Porphyrin **18** (41.7 mg, 41.6 μmol), $[Ir(cod)OMe]_2$ (2.6 mg, 4.0 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (2.2 mg, 8.0 μmol), and bis(pinacolato)diboron (63.5 mg, 25.0 μmol) were purged with argon and then dissolved in 1,4-dioxane (1.0 mL). The mixture was stirred at 100°C for 24 h. After cooling, the reaction mixture was passed through a short silica-gel column with ethyl acetate. Purification by size-exclusion chromatography and recrystallization from dichloromethane/methanol gave the product **19** (44.9 mg, 39.8 μmol, 95%). **19**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 628 (1340), 573 (5640), 541 (4300), 507 (14400), 409 nm (185800 $M^{-1}cm^{-1}$); $^1$H NMR ($CDCl_3$): $\delta$ = 10.16 (s, 2H, *meso*), 8.38 (s, 2H, aromatic imide), 8.04 (d, $J$ = 7.8 Hz, 2H, phenyl), 7.74 (d, $J$ = 7.8 Hz, 2H, phenyl), 7.42 (s, 2H, dimethoxyphenyl), 5.30 (s, 2H, benzylic), 4.04–3.93 (m, 8H, $CH_2CH_3$), 3.77 (t, $J$ = 7.3 Hz, 2H, Hex-1), 3.61 (s, 6H, OMe), 2.59 (s, 6H, Me), 2.41 (s, 6H, Me), 1.70–1.78 (m, 12H, $CH_2CH_3$), 1.58 (s, 12H, pinacol), 1.28–1.43 (m, 8H, Hex-2–5), 0.89 (t, $J$ = 6.9 Hz, 3H, Hex-6), −2.44 ppm (br, 2H, NH); HRMS (ESI): *m/z* calcd for $C_{69}H_{78}BN_6O_8$: 1129.5974 $[M+H]^+$; found: 1129.5961.

Borylation of 10-(3-methoxyphenyl)-5,15-bis(3,5-dioctyloxyphenyl)porphyrinatozinc(II) (**20**): A flask containing $[Ir(OMe)(cod)]_2$ (1.5 mg, 2.3 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (1.2 mg, 4.5 μmol), bis(pinacolato)diboron (38.1 mg, 0.15 mmol), and **20** (114.4 mg, 0.10 mmol) was flushed with argon and then charged with hexane (1.0 mL). The mixture was stirred at 50°C for 24 h. After cooling, the reaction mixture was passed through a short pad of silica gel with dichloromethane. Concentration and purification by recycling preparative GPC–HPLC gave the monoborylated porphyrin **21a** (73.6 mg, 58%) and diborylated porphyrin regioisomers **21b** and **21c** (38.1 mg, 27%, 1:1), along with the starting porphyrin (13.9 mg, 12%). **21a**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 584 (0.01), 547 (0.047), 420 nm (1); $^1$H NMR ($CDCl_3$): $\delta$ = 10.95 (s, 1H, *meso*), 9.73 (s, 1H, β-pyrrole), 9.50 (d, $J$ = 4.1 Hz, 1H, β-pyrrole), 9.21 (d, $J$ = 4.1 Hz, 1H, β-pyrrole), 9.09 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.06 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 8.98 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 8.97 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 7.82 (d, $J$ = 7.4 Hz, 1H, *ortho*-phenyl), 7.75 (s, 1H, *ortho*-phenyl), 7.63 (dd, $J$ = 7.4, 8.8 Hz, 1H, *meta*-phenyl), 7.42 (s, 2H, *ortho*-dioctyloxyphenyl), 7.40 (s, 2H, *ortho*-dioctyloxyphenyl), 7.29 (d, $J$ = 8.8 Hz, 1H, *para*-phenyl), 6.90 (s, 1H, *para*-dioctyloxyphenyl), 6.89 (s, 1H, *para*-dioctyloxyphenyl), 4.16–4.12 (m, 8H, $OCH_2$), 3.93 (s, 3H, $OCH_3$), 1.91–1.85 (m, 8H, $CH_2$), 1.74 (s, 12H, pinacol), 1.55–1.48 (m, 8H, $CH_2$), 1.42–1.26 (m, 32H, $CH_2$), 0.91–0.87 ppm (m, 12H, $CH_3$); HRMS (ESI): *m/z* calcd for $C_{77}H_{102}BN_4O_7Zn$: 1269.7140 $[M+H]^+$; found: 1269.7147. **21b**: $^1$H NMR ($CDCl_3$): $\delta$ = 11.43 (s, 1H, *meso*), 9.72 (s, 2H, β-pyrrole), 9.02 (d, $J$ = 4.6 Hz, 2H, β-pyrrole), 8.93 (d, $J$ = 4.6 Hz, 2H, β-pyrrole), 7.80 (d, $J$ = 7.3 Hz, 1H, *ortho*-phenyl), 7.74 (s, 1H, *ortho*-phenyl) 7.62 (dd, $J$ = 7.3, 8.7 Hz, 1H, *meta*-phenyl), 7.40 (s, 4H, *ortho*-dioctyloxyphenyl), 7.29 (d, $J$ = 8.7 Hz, 1H, *para*-phenyl), 6.91 (s, 2H, *para*-dioctyloxyphenyl), 4.19–4.13 (m, 8H, $OCH_2$), 3.94 (s, 3H, $OCH_3$), 1.92–1.86 (m, 8H, $CH_2$), 1.75 (s, 24H, pinacol), 1.55–1.49 (m, 8H, $CH_2$), 1.42–1.26 (m, 32H, $CH_2$), 0.90–0.86 ppm (m, 12H, $CH_3$). **21c**: $^1$H NMR ($CDCl_3$): $\delta$ = 10.93 (s, 1H, *meso*), 9.73 (s, 1H, β-pyrrole), 9.49 (d, $J$ = 4.1 Hz, 1H, β-pyrrole), 9.20 (d, $J$ = 4.1 Hz, 1H, β-pyrrole), 9.07 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.04 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 8.96 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 8.94 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 8.26 (s, 1H, *ortho*-phenyl), 7.86 (s, 1H, *ortho*-phenyl), 7.75 (s, 1H, *para*-phenyl), 7.43 (s, 2H, *ortho*-dioctyloxyphenyl), 7.40 (s, 2H, *ortho*-dioctyloxyphenyl), 6.91 (s, 1H, *para*-dioctyloxyphenyl), 6.90 (s, 1H, *para*-dioctyloxyphenyl), 4.19–4.13 (m, 8H, $OCH_2$), 4.02 (s, 3H, $OCH_3$), 1.92–1.86 (m, 8H, $CH_2$), 1.73 (s, 12H, pinacol), 1.55–1.49 (m, 8H, $CH_2$), 1.42–1.26 (m, 32H, $CH_2$), 1.40 (s, 12H, pinacol), 0.90–0.86 ppm (m, 12H, $CH_3$). HRMS (ESI) of **21b** and **21c**: *m/z* calcd for $C_{83}H_{113}B_2N_4O_9Zn$: 1395.8004 $[M+H]^+$; found: 1395.8019.

Borylation of 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II) (**22**): The reaction of **22** (149.6 mg, 0.20 mmol) with $[Ir(OMe)(cod)]_2$ (1.0 mg, 1.5 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.8 mg, 3.0 μmol), and bis(pinacolato)diboron (38.1 mg, 0.15 mmol) in mesitylene (2.0 mL) gave **23** (76.2 mg, 44%), along with the diborylated porphyrin (24%) and the starting porphyrin **22** (28%). **23**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 577 (12000), 542 (30000), 415 nm (457000 $M^{-1}cm^{-1}$); $^1H$ NMR ($CDCl_3$): $\delta$ = 11.03 (s, 1H, *meso*), 10.28 (s, 1H, *meso*), 9.78 (s, 1H, β-pyrrole), 9.55 (d, $J$ = 4.4 Hz, 1H, β-pyrrole), 9.43 (d, $J$ = 4.4 Hz, 1H, β-pyrrole), 9.42 (d, $J$ = 4.4 Hz, 1H, β-pyrrole), 9.20 (d, $J$ = 4.4 Hz, 2H, β-pyrrole), 9.19 (d, $J$ = 4.4 Hz, 1H, β-pyrrole), 9.15 (d, $J$ = 4.4 Hz, 1H, β-pyrrole), 8.16 (s, 2H, *ortho*-di-*tert*-butylphenyl), 8.14 (s, 2H, *ortho*-di-*tert*-butylphenyl), 7.85 (s, 1H, *para*-di-*tert*-butylphenyl), 7.84 (s, 1H, *para*-di-*tert*-butylphenyl), 1.72 (s, 12H, pinacol), 1.59 (s, 36H, *tert*-butyl); HRMS (ESI): *m/z* calcd for $C_{54}H_{64}BN_4O_2Zn$: 875.4417 $[M+H]^+$; found: 875.4513.

Borylation of 5,15-dihexylporphyrin (**24**): The reaction of **24** (95.7 mg, 0.20 mmol) with $[Ir(OMe)(cod)]_2$ (0.7 mg, 1.0 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (0.5 mg, 2.0 μmol), and bis(pinacolato)diboron (25.4 mg, 0.10 mmol) in mesitylene (2.0 mL) gave **25** (45.0 mg, 37%), along with the diborylated porphyrin (8%) and the starting porphyrin **24** (46%). **25**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 640 (0.006), 585 (0.015), 542 (0.012), 509 (0.049), 411 nm (1); $^1H$ NMR ($CDCl_3$): $\delta$ = 10.89 (s, 1H, *meso*), 10.11 (s, 1H, *meso*), 10.07 (s, 1H, β-pyrrole), 9.54 (d, $J$ = 4.6 Hz, 2H, β-pyrrole), 9.51 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.50 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.35 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.34 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 5.03 (t, $J$ = 8.3 Hz, 2H, $CH_2$), 4.96 (t, $J$ = 8.3 Hz, 2H, $CH_2$), 2.57–2.51 (m, 4H, $CH_2$), 1.88–1.79 (m, 4H, $CH_2$), 1.78 (s, 12H, pinacol), 1.56–1.50 (m, 4H, $CH_2$), 1.46–1.37 (m, 4H, $CH_2$), 0.97 (t, $J$ = 7.2 Hz, 3H, $CH_3$), 0.97 ppm (t, $J$ = 7.2 Hz, 3H, $CH_3$); HRMS (ESI): *m/z* calcd for $C_{38}H_{50}BN_4O_2$: 605.4028 $[M+H]^+$; found: 605.4048.

Borylation of 5,15-bis(3,5-di-*tert*-butylphenyl)-10-trimethylsilylethynylporphyrinatozinc(II) (**26**): The reaction of **26** (67.7 mg, 80 μmol) with $[Ir(OMe)(cod)]_2$ (2.1 mg, 3.2 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (1.7 mg, 6.4 μmol), and bis(pinacolato)diboron (81.3 mg, 0.32 mmol) in 1,4-dioxane (1.5 mL) gave **27** (54.5 mg, 70%), along with the starting porphyrin **26** (15%). **27**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$) = 600 (17000), 559 (25000), 429 nm (371000 $M^{-1}cm^{-1}$); $^1H$ NMR ($CDCl_3$): $\delta$ = 10.86 (s, 1H, *meso*), 9.76 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.75 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.62 (s, 1H, β-pyrrole), 9.41 (d, $J$ = 4.6 Hz, 2H, β-pyrrole), 9.05 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.04 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 8.99 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 8.11 (s, 2H, *ortho*-di-*tert*-butylphenyl), 8.08 (s, 2H, *ortho*-di-*tert*-butylphenyl), 7.84 (s, 1H, *para*-di-*tert*-butylphenyl), 7.84 (s, 1H, *para*-di-*tert*-butylphenyl), 1.70 (s, 12H, pinacol), 1.60 (s, 36H, *tert*-butyl), 0.63 (s, 9H, TMS); HRMS (ESI): *m/z* calcd for $C_{59}H_{72}BN_4O_2SiZn$: 971.4814 $[M+H]^+$; found: 971.4812.

Borylation of 5,15-bis(3,5-di-*tert*-butylphenyl)-10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)porphyrinatozinc(II) (**28**): The reaction of **28** (87.4 mg, 0.10 mmol) with $[Ir(OMe)(cod)]_2$ (6.6 mg, 10 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (5.4 mg, 20 μmol), and bis(pinacolato)diboron (254.0 mg, 1.0 mmol) in 1,4-dioxane (1.5 mL) gave diborylated product **29** (65.3 mg, 59%). **29**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 588 (0.027), 552 (0.064), 423 nm (1); $^1H$ NMR ($CDCl_3$): $\delta$ = 11.50 (s, 1H, *meso*), 9.90 (d, $J$ = 4.5 Hz, 2H, β-pyrrole), 9.73 (s, 2H, β-pyrrole), 9.10 (d, $J$ = 4.5 Hz, 2H, β-pyrrole), 8.13 (s, 4H, *ortho*-di-*tert*-butylphenyl), 7.85 (s, 2H, *para*-di-*tert*-butylphenyl), 1.87 (s, 12H, pinacol), 1.73 (s, 24H, pinacol), 1.61 (s, 36H, *tert*-butyl); HRMS (ESI): *m/z* calcd for $C_{66}H_{86}B_3N_4O_6Zn$: 1127.6142 $[M+H]^+$; found: 1127.6144.

Borylation of 5-cyano-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (**30**): The reaction of **30** (42.2 mg, 0.059 mmol) with $[Ir(OMe)(cod)]_2$ (2.2 mg, 3.3 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (1.8 mg, 6.7 μmol), and bis(pinacolato)diboron (75 mg, 0.3 mmol) in 1,4-dioxane (0.8 mL) gave borylated product **31** (20.4 mg, 41%). **31**: $^1H$ NMR ($CDCl_3$): $\delta$ = 11.02 (s, 1H, *meso*), 9.63 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.61 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.53 (S, 1H, β-pyrrole), 9.41 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.10 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.04 (d, $J$ = 4.6 Hz, 2H, β-pyrrole), 8.99 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 8.08 (d, $J$ = 1.9 Hz, 2H, *ortho*-di-*tert*-butylphenyl), 8.06 (d, $J$ = 1.9 Hz, 2H, *ortho*-di-*tert*-butylphenyl), 7.85 (t, $J$ = 1.9 Hz, 1H, *para*-di-*tert*-butylphenyl), 7.84 (t, $J$ = 1.9 Hz, 1H, *para*-di-*tert*-butylphenyl), 1.67 (s, 12H, pinacol), 1.5 (br, 24H, *tert*-butyl), −2.40 ppm (s, 2H, NH); HRMS (ESI): *m/z* calcd for $C_{55}H_{65}BN_5O_2$: 838.5235 $[M+H]^+$; found: 838.5266.

Borylation of 5-bromo-10,20-bis(3,5-dioctyloxyphenyl)porphyrin (**32**): The reaction of **32** (158.1 mg, 0.15 mmol) with $[Ir(OMe)(cod)]_2$ (7.5 mg, 11 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (6.0 mg, 23 μmol), and bis(pinacolato)diboron (190.5 mg, 0.75 mmol) in octane (1.5 mL) gave **33** (57.0 mg, 32%), along with the diborylated porphyrin (12%). The *meso*-debrominated β,β′-diborylated product was also obtained in 5% yield. **33**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 650 (0.007), 593 (0.017), 552 (0.015), 517 (0.054), 422 nm (1); $^1H$ NMR ($CDCl_3$): $\delta$ = 10.86 (s, 1H, *meso*), 9.71 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.69 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.57 (s, 1H, β-pyrrole), 9.36 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 9.07 (d, $J$ = 4.6 Hz, 2H, β-pyrrole), 9.02 (d, $J$ = 4.6 Hz, 1H, β-pyrrole), 7.38 (d, $J$ = 1.9 Hz, 2H, *ortho*-di-*tert*-butylphenyl), 7.35 (s, 2H, *ortho*-di-*tert*-butylphenyl), 6.92 (d, $J$ = 2.3 Hz, 1H, *para*-di-*tert*-butylphenyl), 6.91 (d, $J$ = 1.9 Hz, 1H, *para*-di-*tert*-butylphenyl), 4.16 (t, $J$ = 6.6 Hz, 4H, $OCH_2$), 4.15 (t, $J$ = 6.6 Hz, 4H, $OCH_2$), 1.92–1.86 (m, 8H, $CH_2$), 1.70 (s, 12H, pinacol), 1.57–1.49 (m, 8H, $CH_2$), 1.42–1.25 (m, 32H, $CH_2$), 0.88 (t, $J$ = 6.9 Hz, 6H, $CH_3$), 0.87 (t, $J$ = 6.9 Hz, 6H, $CH_3$), −2.89 (s, 2H, NH); HRMS (ESI): *m/z* calcd for $C_{70}H_{97}BBrN_4O_6$: 1179.6690 $[M+H]^+$; found: 1179.6666.

Borylation of 5,5′-linked 10,20,10′,20′-tris(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II) dimer **34**: The reaction of **34** (59.9 mg, 47 μmol) with $[Ir(OMe)(cod)]_2$ (5.3 mg, 8.0 μmol), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (4.3 mg, 16 μmol), and bis(pinacolato)diboron (203.2 mg, 0.80 mmol) in 1,4-dioxane (1.5 mL) gave the tetraborylated product **35** (56.2 mg, 60%), along with the triborylated diporphyrin (26%). **35**: UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ (rel. $I$) = 563 (0.21), 458 (0.88), 426 nm (1); $^1H$ NMR ($CDCl_3$): $\delta$ = 11.55 (s, 2H, *meso*), 9.77 (s, 4H, β-pyrrole), 8.67 (d, $J$ = 5.0 Hz, 4H, β-pyrrole), 8.10 (d, $J$ = 5.0 Hz, 4H, β-pyrrole), 8.09 (s, 8H, *ortho*-di-*tert*-butylphenyl), 7.69 (s, 4H, *para*-di-*tert*-butylphenyl), 1.76 (s, 48H, pinacol), 1.46 (s, 72H, *tert*-butyl); HRMS (ESI): *m/z* calcd for $C_{120}H_{147}B_4N_8O_8Zn_2$: 2000.0345 $[M+H]^+$; found: 2000.0320.

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