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Synthesis of BODIPY-Appended Subporphyrins

Hisashi Sugimoto,[a] Masahiro Muto,[a] Takayuki Tanaka,[a] and Atsuhiro Osuka*[a]

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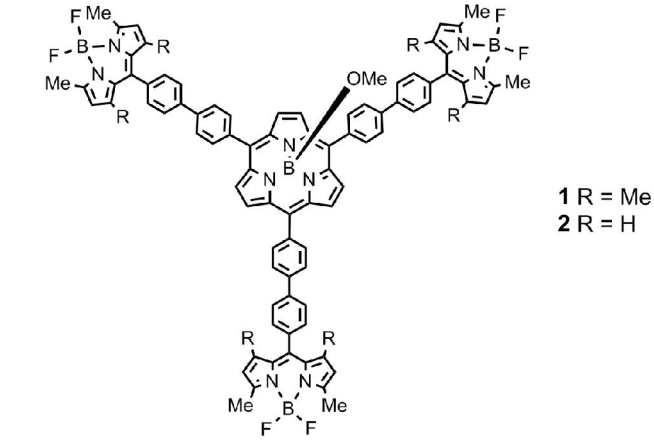
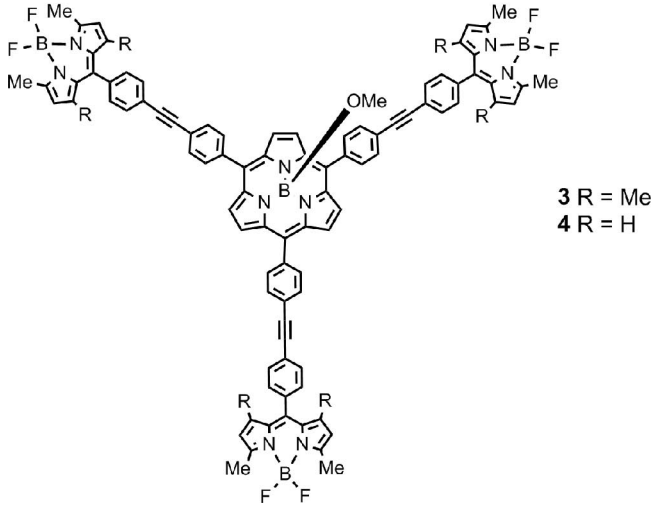
BODIPY–subporphyrin hybrids bridged by a 1,4-biphenylene or 1,4-diphenylethynylene spacer were synthesized either by the palladium-catalyzed Suzuki–Miyaura reaction or the Sonogashira reaction. Their structural and optical properties were examined with respect to the bridge and BODIPY structures. In all cases, intramolecular excitation energy transfer from the subporphyrin core to the BODIPY peripheries is efficient. Depending on the presence or absence of β-methyl groups adjacent to the *meso* position of the BODIPY subunit, the fluorescence is either increased or decreased. It was also found that the electronic interaction between the subporphyrin core and the *meso*-(1,4-phenylene) substituents causes spectral changes for the subporphyrin part, which is not observed for porphyrin counterparts.

Introduction

Since the first report on tribenzosubporphines in 2006,[1] the chemistry of subporphyrins has been actively studied because of their attractive attributes, which include their bowl-shaped structure, 14π-aromatic system, intense green fluorescence, and boron-chelated supramolecular assembly.[2–5] Compared with porphyrins, *meso*-aryl substituents of subporphyrins have a smaller rotation barrier, which leads to large effects on the electronic and optical properties of subporphyrins. Such unique features have allowed the exploitation of novel functionalized chromophores based on subporphyrins. For example, *meso*-oligo(1,4-phenyleneethynylene)-substituted subporphyrins display redshifted and intensified absorption bands and enhanced fluorescence as a consequence of the extension of the π-conjugation network,[3b] and 4-(*N*,*N*-dialkylamino)phenyl-substituted subporphyrins exhibit considerably perturbed absorption and fluorescence spectra owing to intramolecular charge-transfer interactions.[3c] Despite these recent efforts, the chemistry of subporphyrins still remains at the rudimentary stage, and the exploration of subporphyrins that hold novel functions and intriguing properties is desirable.

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (boron dipyrromethene, BODIPY) is a useful pigment with remarkable optical properties such as strong and sharp absorption bands, tunable fluorescence intensity, and photochemical stability.[6] Some BODIPYs are known for their very bright fluorescence with almost quantitative quantum yield and have been used as biochemical labeling reagents and components of an energy-transfer cassette.[7,8] In fact, there are many reports on the utilization of BODIPY as an element of artificial light-harvesting systems, in which light energy





[a] Department of Chemistry, Graduate School of Science, Kyoto University,
Sakyo-ku, Kyoto 606-8502, Japan
Fax: +81-75-753-3970
E-mail: osuka@kuchem.kyoto-u.ac.jp

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is efficiently collected and migrated from a donor part to an acceptor part. Along this line, BODIPY has been employed as an effective energy donor toward porphyrin.[7b,7e] Recently, hexaphyrin–BODIPY hybrids were prepared, in which the energy transfer from BODIPY to [26]hexaphyrin or [28]hexaphyrin proceeds efficiently.[8]

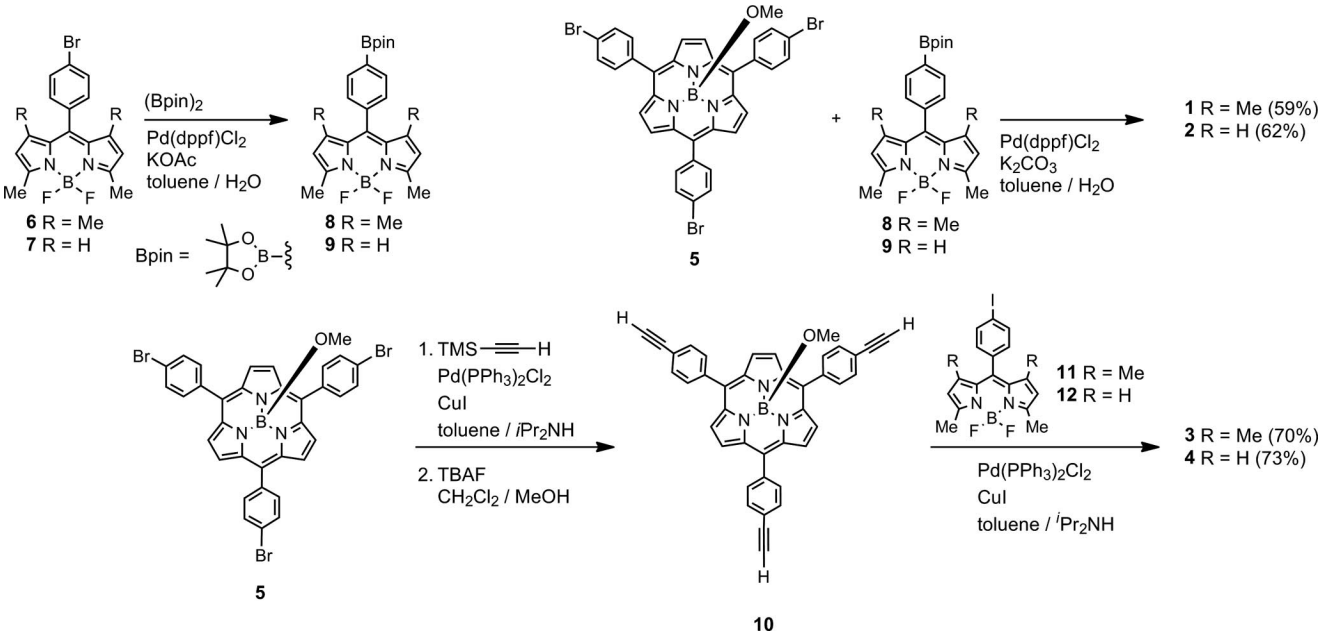
With this background, it occurred to us that covalently linked subporphyrin–BODIPY might be an interesting target, in that (1) the fluorescence of subporphyrins (500–600 nm) overlaps well with the absorption band of BODIPY, which is an important requirement for effective excitation energy transfer, and that (2) the conjugative combination of subporphyrin and BODIPY might lead to even more fluorescent molecular systems. Here we wish to report the synthesis of 1,4-biphenylene- and 1,4-diphenylethynylene-bridged subporphyrin–BODIPY hybrids **1**–**4** and their optical and electrochemical properties.

Results and Discussion

Scheme 1 outlines the synthetic routes to subporphyrin–BODIPY hybrids **1**–**4**. *meso*-Tris(4-bromophenyl)subporphyrin **5**[4a] and *meso*-4-bromophenyl BODIPYs **6** and **7**[6e] were prepared by reported methods. Borylated BODIPYs **8** and **9** were prepared by reaction of **6** and **7** with bis(pinacolato)diboron in the presence of a Pd catalyst (20 mol-%). Suzuki–Miyaura coupling of subporphyrin **5** with borylated BODIPYs **8** and **9** afforded hybrids **1** and **2** in 59 and 62% yield, respectively. The ^{1}H NMR spectra of both **1** and **2** exhibit a singlet due to the β-protons at δ = 8.23 ppm and at δ = 8.26 ppm, respectively, and a single set of signals due to the *meso* substituent groups in accord with their C_3 symmetric structures. These ^{1}H NMR spectra also indicate free rotation of the *meso* substituents in **1** and **2** at room temperature. The synthesis of 1,4-diphenylethynylene-bridged subporphyrin–BODIPY hybrids was achieved in a stepwise manner. Subporphyrin **5** was converted into *meso*-tris(4-ethynylphenyl)subporphyrin **10** by Sonogashira coupling between **5** and trimethylsilylacetylene followed by deprotection with tetrabutylammonium fluoride.[3b] Subsequent Sonogashira coupling of **10** with *meso*-(4-iodophenyl)-substituted BODIPYs **11** and **12** provided subporphyrin–BODIPY hybrids **3** and **4** in 70 and 73% yield, respectively.[6e] The ^{1}H NMR spectra of both **3** and **4** are in line with their structures (see the Supporting Information).

Single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of ethanol into its dichlorobenzene solution. The crystal structure shows C_3 symmetry (Figure 1). In the solid state, the dihedral angles between the plane defined by neighboring C_α–C_{meso}–C_α atoms and adjacent phenylene spacers are relatively small (43.7, 44.7, and 44.9°), which is in line with previous studies.[3a] These stereochemical features are expected to allow strong electronic interaction between the subporphyrin core and the *meso* substituents. On the other hand, the BODIPY units and phenylene spacers are almost perpendicular (81.6, 84.8, and 85.8°) due to the steric hindrance imposed by the β-methyl groups adjacent to the *meso* position, which is unfavorable for the electronic interaction between the subporphyrin core and the BODIPY ends. The B–B distance is about 16 Å, and the bowl depth, which is defined by the distance between the central boron atom and the mean plane of the peripheral six β-carbon atoms, is 1.28 Å.

Figure 2 shows the UV/Vis absorption and fluorescence spectra of **1**–**4** along with those of relevant reference molecules. Subporphyrins **1** and **2** exhibit Soret-like bands at nearly the same positions, 383 and 382 nm, respectively, both of which are clearly redshifted in comparison to that (373 nm) of *meso*-triphenylsubporphyrin **13** (Figure 4). The Soret-like band of **2** is broader than that of **1**. In order to



Scheme 1. Synthesis of subporphyrin–BODIPY hybrids **1**–**4**.

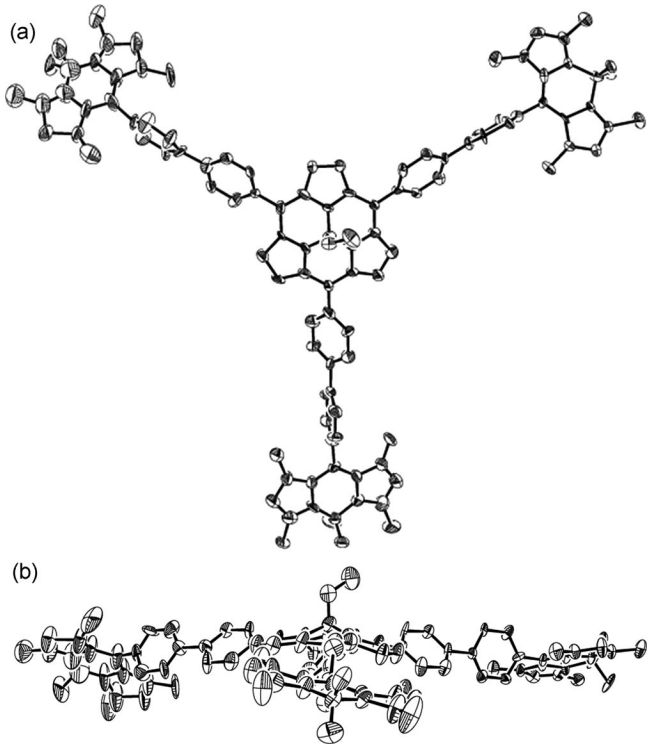


Figure 1. X-ray crystal structure of **1**: (a) top view and (b) side view. Thermal ellipsoids are scaled to 50% probability. Hydrogen atoms are omitted for clarity.

examine the electronic influences of the 4-biphenyl substituents at the *meso* positions, we prepared *meso*-tris(4-biphenyl)-substituted subporphyrin **14** by Suzuki–Miyaura coupling of **5** with pinacolatoboryl benzene in 71% yield (Scheme 2). The X-ray crystal structure of **14** is shown in Figure 3. The Soret-like band of **14** is observed at 382 nm, which is quite similar to those of **1** and **2**. These data indicate that the redshifts of **1** and **2** stem from the electronic interaction of the *meso*-(4-biphenyl) substituents with the subporphyrin core; the BODIPY edges play only a marginal effect. Next, we prepared *meso*-tris(4-terphenyl)-substituted subporphyrin **15** in 77% yield through a similar coupling reaction, which displays a Soret-like band at 385 nm. Interestingly, the fluorescence quantum yield distinctly increases in the order **13** (Φ_F = 0.14) < **14** (Φ_F = 0.26) < **15** (Φ_F = 0.34), probably as a reflection of the increasing size of the effective radiative chromophore.[3b,9] The observed effects of the *meso*-(4-biphenyl) and *meso*-(4-terphenyl) substituents are quite unique for subporphyrin chromophores, as such redshifts and increasing fluorescence quantum yields have never been observed for porphyrin counterparts.[10]

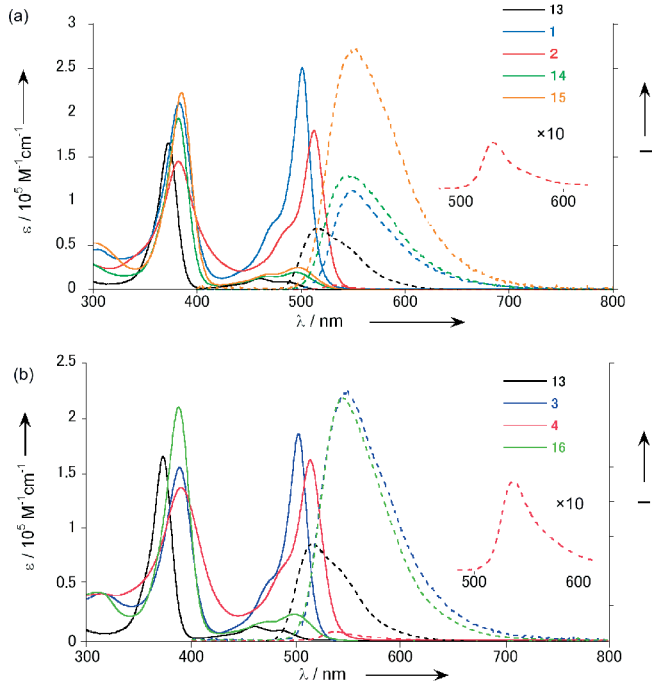
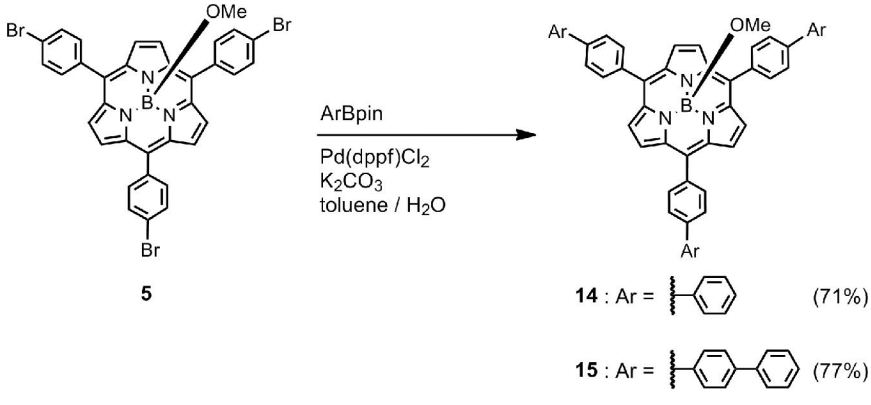


Figure 2. UV/Vis absorption (solid lines) and fluorescence (dashed lines) spectra of (a) **1**, **2**, **13**, **14**, and **15**; (b) **3**, **4**, **13**, and **16** in CH_2Cl_2.

The observed broadening of the Soret-like band of **2** may be ascribed to the conformational distribution of the BODIPY edges that arises from the small steric constraint for their rotation. Subporphyrins **3** and **4** exhibit Soret-like bands at 389 and 390 nm, which are similar to that (388 nm) of *meso*-tris(phenylethynylphenyl)-substituted subporphyrin **16**. Similar to **2**, the Soret-like band of **4** is slightly broader than that of **3**. A small electronic interaction of the subporphyrin and BODIPY can be also seen



Scheme 2. Synthesis of subporphyrins **14** and **15**.

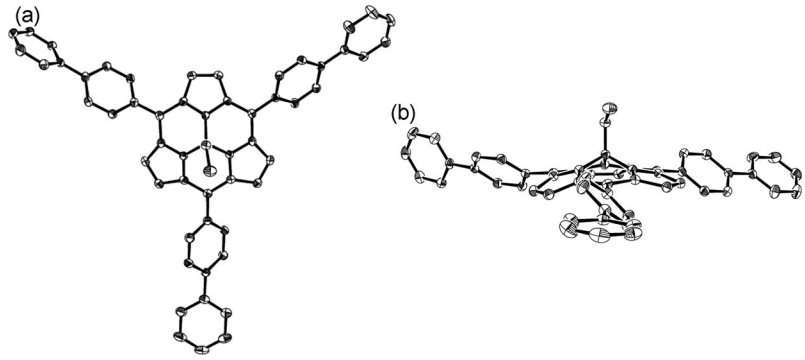


Figure 3. X-ray crystal structure of **14**: (a) top view and (b) side view. Thermal ellipsoids are scaled to 50% probability. Hydrogen atoms are omitted for clarity.

from the absorption bands of BODIPY, which show almost no shift as compared to those of *meso*-phenyl BODIPYs **17** and **18** at 501 and 511 nm, respectively. The UV/Vis absorption spectra of **1**–**4** can be almost reproduced by linear combinations of the corresponding *meso*-oligo(1,4-phenylene)-substituted subporphyrin and BODIPY fragments, indicating that the electronic interaction in the ground state is weak.

Table 1 summarizes the optical properties. The fluorescence spectra of **1**–**4** show emissions from the BODIPY segments, independent of the excitation wavelength either around 380 nm (subporphyrin) or around 500 nm (BODIPY), indicating an efficient excitation energy transfer from the subporphyrin core to the BODIPY segment.[11,12] Mitigated but clear fluorescence is observed for **1** and **3** (Φ_F = 0.20 and 0.29 for the excitation at BODIPY part), whereas the fluorescence is strongly quenched in **2** and **4**; in both cases, $\Phi_F < 0.1\%$. The latter feature may arise from the intrinsic small quantum yield of *meso*-phenyl-1,7-dimethyl BODIPY **17** (Φ_F = 0.19) as compared to that of *meso*-phenyl-1,3,5,7-tetramethyl BODIPY **18** (Φ_F = 0.65; Figure 4).[13] Fluorescence quantum yields of hybrids **1**–**4** are reduced in comparison to those of **17** and **18**. Reasons for these phenomena are not clear at the present stage, but might be due to efficient intramolecular electron-transfer or charge-transfer interaction.

Table 1. Optical properties of **1**–**4** and **13**–**16**.

Compd.	Absorption λ_{max} / nm (ε / 10^5 M^{-1} cm^{-1})	Fluorescence λ_{ex} / nm	λ_{max} / nm	Φ_F
1	383 (2.11)	383	548	0.23
	501 (2.50)	501	548	0.20
2	382 (1.45)	382	530	0.01
	512 (1.80)	512	530	0.01
3	389 (1.56)	389	548	0.36
	502 (1.87)	502	548	0.29
4	390 (1.38)	390	535	0.01
	513 (1.63)	513	535	0.01
13	373 (1.66)	373	516	0.14
14	382 (1.94)	382	548	0.26
15	385 (2.23)	385	548	0.34
16	388 (2.11)	388	554	0.29

Conclusions

BODIPY-appended subporphyrins **1**–**4** were prepared by Suzuki–Miyaura reaction or Sonogashira reaction. Although the intramolecular excitation energy transfer prevails in the singlet excited states of **1**–**4**, the fluorescence quantum yields of **1** and **3** are enhanced, whereas those of **2** and **4** are significantly decreased as compared to that of reference subporphyrin **13**. These trends can be understood in terms of the intrinsic optical properties of reference

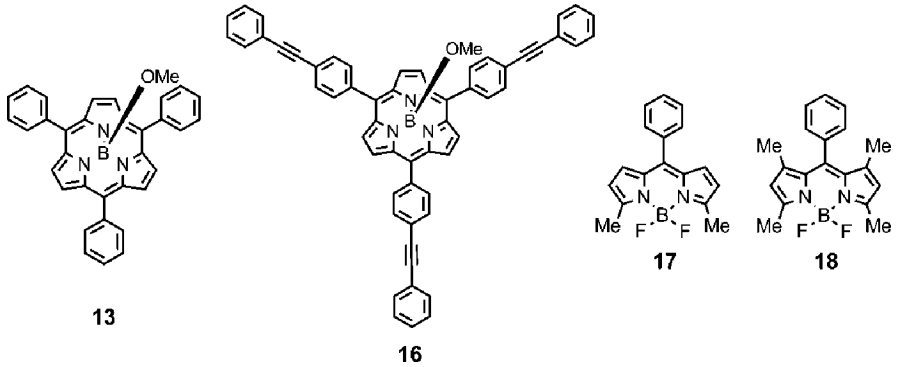


Figure 4. Reference molecules triphenylsubporphyrin **13**, *meso*-tris(phenylethynyphenyl)subporphyrin **16**, *meso*-phenyl-1,7-dimethyl BODIPY **17**, and *meso*-phenyl 1,3,5,7-tetramethyl BODIPY **18**.

BODIPYs **17** and **18**. *meso*-1,4-Oligophenylene substituents influence the optical properties of subporphyrins through conjugative interactions. Exploration of novel subporphyrin-based molecular systems is actively in progress in our laboratory.

Experimental Section

General: All reagents were of the commercial reagent grade and were used without further purification except where noted. Spectroscopic-grade dichloromethane was used as solvent for all spectroscopic studies. Silica gel column chromatography was performed on Wakogel C-200 and C-300. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F254 (Merck 5554). UV/Vis absorption spectra were recorded with Shimadzu UV-3100PC and Shimadzu UV2550 spectrometers. Fluorescence spectra were recorded with a Shimadzu RF-5300PC spectrometer. Absolute fluorescence quantum yields were determined with a Hamamatsu C9920–02S. ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded with a JEOL ECA-600 spectrometer (operating as 600.17 MHz for ^{1}H, 193 MHz for ^{11}B, and 151 MHz for ^{13}C) by using the residual solvent as the internal reference for ^{1}H (δ = 7.26 ppm in $CDCl_3$), $BF_3{\cdot}Et_2O$ as the external reference for ^{11}B (δ = 0.00 ppm in $CDCl_3$), and residual solvent as the internal reference for ^{13}C (δ = 77.16 ppm in $CDCl_3$). High-resolution electrospray-ionization time-of-flight mass spectroscopy [HRMS (ESI-TOF)] was recorded with a Bruker microTOF model by using the positive mode for acetonitrile solutions of samples. Mass spectra were recorded with a Bruker microflex-KR by using the positive-MALDI-TOF method with matrix. Crystallographic data were collected with a Rigaku RAXIS–RAPID apparatus at –150 °C by using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) or a Bruker-Apex X-ray diffractometer equipped with a large area CCD detector at –183 °C. The structures were solved by direct methods (SIR97 or SHELXS-97) and refined with full-matrix least square technique (SHELXL-97). In the event of solvent molecules not being adequately modeled, core molecule **1** was refined without the solvent molecules by a combination of the SHELX-97 and PLATON SQUEEZE programs.[12]

Pinacolatoboryl BODIPY 8: A 20-mL Schlenk tube was charged with BODIPY **6** (171 mg, 424 μmol), bis(pinacolato)diboron (215 mg, 848 μmol), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (35 mg, 85 μmol), KOAc (416 mg, 4.24 mmol), toluene (5 mL), and H_2O (1 mL). The resulting solution was deoxygenated through three freeze–pump–thaw cycles and then stirred at 100 °C for 24 h under a N_2 atmosphere. After being passed through a short Celite pad, the eluent was diluted with CH_2Cl_2 (50 mL). The resulting solution was washed with water and saturated NaCl aqueous solution, and the solvents were evaporated to dryness. The product was separated through a silica gel column (CH_2Cl_2/hexane, 1:1) and recrystallized (CH_2Cl_2/hexane) to give **8** (132 mg, 69% yield) as a red powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90 (d, J = 7.8 Hz, 2 H, Ar-H), 7.29 (d, J = 7.8 Hz, 2 H, Ar-H), 5.97 (s, 2 H, BODIPY-H), 2.55 (s, 6 H, Me), 1.39 (s, 12 H, pinacolato Me), 1.37 (s, 6 H, Me) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 155.5, 143.2, 141.7, 137.9, 135.4, 131.3, 127.4, 121.2, 84.1, 25.0, 14.5, 14.4 ppm. MS (MALDI-TOF+): m/z = 449.02 (calcd. for $C_{25}H_{30}N_2B_1F_2O_2$ 450.14 $[M]^+$). UV/Vis (CH_2Cl_2): λ = 315, 364, 501 nm. Fluorescence (CH_2Cl_2) λ_{ex} = 501 nm, λ_{max} = 511 nm.

Pinacolatoboryl BODIPY 9: A 20-mL Schlenk tube was charged with BODIPY **7** (150 mg, 400 μmol), bis(pinacolato)diboron (233 mg, 920 μmol), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (32 mg, 40 μmol), KOAc (393 mg, 4.00 mmol), toluene (3.3 mL), and H_2O (0.7 mL). The resulting solution was deoxygenated through three freeze–pump–thaw cycles and then stirred at 100 °C for 24 h under a N_2 atmosphere. After the mixture was passed through a short Celite pad, the eluent was diluted with CH_2Cl_2 (50 mL). The resulting solution was washed with water and brine, and the solvents were evaporated to dryness. The product was separated through a silica gel column (CH_2Cl_2/hexane, 1:1) and recrystallized (CH_2Cl_2/hexane) to give **9** (92.2 mg, 55% yield) as a red powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91 (d, J = 7.8 Hz, 2 H, Ar-H), 7.49 (d, J = 8.4 Hz, 2 H, Ar-H), 6.69 (d, J = 4.2 Hz, 2 H, BODIPY-H), 6.26 (d, J = 4.2 Hz, 2 H, BODIPY-H), 2.65 (s, 6 H, Me), 1.38 (s, 12 H, pinacolato Me) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.7, 142.4, 136.7, 134.4, 130.4, 129.7, 119.4, 84.2, 24.9, 14.9, 1.0 ppm. MS (MALDI-TOF+): m/z = 420.80 (calcd. for $C_{23}H_{26}N_2B_1F_2O_2$ 422.08 $[M]^+$). UV/Vis (CH_2Cl_2): λ = 339, 512 nm. Fluorescence (CH_2Cl_2): λ_{ex} = 512 nm, λ_{max} = 532 nm.

BODIPY-Appended Subporphyrin 1: A 10-mL Schlenk tube was charged with 5,10,15-tris(4-bromophenyl)subporphyrin **5** (30.0 mg, 40.6 μmol), BODIPY **8** (60.3 mg, 134 μmol), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (6.6 mg, 8.12 μmol), K_2CO_3 (185 mg, 1.34 mmol), toluene (2 mL), and H_2O (0.4 mL). The resulting solution was deoxygenated through three freeze–pump–thaw cycles and then stirred at 100 °C for 4 d under a N_2 atmosphere. After the mixture was passed through a short Celite pad, the eluent was diluted with CH_2Cl_2 (50 mL). The resulting solution was washed with water and brine, and the solvents were evaporated to dryness. To the residual solid, a mixture of CH_2Cl_2/MeOH (1:1, 50 mL) was added, and the solution was heated at 50 °C for 10 min. The product was separated through a silica gel column (CH_2Cl_2/hexane/ether, 1:2:1) and recrystallized (CH_2Cl_2/MeOH) to give **1** (35.0 mg, 23.8 μmol, 59% yield) as an orange powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.23 (s, 6 H, β-H), 8.22 (d, J = 7.2 Hz, 6 H, Ar-H), 8.06 (d, J = 7.8 Hz, 6 H, Ar-H), 7.98 (d, J = 7.8 Hz, 6 H, Ar-H), 7.48 (d, J = 8.4 Hz, 6 H, Ar-H), 6.04 (s, 6 H, BODIPY-H), 2.60 (s, 18 H, Me), 1.53 (s, 18 H, Me), 0.92 (s, 3 H, OMe) ppm. ^{11}B NMR (193 MHz, $CDCl_3$): δ = 0.79 (t, J = 33.9 Hz, 3 B, BODIPY), –15.15 (s, 1 B, subporphyrin) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 155.9, 143.3, 141.6, 141.2, 141.2, 140.0, 137, 134.7, 134.0, 132.0, 129.0, 128.0, 127.5, 122.6, 121.5, 120.3, 53.6, 47.1, 14.8 ppm. HRMS (ESI-TOF+): m/z = 1436.6283 (calcd. for $C_{90}H_{72}B_4F_6N_9$ 1436.6225 $[M – OMe]^+$). UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 383 (211000), 501 (38600) nm. Fluorescence (CH_2Cl_2) λ_{ex} = 383 nm, λ_{max} = 548 nm, Φ_F = 0.225, λ_{ex} = 501 nm, λ_{max} = 548 nm, Φ_F = 0.202.

BODIPY-Appended Subporphyrin 2: A 10-mL Schlenk tube was charged with 5,10,15-tris(4-bromophenyl)subporphyrin **5** (10.0 mg, 13.5 μmol), BODIPY **9**(18.8 mg, 44.6 μmol), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (2.2 mg, 2.70 μmol), K_2CO_3 (61.6 mg, 446 μmol), toluene (0.8 mL), and H_2O (0.2 mL). The resulting solution was deoxygenated through three freeze–pump–thaw cycles, and then stirred at 100 °C for 4 d under a N_2 atmosphere. After being passed through a short Celite pad, the mixture was diluted with CH_2Cl_2 (50 mL). The resulting solution was washed with water and brine, and the solvents were evaporated to dryness. To the residual solid, a mixture of CH_2Cl_2/MeOH (1:1, 50 mL) was added, and the solution was heated at 50 °C for 10 min. The product was separated through a silica gel column (CH_2Cl_2/hexane/ether, 1:2:1) and recrystallized (CH_2Cl_2/MeOH) to give **2** (11.5 mg, 8.31 μmol, 62% yield) as an orange powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.26 (s, 6 H, β-H), 8.24 (d, J = 7.8 Hz, 6 H, Ar-H), 8.03 (d, J = 7.8 Hz, 6 H, Ar-H), 7.93 (d, J = 7.8 Hz, 6 H, Ar-H), 7.70 (d, J = 8.4 Hz, 6 H, Ar-H), 6.86 (d, J = 4.8 Hz, 6 H, BODIPY-H), 6.33 (d, J = 3.6 Hz, 6

H, BODIPY-H), 2.70 (s, 18 H, Me), 0.92 (s, 3 H, OMe) ppm. ^{11}B NMR (193 MHz, $CDCl_3$): δ = 0.98 (t, J = 66.0 Hz, 3 B, BODIPY), –15.06 (s, 1 B, subporphyrin) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.7, 143.1, 143.0, 141.8, 140.3, 137.8, 135.3, 134.6, 134.3, 132.0, 131.2, 128.2, 127.7, 123.2, 120.9, 120.2, 47.2, 15.1 ppm. HRMS (ESI-TOF+): m/z = 1352.5293 (calcd. for $C_{84}H_{60}B_4F_6N_9$ 1352.5284 [M – OMe]$^+$). UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 382 (127000), 512 (79000) nm. Fluorescence (CH_2Cl_2) λ_{ex} = 383 nm, λ_{max} = 530 nm, Φ_F = 0.007, λ_{ex} = 512 nm, λ_{max} = 530 nm, Φ_F = 0.010.

BODIPY-Appended Subporphyrin 3: A 10-mL Schlenk tube was charged with 5,10,15-tris(4-ethynylphenyl)subporphyrin **10** (10.6 mg, 18.5 μmol), BODIPY **11** (26.6 mg, 59.2 μmol), $Pd(PPh_3)_2Cl_2$ (4.3 mg, 3.70 μmol), CuI (1.4 mg, 7.40 μmol), toluene (0.8 mL), and diisopropylamine (0.8 mL). The resulting solution was deoxygenated through three freeze–pump–thaw cycles and then stirred at 80 °C for 21 h under a N_2 atmosphere. After the mixture was passed through a short Celite pad, the mixture was diluted with CH_2Cl_2 (50 mL). The resulting solution was washed with water and brine, and the solvents were evaporated to dryness. To the residual solid, a mixture of CH_2Cl_2/MeOH (1:1, 50 mL) was added, and the solution was heated at 50 °C for 10 min. The product was separated through a silica gel column (CH_2Cl_2/hexane/ether, 1:2:1) and recrystallized (CH_2Cl_2/MeOH) to give **3** (19.8 mg, 12.9 μmol, 70% yield) as an orange powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.18 (s, 6 H, β-H), 8.11 (d, J = 7.8 Hz, 6 H, Ar-H), 7.91 (d, J = 8.4 Hz, 6 H, Ar-H), 7.77 (d, J = 7.2 Hz, 6 H, Ar-H), 7.36 (d, J = 7.2 Hz, 6 H, Ar-H), 6.02 (s, 6 H, BODIPY-H), 2.58 (s, 18 H, Me), 1.49 (s, 18 H, Me), 0.86 (s, 3 H, OMe) ppm. ^{11}B NMR (193 MHz, $CDCl_3$): δ = 0.75 (t, J = 33.9 Hz, 3 B, BODIPY), –15.20 (s, 1 B, subporphyrin) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 155.8, 143.0, 140.8, 140.7, 137.4, 135.2, 133.2, 132.4, 132.0, 131.2, 128.3, 124.0, 122.5, 122.4, 121.4, 120.0, 90.5, 90.2, 46.8, 29.7, 14.7 ppm. HRMS (ESI-TOF+): m/z = 1508.6159 (calcd. for $C_{90}H_{72}B_4F_6N_9$ 1508.6227 [M – OMe]$^+$). UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 389 (155000), 502 (104000) nm. Fluorescence (CH_2Cl_2): λ_{ex} = 389 nm, λ_{max} = 548 nm, Φ_F = 0.363, λ_{ex} = 502 nm, λ_{max} = 548 nm, Φ_F = 0.297.

BODIPY-Appended Subporphyrin 4: A 10-mL Schlenk tube was charged with 5,10,15-tris(4-ethynylphenyl)subporphyrin **10** (12.0 mg, 20.9 μmol), BODIPY **12** (29.1 mg, 69.0 μmol), $Pd(PPh_3)_2Cl_2$ (4.8 mg, 4.18 μmol), CuI (1.6 mg, 8.36 μmol), toluene (0.8 mL), and diisopropylamine (0.8 mL). The resulting solution was deoxygenated through three freeze–pump–thaw cycles and then stirred at 80 °C for 21 h under a N_2 atmosphere. After the mixture was passed through a short Celite pad, the mixture was diluted with CH_2Cl_2 (50 mL). The resulting solution was washed with water and brine, and the solvents were evaporated to dryness. To the residual solid, a mixture of CH_2Cl_2/MeOH (1:1, 50 mL) was added, and the solution was heated at 50 °C for 10 min. The product was separated through a silica gel column (CH_2Cl_2/hexane/ether, 1:2:1) and recrystallized (CH_2Cl_2/MeOH) to give **4** (22.1 mg, 15.2 μmol, 73% yield) as a red powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (s, 6 H, β-H), 8.12 (d, J = 9.0 Hz, 6 H, Ar-H), 7.92 (d, J = 7.8 Hz, 6 H, Ar-H), 7.74 (d, J = 7.8 Hz, 6 H, Ar-H), 7.56 (d, J = 8.4 Hz, 6 H, Ar-H), 6.77 (d, J = 4.2 Hz, 6 H, BODIPY-H), 6.31 (d, J = 4.2 Hz, 6 H, BODIPY-H), 2.68 (s, 18 H, Me), 0.87 (s, 3 H, OMe) ppm. ^{11}B NMR (193 MHz, $CDCl_3$): δ = 0.93 (t, J = 32.4 Hz, 3 B, BODIPY), –15.20 (s, 1 B, subporphyrin) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 157.9, 141.5, 143.0, 140.9, 137.5, 134.3, 134.2, 133.2, 132.0, 131.5, 130.5, 130.2, 125.1, 122.5, 122.4, 119.6, 91.3, 90.2, 46.9, 15.0 ppm. HRMS (ESI-TOF+) m/z = 1424.5299 (calcd. for $C_{84}H_{60}B_4F_6N_9$ 1424.5286 [M – OMe]$^+$). UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 390 (138000), 513 (121000) nm. Fluorescence (CH_2Cl_2): λ_{ex} = 390 nm, λ_{max} = 535 nm, Φ_F = 0.013, λ_{ex} = 513 nm, λ_{max} = 535 nm, Φ_F = 0.013.

Methoxido[5,10,15-tris(4-biphenylyl)subporphyrinato]boron(III) (14): A 10-mL Schlenk tube was charged with 5,10,15-tris(4-bromophenyl)subporphyrin **5** (19.2 mg, 26.0 μmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (24.4 mg, 119 μmol), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (4.57 mg, 5.60 μmol), K_2CO_3 (118 mg, 857 μmol), toluene (1.8 mL), and H_2O (0.3 mL). The resulting solution was deoxygenated through three freeze–pump–thaw cycles and then stirred at 100 °C for 6 h under a N_2 atmosphere. After the mixture was passed through a short Celite pad, the mixture was diluted with $CHCl_3$. The resulting solution was washed with water and brine, and the solvents were evaporated to dryness. To the residual solid, a mixture of $CHCl_3$/MeOH (1:1, 50 mL) was added, and the solution was heated at 50 °C for 10 min. The product was separated through a silica gel column (CH_2Cl_2/hexane/MeOH, 2:10:1) and recrystallized (CH_2Cl_2/MeOH) to give **14** (13.5 mg, 18.6 μmol, 71% yield) as a red powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.22 (s, 6 H, β-H), 8.18 (d, J = 8.2 Hz, 6 H, Ar-H), 7.95 (d, J = 8.2 Hz, 6 H, Ar-H), 7.81 (d, J = 7.3 Hz, 6 H, Ar-H), 7.55 (t, J = 7.8 Hz, 6 H, Ar-H), 7.44 (t, J = 7.2 Hz, 3 H, Ar-H), 0.89 (s, 3 H, OMe) ppm. ^{11}B NMR (193 MHz, $CDCl_3$): δ = –15.11 (s, 1 B) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.1, 140.8, 136.4, 133.8, 129.1, 127.8, 127.5, 127.4, 122.7, 122.5, 120.3, 47.0 ppm. HRMS (ESI-TOF+): m/z = 698.2770 (calcd. for $C_{51}H_{33}BN_3$ 698.2770 [M – OMe]$^+$). UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 382 (163000), 468 (13000), 495 (17000) nm. Fluorescence (CH_2Cl_2): λ_{ex} = 382 nm, λ_{max} = 548 nm, Φ_F = 0.255.

Methoxido[5,10,15-tris(4-terphenylyl)subporphyrinato]boron(III) (15): A 10-mL Schlenk tube was charged with 5,10,15-tris(4-bromophenyl)subporphyrin **5** (19.2 mg, 26.0 μmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (31.9 mg, 114 μmol), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (4.34 mg, 5.31 μmol), K_2CO_3 (121 mg, 878 μmol), toluene (1.3 mL), and H_2O (0.3 mL). The resulting solution was deoxygenated through three freeze–pump–thaw cycles and then stirred at 100 °C for 9 h under a N_2 atmosphere. After the mixture was passed through a short Celite pad, the mixture was diluted with $CHCl_3$. The resulting solution was washed with water and brine, and the solvents were evaporated to dryness. To the residual solid, a mixture of $CHCl_3$/MeOH (1:1, 50 mL) was added, and the solution was heated at 50 °C for 10 min. The product was separated through a silica gel column (CH_2Cl_2/hexane/MeOH, 2:10:1) and recrystallized (CH_2Cl_2/MeOH) to give **15** (19.1 mg, 19.9 μmol, 77% yield) as a red powder. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.24 (s, 6 H, β-H), 8.20 (d, J = 8.2 Hz, 6 H, Ar-H), 8.01 (d, J = 7.8 Hz, 6 H, Ar-H), 7.90 (d, J = 8.2 Hz, 6 H, Ar-H), 7.79 (d, J = 8.3 Hz, 6 H, Ar-H), 7.72 (d, J = 7.3 Hz, 3 H, Ar-H),7.51 (t, J = 7.8 Hz, 6 H, Ar-H), 7.40 (t, J = 7.8 Hz, 3 H, Ar-H), 0.91 (s, 3 H, OMe) ppm. ^{11}B NMR (193 MHz, $CDCl_3$): δ = –15.08 (s, 1 B) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.1, 140.8, 140.7,140.2, 139.6, 136.5, 133.8, 129.0, 127.9, 127.8, 127.7, 127.6, 127.4, 127.2, 122.5, 120.4, 47.1 ppm. HRMS (ESI-TOF+): m/z = 926.3703 (calcd. for $C_{69}H_{45}BN_3$ 926.3712 [M – OMe]$^+$). UV/Vis (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 385 (223000), 497(25000) nm. Fluorescence (CH_2Cl_2): λ_{ex} = 385 nm, λ_{max} = 548 nm, Φ_F = 0.337.

Crystallographic Data for 1: $C_{91}H_{75}B_4F_6N_9O_1$, M = 1467.84, triclinic, space group $P\bar{1}$ (no. 2), a = 9.086(8) Å, b = 23.79(2) Å, c = 24.84(2) Å, α = 97.060(12)°, β = 95.959(13)°, γ = 93.029(14)°, V = 5288(8) Å^3, $\rho_{calcd.}$ = 0.922 g cm^{-3}, Z = 2, R_1 = 0.1018 [$I > 2\sigma(I)$], wR_2 = 0.2323 (all data), GOF = 0.709.

The contributions to the scattering arising from the presence of the disordered solvents in the crystals were removed by use of the utility SQUEEZE in the PLATON software package.[14]

Crystallographic Data for 14: $C_{56}H_{44}B_1N_3O_1$, M = 4032.2, monoclinic, space group $P\ 2_1/a$ (no. 14), a = 10.7752(18) Å, b = 21.660(5) Å, c = 17.340(7) Å, β = 92.920(7)°, V = 4032.1(13) Å^3, $\rho_{calcd.}$ = 1.321 g cm^{-3}, Z = 4, R_1 = 0.0476 [$I > 2\sigma(I)$], wR_2 = 0.1242 (all data), GOF = 1.070.

CCDC-787281 (for **1**) and -787282 (for **14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Supporting Information (see footnote on the first page of this article): NMR spectra, high-resolution mass spectra (ESI-TOF), and X-ray diffraction analysis.

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