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Synthesis of π-expanded *O*-chelated boron–dipyrromethene as an NIR dye

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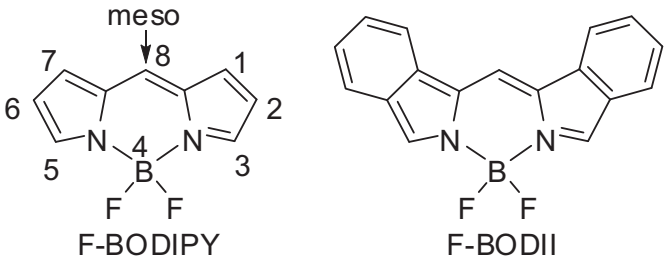
ABSTRACT

A π-expanded BODIPY dye with an intramolecular boronate skeleton was synthesized by retro Diels–Alder reaction of the bicyclo[2.2.2]octadiene (BCOD)-fused BODIPY and the subsequent O-chelation. The photophysical and electrochemical properties were examined by UV–vis, fluorescence, CV measurements, and DFT calculation. This BODIPY exhibited the absorption and emission over a visible–NIR region at 600–850 nm. *O*-chelated BODIPY showed a bathocromic shift compared to F-BODIPYs. This dye showed a bright fluorescence emission at 733 nm with the high Φ value of 0.58.

1. Introduction

Boron–dipyrromethene (BODIPY) is a well-known stable fluorescent dye with strong absorption and emission. This dye is generally composed of a dipyrromethene π-system and a boron-difluoride core. Modification of the BODIPY structure has been developed in order to tune the absorption and emission wavelengths. Introduction of substituents at pyrrole *meso*-position and boron moieties has afforded a variety of BODIPYs, electronic structures of which are greatly influenced not only by the π-system modification at the dipyrromethene moiety but by the substitution of core fluorine atoms.[1–4] In the latter case, substituents making strong bonds with boron atom are employed. Therefore, many BODIPYs with carbon (C-BODIPY)[6] and oxygen (O-BODIPY)[5,7] substituents on the core boron atom have been reported. The first O-BODIPYs have been synthesized by intramolecular substitution of fluorine atoms with phenoxyl groups appended to 3- and 5-positions of the dipyrromethene moiety.[2a,7a–c] The *O*-chelated BODIPY showed a significant red-shift (80 nm) in the UV absorption spectrum and a sharper emission with ca. six-times higher quantum yield than the corresponding precursor. Recently, Kubo et al. have reported that the *O*-chelated boron-di(2*H*-isoindolyl)methenes (BODIIs) have strong absorptions (ϵ=8.3×10^4 M^{-1} cm^{-1}) in NIR region (ca. 750 nm).[7d] In their method, formation of BODIIs according to literature procedure from methyl *o*-methoxybenzoate[5a] followed by intramolecular substitution afforded only *O*-chelated BODIIs without a *meso*-substituent and the molecular structures and emission properties have not been reported. We have already reported the synthesis of BODIIs based on retro Diels–Alder conversion of bicyclo[2.2.2]octadiene (BCOD) to benzene.[1a,c,d] In our method, substituted-BODIIs at *meso*-position, where functional groups could be introduced, are easily obtained.[1d] We herein report the synthesis of *O*-chelated *meso*-phenylBODIIs with NIR absorption and emission.



2. Results and discussion

Synthesis of BODIPYs and BODIIs (**4**, **9**, and **5**) is shown in Scheme 1. *N*-Butoxycarbonyl BCOD-pyrrole-2-carboxylate **1**[8a]

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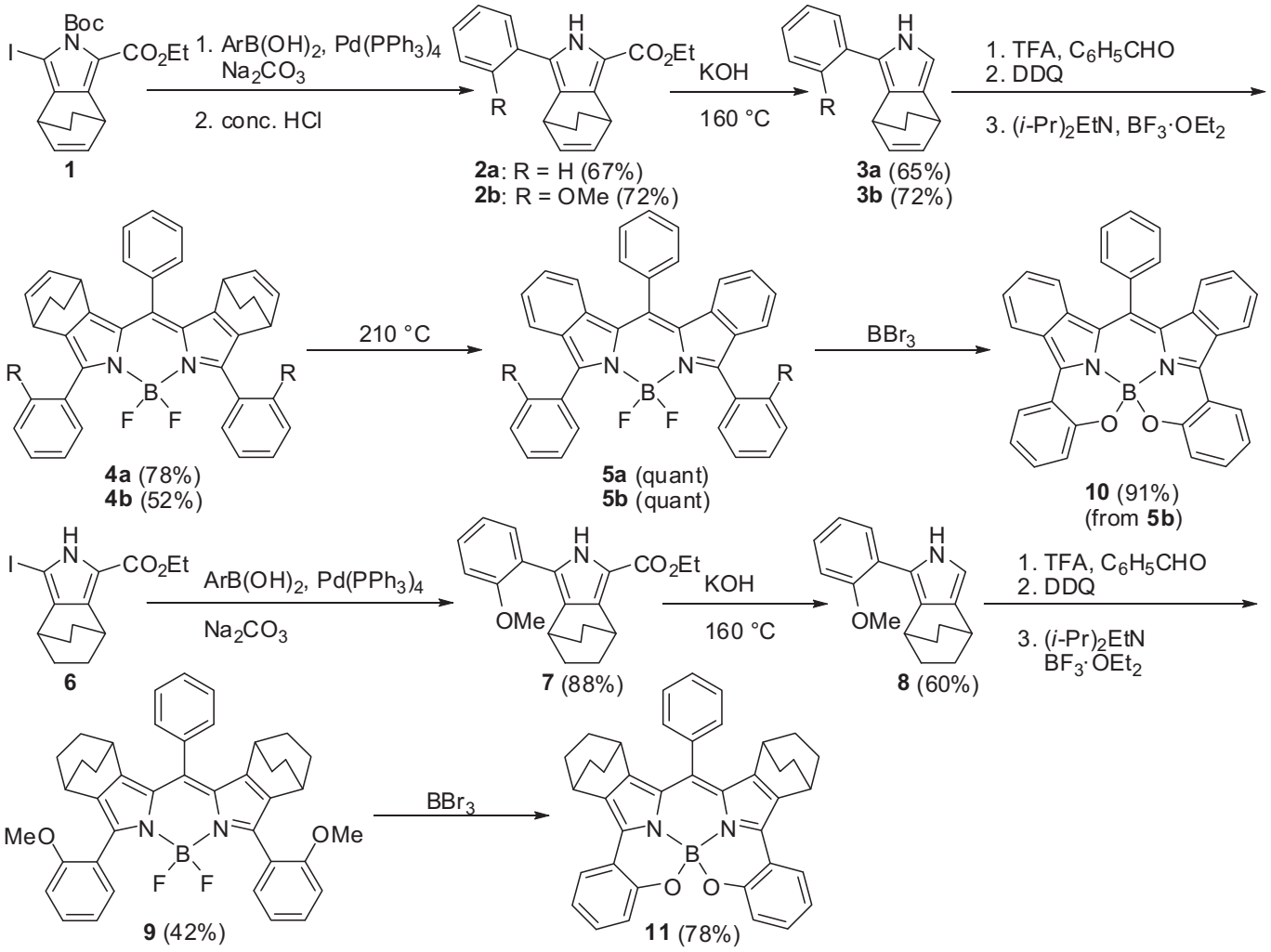

Scheme 1.

reacted with phenyl- and 2-methoxyphenylboronic acids by Suzuki–Miyaura coupling followed by deprotection of Boc groups to give **2a** and **2b** in 67% and 72% yields, respectively. Removal of the ester group of **2a** and **2b** with KOH gave α-free aryl pyrroles **3a** and **3b** in 65% and 72% yields, respectively. Condensation of **3a** and **3b** with benzaldehyde followed by oxidation with DDQ and complexation gave BCOD-fused BODIPYs **4a** and **4b** in 78% and 52% yields, respectively. Thermal treatment of **4a** and **4b** at 210 °C quantitatively gave the corresponding BODIIs **5a** and **5b**. Bicyclo [2.2.2]octene-fused (BCO-fused) BODIPY **9** was prepared in the similar manner starting from **6**.[8b] Demethylation of **5b** and **9** with BBr_3 and simultaneous cyclization afforded constrained compounds **10** and **11** with a spirobi[1,3,2]oxazaborine skeleton in 91% and 78% yields, respectively. When **4b** was treated with BBr_3, however, the corresponding *O*-chelated and brominated product was obtained in low yield.

Thermogravimetric analysis of **4** was carried out in order to determine the temperature of the retro Diels–Alder reaction (Fig. 1). The weight loss from **4a** and **4b** started at 160 and 140 °C, and finished at 240 and 220 °C, respectively. The lost amounts from **4a** and **4b** are 11.1% and 10.1%, which are slightly larger than the calculated ones of 9.7% and 8.8%, respectively.

UV–vis absorption spectra of BODIPYs **4**, **5**, **9**, **10**, and **11** are shown in Fig. 2. Their absorption bands are observed in a visible–NIR region. The BODIPYs **4** and **9** show broad absorption bands around 550 nm similar to those of typical 3,5-diaryl-substituted

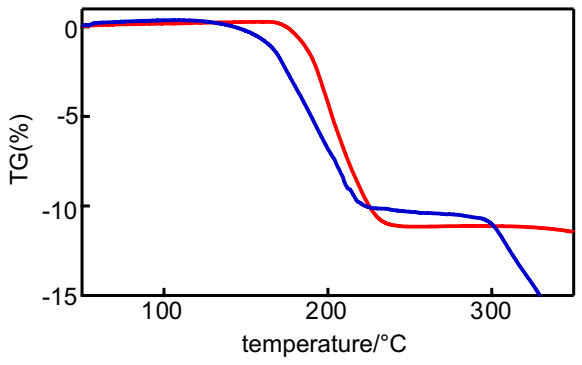

Fig. 1. TG analysis of **4a** (red) and **4b** (blue line).

BODIPYs.[2a] Absorption spectra of BODII **5a** and **5b** are well in accord with the reported value of other BODIIs.[1a,9] The absorption maxima of **4b** and **5b** with *o*-methoxyphenyl group are blue-shifted compared with those of **4a** and **5a** due to insufficient conjugation of *o*-methoxyphenyl groups by steric hindrance.[9] An absorption band of **10** (711 nm) is red-shifted by 80–94 nm compared to those of **5a** and **5b**. An absorption band of **11** is observed at 626 nm, which is red-shifted by 76 nm compared to that of **9**.

Absorption and emission maxima, absolute quantum yields (Φ) and fluorescence lifetime (τ) are summarized in Table 1, and the

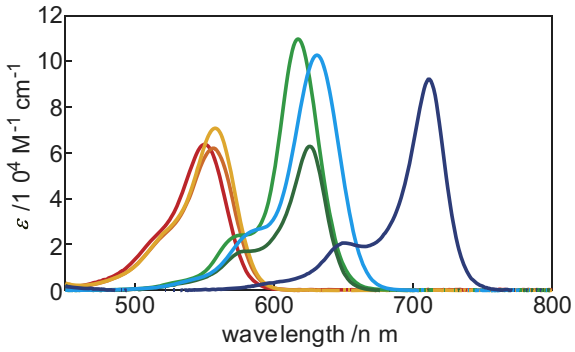

Fig. 2. UV–vis absorption spectra of **9** (red), **4b** (orange), **4a** (yellow), **5b** (light green), **11** (green), **5a** (light blue), and **10** (blue line) in CH_2Cl_2.

Table 1
Photophysical properties

	λ_{abs}/nm (log ϵ)[a]	λ_{em}/nm (Φ)[b]	τ/ns[c]	λ_{ex}/nm
9	550 (4.81)	583 (0.77)	4.5	517
4b	556 (4.79)	587 (0.87)	5.1	517
4a	558 (4.85)	588 (0.87)	6.1	510
5b	617 (5.01)	652 (0.91)	5.8	617
11	626 (4.80)	645 (0.99)	9.6	571
5a	631 (5.01)	664 (0.93)	5.2	583
10	711 (4.96)	733 (0.58)	7.0	651

[a] In CH_2Cl_2 at 10^{-6} M.
[b] In CH_2Cl_2 at 10^{-7} M.
[c] Excited at 532 nm in CH_2Cl_2.

emission spectra are shown in Fig. 3. The BODIPYs **4** and **9** show strong and broad emission bands at 583–588 nm with high Φ values of 0.77–0.87. The emission peaks of **5a** and **5b** are observed at the similar region to the reported BODIIs (664 and 652 nm) with high Φ values of 0.93 and 0.91, respectively. *O*-Chelated BODIPY **11** shows strong fluorescence emission at 645 nm. This band is red-shifted by 62 nm compared to that of precursor **9**. The Φ value (0.99) of **11** is quite high than those of other BODIPY dyes emitting at the same region.[7a] This is probably due to BCO rings blocking the fluorescence quenching by the BODIPY-chromophore stacking and by the *meso*-phenyl-group rotation. The emission band of *O*-chelated BODII **10** appears at 733 nm, value of which is red-shifted by 81 nm compared to **5b**, and the Φ value is 0.58. *O*-Chelated **10** and **11** have longer fluorescence lifetimes of 7.0 and 9.6 ns than **4**, **5**, and **9**. This is due to the lack of wagging of aryl groups.

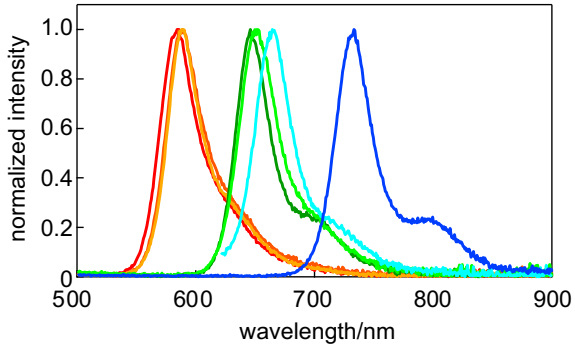

Fig. 3. Normalized fluorescence emission spectra of **9** (red), **4b** (orange), **4a** (yellow), **11** (green), **5b** (light green), **5a** (light blue), and **10** (blue line) in CH_2Cl_2.

Redox potentials of the BODIPYs were measured by CV in CH_2Cl_2 using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte, glassy carbon as a working electrode, Pt wire as a counter electrode, and Ag/Ag^+ as a reference electrode (Table 2 and Fig. S1). All compounds show reversible reduction and oxidation peaks. No obvious effect is observed in the potentials by fusion of BCOD and BCO. The reduction and oxidation potentials of **4b** and **9** are the almost same. Intramolecular spiro ring formation results in the stabilization of LUMO and destabilization of HOMO by effective conjugation of appended aryl groups (Table 2). The lowest oxidation potential is recorded in **10** (0.19 V).

Table 2
Electrochemical data[a], and calculated HOMO and LUMO energy values

	E_{1ox}/V E_{HOMO}/eV[b]	E_{2ox}/V	E^{red}/V E_{LUMO}/eV[b]	E_g/eV[c]	E_{HOMO}/eV[d] E_{LUMO}/eV[d]	E_g/eV[d]
9	0.55 −5.33	—	−1.76 −3.02	2.31	−4.96 −2.19	2.77
4b	0.57 −5.35	—	−1.70 −3.08	2.27	−5.04 −2.26	2.78
4a	0.67 −5.45	—	−1.58 −3.20	2.25	−5.11 −2.41	2.70
5b	0.32 −5.10	(1.17)	−1.63 −3.15	1.95	−4.81 −2.39	2.42
11	0.39 −5.17	(1.08)	−1.64 −3.14	2.03	−4.82 −2.34	2.48
5a	0.37 −5.15	(1.22)	−1.54 −3.24	1.91	−4.80 −2.45	2.35
10	0.19 −4.97	(0.90)	−1.48 −3.30	1.67	−4.65 −2.45	2.20

[a] The redox potentials were measured by CV (V vs Fc/Fc^+, 0.1 M $TBAPF_6$ in CH_2Cl_2 Pt electrode, scan rate=0.1 V s^{-1} Fc/Fc^+=0.25 V vs Ag/Ag^+). In the case of irreversible waves, which are shown in parentheses, E_{2ox} are anodic peak potentials.
[b] $E_{HOMO}(Fc)$=−4.78 eV[10], E_{HOMO}=−4.78 eV−E_{1ox}, ELUMO=−4.78−E_{1red}.
[c] HOMO–LUMO energy gaps obtained by CV.
[d] HOMO and LUMO energy values and gaps calculated by the B3LYP/6-31G(*) density functional theory.

The crystal structures of **4**, **5**, **9**, **10**, and **11** were determined by X-ray diffraction analysis (Figs. 4–6 and Figs.S2–5).[11] The crystallographic data are summarized in Tables S2 and S3. In **5a**, both phenyl rings lie out of the mean plane of the BODIPY chromophore with torsion angles of 56.45° and 58.66°. The BODIPY skeleton is slightly distorted, and the mean plane deviation is 0.0585 Å with respect to the BODIPY mean plane (12 member's atom). The dihedral angle of pyrrole moieties is 8.00°. BODIPY **5b** adopts almost *S*1 symmetry. Both phenyl rings of **5b** lie nearly perpendicularly to the mean plane of BODIPY moiety (80.26° and 89.07°). The BODIPY skeleton is slightly distorted, the dihedral angle of pyrrole moieties is 4.86°, and the mean plane deviation is 0.0508 Å with respect to BODIPY moiety. F–B–F, N–B–N bond angles and F–B, N–B bond lengths of BODIIs **5** are well comparable to the reported values of other BODIIs.[1a,d] *O*-Chelated BODII **10**, however, adopts a considerably distorted structure, and the mean plane deviation is 0.0959 Å. The bond angle of N–B–N is widened to be 108.4(7)°, while that of O–B–O is narrowed to be 106.5(7)°.

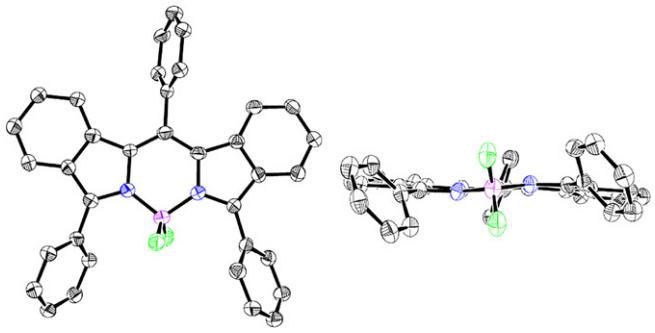

Fig. 4. ORTEP drawing of **5a**. Hydrogen atoms are omitted for clarity.

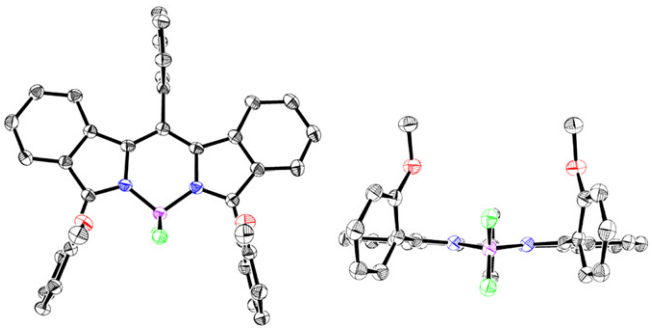

Fig. 5. ORTEP drawing of **5b**. Hydrogen atoms are omitted for clarity.

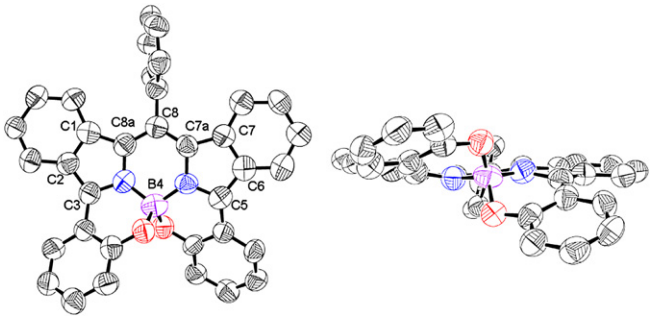

Fig. 6. ORTEP drawing of **10**. Hydrogen atoms are omitted for clarity.

Unexpectedly we obtained yellow crystals of **12** with green crystals of **10** during the recrystallization of **10** from $CHCl_3$/MeOH. The structure of **12** is unambiguously determined to be a bis-methoxide adduct at the 3- and 5-positions of BODII, although the crystal contains mono-chlorinated compound of **12** in ca. 13% as a disordered structure (Supplementary data and Fig. 7). The dihydro BODIPY core of **12** is almost flat, and the heavy distortion observed in **10** is greatly released.[15] The dihedral angle of pyrrole moieties is 4.04°. The mean plane deviation is 0.0541 Å. In **12**, O–B–O angle is larger than that in **10** and N–B–N angle is smaller. These values become close to those of **5a** and **5b** (Table 3). UV–vis absorption of **12** is shown in Fig. 8. Three absorption bands appear at 282, 411, and 434 nm. No fluorescence is observed in **12**. The yellow crystals of **12** were not obtained by recrystallization of **10** from $CHCl_3$/MeOH in the dark. The photo stability of **5b**, **4b**, **10**, and **11** in CH_2Cl_2 at ca. 10^{-5} M was measured by continuous irradiation at the wavelength of absorption maxima with a Xe lamp. After 1 h, 67%, 87%, 69%, and 88% of the initial absorbance were retained, respectively. In *O*-chelated BODIPY, BODII **10** showed low photo stability compared to BODIPY **11**, which was consistent with destabilized HOMO of **10**. Thus, oxidative MeO-addition of **10** afforded **12** with release of ring-strain, although no formation of **12** from **10** was observed under various conditions: a solution of **10** in MeOH at 50 °C, in MeOH/$CHCl_3$ at 50 °C, in MeOH in the presence of HCl, or in THF with NaOMe/MeOH.

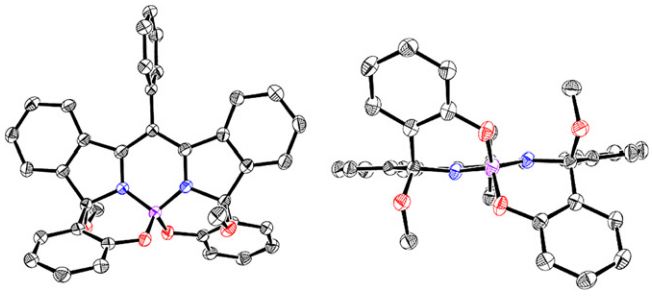

Fig. 7. ORTEP drawing of **12**. Hydrogen atoms are omitted for clarity.

Table 3
Selected distance and angles

	F–B/Å or O–B/Å	F–B–F or O–B–O	N–B/Å	N–B–N
5a	1.374(4), 1.378(4)	111.4(3)°	1.567(4), 1.568(5)	107.5(2)°
5b	1.3681(16), 1.3761(17)	111.54(11)°	1.5737(17), 1.5784(17)	105.83(10)°
10	1.478(10), 1.497(10)	106.5(7)°	1.494(12), 1.506(12)	108.4(7)°
12	1.459(3), 1.468(3)	109.00(17)°	1.524(3), 1.526(3)	105.75(17)°

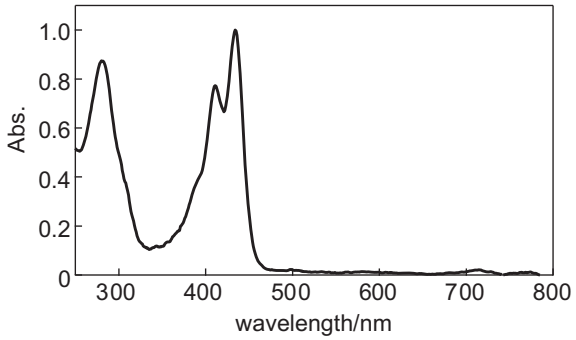

Fig. 8. UV–vis absorption spectrum of **12** in CH_2Cl_2.

3. Conclusion

We have successfully synthesized an *O*-chelated BODII **10** by our methodology, which easily introduced a functional group at *meso*-position. The BODIPYs **4**, **5**, and **9**–**11** exhibit the absorptions and the fluorescence emissions in the visible–NIR region between 580 and 730 nm. The molecular structures of all BODIPYs were fully characterized by the X-ray crystallographic analysis. We have shown that fusion of rigid BCOD or BCO at the 1,2- and 6,7-positions enhances the fluorescence emission by prevention of wagging of the *meso*-phenyl group and stacking of the BODIPY chromophore. The BODIPY chromophore can be effectively expanded not only by the benzo-fusion at the 1,2- and 6,7-positions but also by intramolecular ring-connection of the appended aryl groups at 3- and 5-positions to the core boron atom. This dye **10** was stable and showed a bright fluorescence emission at 733 nm with the Φ value of 0.58, which was relatively high compared to the Φ value of other BODIPYs emitted in NIR region.[3] Further application for *O*-chelated BODIPYs with a *meso*-functional group as NIR dyes are underway, since our methodology has an advantage for the preparation of various *O*-chelated π-expanded-BODIPYs.

4. Experimental section

4.1. General

Melting points were determined on a Yanaco micro melting point apparatus MP500D and are uncorrected. DI–EI and FAB mass spectra were measured on a JEOL JMS-700. MALDI-TOF mass spectra were measured on an Applied Biosystems Voyager de Pro. UV–vis spectra were measured on a JASCO V-570 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL AL-400 at 400 MHz or JEOL JNM-GSX 270 at 270 MHz. The fluorescence emission spectra and the Φ values were measured on a Hamamatsu Photonics K.K. absolute PL quantum yield measurement system C9920-

03. The fluorescence decay was measured, using a C7990-01 NIR fluorescence lifetime measurements system, consisting of a Hamamatsu Photonics K.K. using a 1 ns (FWHM) pulse laser light at 532 nm (45 mW, 14 kHz) from a CrsLas FTSS355-Q YAG laser and a NIR region R5509-43 PMT. Elemental analyses were performed at Integrated Center for Sciences, Ehime University. Pyrrole **1** was prepared according to the literature.[8a] Dried solvents were purchased from Kanto Chemical Co. All solvents used for chromatography were simply distilled prior to use. Ethylene glycol was distilled and stored under an Ar atmosphere. Other chemicals were used as purchased.

4.2. Synthesis

*4.2.1. Pyrrole **2a**.* To a degassed solution of **1** (4.56 g, 10.3 mmol), phenylboronic acid (1.92 g, 15.8 mmol) and $Pd(PPh_3)_4$ (596 mg, 0.516 mmol) in dry DMF (100 ml) was added degassed aqueous Na_2CO_3 (3.36 g/30 ml) under an Ar atmosphere. The mixture was refluxed for 17 h. The reaction mixture was filtered through a Celite pad and concentrated under a reduced pressure. The residue was diluted with $CHCl_3$. The organic extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$. After addition of concd HCl (30 ml) to the crude product in EtOAc (30 ml), the mixture was stirred at room temperature overnight. The mixture was extracted with EtOAc. The organic extract was washed successively with saturated aqueous $NaHCO_3$, water, and brine; dried over Na_2SO_4; and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ followed by recrystallization from $CHCl_3$–hexane to give **2a** (2.01 g, 67%): colorless crystals; mp 160.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ=8.53 (br s, 1H), 7.55–7.51 (m, 2H), 7.45–7.40 (m, 2H), 7.33–7.27 (m, 1H), 6.56–6.51 (m, 2H), 4.35 (m, 1H), 4.34 (q, J=7.3 Hz, 2H), 4.21 (m, 1H), 1.63–1.53 (m, 4H), and 1.39 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=161.90, 138.03, 135.89, 135.34, 132.24, 128.85, 128.66, 127.22, 127.13, 126.17, 113.86, 59.96, 33.75, 33.33, 26.68, 26.17, and 14.52; IR (KBr disk) ν_{max} 3317 (NH), 3051, 2981, 2931, 2863, and 1684 cm^{-1}; MS (FAB) m/z 294 $[M+H]^+$ and 265 $[M-C_2H_4]^+$. Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.76; H, 6.58; N, 4.69.

*4.2.2. Pyrrole **2b**.* To a degassed solution of **1** (6.01 g, 13.6 mmol), 2-methoxyphenylboronic acid (4.00 g, 20.4 mmol) and $Pd(PPh_3)_4$ (749 mg, 0.648 mmol) in dry DMF (130 ml) was added degassed saturated aqueous Na_2CO_3 (4.31 g/40 ml) under an Ar atmosphere. The mixture was refluxed for 21.5 h. The reaction mixture was filtered through a Celite pad and concentrated under a reduced pressure. The residue was diluted with $CHCl_3$. The organic extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. After addition of concd HCl (45 ml) to the residue in EtOAc (90 ml), the mixture was stirred at room temperature overnight. The mixture was extracted with EtOAc. The organic extract was washed successively with saturated aqueous $NaHCO_3$, water, and brine; dried over Na_2SO_4; and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$. Recrystallization from $CHCl_3$–hexane to give **2b** (3.13 g, 72%): colorless crystals; mp 141.6–142.1 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ=9.33 (br s, 1H), 7.63–7.59 (m, 1H), 7.30–7.23 (m, 1H), 7.07–6.97 (m, 2H), 6.57–6.50 (m, 2H), 4.43 (m, 1H), 4.33 (q, J=7.3 Hz, 2H), 4.22 (m, 1H), 3.91 (s, 3H), 1.63–1.54 (m, 4H) and 1.39 (t, J=7.3 Hz, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ=161.74, 155.71, 137.10, 135.92, 135.57, 129.52, 128.89, 128.15, 124.14, 121.02, 120.75, 113.00, 111.39, 59.75, 55.56, 34.03, 33.69, 26.60, 26.21, and 14.57; IR (KBr disk) ν_{max} 3305 (NH), 3047, 2993, 2939, 2866, and 1676 cm^{-1}; MS (FAB) m/z 323$[M]^+$ and 295 $[M-C_2H_4]^+$. Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.22; H, 6.61; N, 4.30.

*4.2.3. Pyrrole **7**.* To a degassed solution of **6** (618 mg, 1.79 mmol), 2-methoxyphenylboronic acid (431 mg, 2.83 mmol) and $Pd(PPh_3)_4$ (9 mg, 0.008 mmol) in dry DMF (14 ml) was added a degassed aqueous Na_2CO_3 (569 mg/5 ml) under an Ar atmosphere. The mixture was refluxed for 5 h. The reaction was quenched by addition of 1 M HCl (10 ml), brine (10 ml), and $CHCl_3$ (10 ml). The organic extract was separated and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ followed by recrystallization from $CHCl_3$–hexane to give **7** (513 mg, 88%): colorless crystals; mp 141.6–142.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ=9.53 (br s, 1H), 7.57 (dd, J=7.7 and 1.8 Hz, 1H), 7.28–7.23 (m, 1H), 7.03–6.97 (m, 2H), 4.33 (q, J=7.1 Hz, 2H), 3.93 (s, 3H), 3.58 (m, 1H), 3.35 (m, 1H), 1.82–1.76 (m, 4H), 1.46–1.20 (m, 4H), and 1.37 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=161.87, 155.60, 135.71, 129.01, 127.97, 127.73, 124.94, 120.94, 120.80, 113.64, 111.26, 59.68, 55.58, 28.08, 27.64, 26.96 (2C), 26.54 (2C), and 14.64; IR (KBr disk) ν_{max} 3305 (NH), 3047, 2972, 2945, 2860, and 1670 cm^{-1}; MS (FAB) m/z 325 $[M]^+$. Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.82; H, 7.07; N, 4.30.

*4.2.4. Pyrrole **3a**.* A suspension of **2a** (1.57 g, 5.36 mmol) and KOH (2.65 g, 47.3 mmol) in ethylene glycol (48 ml) was heated at 175 °C for 2 h under an Ar atmosphere in the dark. The reaction mixture was cooled to room temperature. After addition of water, the mixture was extracted with $CHCl_3$. The organic extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ followed by recrystallization from $CHCl_3$–hexane to give **3a** (775 mg, 65%): pale pink crystals; mp 200.0–201.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 (br s, 1H), 7.44 (m, 2H), 7.37 (m, 2H), 7.19 (m, 1H), 6.54 (m, 2H), 6.49 (d, J=2.2 Hz, 1H), 4.19 (m, 1H), 3.86 (m, 1H), and 1.64–1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=136.11, 135.79, 133.60, 131.15, 128.72, 126.65, 125.55, 125.08, 122.75, 108.35, 33.34, 33.32, 27.35, and 27.13; IR (KBr disk) ν_{max} 3359 (NH), 3039, 2962, 2931, and 2858 cm^{-1}; MS (FAB) m/z 221 $[M]^+$ and 193$[M-C_2H_4]^+$. Anal. Calcd for $C_{16}H_{15}N\cdot 1/16H_2O$: C, 86.40; H, 6.83; N, 6.33. Found: C, 86.28; H, 6.88; N, 6.37.

*4.2.5. Pyrrole **3b**.* A suspension of **2b** (646 mg, 2.00 mmol) and KOH (0.800 g, 14.3 mmol) in ethylene glycol (20 ml) was heated to 160 °C for 2 h under an Ar atmosphere in the dark. The reaction mixture was cooled to room temperature. After addition of water, the mixture was extracted with $CHCl_3$. The organic extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by silica gel column chromatography with $CHCl_3$ give **3b** (363 mg, 72%): pale pink crystals; mp >135 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.74 (br s, 1H), 7.61 (dd, J=7.6 and 1.2 Hz, 1H), 7.16 (m, 1H), 7.01 (m, 1H), 6.95 (d, J=8.3 Hz, 1H), 6.56–6.51 (m, 3H), 4.23 (m, 1H), 3.88 (s, 3H), 3.86 (m, 1H), and 1.64–1.55 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=154.95, 136.35, 135.88, 130.21, 127.95, 127.49, 126.29, 122.34, 121.07, 119.83, 111.36, 107.48, 55.57, 34.07, 33.40, 27.41, and 27.12; IR (KBr disk) ν_{max} 3444 (NH), 3047, 2970, 2927, 2897, and 2862 cm^{-1}; MS (70 eV) m/z (relative intensity) 251 (M^+, 36) and 223 ($M^+-C_2H_4$, 100). Anal. Calcd for $C_{17}H_{17}NO\cdot 1/8H_2O$: C, 74.71; H, 7.19; N, 3.96. Found: C, 74.67; H, 7.17; N, 3.91.

*4.2.6. Pyrrole **8**.* A suspension of **7** (811 mg, 2.49 mmol) and KOH (1.10 g, 19.6 mmol) in ethylene glycol (25 ml) was heated to 160 °C for 2 h under an Ar atmosphere in the dark. The reaction mixture was cooled to room temperature. After addition of water, the mixture was extracted with $CHCl_3$. The organic extract was washed successively with saturated aqueous $NaHCO_3$, water, and brine;

dried over Na_2SO_4; and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ followed by recrystallization from $CHCl_3$–hexane to give **8** (360 mg, 60%): purple crystals; mp 147.5–146.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.97 (br s, 1H), 7.57 (dd, J=7.6 and 1.7 Hz, 1H), 7.17–7.13 (m, 1H), 6.97 (m, 2H), 6.58 (d, J=2.2 Hz, 1H), 3.90 (s, 3H), 3.40 (m, 1H), 3.02 (m, 1H), 1.84–1.74 (m, 4H), and 1.50–1.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=154.88, 128.58, 128.06, 126.09, 125.94, 122.46, 121.04, 120.18, 111.24, 108.07, 55.50, 28.20, 27.61, 27.57, and 27.41; IR (KBr disk) ν_{max} 3452 (NH), 3059, 3012, 2935, 2858 cm^{-1}; MS (70 eV) m/z (relative intensity) 253 (M^+, 82) and 224($M^+-C_2H_4$, 100); HRMS calcd for $C_{19}H_{19}NO$, 253.1467; found 253.1467.

4.2.7. BCOD-fused triphenyldipyrromethene. To a solution of **3a** (338 mg, 1.53 mmol) and benzaldehyde (0.077 ml, 0.77 mmol) in dry CH_2Cl_2 (10 ml) were added three drops of TFA under a N_2 atmosphere. The mixture was refluxed overnight in the dark. After cooling to room temperature, DDQ (360 mg, 1.63 mmol) was added, and the mixture was stirred overnight. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic extract was washed successively with saturated aqueous $NaHCO_3$, water, and brine; dried over Na_2SO_4; and concentrated under a reduced pressure. The residue was purified by column chromatography on alumina with hexane–EtOAc to give the dipyrromethene (321 mg, 79%): red crystals: mp 198.7–199.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ=13.30 (br s, 1H), 7.86 (m, 4H), 7.59–7.45 (m, 9H), 7.36 (m, 2H), 6.46–6.41 (m, 2H), 6.17–6.12 (m, 2H), 4.28–4.26 (m, 2H), 2.55–2.53 (m, 2H), 1.48–1.44 (m, 4H), and 1.24–1.20 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=149.35, 149.27, 145.87, 145.82, 137.82, 137.78, 137.27, 137.25, 136.90, 135.39, 135.33, 134.98, 134.28, 134.25, 133.91, 133.89, 129.94, 129.67, 129.34, 128.64, 128.44, 127.90, 127.88, 127.81, 127.70, 127.62, 126.96, 126.94, 35.37, 34.85, 26.60, 26.55, 25.94, and 25.90; MS (FAB) m/z 529 $[M+H]^+$ and 500 $[M+H-2C_2H_4]^+$. Anal. Calcd. For $C_{39}H_{32}N_2\cdot H_2O$ C, 85.68; H, 6.27; N, 5.12. Found: C, 85.52; H, 6.00; N, 5.07.

*4.2.8. BODIPY **4a**.* A solution of BCOD-fused triphenyldipyrromethene (89 mg, 0.17 mmol) and (i-Pr)$_2$EtN (0.088 ml) in toluene (5 ml) was stirred at room temperature for 30 min. After addition of $BF_3\cdot OEt_2$ (0.134 ml), the mixture was refluxed for 15 min. The mixture was poured into water and extracted with $CHCl_3$. The organic extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ to give **4a** (97 mg, 99%): red crystals; mp >180 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.66–7.33 (m, 15H), 6.36 (m, 2H), 6.10 (m, 2H), 3.82 (m, 2H), 2.66 (m, 2H), 1.41 (m, 4H), and 1.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=150.98, 149.31, 140.77, 139.11, 135.75, 134.98, 134.01, 133.89, 131.82, 129.58, 129.54, 129.50, 129.47, 129.20, 129.15, 128.91, 128.58, 128.11, 128.02, 127.96, 127.80, 35.35, 35.33, 33.55, 33.52, 26.39, 26.34, 26.00, and 25.95; UV–vis (CH_2Cl_2) λ_{abs} nm (log ϵ) 405 (4.05) and 558 (4.85); MS (FAB) m/z 577 $[M+H]^+$, 558 $[M+H-F]^+$, 521 $[M+H-2C_2H_4]^+$, and 502 $[M+H-F-2C_2H_4]^+$. Anal. Calcd. For $C_{39}H_{31}BF_2N_2\cdot 3/4H_2O$: C, 79.39; H, 5.55; N, 4.75. Found: C, 79.43; H, 5.31; N, 5.05.

*4.2.9. BODIPY **4b**.* To a solution of **3b** (531 mg, 2.11 mmol) and benzaldehyde (0.110 ml, 1.10 mmol) in dry CH_2Cl_2 (10 ml) were added three drops of TFA under an Ar atmosphere. The mixture was refluxed for 20 h in the dark. After cooling to room temperature, DDQ (345 mg, 1.56 mmol) was added, and the mixture was stirred for additional 1 h. After addition of (i-Pr)$_2$EtN (0.51 ml) and $BF_3\cdot OEt_2$ (0.80 ml), the mixture was refluxed for 30 min. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic extract was washed successively with saturated aqueous $NaHCO_3$, water, and brine; dried over Na_2SO_4; and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2. Recrystallization from CH_2Cl_2–MeOH gave **4b** (349 mg, 52%) as a mixture of rotamer: red crystals; mp >170 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.73 (m, 1H), 7.59–748 (m, 6H), 7.37–7.23 (m, 2H), 7.02–6.85 (m, 4H), 6.37–6.04 (m, 4H), 3.80–3.67 (m, 6H), 3.51 (m, 2H), 2.63 (m, 2H), and 1.54–1.24 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, typical signals) δ=157.15, 157.07, 157.00, 156.98, 156.91, 149.80, 149.78, 149.62, 149.48, 149.47, 149.45, 149.15, 149.13, 146.07, 146.05, 145.88, 145.73, 145.71, 145.55, 140.93, 140.89, 140.74, 140.69, 140.38, 140.35, 140.32, 140.28, 140.04, 139.86, 139.77, 135.86, 135.79, 135.66, 135.54, 135.16, 134.28, 134.00, 133.83, 132.62, 132.57, 132.36, 132.26, 131.88, 131.82, 131.65, 131.57, 129.94, 129.87, 129.58, 129.36, 129.01, 128.88, 128.84, 128.70, 128.64, 128.56, 128.44, 128.38, 128.03, 127.94, 127.91, 127.80, 121.45, 121.36, 121.11, 120.18, 120.15, 120.10, 120.06, 111.01, 110.77, 110.46, 110.44, 110.22, 55.78, 55.76, 55.71, 55.55, 55.46, 55.43, 55.38, 55.25, 35.31, 35.28, 35.21, 34.06, 26.37, 26.27, 26.05, 25.89, and 25.57; UV–vis (CH_2Cl_2) λ_{abs} nm (log ϵ) 395 (4.07) and 556 (4.79); MS (FAB) m/z 636 $[M]^+$, 617 $[M-F]^+$, and 580 $[M-2C_2H_4]^+$. Anal. Calcd for $C_{41}H_{35}BF_2N_2O_2$: C, 77.36; H, 5.54; N, 4.40. Found: C, 77.61; H, 5.49; N, 4.41.

*4.2.10. BODIPY **9**.* To a solution of **8** (196 mg, 0.775 mmol) and benzaldehyde (0.040 ml, 0.40 mmol) in dry CH_2Cl_2 (5 ml) was added a drop of TFA under an Ar atmosphere. The mixture was refluxed for 18 h in the dark. After cooling to room temperature, DDQ (186 mg, 0.820 mmol) was added, and the mixture was stirred for additional 2 h. After addition of (i-Pr)$_2$EtN (0.185 ml) and $BF_3\cdot OEt_2$ (0.30 ml), the mixture was refluxed for 30 min. The reaction mixture was poured into water and extracted with $CHCl_3$. The organic extract was washed successively with saturated aqueous $NaHCO_3$, water, and brine; dried over Na_2SO_4; and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2. Recrystallization from CH_2Cl_2–MeOH gave **9** (103 mg, 42%) as a rotamer (38:62): red crystals; mp >350 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.77 (d, J=7.6 Hz, 1H), 7.61–7.44 (m, 6H), 7.32–7.25 (m, 2H), 7.04–6.84 (m, 4H), 3.76 and 3.67 (s, 6H), 2.61 (m, 2H), 1.75 (m, 2H), and 1.76–1.05 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$, typical signals) δ=157.16, 157.11, 148.27, 148.09, 147.40, 147.05, 139.96, 138.08, 135.49, 135.46, 132.50, 132.45, 132.40, 131.77, 131.70, 130.33, 129.86, 129.83, 129.45, 129.24, 128.76, 128.72, 128.67, 128.63, 127.81, 127.77, 127.69, 126.83, 121.70, 121.40, 120.15, 120.09, 110.65, 110.47, 55.57, 55.38, 29.37, 27.76, 26.57, 26.48, 26.44, 26.43, 26.34, 26.23, 26.15, and 26.03; UV–vis (CH_2Cl_2) λ_{abs} nm (log ϵ) 382 (4.09) and 550 (4.81); MS (70 eV) m/z (relative intensity) 641 (M^+, 100). Anal. Calcd for $C_{41}H_{39}BF_2N_2O_2\cdot 1/4H_2O$: C, 76.34; H, 6.17; N, 4.34. Found: C, 76.08; H, 6.15; N, 4.26.

*4.2.11. BODIIs **5**.* BCOD-fused BODIPYs **4a** and **4b** (ca. 10 mg each) were heated at 210 °C under a reduced pressure for 2 h in a glass tube to give **5a** and **5b** in quantitative yields.

*4.2.11.1. BODII **5a**.* Blue crystals; mp >350 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.80–7.78 (m, 4H), 7.74–7.68 (m, 3H), 7.64–7.62 (m, 2H), 7.52–7.43 (m, 8H), 7.11–7.02 (m, 4H), 6.23 (d, J=8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=151.51, 136.27, 135.11, 134.15, 130.99, 130.87, 130.12, 130.09, 130.06, 129.44, 129.29, 129.21, 128.89, 128.62, 127.97, 126.21, 124.51, 123.38, and 121.22; UV–vis (CH_2Cl_2) λ_{abs} nm (log ϵ) 338 (4.30), 351 (4.34), and 631 (5.01); MS (MALDI-TOF) m/z 520 $[M]^+$. Anal. Calcd for $C_{35}H_{23}BF_2N_2$: C, 80.78; H, 4.45; N, 5.38. Found: C, 80.56; H, 4.15; N, 5.64.

*4.2.11.2. BODII **5b**.* Blue crystals (41:59 rotamer mixture); mp 187.7–188.0 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.73–7.58 (m, 6H), 7.52 (m, 1H), 7.40 (m, 2H), 7.28–7.23 (m, 2H), 7.08–6.96 (m, 8H), 6.26–6.19 (m, 2H), 3.75 and 3.68 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, typical signals) δ=157.56, 157.51, 149.19, 148.92, 136.06, 135.27, 135.24, 133.62, 132.43, 132.40, 132.36, 131.93, 131.87, 131.41,

131.39, 131.32, 130.66, 130.64, 129.27, 129.25, 129.21, 129.10, 129.02, 128.96, 128.89, 128.18, 126.09, 123.82, 123.34, 123.26, 121.05, 121.03, 120.24, 120.17, 120.06, 120.01, 111.00, 110.85, 55.82, and 55.62; UV–vis (CH_2Cl_2) λ_{abs} nm (log ϵ) 348 (4.33) and 617 (5.04); MS (FAB) m/z 580 $[M]^+$ and 561 $[M-F]^+$. Anal. Calcd for $C_{37}H_{27}BF_2N_2O_2$: C, 76.56; H, 4.69; N, 4.83. Found: C, 76.59; H, 4.72; N, 4.79.

4.2.12. O-Chelated BODII ***10***. 1.0 M solution of BBr_3 in CH_2Cl_2 (1.2 ml) was added dropwise to **5b** (53 mg, 0.092 mmol) over 1 min at 0 °C. The solution was allowed to warm to room temperature and stirred at the same temperature for 4 h. After filtration with a Celite pad, the filtrate was concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2. Recrystallization from CH_2Cl_2–MeOH gave **10** (43 mg, 91%): green crystals; mp >350 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.28–8.22 (m, 4H), 7.70–7.66 (m, 5H), 7.42–7.12 (m, 8H), 7.00 (d, J=8.1 Hz, 2H), and 6.59 (d, J=8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=153.47, 142.30, 134.51, 134.33, 131.92, 129.36, 129.33, 129.21, 128.81, 128.25, 125.87, 125.12, 122.92, 121.37, 120.62, 120.33, and 119.64; UV–vis (CH_2Cl_2) λ_{abs} nm (log ϵ) 313 (4.49), 365 (4.44), 651 (4.31), and 711 (4.96); MS (FAB) m/z 512 $[M]^+$. Anal. Calcd for $C_{35}H_{21}BN_2O_2 \cdot 1/4H_2O \cdot 1/2CH_2Cl_2$: C, 76.23; H, 4.05; N, 5.01. Found: C, 76.39; H, 4.13; N, 5.01. HRMS calcd for $C_{35}H_{22}BN_2O_2$, 513.1774; found 513.1781.

4.2.13. O-Chelated BODIPY ***11***. BBr_3 (1.0 M solution) in CH_2Cl_2(1.0 ml) was added dropwise to **9** (49 mg, 0.077 mmol) over 1 min at 0 °C. The solution was allowed to warm to room temperature and stirred at the same temperature for 3h. After filtration with a Celite pad, the filtrate was concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 followed by recrystallization from CH_2Cl_2–MeOH to give **11** (34 mg, 78%): green crystals; mp >350 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.89–7.58 (dd, J=7.8 Hz, 1.5 Hz, 2H), 7.54–7.44 (m, 5H), 7.30–7.26 (m, 2H), 7.03–6.99 (m, 2H), 6.92 (dd, J=8.3 Hz, 1.0 Hz, 2H), 3.52 (m, 2H), 2.08 (m, 2H), 1.82–1.75 (m, 2H), 1.66–1.49 (m, 6H), 1.45–1.37 (m, 2H), 1.33–1.23 (m, 2H), 1.19–1.11 (m, 2H), and 0.95–0.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=154.31, 148.72, 142.28, 135.74, 134.53, 134.47, 131.14, 129.09, 129.04, 128.82, 127.92, 126.08, 120.39, 119.91, 119.64, 28.96, 28.39, 26.82, 26.29, 26.18, and 25.90; UV–vis (CH_2Cl_2) λ_{abs} nm (log ϵ) 316 (4.64), 416 (4.02), and 626 (4.80); MS (FAB) m/z 572 $[M]^+$. Anal. Calcd for $C_{39}H_{33}BN_2O_2 \cdot H_2O$: C, 79.32; H, 5.97; N, 4.74. Found: C, 79.22; H, 5.72; N, 5.09. HRMS calcd for $C_{39}H_{33}BN_2O_2$, 572.2635; found 572.2646.

4.2.14. DimethoxydihydroBODII ***12***. Yellow crystals; UV–vis (CH_2Cl_2) λ_{abs} nm 282, 411, and 434; MS (FAB) m/z 574 $[M]^+$, 543 $[M-MeO]^+$, and 512 $[M-2MeO]^+$; HRMS calcd for $C_{37}H_{28}BN_2O_4$, 575.2142; found 575.2139.

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.03.016. These data include MOL files and InChIKeys of the most important compounds described in this article.

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