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3,5-Bis(benzothiazolyl)-Substituted BODIPY Dyes

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A number of new BODIPY dyes with benzothiazolyl substituents have been synthesized that exhibit long-wavelength absorption and act as strong fluorophores. The optical properties of the dyes were studied by using spectroscopic methods and quantum-chemical calculations. The structural peculiarities of the dyes obtained, in comparison to their analogues, were studied by X-ray analysis.

Introduction

Borondipyrromethene dyes (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene, BODIPY, BDP) have found numerous applications in biochemistry and molecular biology owing to their excellent thermal, chemical, and photochemical stability, high molar absorptivity, high fluorescence quantum yield and low sensitivity to both solvent polarity and pH.[1]

However, because the absorption maxima of the majority of BODIPYs are below 600 nm, and because long-wavelength dyes are important for both basic and applied research,[2] many synthetic approaches have been developed to modify the BODIPY core to obtain structures absorbing at longer wavelengths.[1d] One of the most promising approaches to the modification of BODIPY is its peripheral functionalization.

Substitution of BODIPY at the 3- and 5-positions with aryl units usually results in a redshift of the absorption maximum, and there are many 3,5-diaryl-substituted dyes described in the literature.[3] In comparison to dye **1**,[3a] the bathochromic effect in compound **2**[3b] is approximately 50 nm (Scheme 1). However, only a few BODIPYs substituted with heterocyclic rings at the 3- and 5-positions are known.[4] The first representative, dye **3**, which is substituted with benzothiophene moieties,[4a] shows a redshift of the absorption maximum of near 30 nm, compared to BODIPY **2**.

Another example is dye **4**, with thienyl substituents in the BODIPY core.[4b] As shown in Scheme 1, dye **4** demonstrates a 69 nm redshift in comparison to **2**. Given that the electronic properties of thiophene rings are very similar to those of the phenyl rings, the reason for such spectral differences could be explained in terms of the reduced steric hindrance on changing from 6- to 5-membered rings. Therefore, one of the main factors that affect the optical properties of such dyes is the efficient conjugation of the BODIPY core with the π-system of the substituents; this can be partly confirmed by comparing dyes **2** and **5**.[3d]

This paper addresses the synthesis and study of bis-(benzothiazolyl)-substituted BODIPY dyes.

Results and Discussion

The parent compound that was chosen for the synthesis of the desired dyes, was 2-(pyrrol-2-yl)benzothiazole (**6**).[5] According to the literature,[5a] it has been synthesized from *N*-(ethoxycarbonyl)pyrrole-2-carbothioamide, and more recently[5b] pyrrole **6** was prepared starting from 2-formylpyrrole by using $Sc(OTf)_3$ as the catalyst. We succeeded in the synthesis of derivative **6** in good yield (91%) from accessible 2-cyanopyrrole[6] on a preparative scale (Scheme 2).

The condensation reaction of pyrroles with aromatic aldehydes occurred readily,[1,3] however, when electron-acceptor substituents were present on the pyrrole ring [e.g., 2-(pyrrol-2-yl)pyridine] drastic reaction conditions were required.[7] In the latter case, the product was prepared in poor yield and involved a tedious purification stage. We found that heating of pyrrole **6** with benzaldehyde and 4-methoxybenzaldehyde, in the presence of catalytic amounts of acetic acid and aniline, gives rise to compounds **7a** and **7b** in good yields (Scheme 3).

The oxidation of compounds **7a** and **7b** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) led to dipyrromethenes **8a** and **8b**, respectively. Because the reaction between (benzothiazolyl)pyrrole **6** and 4-hydroxybenzaldehyde did not succeed, dipyrromethene **8c** was obtained by cleaving methoxy derivative **8b** with hydrobromic acid in acetic acid. Compounds **8a**–**c** were treated with boron trifluoride–diethyl ether in the presence of Hünig's base to yield 3,5-bis(benzothiazolyl)-substituted BODIPY dyes **9a**–**c** (Scheme 3).

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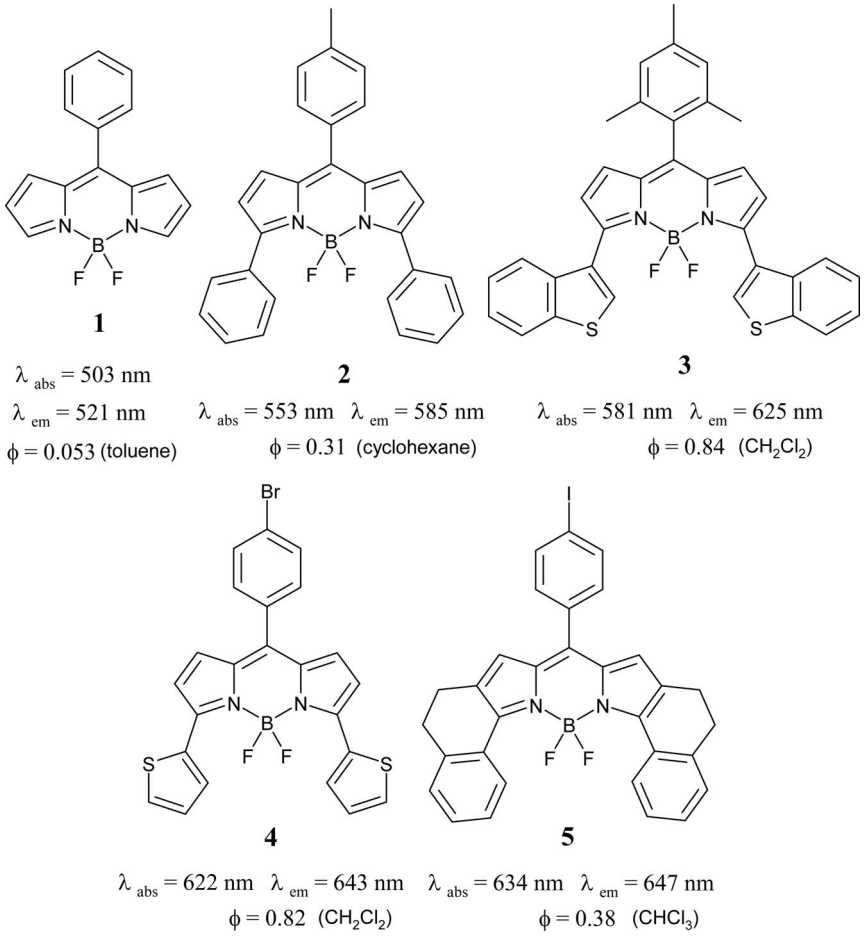
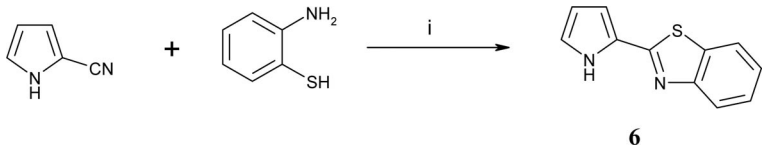


Scheme 1.



Scheme 2. Reagents and conditions: (i) 140 °C, 2 h.

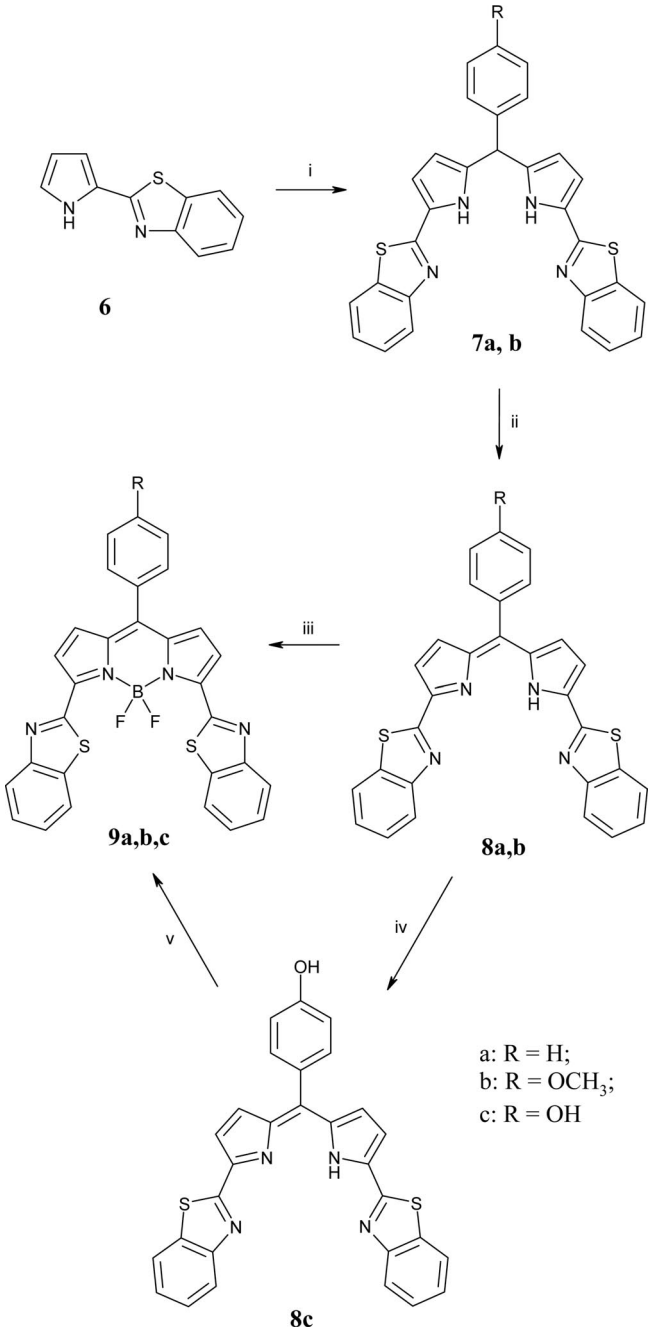
For all BODIPYs synthesized, an intensive absorption band near 620 nm was observed that showed almost no dependence on the solvent polarity. Molar absorption coefficients of the dyes were in the range of 40000–57000 $M^{-1} cm^{-1}$, which is comparable with another BODIPYs.[1,3] Dyes **9a**–**c** are fluorophores and exhibit strong emission near 640 nm (Figure 1, Table 1). Fluorescent quantum yields (Φ) are high and reach maximum values for **9b**.

Dye **9c**, containing a hydroxy group at the terminal position, was further explored for the purpose of altering its optical properties by treatment with basic reagents. On addition of excess pyridine to a solution of **9c**, the absorption spectrum hardly changed, whereas the fluorescence of **9c** drastically decreased (Table 1). Similar effects were observed for other BODIPY hydroxy derivatives.[8]

Besides long-wavelength absorption bands, dyes **9a**–**c** also exhibited relatively intensive short-wavelength absorption bands (Figure 1).

For a better understanding of the origin of the electronic transitions, DFT/B3LYP/6-31 G(dp) calculations for dye **9b** were performed. The Firefly QC package,[9a] which is partially based on the GAMESS (US)[9b] source code, was used to perform the calculations.

Analysis of the calculated absorption spectrum of dye **9b** shows that the long-wavelength band corresponds to the electronic transition $S_0 \rightarrow S_1$. The short-wavelength band, located in the region of 460 nm, bears three electronic transitions: $S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$, and $S_0 \rightarrow S_4$, each roughly composed, to a considerable degree, by three transitions (H-1→L, H-2→L, and H-3→L). HOMO–1, HOMO–2, and HOMO–3 are local orbitals that lie very close to one another in energy



Scheme 3. Reagents and conditions: (i) aniline, ArCHO, acetic acid, 140 °C, 15 h; (ii) DDQ, CH_2Cl_2, room temp., 30 min; (iii) $BF_3{\cdot}Et_2O$, *i*Pr_2EtN, CH_2Cl_2, room temp., 1 h; (iv) R = OCH_3, HBr 48%, acetic acid, reflux, 16 h; (v) $BF_3{\cdot}Et_2O$, N*i*Pr_2Et, CH_2Cl_2, room temp., 3 h.

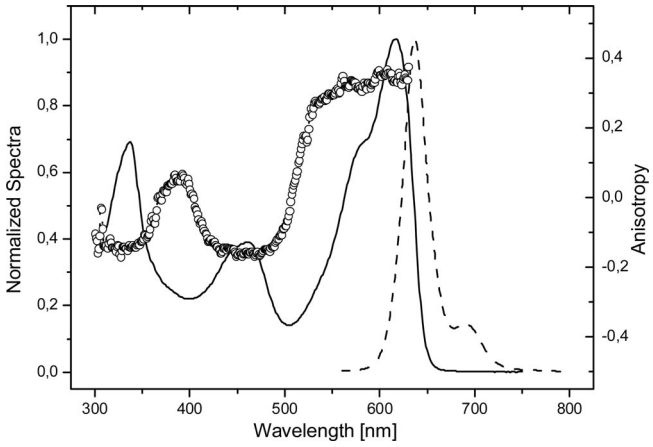


Figure 1. Absorption (—), fluorescence (----), and excitation anisotropy (○) spectra of **9b** in glycerol.

Table 1. Optical properties of the synthesized dyes.

Entry	Dye	Solvent	λ_{abs}[a] [nm]	$\varepsilon{\cdot}10^{-3}$ [$M^{-1}cm^{-1}$]	λ_{em}[b] [nm]	Φ
1	**9a**	EtOH	619	48	639	0.43
			403	13		
2	**9a**	CH_2Cl_2	623	48	643	0.86
			399	14		
3	**9a**	DMF	620	40	642	0.66
			406	12		
4	**9b**	EtOH	616	47	637	0.94
			460	18		
5	**9b**	CH_2Cl_2	624	57	643	1.00
			460	21		
6	**9b**	DMF	617	44	641	0.81
			468	18		
7	**9c**	CH_2Cl_2	618	54	639	0.53
			448	18		
8	**9c**	CH_2Cl_2 + Py	616	54	638	0.11

[a] $c = 2\times10^{-5}$ M. [b] Excitation at 550 nm.

Table 2. Calculated energy of molecular orbitals for dye **9b**.

	HOMO–3 [eV]	HOMO–2 [eV]	HOMO–1 [eV]	HOMO [eV]	LUMO [eV]
9b	–6.26	–6.25	–6.18	–5.44	–3.06

(Table 2); H-2 and H-3 are degenerate, with the electron density mainly localized on the benzothiazole substituent (Table 2, Figure 2).

The position of highest electronic transitions in the short-wavelength region is illustrated by the fluorescence excitation anisotropy spectrum (Figure 1). Two minimums at approximately 460 and 330 nm, were observed for dye **9b** in glycerol solution that correspond to electronic transitions with dipole moments at an angle to the dipole moment of the transition $S_0 \rightarrow S_1$. The anisotropy in both minimums was –0.16 and, hence, according to the equation $r = (3\cos^2\beta - 1)/5$,[10] the angles amount to approximately 75° each.

To analyze the structural peculiarities of the synthesized dyes and their known analogous, the molecular structure of compound **9b** was determined by single-crystal X-ray diffraction. A perspective view of molecule **9b** is given in Figure 3. The central six-membered ring B(1)N(3)C(13)C(12)-C(11)N(2) is not planar (the maximum deviation from the least-square plane is 0.075 Å) and has a *semi-boat* conformation. The heterocycles C(8–11)N(2) and C(13–16)N(3) are planar to within 0.001 Å, whereas the C(1–7)S(1)N(1) and C(17–23)S(2)N(4) substituents are twisted around the

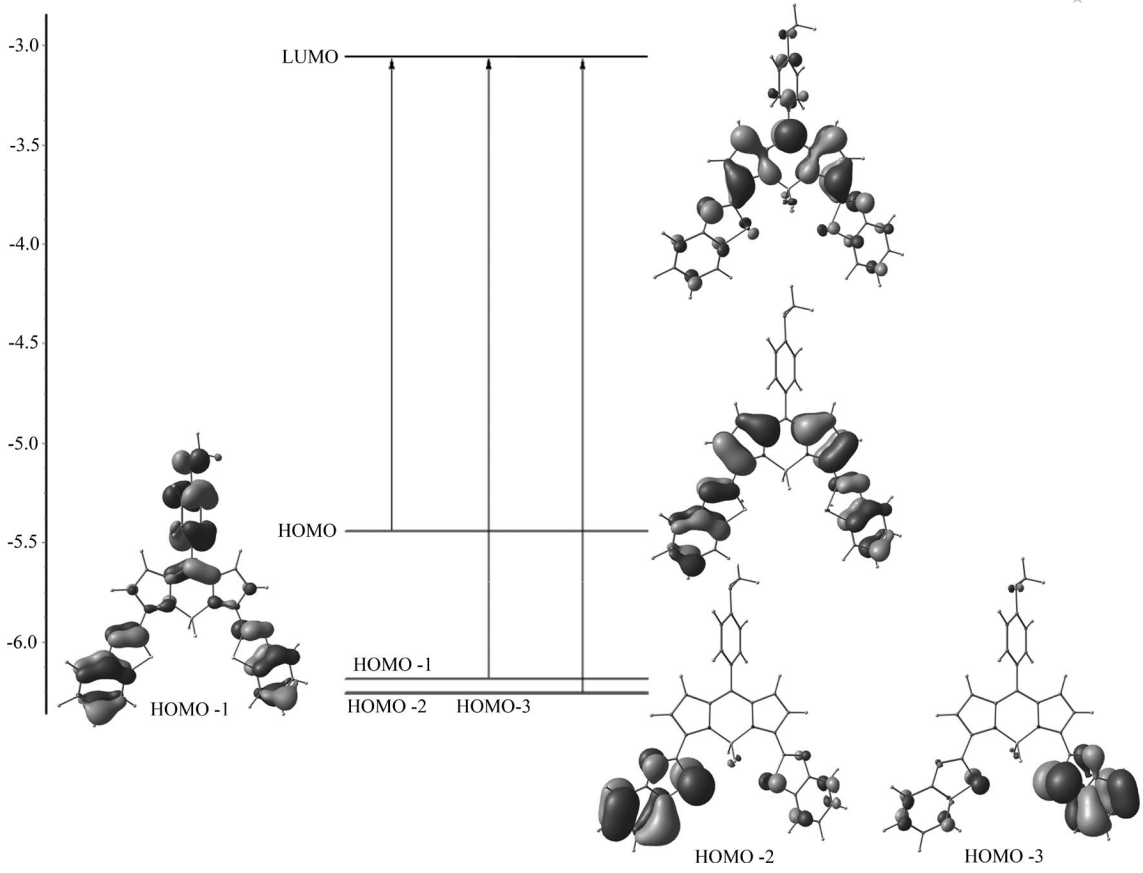


Figure 2. Molecular orbitals and electronic transitions for dye **9b**.

central C(8–16)N(3)B(1)N(2) system by 43.86° and 50.41°, respectively. Due to intramolecular steric interactions, substituents C(1–7)S(1)N(1) and C(17–23)S(2)N(4) are almost orthogonal (the dihedral angle is 85.55°). The dihedral angle between the C(24–29) and C(8–16)N(3)B(1)N(2) systems is 48.43°.

According to the literature,[4b] the dihedral angles between the BODIPY chromophore and the thienyl substituents for dye **4** in the crystal state (Scheme 1) are 25.2° and 21.6°, respectively, leaving the sulfur atoms on the edges turned out. Unlike compound **4**, the X-ray analysis of BODIPY **9b** reveals that the sulfur atoms of the benzothiazolyl substituents are turned towards the fluorine atom, with interatomic distances of 2.92 Å and 3.10 Å, respectively, which is shorter than the sum of sulfur and fluorine van der Waals radii.[11a] There is a report in the literature that refers to S–F intramolecular interactions[11b] and, evidently, a weak intramolecular bonding of a similar type may also occur in this case.

However, the dihedral angles for such BODIPY dyes in the solid state cannot be responsible for the spectral properties in solution due to the strong dependence upon the crystal packing (Figure 4).[3c,4b]

Since the synthesized dyes, like the majority of BODIPYs, show very weak solvatochromism,[1,3] the optimized calculated geometry in the gas phase could adequately model the optical properties of such dyes in solution.

To clarify the relationship between the structure and optical properties of the synthesized BODIPY, we have analyzed the calculated dihedral angles around the bonds between the BODIPY chromophore and the substituents for a series of BODIPYs (**2**, **4**, **5**, and **9b**).

In the pair of compounds **2** and **5**, the substituents are equivalent in their electronic properties. The only difference being that in dye **5** the rotation around the aryl–pyrrole bond is prevented by the ethylene bridge. For this pair, the DFT calculations give dihedral angles of 34.6° and 18.0°, respectively (Table 3), and the absorption band of dye **5** is 80 nm redshifted in comparison to **2**.

For dyes **4** and **9b**, the calculations give the following conformations with the lowest energy: the thienyl substituents and the BODIPY system in **4** subtend an angle of 22.1°, with the sulfur atoms twisted into different directions; in the case of **9b**, the sulfur atoms are turned towards the fluorine atoms, the dihedral angles amounting to approximately 16°.

The fact that the optical properties of BODIPYs **4** and **9b** are very similar can be explained on the basis of two factors: The first factor is the dihedral angle between the central framework and the substituents, which – as illustrated by the difference between the pair of **2** and **5** – plays a crucial role. The second factor is the electronic effect of the substituents, which is difficult to quantify correctly, owing to the different dihedral angles; however, the thienyl

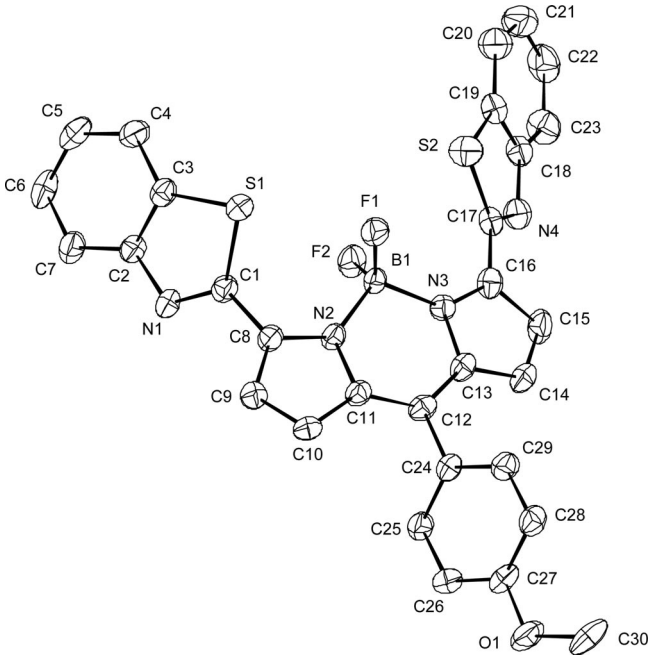


Figure 3. Molecular structure of compound **9b**. Selected bond lengths [Å] and angles [°]: N(2)–C(8) 1.358(4), N(2)–B(1) 1.575(2), N(3)–C(16) 1.363(4), N(3)–B(1) 1.553(2), C(1)–C(8) 1.461(4), C(8)–C(9) 1.402(4), C(9)–C(10) 1.357(4), C(10)–C(11) 1.414(4), C(11)–C(12) 1.399(4), C(12)–C(13) 1.401(4), C(12)–C(24) 1.482(4), C(13)–C(14) 1.402(4), C(14)–C(15) 1.362(5), C(15)–C(16) 1.393(4), C(16)–C(17) 1.457(4); C(27)–O(1)–C(30) 117.8(3), C(8)–N(2)–B(1) 128.2(2), C(16)–N(3)–B(1) 127.1(2), C(11)–C(12)–C(24) 121.7(3), C(13)–C(12)–C(24) 118.2(3), N(2)–C(8)–C(1) 127.1(3), C(1)–C(8)–C(9) 123.5(3), N(3)–C(16)–C(17) 127.0(3), C(15)–C(16)–C(17) 123.5(3).

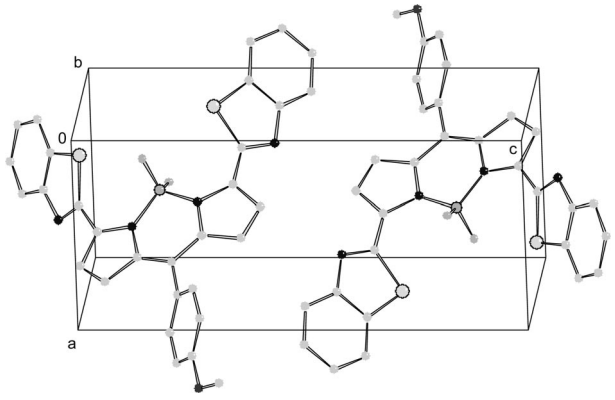


Figure 4. Crystal packing of compound **9b**.

Table 3. Calculated bond lengths and dihedral angles between BODIPY core and substituent in α-position.

	2	**4**	**5**	**9b**
Bond length (B3LYP) [Å]	1.472	1.448	1.463	1.458
Dihedral angle [°]	34.6	22.1	18.0	16.1

substituent probably has a larger polar effect. In the pair of dyes **4** and **9b** the combination of these factors results in almost equal optical properties.

Conclusions

A synthesis of 2-(1*H*-pyrrol-2-yl)benzothiazole has been developed that enabled a number of new BODIPY dyes with benzothiazolyl substituents to be generated. Although the molar absorption coefficients of the dyes are moderate, they exhibit intense fluorescence (up to 100%). The dyes obtained have relatively intense short-wavelength absorption bands arising from the three highest electronic transitions. The substitution of BODIPY with benzothiazolyl moieties leads to exactly the same optical properties as observed for thienyl-substituted BODIPY. Unlike BODIPY **4**, in case of dye **9b**, S–F intramolecular bonding occurs in the solid state.

Experimental Section

General: Electronic absorption spectra were recorded with a Shimadzu UV-3100 spectrophotometer. Emission spectra were recorded with a Solar 2303M instrument. The fluorescence quantum yields were determined by using indodicarbocyanine iodide (Φ = 0.25, EtOH) as a reference according to the literature.[12] ^{1}H NMR spectra were recorded with Varian VXR-300 and Bruker Avance DRX 500 instruments. LC/MS spectra were recorded with a chromatography/mass spectrometric system that consisted of an Agilent 1100 Series high-performance liquid chromatograph equipped with an Agilent LC\MSD SL diode-matrix and mass-selective detector.

2-(1*H*-Pyrrol-2-yl)benzothiazole (6): A mixture of 2-cyanopyrrole (13.7 g, 0.15 mol) and 2-aminothiophenole (20 g, 0.16 mol) was heated at 135–140 °C for 2 h. After cooling, the solid was filtered and washed with hexane and *i*PrOH to give the title compound (27 g, 90.6%); m.p. 155–156 °C (CCl_4) (ref.[5a] 167–168 °C). $C_{11}H_8N_2S$ (200.26): calcd. C 65.97, H 4.03, N 13.99; found C 66.09, H 4.08, N 13.91. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.34 (dd, $^3J_{H,H}$ = 2.4, 2.7 Hz, 1 H, py-H^4), 6.90 (br. s, 1 H, py-H^5), 6.95 (br. s, 1 H, py-H^3), 7.33 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, benzo-H^5), 7.44 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, benzo-H^6), 7.85 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, benzo-H^7), 7.91 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, benzo-H^4), 10.76 (br. s, 1 H, NH) ppm.

1,9-Bis(2-benzothiazolyl)-5-phenyl-5,10-dihydrodipyrrin (7a): A mixture of compound **6** (4 g, 0.02 mol), benzaldehyde (1.18 g, 0.011 mol), acetic acid (1 g, 0.017 mol), and aniline (0.5 g, 0.005 mol) was heated at 140 °C under a flow of argon for 15 h. After cooling, the product was solidified by the addition of acetonitrile and washed with toluene to give compound **7a** (3.36 g, 69%); m.p. 226–228 °C (toluene). $C_{29}H_{20}N_4S_2$ (488.64): calcd. C 71.28, H 4.13, N 11.47; found C 71.06, H 4.10, N 11.58. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.20 (br. s, 3 H, PhC*H*, 2 py-H), 6.55 (br. s, 2 H, py-H), 6.96–7.10 (m, 2 H, ArH), 7.15–7.35 (m, 7 H, 4 benzo-H, 3 ArH), 7.70 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, benzo-H), 7.80 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, benzo-H), 11.30 (br. s, 2 H, NH) ppm.

1,9-Bis(2-benzothiazolyl)-5-(4-methoxyphenyl)-5,10-dihydrodipyrrin (7b): The product was synthesized as for **7a**. Yield: 56%; m.p. 213–214 °C (toluene). $C_{30}H_{22}N_4OS_2$ (518.66): calcd. C 69.47, H 4.28, N 10.80; found C 69.34, H 4.19, N 10.84. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.74 (s, 3 H, OCH_3), 5.13 (s, 1 H, ArC*H*), 5.22 (br. s, 2 H, py-H), 6.52 (br. s, 2 H, py-H), 6.68 (d, $^3J_{H,H}$ = 9.3 Hz, 2 H, ArH), 6.90 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, ArH), 7.15–7.35 (m, 4 H, benzo-H), 7.66 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, benzo-H), 7.77 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, benzo-H), 11.23 (br. s, 2 H, NH) ppm.

1,9-Bis(2-benzothiazolyl)-5-phenyldipyrrin (8a): To a stirred solution of compound **7a** (0.75 g, 1.5 mmol) in CH_2Cl_2 (750 mL) at room temp., DDQ (0.37 g, 1.6 mmol) was added. After 15 min, the solution was filtered to remove solid material. The solvent was distilled off to afford **8a** (0.74 g, 100%); m.p. 243 °C (toluene). $C_{29}H_{18}N_4S_2$ (486.62): calcd. C 71.58, H 3.73, N 11.51; found C 71.85, H 3.81, N 11.66. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.81 (d, $^3J_{H,H}$ = 4.2 Hz, 2 H, py-H), 7.18 (d, $^3J_{H,H}$ = 4.2 Hz, 2 H, py-H), 7.45–7.65 (m, 9 H, 5 ArH, 4 benzo-H), 8.03 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, benzo-H), 8.17 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, benzo-H) ppm. MS (APCI): *m*/*z* = 487 [M + H]$^+$.

1,9-Bis(2-benzothiazolyl)-5-(4-methoxyphenyl)dipyrrin (8b): The product was synthesized as for **8a**. Yield: 90%; m.p. 208–209 °C (toluene). $C_{30}H_{20}N_4OS_2$ (516.65): calcd. C 69.74, H 3.90, N 10.84; found C 69.63, H 3.92, N 11.01. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.90 (s, 3 H, OCH_3), 6.83 (d, $^3J_{H,H}$ = 4.2 Hz, 2 H, py-H), 7.02 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.16 (d, $^3J_{H,H}$ = 4.2 Hz, 2 H, py-H), 7.44 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, benzo-H), 7.48–7.58 (m, 4 H, 2 ArH + 2 benzo-H), 7.98 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, benzo-H), 8.13 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, benzo-H) ppm. MS (APCI): *m*/*z* = 517 [M + H]$^+$.

1,9-Bis(2-benzothiazolyl)-5-(4-hydroxyphenyl)dipyrrin (8c): A solution of **8b** (1.4 g, 2.7 mmol) and hydrobromic acid (46%, 30 mL) in acetic acid (140 mL) was refluxed for 16 h. The reaction mixture was diluted with an equal volume of water, and aqueous ammonia (25 mL) was added. The precipitate was filtered off to give the crude material (0.89 g). Additional product (0.34 g) was obtained from the mother liquor. The crude product was recrystallized from acetic acid to afford **8c** (0.87 g, 64%); m.p. 255–256 °C (HOAc). $C_{29}H_{18}N_4OS_2$ (502.62): calcd. C 69.30, H 3.61, N 11.15; found C 69.22, H 3.58, N 11.19. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): δ = 6.91 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, py-H), 6.99 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, ArH), 7.27 (d, $^3J_{H,H}$ = 4.0 Hz, 2 H, py-H), 7.49 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, ArH), 7.56 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, benzo-H), 7.64 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, benzo-H), 8.17 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, benzo-H), 8.28 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, benzo-H), 10.20 (s, 1 H, OH), 13.76 (s, 1 H, NH) ppm. MS (APCI): *m*/*z* = 503 [M + H]$^+$.

3,5-Bis(2-benzothiazolyl)-4,4-difluoro-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene (9a): Compound **8a** (0.5 g, 1.03 mmol) was dissolved in anhydrous CH_2Cl_2 (200 mL), and subsequently boron trifluoride–diethyl ether (2.25 g, 2 mL, 16 mmol) and Hünig's base (1.29 g, 10 mmol) were added. After 30 min of stirring, the solvent was distilled off, and the residue was purified by chromatography on silica gel by using a mixture of ethyl acetate/hexane (1:3) to give BODIPY **9a** (0.61 g, 56%); m.p. 195–196 °C. $C_{29}H_{17}BF_2N_4S_2$ (534.42): calcd. C 65.18, H 3.21, N 10.48; found C 65.12, H 3.26, N 10.40. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.96 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, py-H), 7.35 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, py-H), 7.47 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, benzo-H), 7.52–7.65 (m, 7 H, 5 ArH + 2 benzo-H), 7.97 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, benzo-H), 8.21 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, benzo-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ = –135.63 (m) ppm. MS (APCI): *m*/*z* = 535 [M + H]$^+$.

3,5-Bis(2-benzothiazolyl)-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (9b): The product was synthesized as for **9a**. Yield: 63%; m.p. 265–266 °C. $C_{30}H_{19}BF_2N_4OS_2$ (564.45): calcd. C 63.84, H 3.39, N 9.93; found C 63.57, H 3.48, N 10.14. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.94 (s, 3 H, OCH_3), 7.06 (d, $^3J_{H,H}$ = 4.8 Hz, 2 H, py-H), 7.10 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.47 (t, $^3J_{H,H}$ = 8.1 Hz, 2 H, benzo-H), 7.51–7.64 (m, 6 H, 2 ArH + 2 py-H + 2 benzo-H), 8.03 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, benzo-H), 8.16 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, benzo-H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ = –133.15 (m) ppm. MS (APCI): *m*/*z* = 565 [M + H]$^+$.

3,5-Bis(2-benzothiazolyl)-4,4-difluoro-8-(4-hydroxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (9c): Compound **8c** (0.3 g, 0.6 mmol) was suspended in anhydrous CH_2Cl_2 (300 mL), and a solution of boron trifluoride–diethyl ether (1.42 g, 10 mmol) in CH_2Cl_2 (20 mL) was added dropwise. The mixture was stirred for 1 h, then a solution of Hünig's base (1.1 g, 8.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise to the resulting mixture. The solution was stirred for 2 h, and the solvent was distilled off. The residue was purified by chromatography on silica gel by using ethyl acetate as eluent. The solution was concentrated in vacuo almost to dryness, and then diluted with an equal volume of hexane. The precipitate was filtered to afford **9c** (0.13 g, 39%); m.p. 205 °C (dec.). $C_{29}H_{17}BF_2N_4OS_2$ (550.42): calcd. C 63.28, H 3.11, N 10.18; found C 63.61, H 3.23, N 10.29. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 7.05 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, ArH), 7.15 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, py-H), 7.47 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, py-H), 7.50–7.70 (m, 6 H, 2 ArH + 4 benzo-H), 8.17 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, benzo-H), 8.26 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, benzo-H), 10.44 (s, 1 H, OH) ppm. ^{19}F NMR (282 MHz, [D$_6$]DMSO, $CFCl_3$): δ = –131.36 (m) ppm. MS (APCI): *m*/*z* = 503 [M – BF_2].

X-ray Structure Determination for 9b: Crystal data: $C_{30}H_{19}B_1F_2N_4O_1S_2$; M = 564.45; system: triclinic; space group: $P\bar{1}$ (no. 2); unit-cell dimensions: a = 6.712(2), b = 12.055(3), c = 15.570(5) Å, α = 82.844(8), β = 87.078(9), γ = 88.868(8)°; V = 1248.2(6) Å^3; Z = 2; calculated density: 1.502 g cm^{-3}; μ = 0.263 mm^{-1}; F(000) = 580; crystal size ca. 0.10 × 0.20 × 0.50 mm. All crystallographic measurements were performed at 123 K with a Bruker Smart Apex II diffractometer operating in the ω- and ϕ-scan modes. The cell parameters were obtained from the least-squares treatment of 2358 reflections in the θ range of 2.6–21.6°. The intensity data were collected within the range of $2.1° \leq \theta \leq 26.4°$ by using Mo-K_α radiation (λ = 0.71078 Å). The intensities of 10821 reflections were collected (4832 unique reflections, R_{int} = 0.001). Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms by using the SHELXS97 and SHELXL97 programs[13,14] and CRYSTALS program package.[15] SADABS absorption correction was applied.[16] In the refinement, 4832 reflections [2429 reflections with $I \geq 3\sigma(I)$] were used. Convergence was obtained at R_1 = 0.0372 and wR_2 = 0.0359, GOF = 1.165 (352 parameters; observed/variable ratio 6.90; largest and smallest peaks in the final difference map 0.24 and –0.25 e/Å^3). In the refinement, the Chebychev weighting scheme[17] was used (weighting coefficients: 0.924, –0.734, 0.756, –0.302, 0.136). CCDC-755495 contains 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.

[1] a) A. Loudet, K. Burgess, *Chem. Rev.* **2007**, *107*, 4891–4932; b) G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem. Int. Ed.* **2008**, *47*, 1184–1201; c) T. E. Wood, A. Thompson, *Chem. Rev.* **2007**, *107*, 1831–1861; d) A. B. Descalzo, H.-J. Xu, Z. Shen, K. Rurack, *Ann. N. Y. Acad. Sci.* **2008**, *1130*, 164–171; e) R. P. Haugland, *The Handbook – A Guide to Fluorescence Probes and Labeling Technologies*, 10th ed., Invitrogen Corp., Eugene, OR, **2005**.

[2] a) J. Fabian, H. Nakazumi, M. Matsuoka, *Chem. Rev.* **1992**, *92*, 1197–1226; b) *Near-Infrared Dyes for High Technology Application* (Eds.: S. Dahne, U. Resch-Genger, O. S. Wolfbeis), Kluwer Academic, Dordrecht, **1998**.

[3] a) R. W. Wagner, J. S. Lindsey, *Pure Appl. Chem.* **1996**, *68*, 1373–1380; b) T. Rohan, W. Qin, N. Boens, W. Dehaen, *Eur. J. Org. Chem.* **2006**, 4658–4663; c) A. Burghart, H. Kim, M. B. Welch, L. H. Thoresen, J. Reibenspies, K. Burgess, F. Bergstrom, L. B.-Å. Johansson, *J. Org. Chem.* **1999**, *64*, 7813–7819; d) J. Chen, A. Burghart, A. Derecskei-Kovacs, K. Burgess, *J. Org. Chem.* **2000**, *65*, 2900–2906; e) J. Chen, J. Reibenspies, A. Derecskei-Kovacs, K. Burgess, *Chem. Commun.* **1999**, 2501–2502.
[4] a) E. Yu. Schmidt, B. A. Trofimov, A. I. Mikhaleva, N. V. Zorina, N. I. Protzuk, K. B. Petrushenko, I. A. Ushakov, M. Yu. Dvorko, R. Méallet-Renault, G. Clavier, T. T. Vu, H. T. T. Tran, R. B. Pansu, *Chem. Eur. J.* **2009**, *15*, 5823–5830; b) S. Rihn, P. Retailleau, N. Bugsaliewicz, A. De Nicola, R. Ziessel, *Tetrahedron Lett.* **2009**, *50*, 7008–7013; c) R. Haugland, H. Kang, *US Pat*. 5248782, **1993**.
[5] a) B. George, E. P. Papadopoulos, *J. Org. Chem.* **1977**, *42*, 441–443; b) T. Itoh, K. Nagata, H. Ishikawa, A. Ohsawa, *Heterocycles* **2004**, *63*, 2769–2783.
[6] H. J. Anderson, *Can. J. Chem.* **1959**, *37*, 2053–2058.
[7] R. J. P. Corriu, V. Huynh, J. Iqbal, J. J. E. Moreau, C. Vernhet, *Tetrahedron* **1992**, *48*, 6231–6244.
[8] a) M. Baruah, W. Qin, N. Basarić, W. M. De Borggraeve, N. Boens, *J. Org. Chem.* **2005**, *70*, 4152–4157; A. Coskun, E. Deniz, E. U. Akkaya, *Org. Lett.* **2005**, *7*, 5187–5189; T. Gareis, C. Huber, O. S. Wolfbeis, J. Daub, *Chem. Commun.* **1997**, 1717–1718.
[9] a) A. A. Granovsky, *FIREFLY*, version 7.1.G, http://classic.chem.msu.su/gran/firefly/index.html; b) M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347–1363.
[10] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd ed., Kluwer Academic Plenum Publishers, New York, **1999**.
[11] a) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451; b) D. J. Crouch, P. J. Skabara, M. Heeney, I. McCulloch, S. J. Colesc, M. B. Hursthouse, *Chem. Commun.* **2005**, 1465–1467.
[12] S. Fery-Forgues, D. Lavabre, *J. Chem. Educ.* **1999**, *76*, 1260–1264.
[13] G. M. Sheldrick, *SHELXS97 – Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1997**.
[14] G. M. Sheldrick, *SHELXL97 – Program for the Refinement of crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.
[15] D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge, *CRYSTALS*, Issue 10, Chemical Crystallography Laboratory, University of Oxford, **1996**.
[16] G. M. Sheldrick, *SADABS – Program for scaling and correction of area detector data*, University of Göttingen, Germany, **1996**.
[17] J. R. Carruthers, D. J. Watkin, *Acta Crystallogr., Sect. A* **1979**, *35*, 698–699.

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