CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200802541

Functionalization of Boron Dipyrrin (BODIPY) Dyes through Iridium and Rhodium Catalysis: A Complementary Approach to α- and β-Substituted BODIPYs

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Abstract: Iridium-catalyzed direct borylation has been applied to *meso*-substituted dipyrromethane and boron dipyrrin (BODIPY) dyes. Borylation is highly regioselective and complementary: it occurs exclusively at the α position for *meso*-mesityldipyrromethane and at the β positions for *meso*-mesityl BODIPY dye. This regioselective borylation enables a variety of α- and β-substituted BODIPY dyes to be synthesized. Introduction of α,β-enoate and α,β,γ,δ-dienoate functions into BODIPY dyes at the α or β positions was achieved by rhodium-catalyzed Heck-type addition of the borylated compounds to acrylate and 2,4-pentadienoate esters. This functionalization has a significant effect on the electronic properties of BODIPY dyes, as seen in substantial redshift of the absorption and emission spectra. Comparative studies showed that the α- and β-substituted series of BODIPY dyes show substantially different photophysical properties, and thus the importance of the position to be functionalized is highlighted.

Keywords: boron · C–C coupling · dyes/pigments · iridium · rhodium

Introduction

Boron dipyrrins (BODIPYs) have received much interest in research areas such as labeling reagents,[1] fluorescent switches,[2] chemosensors,[3] light-harvesting systems,[4] and dye-sensitized solar cells[5] owing to their advantageous photophysical properties such as photostability, high absorption coefficients, and high fluorescence quantum yields.[6] Furthermore, BODIPY dyes are amenable to modifications, which allow fine-tuning of properties by introduction of suitable substituents at appropriate positions of the dipyrrin framework. One of the challenges has been the synthesis of BODIPY derivatives that emit at longer wavelengths with high fluorescence quantum yields. Post-modification methods used to attain this goal include halogenation,[7] Sonogashira coupling,[8] Knoevenagel-type condensation,[9,2b] and palladium-catalyzed direct C–H functionalization.[10] Other strategies, such as replacement of the *meso* carbon atom by a nitrogen atom[11] and extension of the π conjugation by the fusion of aryl moieties with isoindole[12] or furan,[13] are also quite useful.

Recently, iridium-catalyzed direct borylation of aromatic compounds via C–H bond activation has proved to be a powerful tool for organic synthesis.[14] In addition, the use of organoboranes with rhodium catalysis has been extensively explored for new types of C–C bond formation.[15] We have applied these novel metal-catalyzed methodologies to porphyrin chemistry, and established highly regioselective iridium-catalyzed β-borylation of porphyrins.[16] Facile introduction of α,β- and α,β,γ,δ-unsaturated ester functions into porphyrins has also been achieved by rhodium-catalyzed Heck-type addition of borylated porphyrins to acrylate and 2,4-pentadienoate esters.[17]

Here we focus on BODIPY as a substrate for functionalization by a similar strategy. BODIPY and porphyrin have the same dipyrrin building blocks and both have β-pyrrolic positions. We anticipated that a combination of iridium-catalyzed borylation and rhodium-catalyzed Heck-type addition would also be applicable to BODIPY dyes and offer method for functionalization of BODIPYs with fine-tuned photophysical properties. Here we disclose α- and β-selective functionalization of BODIPYs, which allow a direct

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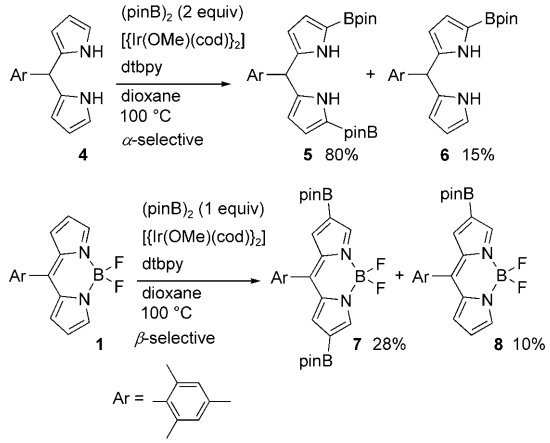
comparison between α- and β-extended conjugation for BODIPY dyes.

Results and Discussion

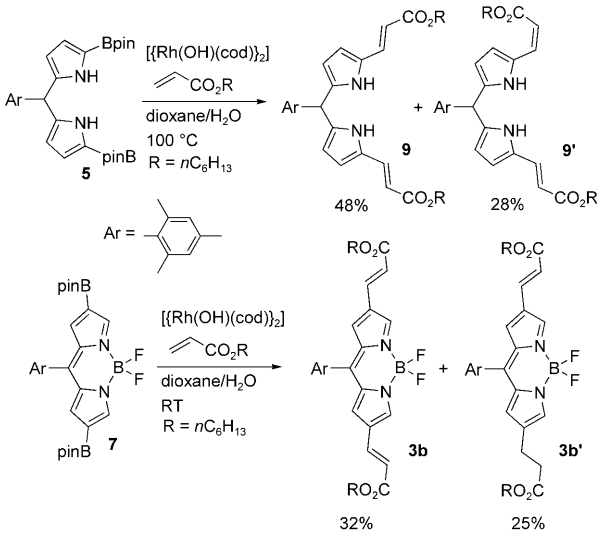
Synthesis of the BODIPY dyes: The *meso*-mesityl dipyrromethane **4** and *meso*-mesityl BODIPY **1** were synthesized according to the reported procedures.[18] Inspired by borylation of pyrrole,[19] we examined borylation of **4** (Scheme 1).



Scheme 1. Regioselective borylation of dipyrromethane **4** and BODIPY **1**. pin = pinacolato.

Treatment of **4** (1.0 equiv) with bis(pinacolato)diboron (2.0 equiv) in the presence of a catalyst generated from [{Ir(OMe)(cod)}$_2$] (1.0 mol%; cod = 1,5-cyclooctadiene) and 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dtbpy, 2.0 mol%) in dioxane provided α,α′-diborylated product **5** in high yield (80%) with perfect regioselectivity at the α positions. About 15% of monoborylated compound **6** was also obtained. The same strategy was applied to BODIPY **1**, but diborylated compound **7** was isolated only in about 20% yield. Although the yield was not as high as that of *meso*-substituted dipyrromethane **4**, the highly regioselective borylation at the β position prompted us to find optimal conditions for the borylation. Changing reaction conditions such as temperatures and solvent did not improve the yield distinctly, but the yield increased from 20 to 28% when 1.0 equiv of diboron reagent was used instead of 2.0 equiv. The low yield probably results from the instability of the BODIPY dyes under the reaction conditions in the presence of an excess of bis(pinacolato)diboron. Eventually, we obtained the β,β′-diborylated and β-monoborylated BODIPYs in 28 and 10% yield, respectively.

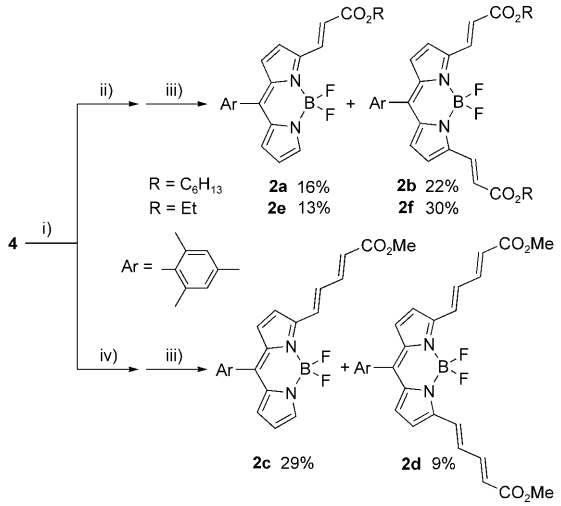
Borylation of *meso*-mesityl dipyrromethane and BODIPY occurs with exclusively at α and β positions, respectively, and this allows complementary synthesis of α- and β-functionalized BODIPY dyes. We then attempted introduction of unsaturated ester functions by means of Rh-catalyzed Heck-type addition (Scheme 2). Treatment of diboryldipyrromethane **5** with hexyl acrylate in the presence of [{Rh(OH)(cod)}$_2$] as catalyst in dioxane/water (10/1) at 100 °C afforded the desired α,α′ double addition products as a mixture of *E*,*E* isomer **9** and *E*,*Z* isomer **9′**. On the other hand, the corresponding reaction of diborylated BODIPY **7** furnished α,α′-diacrylate BODIPY **3b** in 32% yield along with partially saturated compound **3b′**. Unfortunately, the borylated products are not stable enough for purification by column chromatography on silica gel and should be purified by preparative GPC-HPLC. To eliminate tedious separation and decomposition of the products on silica gel, we then developed a procedure for the synthesis of BODIPY dyes without separation of the borylated intermediates.



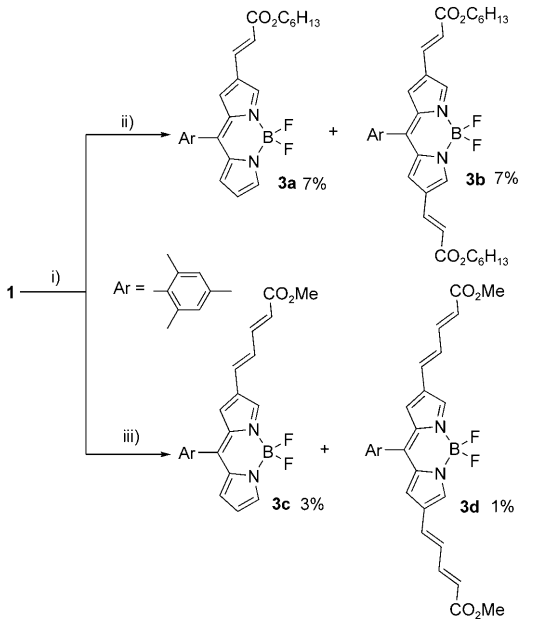
Scheme 2. Rhodium-catalyzed addition to acrylate esters.

To prepare α-substituted BODIPYs, *meso*-mesityldipyrromethane **4** was borylated under the standard conditions to yield a mixture of diborylated and monoborylated dipyrromethanes **5** and **6** (Scheme 3). Without separation of unstable borylated intermediates, treatment of the crude mixture with hexyl acrylate or ethyl acrylate in the presence of [{Rh(OH)(cod)}$_2$] as catalyst in dioxane and water at 100 °C afforded the desired α-acrylate dipyrromethanes. Oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in THF at room temperature afforded the corresponding dipyrrin products. Finally, treatment of the dipyrrins with triethylamine and BF_3•OEt_2 in toluene at room temperature furnished the corresponding α-acrylate BODIPYs **2a** and **2b** in 16 and 22% yield or **2e** and **2f** in 13 and 30% yield, respectively, in four steps. Reaction with methyl 2,4-pentadienoate allows further elongation of conjugation: using methyl 2,4-pentadienoate provides **2c** and **2d** in 29% and 9% yield, respectively. The ratio of the monosubstituted product to the disubstituted product increased in comparison to that of the borylated dipyrromethanes because of partial deborylation during the Heck-type addition reaction.

To obtain β-substituted BODIPYs, we started from unsubstituted BODIPY **1** (Scheme 4). After borylation with 1.0 equiv of bis(pinacolato)diboron under iridium catalysis,



Scheme 3. Synthesis of α-substituted BODIPYs without isolation of borylated intermediates. i) bis(pinacolato)diboron, [[Ir(OMe)(cod)}$_2$], dtbpy, dioxane, 100 °C; ii) hexyl or ethyl acrylate, [{Rh(OH)(cod)}$_2$], dioxane, H_2O, 100 °C; iii) DDQ/THF, then BF_3·OEt_2, Et_3N, toluene; iv) methyl 2,4-pentadienoate, [{Rh(OH)(cod)}$_2$], dioxane, H_2O, 100 °C.



Scheme 4. Synthesis of β-substituted BODIPYs without isolation of borylated intermediates. i) bis(pinacolato)diboron, [{Ir(OMe)(cod)}$_2$], dtbpy, dioxane, 100 °C; ii) hexyl acrylate, [{Rh(OH)(cod)}$_2$], dioxane, H_2O, RT; iii) methyl 2,4-pentadienoate, [{Rh(OH)(cod)}$_2$], dioxane, H_2O, RT.

the reaction mixture was treated with hexyl acrylate or methyl 2,4-pentadienoate directly in the presence of the rhodium catalyst in dioxane and water at room temperature to give the desired β-substituted BODIPYs **3a** in 7 and **3b** in 7% yield or **3c** in 3 and **3d** in 1% yield. Unfortunately, the yields of isolated products were low because the product mixture contained saturated byproducts such as **3b'** due to 1,4-conjugate addition, and thus repeated chromatographic purification was necessary.

X-Ray diffraction analysis of BODIPY dyes: Single crystals suitable for X-ray diffraction studies were obtained for **2f**, **2d**, and **3d**. Figure 1 depicts the structures of these compounds. The crystallographic data are summarized in Table 2. The unsaturated ester moieties and the C_9BN_2 frameworks adopt a coplanar conformation for all compounds, as clearly seen in the side views. This orientation allows effective electronic conjugation between the C_9BN_2 framework and the double bonds. The lack of a clear distinction between the C–C bond lengths of the dipyrrin backbone and the substituted double bonds for the three compounds indicates substantial delocalization of the π systems. The mesityl groups are perpendicular to the mean C_9BN_2 plane with dihedral angles of 76.65, 71.58, and 73.95° for **2f**, **2d**, and **3d**, respectively.

Photophysical characterization: UV/Vis absorption and fluorescence spectra of the BODIPY dyes were recorded in CH_2Cl_2. Figures 2 and 3 show the absorption and emission spectra of the α- and β-substituted BODIPY dyes, along with those of unsubstituted BODIPY **1**. The α-substituted dyes exhibit the typical absorption characteristics of BODIPY dyes, that is, a narrow absorption band with a maximum above 540 nm assigned to the S_0–S_1 transition and a weak and broad absorption band attributed to the S_0–S_2 transition.[20] The absorption maxima are redshifted significantly from 501 to 641 nm with extending conjugation, while there is almost no change in spectral shape. The absorption coefficients are increasingly enhanced compared with unsubstituted BODIPY **1**. Disubstituted compounds **2b** and **2d** have higher absorption coefficients than the corresponding monosubstituted compounds **2a** and **2c**, that is, extended conjugation at the α positions of BODIPY dyes has a hyperchromic effect. All the α-substituted BODIPYs show narrow fluorescence emission bands with the mirror-image shape of the absorption bands and small Stokes shifts. The emission maximum of **2d** is shifted to 651 nm, reaching into the near-infrared spectral region while maintaining a relatively high quantum yield ($\Phi_f = 0.53$). Mono- and disubstituted BODIPYs show good dispersion of UV/Vis absorbance and fluorescence emission: the α-substituted BODIPYs are colorful and brilliant to the naked eye when irradiated under the UV light (Figure 4, **2a**–**2d**).

In the case of β-substituted BODIPY dyes, the absorption and emission spectra also exhibit substantial redshifts as the conjugation extends, but the shapes tend to become broader with increasing conjugation. The extinction coefficient of β-substituted BODIPYs decreases compared with unsubstituted BODIPY **1**, but the relative area of each S_0–S_1 absorption band increases and is comparable to that of α-substituted BODIPYs. This indicates that the oscillator strength is also enhanced in the β-substituted series by the unsaturated substituents. The sharpness of the fluorescence emissions is characterized by full width at half maximum (fwhm), which increases from 937 cm^{-1} for **1** to 1400 cm^{-1} for **3d**. The emission spectra of monosubstituted BODIPYs **3a** and **3c** are distinctly broader than those of the corresponding disubstituted BODIPYs **3b** and **3d**. The emission quantum yields

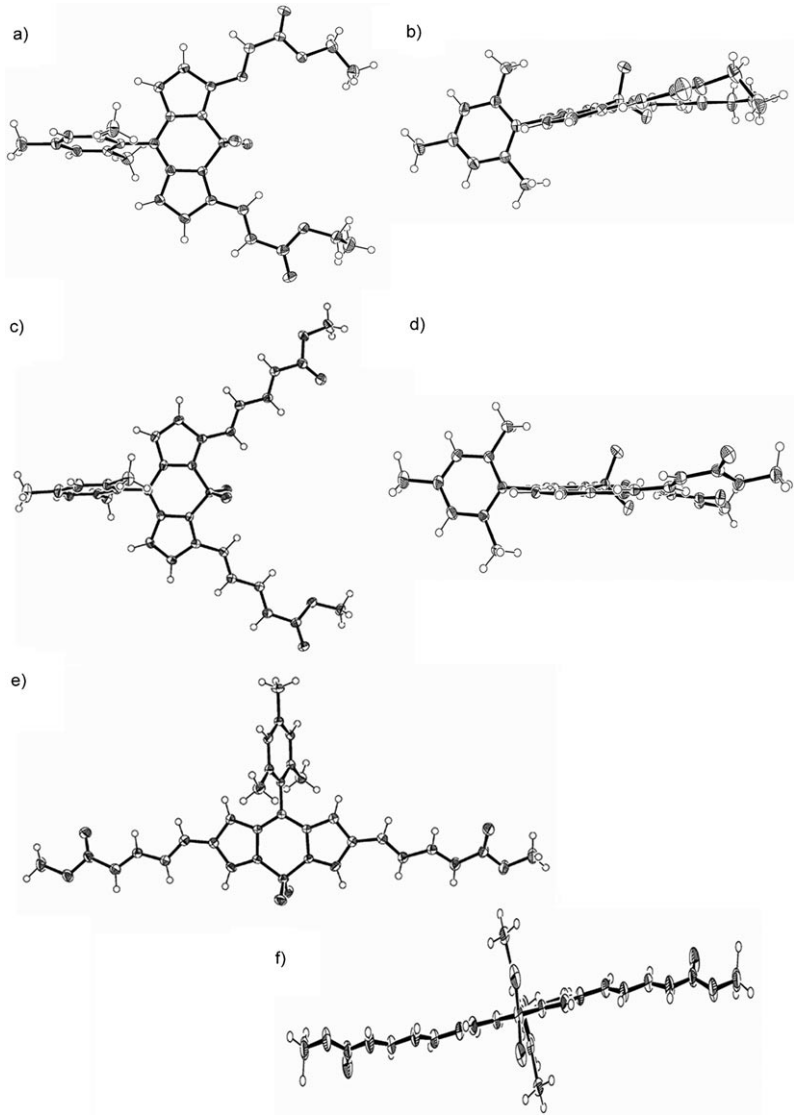


Figure 1. X-ray structures of **2f**, **2d**, and **3d**. a) Top and b) side views of **2f**; c) top and d) side views of **2d**; e) top and f) side views of **3d**. Thermal ellipsoids at 50% probability.

Table 1. Spectral properties of BODIPY dyes in CH_2Cl_2.

	UV/Vis			Emission		Stokes shift [cm^{-1}]	Φ_f
	λ_{max} [nm]	ε_{max} [$M^{-1}cm^{-1}$]	Relative area[a]	λ_{em} [nm]	FWHM [cm^{-1}]		
1	501	6.32×10^4	1.0	514	937	505	0.92 (0.93)[b]
2a	545	8.74×10^4	1.13	554	714	298	0.82
2b	593	9.27×10^4	1.30	601	608	224	0.92
2c	566	1.07×10^5	1.33	575	649	277	0.96
2d	641	1.43×10^5	1.75	651	541	240	0.53
2e	545	9.16×10^4	1.17	554	698	298	0.96
2f	593	1.25×10^5	1.43	602	594	252	0.98
3a	538	5.72×10^4	1.45	563	1565	825	0.48
3b	579	6.07×10^4	1.48	606	1371	769	0.68
3c	557	3.96×10^4	1.36	623	2279	1902	0.019
3d	633	5.71×10^4	1.83	662	1400	692	0.054

[a] The relative area of each S_0–S_1 absorption band was obtained by integration of the spectrum after conversion to the wavenumber scale. [b] Quantum yield of **1** in toluene reported in the literature.[18c]

decrease distinctly, and BODIPY **3d** exhibits an emission yield of only 0.054, about one-tenth of that of the corresponding α-substituted BODIPY **2d**. Consequently, it is not as brilliant as the α-substituted BODIPYs (Figure 4, **3a**–**3d**). The absorption is blueshifted and the emission redshifted in comparison to the corresponding α-substituted BODIPYs, that is, the Stokes shifts of β-substituted BODIPYs are larger than those of the corresponding α-substituted BODIPYs. Spectra data for all α- and the β-substituted BODIPY dyes in CH_2Cl_2 are collected in Table 1.

Conclusions

We have developed the regioselective borylation of *meso*-substituted dipyrromethane at the α positions and BODIPY dyes at the β positions. The high regioselectivity of the borylation procedure offers a new way to synthesize different kinds of α- or β-substituted BODIPY dyes by means of transition metal catalyzed reactions. Thus, a series of α- and β-substituted BODIPY dyes with different lengths of conjugation were synthesized by rhodium-catalyzed Heck-type addition of borylated intermediates to acrylate and 2,4-pentadienoate esters. The extended conjugation has significant effects on the spectral properties of BODIPY dyes and induces substantial redshifts of the absorption and emission spectra. The α-substituted series exhibits higher absorption coefficients and fluorescence quantum yields, sharp fluorescence peaks, and smaller Stokes shifts, while the β-substituted series shows lower absorption coefficients and fluorescence quantum yields, broader fluorescence peaks, and larger Stokes shifts with extending conjugation. These findings reveal that properties of BODIPY dyes can be finely tuned not only by extended conjugation but also by means of the position of modification.

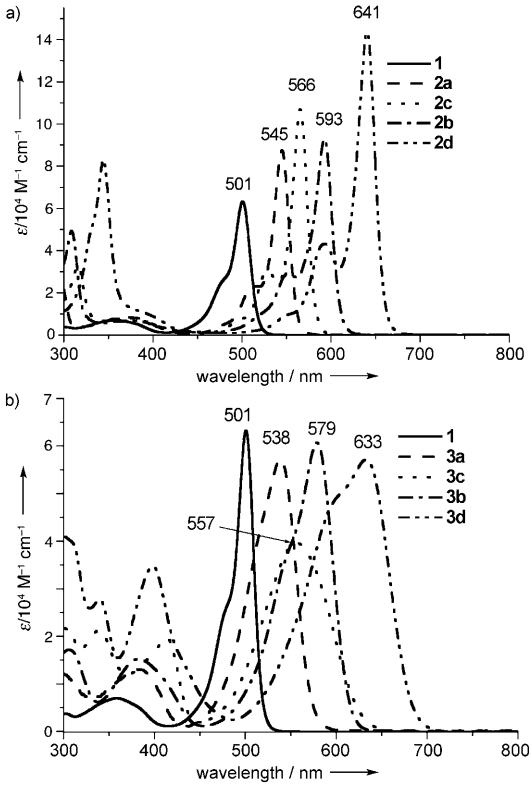


Figure 2. UV/Vis absorption spectra of α- and β-substituted BODIPYs as well as unsubstituted BODIPY **1** in CH_2Cl_2.

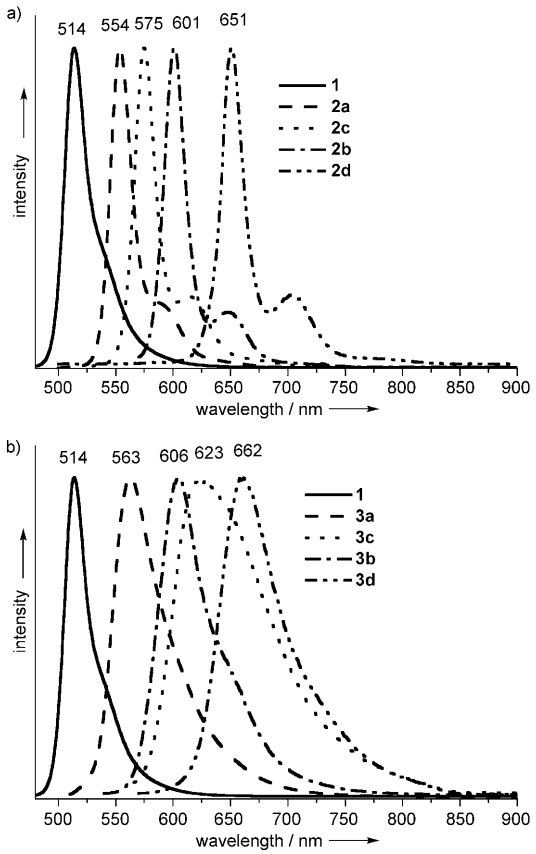


Figure 3. Normalized fluorescence emission spectra of α- and β-substituted BODIPYs as well as unsubstituted BODIPY **1** in CH_2Cl_2.

Table 2. Crystallographic details for **2f**, **2d**, and **3d**.

	2f	**2d**	**3d**
empirical formula	$C_{28}H_{29}BF_2N_2O_4$	$C_{30}H_{29}BF_2N_2O_4$	$C_{30}H_{29}BF_2N_2O_4$
M	506.35	530.36	530.36
crystal system	orthorhombic	monoclinic	monoclinic
space group	*Pbcn*	$P2_1/c$	$P2_1/n$
a [Å]	14.175(3)	21.529(4)	9.210(4)
b [Å]	16.132(3)	15.387(3)	17.869(7)
c [Å]	24.474(7)	8.1029(15)	16.664(6)
α [°]	90.00	90.00	90.00
β [°]	90.00	97.535(4)	100.783(7)
γ [°]	90.00	90.00	90.00
V [Å^3]	5596(2)	2661.0(9)	2693.9(18)
Z	8	4	4
ρ_{calcd} [g cm^{-3}]	1.275	1.324	1.308
μ [mm^{-1}]	0.094	0.096	0.095
F(000)	2262	1112	1112
crystal size [mm]	0.60×0.50×0.20	0.80×0.60×0.15	0.50×0.20×0.20
$2\theta_{max}$ [°]	55.0	50.0	56.0
T [K]	123(2)	90(2)	90(2)
total reflns	48861	13770	13793
unique reflns	6409	4685	5932
reflns used	6409	4685	5932
parameters	351	357	394
absorption correction	none	none	none
R_1	0.0613	0.0343	0.0510
wR_2	0.1894	0.1028	0.1419
GOF	1.077	1.087	1.026

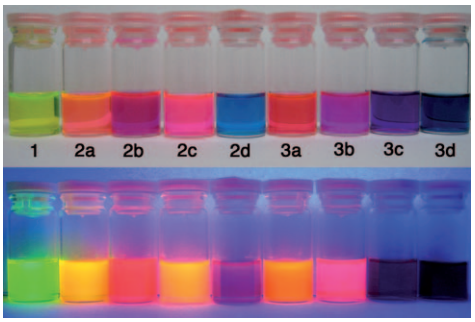


Figure 4. Photograph of solutions of BODIPY dyes without (upper row) and with UV irradiation (bottom row).

Experimental Section

Instrumentation and materials: ^{1}H NMR (600 MHz) spectra were recorded on a JEOL ECA-600 spectrometer. UV/Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. Fluorescence emission spectra were measured on Shimadzu RF-5300PC spectrometer. Quantum yields were determined by the absolute method with a Hamamatsu C9920-01 calibrated integrating-sphere system. Mass spectra were recorded on a Bruker microTOF. Recycling preparative GPC-HPLC was carried out on JAI LC-908 with preparative JAIGEL-2H and 2.5H columns. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Solvents used for spectroscopic measurements were all of spectral grade.

Crystallographic data collection and structure refinement: Data for **2f** were collected at low temperature (−153 °C) on a Rigaku RAXIS-RAPID with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), and data for **2d** and **3d** at −183 °C on a Bruker SMART APEX with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Details of the crystallographic data are listed in Table 2. The structures were solved by direct methods (Sir 97[21] or SHELXS-97[22]) and full-matrix least-squares techniques (SHELXL-97).[22] CCDC 709675 (**2f**), 709674 (**2d**) and 709676 (**3d**) 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/data_request/cif.

General procedure for the synthesis of α-substituted BODIPY dyes: *meso*-Mesityldipyrromethane (264 mg, 1.0 mmol, 1.0 equiv), bis(pinacolato)diboron (508 mg, 2.0 mmol, 2.0 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (5.4 mg, 0.02 mmol, 0.02 equiv), and $[\{Ir(cod)(OMe)\}_2]$ (6.63 mg, 0.01 mmol, 0.01 equiv) were added to a Schlenk flask, which was evacuated and purged with argon five times, and then charged with dried 1,4-dioxane (3.0 mL). The mixture was stirred at reflux for 24 h under argon (oil-bath temperature: 100–105 °C). After removal of the solvents under vacuum, the residue was dissolved in CH_2Cl_2. The solution was filtered through a short pad of Florisil (ca. 1.5 cm high, eluent: CH_2Cl_2), which was washed with CH_2Cl_2 to remove the catalyst and insoluble salts. The solvent was removed and the residue dried in vacuum to give the crude borylated compounds (508 mg, a colorless glassy solid) without separation. The borylated compound (258 mg, 0.5 mmol, 1.0 equiv) and the catalyst $[\{Rh(cod)(OH)\}_2]$ (11.4 mg, 0.025 mmol, 0.05 equiv) were added to a Schlenk flask, which was evacuated and purged with argon three times, and then charged with dioxane (2.5 mL), H_2O (250 μL), and hexyl acrylate (365 μL, 2.0 mmol, 4.0 equiv). The mixture was stirred at reflux for 24 h under argon (oil-bath temperature: 100–105 °C). After removal of the solvent, the residue was dissolved in 5 mL of THF, and DDQ (114 mg, 0.5 mmol, 1.0 equiv) was added to the solution. After stirring at room temperature for 15 min, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was washed with water and dried over Na_2SO_4. Solvents were removed and the residue was dissolved in 5 mL of toluene. After purging with argon for 15 min, triethylamine (0.8 mL, 5.0 mmol, 10 equiv) was added to the reaction mixture followed by $BF_3{\cdot}OEt_2$ (0.8 mL, 5.0 mmol, 10 equiv). The mixture was stirred at room temperature for 30 min, quenched with a saturated aqueous solution of $NaHCO_3$, and extracted with CH_2Cl_2. The organic layer was washed with water and dried over Na_2SO_4. Solvents were removed and the residue was filtered through a short pad of silica gel (eluent: CH_2Cl_2) to remove insoluble salts and polar byproducts. The mixture was purified by GPC (BioRad Bio-Beads SX-1, packed in a 3.0×60 cm gravity-flow column; eluent: THF) to afford four major bands (in order of elution): 1) unidentified byproduct, 2) α,α′-diacrylate BODIPY **2b** (oil, 71 mg, 22% yield), 3) α-monoacrylate BODIPY **2a** (oil, 39 mg, 16% yield), and **4**) unsubstituted BODIPY **1**.

BODIPY 2a: ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (t, 3H; $J = 6.8$ Hz, CH_3 in hexyl), 1.25–1.69 (m, 8H; CH_2 in hexyl), 2.09 (s, 6H; CH_3 in mesityl), 2.36 (s, 3H; CH_3 in mesityl), 4.23 (t, 2H; $J = 6.8$ Hz; OCH_2 in hexyl), 6.51 (d, $J = 4.1$ Hz, 1H; pyrrole H), 6.56 (d, $J = 16.0$ Hz, 1H; double bond), 6.62 (d, $J = 4.6$ Hz, 1H; pyrrole H), 6.69 (d, $J = 4.1$ Hz, 1H; pyrrole H), 6.79 (d, $J = 4.1$ Hz, 1H; pyrrole H), 6.96 (s, 2H; ArH), 7.95 (s, 1H; pyrrole H), 8.10 ppm (d, $J = 16.5$ Hz, 1H; double bond); MS (ESI-TOF): m/z 487.2345 $[M+Na^+]$, calcd m/z 487.2344 $[M+Na^+]$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 545 nm (8.74×10^4 M^{-1} cm^{-1}).

BODIPY 2b: ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (t, 6H; $J = 6.8$ Hz, CH_3 in hexyl), 1.25–1.74 (m, 16H; CH_2 in hexyl), 2.09 (s, 6H; CH_3 in mesityl), 2.36 (s, 3H; CH_3 in mesityl), 4.26 (t, 4H; $J = 6.9$ Hz; OCH_2 in hexyl), 6.59 (d, $J = 16.0$ Hz, 2H; double bond), 6.63 (d, $J = 4.1$ Hz, 2H; pyrrole H), 6.83 (d, $J = 4.6$ Hz, 2H; pyrrole H), 6.96 (s, 2H; ArH), 8.14 (d, $J = 16.0$ Hz, 2H; double bond); MS (ESI-TOF): m/z 641.3316 $[M+Na^+]$, calcd m/z 641.3339 $[M+Na^+]$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 593 nm (9.27×10^4 M^{-1} cm^{-1}).

BODIPYs 2c and 2d: The general procedure was followed, but methyl 2,4-pentadienoate was used instead of hexyl acrylate. Final purification was performed by column chromatography on silica gel (THF/hexane = 1/10) and recrystallization (CH_2Cl_2/hexane) to give BODIPY **2c** (powder) in 29% yield and BODIPY **2d** (powder) in 9% yield.

BODIPY 2c: ^{1}H NMR (CD_2Cl_2): $\delta = 2.08$ (s, 6H; CH_3 in mesityl), 2.35 (s, 3H; CH_3 in mesityl), 3.75 (s, 3H; OCH_3), 6.11 (d, $J = 15.1$ Hz, 1H; double bond), 6.49 (m, 1H; pyrrole H), 6.62 (d, $J = 4.1$ Hz, 1H; pyrrole H), 6.64 (d, $J = 4.5$ Hz, 1H; pyrrole H), 6.85 (d, $J = 4.1$ Hz, 1H; pyrrole H), 6.97 (s, 2H; ArH), 7.10 (dd, $J = 15.5$, 11.5 Hz, 1H; double bond), 7.42 (d, $J = 15.6$ Hz, 1H; double bond), 7.52 (dd, $J = 15.1$, 11.0 Hz, 1H; double bond), 7.84 ppm (s, 1H; pyrrole H); MS (MALDI-TOF): m/z 420.94 $[M^+]$, calcd m/z 420.26 $[M^+]$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 566 nm (1.07×10^5 M^{-1} cm^{-1}).

BODIPY 2d: ^{1}H NMR (CD_2Cl_2): $\delta = 2.09$ (s, 6H; CH_3 in mesityl), 2.36 (s, 3H; CH_3 in mesityl), 3.76 (s, 6H; OCH_3), 6.12 (d, $J = 15.1$ Hz, 2H; double bond), 6.59 (d, $J = 4.1$ Hz, 2H; pyrrole H), 6.88 (d, $J = 4.6$ Hz, 2H; pyrrole 1H), 6.98 (s, 2H; ArH), 7.11 (dd, $J = 15.6$, 11.5 Hz, 2H; double bond), 7.44 (d, $J = 15.6$ Hz, 1H; double bond), 7.55 ppm (dd, $J = 15.1$, 11.5 Hz, 1H; double bond); MS (ESI-TOF): m/z 553.2088 $[M+Na^+]$, calcd m/z 553.2086 $[M+Na^+]$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 641 nm (1.43×10^5 M^{-1} cm^{-1}).

BODIPYs 2e and 2f: The general procedure was followed, but ethyl acrylate was used instead of hexyl acrylate. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 1:10) to give BODIPY **2e** (oil) in 13% yield and BODIPY **2f** (powder, recrystallized from CH_2Cl_2/hexane) in 30% yield.

BODIPY 2e: ^{1}H NMR ($CDCl_3$): $\delta = 1.36$ (t, 3H; $J = 7.4$ Hz, CH_3 in ethyl), 2.09 (s, 6H; CH_3 in mesityl), 2.36 (s, 3H; CH_3 in mesityl), 4.31 (q, 2H; $J = 7.3$ Hz; OCH_2 in ethyl), 6.51 (d, $J = 3.7$ Hz, 1H; pyrrole H), 6.56 (d, $J = 16.1$ Hz, 1H; double bond), 6.62 (d, $J = 4.6$ Hz, 1H; pyrrole H), 6.69 (d, $J = 4.1$ Hz, 1H; pyrrole H), 6.79 (d, $J = 4.5$ Hz, 1H; pyrrole H), 6.96 (s, 2H; ArH), 7.95 (s, 1H; pyrrole H), 8.10 ppm (d, $J = 16.5$ Hz, 1H; double bond); MS (ESI-TOF): m/z 431.1705 $[M+Na^+]$, calcd m/z 431.1717 $[M+Na^+]$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 545 nm (9.16×10^4 M^{-1} cm^{-1}).

BODIPY 2f: ^{1}H NMR ($CDCl_3$): $\delta = 1.38$ (t, 6H; $J = 6.8$ Hz, CH_3 in ethyl), 2.09 (s, 6H; CH_3 in mesityl), 2.36 (s, 3H; CH_3 in mesityl), 4.32 (q, 4H; $J = 7.3$ Hz; OCH_2 in hexyl), 6.59 (d, $J = 16.0$ Hz, 2H; double bond), 6.63 (d, $J = 4.6$ Hz, 2H; pyrrole H), 6.83 (d, $J = 4.6$ Hz, 2H; pyrrole H), 6.96 (s, 2H; ArH), 8.13 ppm (d, $J = 16.0$ Hz, 2H; double bond); MS (ESI-TOF): m/z 529.2058 $[M+Na^+]$, calcd m/z 529.2086 $[M+Na^+]$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 593 nm (1.25×10^5 M^{-1} cm^{-1}).

General procedure for the synthesis of β-substituted BODIPY dyes: *meso*-Mesityl BODIPY (**1**, 100 mg, 0.32 mmol, 1.0 equiv), bis(pinacolato)diboron (81.7 mg, 0.32 mmol, 1.0 equiv), 4,4′-di-*tert*-butyl-2,2′-bipyridyl (4.3 mg, 0.016 mmol, 0.05 equiv), and $[Ir(cod)OMe]_2$ (5.3 mg, 0.008 mmol, 0.025 equiv) were added to a Schlenk flask, which was evacuated and purged with argon five times, and then charged with dried dioxane (3.0 mL). The mixture was stirred at reflux for 16 h under argon. After removal of the solvent under vacuum, the residue was dissolved in CH_2Cl_2. The solution was passed through a short pad of Florisil (ca. 1.5 cm high, eluent: CH_2Cl_2) to remove the catalyst and insoluble salts. Then the crude product was transferred to a 50 mL round-bottomed-flask and the solvent removed under vacuum to give the borylated products. $[\{Rh(cod)(OH)\}_2]$ (7.3 mg, 0.016 mmol, 0.05 equiv) was added to the flask, which was then purged with argon and charged with hexyl acrylate (226 μL, 1.29 μmol, 4 equiv), H_2O (300 μL), and dioxane (3.0 mL). The mixture was stirred at room temperature for 24 h under argon. The solvent was evaporated under vacuum, and the crude product purified by chromatography on silica gel (CH_2Cl_2/hexane = 3/1) to provide BODIPY **3a** (oil) in 7% yield and BODIPY **3b** (powder) in 7% yield.

BODIPY 3a: ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.8$ Hz, 3H; CH_3 in hexyl), 1.25–1.65 (m, 8H; CH_2 in hexyl), 2.10 (s, 6H; CH_3 in mesityl), 2.38 (s, 3H; CH_3 in mesityl), 4.14 (t, $J = 6.8$ Hz, 2H; OCH_2 in hexyl), 6.17 (d, $J = 16.0$ Hz, 1H; double bond), 6.54 (d, $J = 3.7$ Hz, 1H; pyrrole H), 6.73 (s, 1H; pyrrole H), 6.77 (d, $J = 4.1$ Hz, 1H; pyrrole H), 6.97 (s, 2H; ArH), 7.47 (d, $J = 16.0$ Hz, 1H; double bond), 8.00 (s, 1H; pyrrole H), 8.03 ppm (s, 1H; pyrrole H); MS (ESI-TOF): m/z 487.2338 $[M+Na^+]$,

calcd *m/z* 487.2344 [*M*+Na$^+$]; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 538 nm ($5.72\times10^4\,M^{-1}cm^{-1}$).

BODIPY 3b: ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 6H; CH_3 in hexyl), 1.30–1.70 (m, 16H; CH_2 in hexyl), 2.10 (s, 6H; CH_3 in mesityl), 2.39 (s, 3H; CH_3 in mesityl), 4.15 (t, *J* = 6.4 Hz, 4H; OCH_2 in hexyl), 6.21 (d, *J* = 16.0 Hz, 2H; double bond), 6.79 (s, 2H; pyrrole H), 6.99 (s, 2H; ArH), 7.46 (d, *J* = 16.0 Hz, 2H; double bond), 8.12 ppm (s, 2H; pyrrole H); MS (ESI-TOF): *m/z* 641.3343 [*M*+Na$^+$], calcd *m/z* 641.3339 [*M*+Na$^+$]; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 579 nm ($6.07\times10^4\,M^{-1}cm^{-1}$).

BODIPYs 3c and 3d: The general procedure was followed, but methyl 2,4-pentadienoate was employed instead of hexyl acrylate. After removal of the solvent, the residue was purified by column chromatography on silica gel (THF/hexane = 1/10) to provide BODIPY **3c** (powder, recrystallized from CH_2Cl_2/hexane) in 3% yield and BODIPY **3d** (powder, recrystallized from CH_2Cl_2/hexane) in 1% yield.

BODIPY 3c: ^{1}H NMR ($CDCl_3$): δ = 2.11 (s, 6H; CH_3 in mesityl), 2.38 (s, 3H; CH_3 in mesityl), 3.75 (s, 3H; OCH_3), 5.89 (d, *J* = 15.1 Hz, 1H; double bond), 6.51 (d, *J* = 3.7 Hz, 1H; pyrrole H), 6.61–6.71 (m, 3H; pyrrole 1H and double bond 2H), 6.72 (d, *J* = 4.1 Hz, 1H; pyrrole H), 6.98 (s, 2H; ArH), 7.35 (dd, *J* = 15.1, 10.5 Hz, 1H; double bond), 7.96 (s, 1H; pyrrole H), 8.03 ppm (s, 1H; pyrrole H); MS (MALDI-TOF): *m/z* 420.75 [*M*$^+$], calcd *m/z* 420.26 [*M*$^+$]; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 557 nm ($3.96\times10^4\,M^{-1}cm^{-1}$).

BODIPY 3d: ^{1}H NMR ($CDCl_3$): δ = 2.12 (s, 6H; CH_3 in mesityl), 2.39 (s, 3H; CH_3 in mesityl), 3.75 (s, 3H; OCH_3), 5.91 (d, *J* = 15.5 Hz, 2H; double bond), 6.62–6.70 (m, 6H; pyrrole 2H and double bond 4H), 7.00 (s, 2H; ArH), 7.35 (dd, *J* = 15.5, 10.1 Hz, 2H; double bond), 8.07 ppm (s, 1H; pyrrole H); MS (MALDI-TOF): *m/z* 530.18 [*M*$^+$], calcd *m/z* 530.37 [*M*$^+$]; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 633 nm ($5.71\times10^4\,M^{-1}cm^{-1}$).

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 18685013) from MEXT, Japan. Financial support from the Sumitomo Foundation is gratefully acknowledged. J.C. thanks the JSPS for a postdoctoral fellowship.

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Received: December 4, 2008
Revised: February 25, 2009
Published online: May 5, 2009

