JOC The Journal of Organic Chemistry

ARTICLE

pubs.acs.org/joc

1,7-Disubstituted Boron Dipyrromethene (BODIPY) Dyes: Synthesis and Spectroscopic Properties

Volker Leen,[†] Dominique Miscoria,[†] Shouchun Yin,[†,‡] Aleksander Filarowski,[†,§] Joseph Molisho Ngongo,[†,∥] Mark Van der Auweraer,[†] Noël Boens,[†] and Wim Dehaen*[,†]

[†]Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200f - bus 02404, 3001 Leuven, Belgium

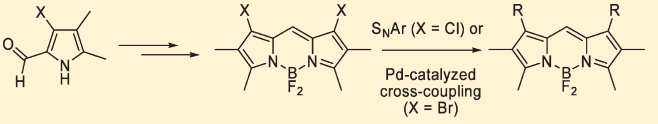
[‡]College of Material Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, People's Republic of China

[§]Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

[∥]Faculty of Science, Université de Kinshasa, B.P. 190 Kinshasa XI, Democratic Republic of the Congo

Supporting Information

ABSTRACT: 1,7-Dihalogenated boron dipyrromethene dyes were successfully synthesized and substituted, thus providing an entry to the final, elusive reactivity pattern. The spectroscopic properties of 1,7-disubstituted BODIPY dyes were studied and are discussed as a function of their structure.



INTRODUCTION

One of the major reasons for the vast increase in the use of boron dipyrromethene (BODIPY) dyes is undoubtedly their potential for derivatization.[1] With limited synthetic effort, a large number of functional groups can be introduced through well-documented synthetic approaches to the BODIPY core. Moreover, in recent years, several reactive BODIPY scaffolds have been reported, which allow a nearly unlimited structural variation.

Upon analysis of the literature data on such reactive BODIPY dyes, it is clear that substitution at almost all positions has been investigated (Figure 1). The most straightforward method, electrophilic substitution at the 2,6-positions, has found widespread use due to its easy accessibility from 2,4-dimethylpyrrole.[1] Halogenated systems arising from such protocols have also been subjected to transition-metal-catalyzed cross-coupling reactions.[2] Furthermore, the 2,6-positions are susceptible to direct hydrogen substitution with both alkenyl and aryl groups.[3] Similar nucleophilic substitution reactions and palladium-catalyzed functionalization reactions have been reported for 8-thiomethylated BODIPY dyes, with the thioether acting as a pseudohalogen.[4] Recently, the use of 3,5-halogenated systems has been attracting a great deal of attention, because these dyes show excellent reactivity in both nucleophilic aromatic substitution and Pd-catalyzed cross-coupling reactions.[5] As an alternative to halogenated systems, it was shown that the 3,5-hydrogens can be substituted directly by nucleophiles, either by an oxidative mechanism or via vicarious elimination.[6] Such substitutions at the 3,5-positions tend to have profound effects on the spectral properties. Finally, substitution of the 4-fluorine atoms by carbon and oxygen nucleophiles has been shown to be a versatile method for the introduction of functionality.[7]

As such, 1,7-disubstitution and the effect thereof on the spectral properties remain largely unexplored. These positions

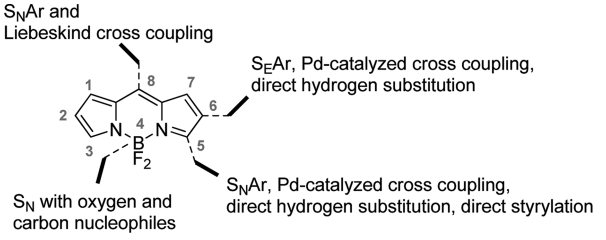


Figure 1. Overview of the methods of direct derivatization of the BODIPY core.

are rather electron poor and are expected to show reactivity similar to that for the 3,5- and 8-positions. Additionally, the structural arrangement of new substituents on these 1,7-positions allows integration of cooperative effects in the design of new sensors.[8] Therefore, we set out to prepare and evaluate the spectroscopic characteristics of such 1,7-disubstituted BODIPY dyes.

RESULTS AND DISCUSSION

Synthesis. Since direct halogenation of the BODIPY core would preferably halogenate other positions, the use of this approach can only be effective through blockage of all the other positions.

Such 2,3,5,6,8-pentasubstituted dyes can be conveniently prepared through standard BODIPY preparations with substituted pyrroles. For example, condensation of 2,3-dimethylpyrrole (**1**) with acetyl chloride in dichloromethane, followed by in situ

Received: May 30, 2011
Published: September 12, 2011

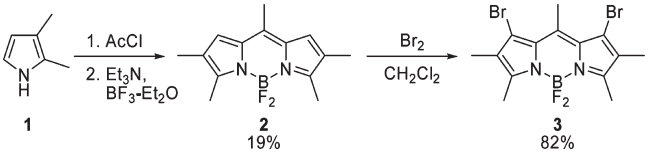
complex formation, afforded the BODIPY dye **2** in a typical yield (Scheme 1). Bromination of this dye was fast with molecular bromine in dichloromethane, and the desired 1,7-dibrominated dye **3** was isolated in excellent yield and on a large scale. Although direct iodination is also possible, the resulting compounds are exceedingly difficult to purify and, hence, were not further examined. In theory, BODIPY compounds such as **3**, where the 1,7-positions are halogenated, are accessible starting from 4-halogenated pyrroles where the 5-position is unsubstituted and at least the 2-position is blocked (e.g., 4-bromo-2-methyl-1*H*-pyrrole). Unfortunately, such starting pyrroles are unstable and, furthermore, have limited synthetic accessibility.

However, attempts to subject dyes such as **3** to Pd-catalyzed cross-coupling reactions showed that reactions were always accompanied by reductive dehalogenation, and the resulting reaction products could not be purified by common column chromatography. These side reactions occurred under the Suzuki, Stille, Heck, and Sonogashira protocols. As steric crowding of the intermediate palladium complex was reasoned to be a plausible origin of this side reaction, we switched to meso-unsubstituted systems.

In this case, halogenation of the meso position could interfere; therefore, halogenation at the pyrrole stage was desirable. Moreover, placing a hydrogen substituent at the 8-position would require working with aldehydes. From these premises, a strategy was designed that would use the decarbonylative condensation of two pyrrole carbaldehydes to dipyrromethenes, and the corresponding BODIPY dyes, as discovered by Burgess et al.[9]

Thus, 2,3-dimethylpyrrole (**1**)[10] was formylated in moderate yield under Vilsmeier–Haack conditions, setting the stage for halogenation studies (Scheme 2). From a screening of pyrrole halogenation protocols, the chlorinated and brominated derivatives **5a,b** were isolated as highly crystalline solids. The yield of chlorination was significantly lower than that of bromination, without a clear reason and despite numerous attempts at improvement. Subjecting the aldehydes **5** to phosphorus oxychloride in dichloromethane efficiently gave the corresponding dipyrromethenes. After a standard complexation with boron trifluoride etherate, the 1,7-dihalogenated BODIPY dyes **6** were isolated as the sole product from the reaction, in good yield. Using aldehyde **4** directly leads to 1,7,8-unsubstituted BODIPY **6c**, which will be used as a reference for the spectroscopic properties.

Scheme 1. Synthesis of a 1,7-Dihalogenated Meso-Substituted BODIPY Dye



Substitution. Gratifyingly, the compounds **6a,b** showed excellent reactivity in Pd-catalyzed reactions, because dehalogenation was no longer a problem.

The double Suzuki cross-coupling reaction of the 1,7-dibrominated dye **6b** with benzene boronic acid proceeded in excellent yield, under standard conditions (i.e., refluxing toluene and aqueous Na_2CO_3 with $Pd(PPh_3)_4$ as catalyst). Conducting the same reaction with 2-thienyl boronic acid also furnished the substituted product **7b** in good yield (Table 1).

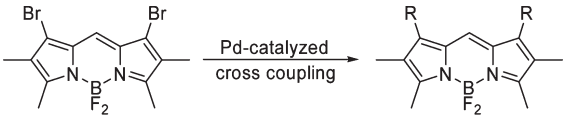
Similar observations could be made for the Stille reaction, where a cross-coupling reaction with the corresponding tin reagents cleanly led to the doubly substituted products in near-quantitative yield. As noted in previous cross-coupling reactions with halogenated BODIPY dyes, the use of the mildly electron donating ligand trifurylphosphine leads to more efficient transmetalation and acceptable reaction times.[5]

The Sonogashira reaction with phenylethyne in DMF was exceptionally fast, even with low catalyst loadings, and the 1,7-disubstituted product **7c** was isolated in high yield after just 30 min.

Similarly, cross coupling of **6b** with styrene in a Heck reaction resulted in the 1,7-disubstituted product **7d**.

In these Pd-catalyzed reactions, selective monocoupling was not achieved, indicating that the first cross-coupling reaction does not reduce the reactivity of the remaining bromine significantly. For the

Table 1. Palladium-Catalyzed Derivatization of 1,7-dibromoBODIPY 6b

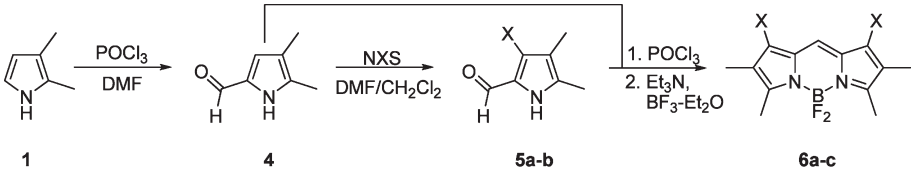


6b **7a-d**

reacn type	R	reacn time/h	yield/%[a]	product
Suzuki[b]	Ph	16	81	**7a**
	2-thienyl	16	65	**7b**
Stille[c]	Ph	2	96	**7a**
	2-thienyl	7	90	**7b**
Sonogashira[d]	PhC≡C	0.5	76	**7c**
Heck[e]	PhCH=CH	2	62	**7d**

[a] Isolated yields for the reaction on a 0.2 mmol scale. [b] Conditions: toluene/Na_2CO_3(aq) (1 M), $Pd(PPh_3)_4$, boronic acid (2.2 equiv), 100 °C. [c] Conditions: 1,4-dioxane, $Pd_2(dba)_3$ (5%), trifurylphosphine (5%), $RSnBu_3$ (2.2 equiv), Na_2CO_3 (3 equiv), 100 °C. [d] Conditions: DMF/Et_3N (8/2 v/v), $Pd_2(dba)_3$ (5%), trifurylphosphine (10%), CuI (10%), PhC≡CH (2.6 equiv), 60 °C. [e] Conditions: DMF, Et_3N (6 equiv), styrene (2.6 equiv), $Pd(PPh_3)_4$, 65 °C.

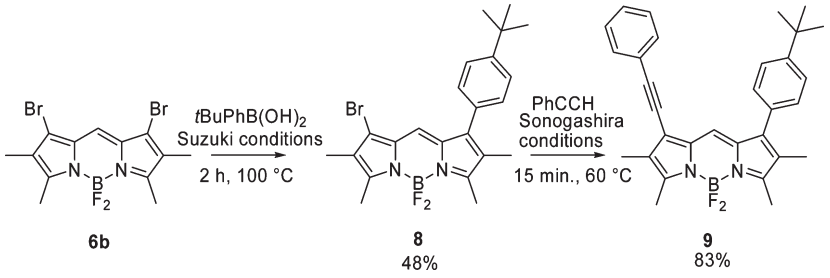
Scheme 2. Halogenation–Condensation Approach of Pyrrole Carbaldehydes to 1,7-Dihalogenated BODIPY Fluorophores



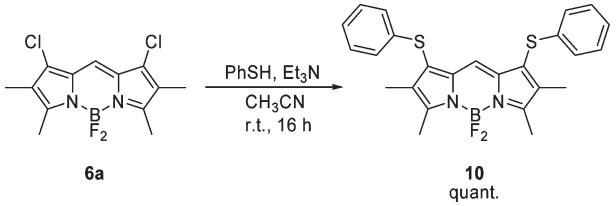
1 **4** 51% **5a-b** **a**: X = Cl (33%) **b**: X = Br (88%) **6a-c** **a**: X = Cl (48%) **b**: X = Br (70%) **c**: X = H (60%)

dx.doi.org/10.1021/jo201082z |*J. Org. Chem.* 2011, 76, 8168–8176

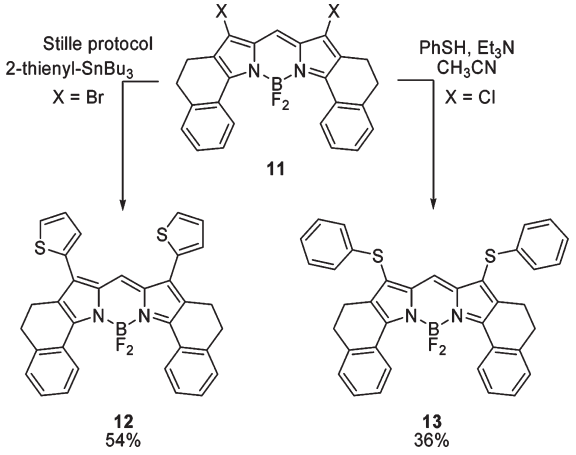
Scheme 3. Synthesis of Asymmetrically Substituted Product through Sequential Palladium-Catalyzed Substitution



Scheme 4. Nucleophilic Substitution of 1,7-Dichlorinated Dye 6a with Thiophenol



Scheme 5. Derivatization of Rotationally Restricted 1,7-Dihalogenated BODIPY



synthesis of asymmetric 1,7-disubstituted BODIPYs, the desired monohalogenated intermediate has to be separated from a mixture of remaining starting material **6b** and the 1,7-disubstituted product.

As an example of such synthesis, the product **8** of a single Suzuki reaction with 1 equiv of aryl boronic acid was prepared in 48% yield (Scheme 3). This product (**8**) was subsequently transformed into the asymmetric dye **9** by means of the Sonogashira protocol. Attesting to the exceptional reactivity toward the Sonogashira alkynation, the reaction was complete after 15 min in excellent yield.

As for the 3,5-dihalogenated dyes, the 1,7-positions are rather electron poor, and this may render them susceptible to nucleophilic aromatic substitution. Nonetheless, only strongly nucleophilic thiolate anions were able to participate in the reaction with the 1,7-dichloro derivative **6a**, yielding the double thioether **10** (Scheme 4). All attempts to introduce nitrogen, oxygen, and carbon nucleophiles failed, with the starting material as the only recovered product. This lowering of the reactivity of the 1,7- compared to the 3,5-positions is likely to be due to their smaller HOMO coefficients.

Evidently, the synthetic strategy outlined in Scheme 2 can also be applied to other 2,3-substituted pyrroles different from 2,3-dimethylpyrrole, which would allow the introduction of different functionalities or the extension of conjugation. Thus, passing through a reaction sequence similar to that in in Scheme 2 with 4,5-dihydrobenzo[*g*]indole as starting material resulted in the 1,7-dihalogenated, conformationally restricted BODIPY **11** (X = Cl, Br).

The reactivity of **11** is comparable to that of **6a,b** (Scheme 5). The double Stille reaction affords **12**, isolated in moderate yield. The lowered yield in the case of S_NAr with thiophenol to **13** is associated with inefficient separation from trace impurities.

UV−Vis Spectroscopic Properties. Generally, the introduction of new substituents directly on the BODIPY scaffold has a profound effect on the spectroscopic characteristics of the dye. When we isolated the reaction products, we immediately noticed that the bathochromic shift induced by the extended conjugation was not as strong as previously observed for analogous 3,5-disubstituted BODIPY compounds. For all the 1,7-disubstituted dyes, the Stokes shift $\Delta\bar{\nu}$ is rather small, being in the normal range for classic BODIPY dyes (Table 2). The visible absorption (λ_{abs}(max)) and fluorescence emission maxima (λ_{em}(max)) of **7a** are blue-shifted in comparison to these values for 3,5-diphenyl BODIPY analogues by about 10 and 35 nm, respectively, resulting in much reduced Stokes shifts $\Delta\bar{\nu}$ (360−370 cm^{-1} for **7a** vs 1000−1100 cm^{-1} for 3,5-diphenyl derivatives).[11] Compound **7b** with 2-thienyl substituents at the 1,7-positions has λ_{abs}(max) and λ_{em}(max) values which are blue-shifted by about 70 nm compared to those for a 3,5-di(2-thienyl) BODIPY analogue.[12] λ_{abs}(max) and λ_{em}(max) values of the 1,7-distyryl dye **7d** are also hypsochromically shifted in comparison to around 630−640 and 640−650 nm, respectively, for 3,5-distyryl BODIPYs.[11,13] Similar blue shifts are found for the 1,7-diethynylphenyl derivative (**7c**) in comparison to the 3,5-substituted counterparts with λ_{abs}(max) 605−615 nm and λ_{em}(max) 620−630 nm.[11] Our preliminary quantum chemical calculations indicate that the smaller effect of 1,7- compared to that for 3,5-substituents may be due to the fact that the HOMO has smaller coefficients in the 1,7-positions compared to the 3,5-positions.

The absorption and emission spectra of **7** all shift to longer wavelengths upon increasing polarizability of the solvent, while $\Delta\bar{\nu}$ does not depend much upon the solvent. This suggests that there is no difference in the permanent dipole moments of the ground state (S_0) and excited state (S_1) for **7**. The larger Stokes shifts of **7b,d** compared to those for **7a,c** must therefore be due to

dx.doi.org/10.1021/jo201082z |*J. Org. Chem.* 2011, 76, 8168–8176

Table 2. Selected Spectroscopic/Photophysical Data (Absorption Maximum λ_{abs}(max), Fluorescence Emission Maximum λ_{em}(max), Stokes Shift $\Delta\bar{\nu}$, and Fluorescence Quantum Yield Φ) of 1,7-Substituted BODIPY Dyes in Several Solvents

BODIPY	solvent[a]	λ_{abs}(max)/nm	λ_{em}(max)/nm	$\Delta\bar{\nu}$[b]/cm^{-1}	Φ
6c	MeOH	532	542	347	0.88
	MeCN	532	542	347	0.70
	THF	534	544	344	0.93
	toluene	539	548	305	0.91
7a	MeOH	538	549	372	0.94
	MeCN	538	549	372	0.93
	THF	541	552	368	0.99
	toluene	545	556	363	0.97
7b	MeOH	548	572	766	0.44
	MeCN	548	571	735	0.52
	THF	551	572	666	0.57
	toluene	555	578	717	0.57
7c	MeOH	570	580	302	1.00
	MeCN	570	579	273	1.00
	THF	573	583	299	1.00
	toluene	577	588	324	1.00
7d	MeOH	572	588	476	0.72
	MeCN	572	589	505	0.55
	THF	577	595	524	0.41
	toluene	582	603	598	0.44
8	MeOH	534	543	322	0.06
	MeCN	534	545	372	0.06
	THF	536	546	342	0.07
	toluene	540	550	348	0.10
9	MeOH	554	563	289	0.21
	MeCN	554	565	341	0.19
	THF	556	567	344	0.22
	toluene	560	571	344	0.26
10	MeOH	550	568	576	0.07
	MeCN	551	567	512	0.11
	THF	553	568	478	0.15
	toluene	556	572	503	0.30
12	MeOH	634	648	341	0.56
	MeCN	636	650	339	0.84
	THF	640	651	264	0.86
	toluene	646	664	420	0.87
13	MeOH	643	663	469	0.59
	MeCN	640	661	496	0.41
	THF	644	663	445	0.88
	toluene	649	668	438	0.79

[a] The solvents are listed according to increasing refractive index at 20 °C (methanol (1.3288), acetonitrile (1.34423), tetrahydrofuran (THF, 1.4050), toluene (1.4961)). [b] Stokes shift (=1/λ_{abs}(max) − 1/λ_{em}(max)).

a larger change in excited-state geometry. This is also reflected in the increased width of the fluorescence emission spectra of **7b,d** compared to those of **7a,b** (see Figure 2). The more extensive red shift for **7c,d** in comparison to **7a,b** is not surprising because triple and double bonds are more available for delocalization than aromatic moieties, since for the latter delocalization leads to a partial loss of aromaticity. Furthermore, steric strain with the

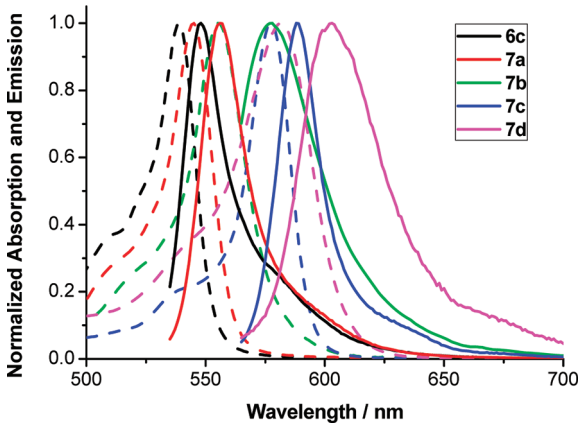


Figure 2. Normalized absorption (dashed) and emission (full) profiles of 1,7-diaryl-substituted BODIPY dyes in toluene, either connected directly (**7a**, phenyl; **7b**, 2-thienyl) or connected through a double bond (**7d**, ethenylphenyl), or a triple bond (**7c**, ethynylphenyl), in comparison to the unsubstituted standard dye **6c**.

methyl groups in 2,6-positions will lead to a rotation out of the plane of the phenyl (in **7a**) and 2-thienyl (in **7b**) moieties and decrease further the electron delocalization over those groups. The 1,7-diethynylphenyl dye **7c** has the highest fluorescence quantum yield, Φ (1.00), in accordance with observations made for a 3,5-diethynylphenyl BODIPY analogue.[11] Styryl substituents (in **7d**) produce the largest bathochromic shifts in both the absorption and emission spectra, followed by ethynylphenyl substituents (in **7c**), while phenyl groups (in **7a**) generate the smallest bathochromic shifts compared to the reference 2,3,5,6-tetramethylBODIPY (**6c**) with no substituents at the 1,7-positions. The same red-shift trend (styryl > ethynylphenyl > phenyl) has been observed already for BODIPYs with these functionalities at the 3,5-positions, and quantum chemical calculations have provided a rationale for these spectral shifts.[11] The smaller fluorescence quantum yields Φ of **7b,d** in comparison to those for **7a,c** can be associated with an increased change in equilibrium geometry upon excitation, which is also suggested by the larger Stokes shift $\Delta\bar{\nu}$ and the broader absorption and emission spectra of **7b,d** (Figure 2). This displacement of the potential energy surface of the S_1 state versus that of the S_0 state—referred to as exciton phonon coupling—will lead to increased Franck−Condon factors between the low vibrational levels of the S_1 state and isoenergetic higher vibrational levels of the S_0 state.[14] The type of vibration involved in this process is less clear, but it certainly is no high-frequency stretching mode of the conjugated system. In this case, one would observe a prolonged vibrational progression rather than band broadening and an increased Stokes shift. Moreover, an increased coplanarity of the styryl (**7d**) or thienyl moieties (**7b**) with the BODIPY moiety in the excited state can be excluded. Indeed, as observed for oligoarylenes or oligoarylene vinylenes, such increased coplanarity in the excited state would lead to a broadening of the absorption bands rather than of the emission spectra, in contrast to the observations made for **7b,d**.[15]

Heavy-atom quenching by Br in compound **8** may account for the much lower Φ value in comparison to that for the standard dye **6c**. It is unlikely that this reduced fluorescence quantum yield Φ is due to exciton phonon coupling with torsions of the phenyl group, because this should also be observed for **7a**. Furthermore, the small Stokes shift $\Delta\bar{\nu}$ and features of the spectra do not

dx.doi.org/10.1021/jo201082z |J. Org. Chem. 2011, 76, 8168–8176

Table 3. Molar Absorption Coefficients ε_{max} (± Standard Error) and Brightness at the Given Absorption Maxima λ_{abs}(max) for a Selection of BODIPY Dyes in the Solvents of Table 2

BODIPY	solvent	λabs-(max)/nm	$\varepsilon_{max}/10^3$ M^{-1} cm^{-1}	max brightness Φ × $\varepsilon_{max}/10^4$ M^{-1} cm^{-1}
6c	MeOH	532	42 ± 3	3.74
	MeCN	532	53 ± 2	3.71
	THF	534	68.9 ± 0.5	6.41
	toluene	539	45 ± 7	4.13
7a	MeOH	538	70 ± 8	6.63
	MeCN	538	88.0 ± 0.2	8.18
	THF	541	91 ± 2	9.05
	toluene	545	84.8 ± 0.5	8.22
10	MeOH	550	73 ± 2	0.51
	MeCN	551	69 ± 1	0.76
	THF	553	94 ± 2	1.41
	toluene	556	86 ± 3	2.57

suggest such increased exciton phonon coupling. The blue shift of λ_{abs}(max) and λ_{em}(max) upon increasing solvent polarity and the independence of $\Delta\bar{\nu}$ of the solvent polarity indicate that no significant change of the permanent dipole occurs in the excited state S_1 of **8**. After the Sonogashira reaction of the remaining Br in derivative **8**, both λ_{abs}(max) and λ_{em}(max) of **9** shift bathochromically about 20 nm in comparison to **8**, indicative of the extension of conjugation by the ethynylphenyl group. Φ of **9** increases 3-fold in relation to that of **8** but remains substantially lower than that of **6c**. It is unlikely that this low Φ value can be attributed to exciton phonon coupling with rotational modes of the *p-tert*-butylphenyl group because **7a,c** with similar substituents have Φ values close to 1.0. Also, the small Stokes shift and the features of absorption and emission spectra exclude such exciton phonon coupling.

The λ_{abs}(max) and λ_{em}(max) values of **10** are shifted to wavelengths slightly longer than those of **7a** due to conjugation with the sulfur that can act as electron donor or electron acceptor (involving respectively 3p and 3d orbitals). However, there is no charge-transfer character of the excited state, because the emission spectra shift to shorter wavelength upon increasing the solvent polarity (which for the solvents used is accompanied by a decrease in the polarizability of the solvent). Moreover, the Stokes shift $\Delta\bar{\nu}$ is (within experimental error) independent of the solvent polarity, indicative of equality of the dipole moments of S_0 and S_1. The small fluorescence quantum yield Φ of **10** is surprising. The small Stokes shift (intermediate between those of **7a** and **7b**) excludes that this is due to extensive exciton phonon coupling. Considering the inefficient intersystem crossing in other sulfur-substituted BODIPYs,[16] it is also not evident to attribute the small Φ to enhanced intersystem crossing. In contrast to the case for the other 1,7-disubstituted BODIPYs, the Φ value of **10** decreases markedly upon increasing solvent polarity. Similar results were obtained earlier for other BODIPY analogues with weakly electron releasing substituents at the 8-, 3-, and 3,5-positions.[17] Also for those compounds, Φ sometimes decreased with increasing solvent polarity, even in the absence of a red shift of λ_{em}(max).

The ring-fused compounds **12** and **13** absorb and fluoresce in the red spectral range due to the extended conjugation combined with the restricted rotational mobility (and increased coplanarity) of the aromatic substituents. The absorption and fluorescence emission maxima of conformationally constrained **12** are bathochromically shifted by ∼90 and ∼80 nm, respectively, in comparison to those for **7b** with four methyl groups at the 2,3,5,6-positions. Similarly, λ_{abs}(max) and λ_{em}(max) of ring-fused **13** are red-shifted by ∼90 and ∼95 nm, respectively, in relation to those for **10**. In analogy to what was observed for dyes **7**, the solvent dependence of λ_{abs}(max), λ_{em}(max), and $\Delta\bar{\nu}$ of **12** and **13** suggests that there is no change in dipole moment between the S_0 and S_1 states. The quantum yields Φ of conformationally restricted **12** and **13** are substantially higher than those of the respective analogues **7b** and **10** with a 2,3,5,6-tetramethyl substitution pattern, while the Stokes shifts are smaller. Comparable effects have been found for other ring-fused BODIPY dyes.[18] This suggests that the change in the equilibrium geometry in the excited state of **12** (respectively **13**) is smaller than in **7b** (respectively **10**), which will lead to less extensive exciton phonon coupling. The Φ value of **13** is significantly larger than that of **10** and approaches the Φ value of **12**. This supports our earlier assumption that the small Φ value of **10** is not related to a heavy-atom effect, as the latter should also be observed for **13**. In analogy to **10** and **12** and in contrast with the other molecules discussed here, the Φ value of **13** clearly decreases with increasing solvent polarity. This could suggest internal conversion induced by interaction with a state with charge transfer character situated a short distance above the S_1 state.

An important photophysical property of a fluorescent dye is its brightness,[19] defined as the product of the fluorescence quantum yield Φ and the molar absorption coefficient $\varepsilon(\lambda)$ at wavelength λ. The maximum brightness values, corresponding to the ε_{max} values at λ_{abs}(max), of a selection of BODIPY dyes (1,7-unsubstituted **6c**, 1,7-diphenyl **7a**, and 1,7-dithiophenyl **10**) in the solvents used in Table 2 are compiled in Table 3. The ε_{max} values are in line with those of reported BODIPY dyes. The maximum brightness is the smallest for **10**, due to the consistently low Φ value. In contrast, 1,7-diphenyl BODIPY **7a** has the highest brightness, as a result of the favorable combination of large ε_{max} and high Φ. Intermediate brightness values are found for **6c**, owing to the small ε_{max} in combination with high Φ.

CONCLUSION

1,7-DihaloBODIPY dyes are readily synthesized in a sequence of high-yielding steps, thus providing an entry to the final missing arrangement of substituents on the boron dipyrromethene scaffold. Even though the changes in spectral properties are somewhat attenuated in comparison to other substitution patterns, they nevertheless combine high fluorescence quantum yields with red-shifted absorption and fluorescence emission spectra. Because of the beneficial alignment of the introduced group, these systems may prove especially useful in the preparation of new sensors with improved properties.[20]

EXPERIMENTAL SECTION

All reactions were carried out in flame-dried glassware, but no special precautions were taken for the exclusion of moisture. Solvents were not dried prior to use.

^{1}H NMR spectra (300 MHz) in $CDCl_3$ were recorded at room temperature and referenced to tetramethylsilane (0.00 ppm) as an

internal standard. ^{13}C NMR spectra (75 MHz) in $CDCl_3$ were referenced to the $CDCl_3$ (77.16 ppm) signal.

Freshly prepared samples in 1 cm quartz cells were utilized to perform all UV−vis absorption and fluorescence measurements. For the determination of the relative fluorescence quantum yields (Φ) in solution, only dilute solutions with an absorbance below 0.1 at the excitation wavelength were used. Rhodamine 6G in ethanol (for UV spectroscopy, ACS reagent, Φ = 0.88) and cresyl violet in methanol (≥99.9%, ACS spectrophotometric grade, Φ = 0.55) were used as references to determine Φ values. In all cases, correction for the refractive index was applied. Molar absorption coefficients $\varepsilon(\lambda)$ were obtained from the linear regression analysis of the absorbance $A(\lambda)$ versus dye concentration C data. Between 4 and 10 such $\{A(\lambda), C\}$ data points were used in each regression analysis. All spectroscopic measurements were done at 20 °C.

2,3-Dimethylpyrrole (**1**) and 4,5-dihydro-1*H*-benzo[*g*]indole were prepared in a Trofimov reaction according to a literature procedure.[10]

2,3,5,6,8-Pentamethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (2). 2,3-Dimethylpyrrole (**1**; 0.70 g, 7.5 mmol) was dissolved in CH_2Cl_2 (10 mL), followed by the addition of acetyl chloride (0.291 g, 264 μL, 3.7 mmol). The mixture was refluxed for 2 h and cooled to 0 °C by means of an ice bath, followed by the addition of triethylamine (5 mL). After 10 min at 0 °C, boron trifluoride etherate (5 mL) was added and the reaction mixture was stirred at room temperature for 16 h. The solution was poured into diethyl ether (200 mL) and thoroughly washed with water. The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. Chromatographic purification (silica; CH_2Cl_2-petroleum ether, 1/1 (v/v)) yielded the compound as an orange solid (175 mg, 18%): mp 161−165 °C; ^1H NMR δ 6.82 (s, 2H), 2.49 (s, 6H), 2.35 (s, 3H), 2.02 (s, 6H) ppm; ^{13}C NMR δ 154.7, 137.5, 133.3, 127.1, 125.2, 15.0, 12.6, 11.2 ppm; LRMS (EI, 70 eV; m/z) 262; HRMS (m/z) calcd for $C_{14}H_{17}BF_2N_2$ 262.145 29, found 262.144 99.

1,7-Dibromo-2,3,5,6,8-pentamethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (3). A solution of 2,3,5,6,8-pentamethyl-BODIPY (0.178 g, 0.679 mmol) and $NaHCO_3$ (130 mg, 1.5 mmol, 2.2 equiv) was stirred at 0 °C, followed by the slow addition of bromine (217 mg, 1.36 mmol, 2 equiv). The resulting reaction mixture was stirred at room temperature for 2 h, followed by quenching of the reaction with an aqueous $Na_2S_2O_3$ solution. The organic layer was extracted with water, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography (silica; CH_2Cl_2/petroleum ether, 1/1 (v/v)): red solid (234 mg, 82%); mp >300 °C; ^1H NMR δ 3.08 (s, 3H), 2.52 (s, 6H), 2.05 (s, 6H) ppm; ^{13}C NMR δ 152.8, 141.7, 129.1, 118.9, 16.6, 13.2, 10.9 ppm (one aromatic carbon not observed); LRMS (EI, 70 eV; m/z) 420; HRMS (m/z) calcd for $C_{14}H_{15}BBr_2F_2N_2$ 419.964 27, found 419.963 28.

4,5-Dimethyl-1*H*-pyrrole-2-carbaldehyde (4). To *N*,*N*-dimethylformamide (DMF, 18.7 mmol, 1.44 mL) at 0 °C was added phosphorus oxychloride (37.4 mmol, 5.74 mL, 3 equiv) dropwise, and the resulting suspension was stirred at room temperature for 1 h. The mixture was cooled to 0 °C, and 2,3-dimethylpyrrole (12.5 mmol, 1.187 g) in dichloromethane (50 mL) was added, followed by stirring at room temperature for 16 h. The reaction was quenched by the rapid addition of excess Na_2CO_3 (50 mmol in 50 mL of H_2O), followed by heating to reflux for 1 h. The mixture was cooled and extracted with dichloromethane (2 × 100 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness. The crude solid was purified by flash chromatography (silica; CH_2Cl_2/ethyl acetate, 9/1 (v/v)) to yield the aldehyde as an off-white solid (1.170 g, 9.54 mmol, 51%): mp 118−123 °C; ^1H NMR δ 10.25 (s, br, 1H, NH), 9.27 (s, 1H), 6.74 (d, 1H, J = 2.07 Hz), 2.28 (s, 3H), 2.03 (s, 3H) ppm; ^{13}C NMR δ 177.6, 136.8, 130.4, 123.8, 119.2, 11.61, 10.9 ppm; MS (EI, 70 eV; m/z) 123.

3-Chloro-4,5-dimethyl-1*H*-pyrrole-2-carbaldehyde (5a). Pyrrole carbaldehyde **4** (1.254 g, 10 mmol) was dissolved in a mixture of DMF and CH_2Cl_2 (1/3 (v/v); 40 mL), and the mixture was cooled to 0 °C. *N*-Chlorosuccinimide (1.6 g, 12 mmol, 1.15 equiv) was added, and the mixture was stirred at 0 °C for 30 min. Subsequently, the darkened mixture was partitioned between diethyl ether (300 mL) and water (300 mL). The organic layer was separated, extracted with water, dried over $MgSO_4$, filtered, and concentrated in vacuo. After column chromatography (silica; CH_2Cl_2/ethyl acetate, 9/1 (v/v)) the pure solid was obtained as off-white crystals (525 mg, 3.30 mmol, 33%): mp 106−107 °C; ^1H NMR δ 11.13 (s, 1H), 9.42 (s, 1H), 2.29 (s, 3H), 1.97 (s, 3H) ppm; ^{13}C NMR δ 175.8, 136.8, 126.3, 125.7, 117.4, 11.9, 8.2 ppm; MS (EI, 70 eV; m/z) 156, 158; HRMS (m/z) calcd for C_7H_8ClNO 157.029 44, found 157.029 16.

3-Bromo-4,5-dimethyl-1*H*-pyrrole-2-carbaldehyde (5b). Pyrrole carbaldehyde **4** (246.3 mg, 2 mmol) was dissolved in a mixture of DMF and CH_2Cl_2 (1/3 (v/v); 8 mL), and the mixture was cooled to 0 °C. *N*-Bromosuccinimide (462.7 mg, 2.3 mmol, 1.15 equiv) was added, and the mixture was stirred at 0 °C for 30 min. The darkened mixture was partitioned between diethyl ether and water. The organic layer was separated, extracted with water, dried over $MgSO_4$, filtered, and concentrated in vacuo. After column chromatography (silica; CH_2Cl_2/ethyl acetate, 9/1 (v/v)) the pure solid was obtained as off-white crystals (355 mg, 1.76 mmol, 88%): mp 144−148 °C; ^1H NMR δ 10.94 (s, 1H), 9.30 (s, 1H), 2.24 (s, 3H), 1.91 (s, 3H) ppm; ^{13}C NMR δ 177.1, 136.9, 127.0, 119.4, 113.7, 12.1, 9.6 ppm; MS (EI, 70 eV; m/z) 201, 203; HRMS (m/z) calcd for C_7H_8BrNO 200.978 93, found 200.977 708.

3-Chloro-4,5-dihydro-1*H*-benzo[*g*]indole-2-carbaldehyde (S1). To a stirred solution of dihydrobenzindole aldehyde[9] (197 mg, 1 mmol) and $NaHCO_3$ (102 mg, 1.2 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL) was added sulfuryl chloride (1 mL of a 1 M solution in CH_2Cl_2) while the temperature was kept at 0 °C. The resulting mixture was stirred for 16 h, followed by pouring it into aqueous $NaHCO_3$. Dichloromethane (50 mL) was added, and the solution was extracted with water and subsequently with brine. The organic layer was collected, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography (silica; CH_2Cl_2/ethyl acetate, 9/1 (v/v)) to yield a white, crystalline solid (78 mg, 34%): mp 199−206 °C; ^1H NMR δ 10.60 (s, br, 1H, NH), 9.64 (s, 1H), 7.68 (d, 1H, J = 7.35 Hz), 7.30 (m, 3H), 2.98 (t, 2H, J = 7.35 Hz), 2.75 (t, 2H, J = 7.74 Hz) ppm; ^{13}C NMR δ 176.6, 137.4, 135.8, 128.9, 128.8, 127.7, 127.3, 126.7, 123.6, 121.8, 120.7 ppm; LRMS (EI, 70 eV; m/z): 231; HRMS (m/z) calcd for $C_{13}H_{10}ClNO$ 231.045 09, found 231.043 46.

3-Bromo-4,5-dihydro-1*H*-benzo[*g*]indole-2-carbaldehyde (S2). To a stirred solution of dihydrobenzindole aldehyde[9] (394 mg, 2 mmol) and $NaHCO_3$ (168 mg, 2 mmol, 2 equiv) in CH_2Cl_2 (10 mL) was added bromine (320 mg, 2 mmol, 1 equiv), while the temperature was kept at 0 °C. The resulting mixture was stirred at room temperature for 2 h, followed by pouring it into aqueous $Na_2S_2O_3$. Dichloromethane (50 mL) was added, and the solution was extracted with water and subsequently with brine. The organic layer was collected, dried over $MgSO_4$, filtered, and evaporated to dryness. The crude mixture was purified by column chromatography (silica; CH_2Cl_2/ethyl acetate, 9/1 (v/v)) to yield a white, crystalline solid (385 mg, 70%): mp 208−210 °C; ^1H NMR δ 10.14 (s, br, 1H, NH), 9.57 (s, 1H), 7.54 (d, 1H, J = 6.6 Hz), 7.26 (m, 3H), 2.99 (t, 2H, J = 7.53 Hz), 2.73 (t, 2H, J = 7.53 Hz) ppm; ^{13}C NMR δ 177.7, 137.4, 128.9, 128.8, 128.7, 127.3, 126.3, 115.9, 121.3, 110.0, 29.0, 19.9 ppm; LRMS (EI, 70 eV; m/z) 275; HRMS (m/z) calcd for $C_{13}H_{10}BrNO$ 276.992 54, found 276.993 85.

1,7-Dichloro-2,3,5,6-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (6a). The compound was obtained according to General Procedure for the Decarbonylative Condensation as a purple solid (151 mg, 48%): mp >300 °C; ^1H NMR δ 7.19 (s), 2.51 (s, 6H), 2.01 (s, 6H) ppm; ^{13}C NMR δ 155.8, 131.4, 130.3, 125.3, 118.7, 13.4, 8.9 ppm; MS (EI, 70 eV; m/z) 316; HRMS (m/z) calcd for $C_{13}H_{13}BF_2N_2Cl_2$ 316.051 69, found 316.051 54.

1,7-Dibromo-2,3,5,6-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (6b). *General Procedure for the Decarbonylative Condensation.* To a solution of brominated pyrrole carbaldehyde **5b** (400 mg, 2 mmol) in dichloromethane (10 mL) at 0 °C was added phosphorus oxychloride (920 mg, 550 μL, 6 mmol), and the resulting mixture was stirred at room temperature for 16 h. Triethylamine (2.023 g, 2.78 mL, 20 mmol, 10 equiv) was added dropwise at 0 °C, followed 10 min later by boron trifluoride etherate (2.78 mL, 22 mmol, 11 equiv). The mixture was stirred at room temperature for 2 h and subsequently poured into diethyl ether (200 mL). The ether solution was extracted with water (3 × 200 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified by column chromatography (silica; petroleum ether/ethyl acetate, 9/1 (v/v)) to yield a dark red solid (284 mg, 70%): mp >300 °C; ^{1}H NMR δ 7.12 (s, 1H), 2.52 (s, 6H), 2.02 (s, 6H) ppm; ^{13}C NMR δ 156.0, 132.0, 127.9, 121.0, 120.4, 13.4, 10.4 ppm; MS (EI, 70 eV; *m*/*z*) 404, 406, 408; HRMS (*m*/*z*) calcd for $C_{13}H_{13}BF_2N_2Br_2$ 406.974 13, found 406.973 46 (45.56%).

2,3,5,6-Tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (6c). The compound was obtained according to General Procedure for the Decarbonylative Condensation as a purple solid (149 mg, 60%): mp 229−232 °C; ^{1}H NMR δ 6.82 (s, 1H), 6.65 (s, 2H), 2.50 (s, 6H), 2.02 (s, 6H) ppm; ^{13}C NMR δ 156.3, 133.1, 128.0, 124.5, 12.8, 11.1 ppm; MS (EI, 70 eV; *m*/*z*) 248; HRMS (*m*/*z*) calcd for $C_{13}H_{15}BF_2N_2$ 248.129 64, found 248.129 69.

1,7-Diphenyl-2,3,5,6-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (7a). *General Procedure for the Suzuki Reaction.* BODIPY **6b** (40.6 mg, 0.1 mmol) was dissolved in toluene (1 mL), followed by the addition of benzene boronic acid (26 mg, 0.22 mmol, 2.2 equiv), $Pd(PPh_3)_4$ (11 mg, 0.01 mmol, 10%), and aqueous Na_2CO_3 (1 mL of a 1 M solution). The resulting mixture was flushed with nitrogen and refluxed for 3 h or until TLC analysis showed complete reaction. The mixture was extracted with diethyl ether (200 mL), and the organic layer was collected, dried over $MgSO_4$, and evaporated to dryness. The crude solid was purified chromatographically to yield the target compound as a purple solid (32 mg, 81%): mp 238−241 °C; ^{1}H NMR δ 7.43−7.33 (m, 8H), 7.27 (d, 2H, *J* = 1.53 Hz), 2.60 (s, 6H), 2.03 (s, 6H) ppm; ^{13}C NMR δ 155.2, 141.9, 133.2, 132.7, 129.8, 128.7, 127.9, 124.9, 124.1, 13.0, 9.8 ppm; MS (EI, 70 eV; *m*/*z*) 400; HRMS (*m*/*z*) calcd for $C_{25}H_{23}BF_2N_2$ 400.192 24, found 400.192 24.

General Procedure for the Stille Reaction. To a solution of 1,7-dibromoBODIPY **6b** in dioxane (1 mL) was added $Pd_2(dba)_3$ (5 μmol, 4.5 mg, 5%), tris(2-furyl)phosphine (5 mmol, 1.2 mg, 5%), fenyltributyltin (0.22 mmol, 72 mL, 2.2 equiv), and Na_2CO_3 (0.30 mmol, 32 mg, 3 equiv). The reaction mixture was heated to reflux until TLC analysis indicated complete reaction. The mixture was cooled to room temperature and evaporated to dryness. After purification via column chromatography (silica; petroleum ether/CH_2Cl_2, 1/1 (v/v)), the compound was obtained as a purple solid (38 mg, 96%).

1,7-Bis(2-thienyl)-2,3,5,6-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (7b). The compound was obtained according to General Procedure for the Suzuki Reaction and General Procedure for the Stille Reaction as a purple solid (37 mg, 90%): mp 240−242 °C; ^{1}H NMR δ 7.47 (s, 1H), 7.42 (d, 2H, *J* = 5.04 Hz), 7.14 (t, 2H, *J* = 5.04 Hz), 7.08 (d, 2H, *J* = 2.76 Hz), 2.58 (s, 6H), 2.14 (s, 6H) ppm; ^{13}C NMR δ 155.6, 134.4, 132.8, 128.1, 128.0, 127.8, 127.2, 125.0, 123.7, 13.0, 10.3 ppm; MS (EI, 70 eV; *m*/*z*) 412; HRMS (*m*/*z*) calcd for $C_{21}H_{19}BF_2N_2S_2$ 412.105 08, found 412.107 42.

1,7-Bis(phenylethynyl)-2,3,5,6-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (7c). *General Procedure for the Sonogashira Reaction.* 1,7-DibromoBODIPY **6b** (0.1 mmol, 40.6 mg), $Pd_2(dba)_3$ (5 mmol, 4.6 mg, 5%), tris(2-furyl)phosphine (5 μmol, 2.4 mg, 10%), and CuI (10 μmol, 10%) were dissolved in a mixture of DMF and triethylamine (8/2 (v/v), 1 mL) and flushed with nitrogen. Phenylacetylene (0.26 mmol, 27 mg, 28.5 μL, 2.6 equiv) was added, and the mixture was stirred at 60 °C for 30 min. The reaction mixture was poured into diethyl ether (200 mL) and repeatedly washed with water. The organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness. After purification via column chromatography (silica, petroleum ether/CH_2Cl_2, 2/1 (v/v)), the compound was obtained as a purple solid (34 mg, 76%): mp >300 °C; ^{1}H NMR δ 7.58−7.56 (m, H), 7.37 (t, 6H, *J* = 3.03 Hz), 7.34 (s, 1H), 2.52 (s, 6H), 2.14 (s, 6H) ppm; ^{13}C NMR δ 155.9, 135.3, 131.9, 130.3, 128.9, 128.8, 128.6, 123.1, 119.8, 100.4, 82.2, 12.9, 10.3 ppm; MS (EI, 70 eV; *m*/*z*) 448; HRMS (*m*/*z*) calcd for $C_{29}H_{23}BF_2N_2$ 448.192 24, found 448.195 25.

1,7-Bis(phenylethenyl)-2,3,5,6-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (7d). 1,7-DibromoBODIPY (**6b**; 0.1 mmol, 40.6 mg) was dissolved in DMF (1 mL), followed by the addition of triethylamine (0.4 mmol, 56 μL, 4 equiv), styrene (0.30 mmol, 30 μL, 2.6 equiv), and $Pd(OAc)_2$ (10 μmol, 2 mg, 10%). The mixture was flushed with nitrogen and stirred under a nitrogen atmosphere at 65 °C until the reaction was complete. The reaction mixture was poured into diethyl ether (200 mL) and repeatedly washed with water. The organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness. After purification via column chromatography (silica; petroleum ether/CH_2Cl_2, 2/1 (v/v)), the compound was obtained as a purple solid (28 mg, 62%): mp 275−278 °C; ^{1}H NMR δ 7.53 (d, 4H, *J* = 7.35 Hz), 7.41−7.30 (m, 7H), 7.20, 7.14 (d, 2H, *J* = 16.38 Hz), 7.02, 6.96 (d, 2H, *J* = 16.38 Hz), 2.55 (s, 6H), 2.18 (s, 6H) ppm; ^{13}C NMR δ 158.3, 153.0, 138.6, 137.0, 135.0 133.5, 131.9, 131.2, 128.8, 128.5, 127.8, 126.7, 126.4, 125.1, 120.8, 119.7, 118.9, 118.4, 13.3, 13.1, 12.9, 10.6, 10.26, 10.21 ppm; MS (EI, 70 eV; *m*/*z*) 452; HRMS (*m*/*z*) calcd for $C_{29}H_{27}BF_2N_2$ 452.223 54, found 452.223 64.

1-(4-*tert*-Butylphenyl)-2,3,5,6-tetramethyl-7-bromo-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (8). Obtained from General Procedure for the Suzuki Reaction on 1,7-dibromoBODIPY (**6b**; 22 mg, 48%): mp 216−219 °C; ^{1}H NMR δ 7.52 (d, 2H, *J* = 8.32 Hz), 7.27 (d, 2H, *J* = 8.32 Hz), 6.96 (s, 1H), 2.57 (s, 3H), 2.53 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.38 (s, 9H) ppm; ^{13}C NMR δ 158.5, 152.6, 151.5, 143.3, 133.4, 131.4, 129.8, 129.5, 126.2, 126.1, 125.8, 122.5, 31.9, 31.4, 13.2, 13.1, 10.3, 9.9 ppm; LRMS (EI, 70 eV; *m*/*z*): 458; HRMS (*m*/*z*) calcd for $C_{23}H_{26}BBrF_2N_2$ 458.134 05, found 458.134 87.

1-(4-*tert*-Butylphenyl)-2,3,5,6-tetramethyl-7-(phenylethynyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (9). Obtained from General Procedure for the Sonogashira Reaction (see under **7c**) on monobromoBODIPY (**8**; 40 mg, 83%): mp 242−247 °C; ^{1}H NMR δ 7.52 (d, 2H, *J* = 8.28 Hz), 7.46 (m, 2H), 7.33 (m, 6H), 7.11 (s, 1H), 2.60 (s, 3H), 2.52 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 1.39 (s, 9H) ppm; ^{13}C NMR δ 158.2, 152.8, 151.4, 143.1, 134.8, 133.6, 131.7, 130.0, 139.6, 128.8, 128.7, 128.5, 125.9, 125.7, 123.2, 122.1, 99.3, 82.5, 34.9, 31.4, 13.2, 12.7, 10.2, 9.9 ppm; LRMS (EI, 70 eV; *m*/*z*): 480; HRMS (*m*/*z*) calcd for $C_{31}H_{31}BF_2N_2$ 480.254 84, found 480.256 81.

1,7-Bis(phenylsulfenyl)-2,3,5,6-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (10). *Nucleophilic Substitution Procedure.* To a solution of BODIPY **6a** (0.1 mmol) in acetonitrile (1.5 mL) were added triethylamine (0.5 mmol, 50.6 mg, 5 equiv) and thiophenol (0.5 mmol, 55 mg, 5 equiv). The resulting mixture was stirred at room temperature until the reaction was complete, as indicated by TLC analysis. The reaction mixture was poured into diethyl ether (200 mL) and repeatedly washed with aqueous Na_2CO_3. The organic layer was dried over $MgSO_4$, filtered, and evaporated to dryness. After purification via column chromatography (silica, petroleum ether/CH_2Cl_2, 2/1 (v/v)), the compound was obtained as a purple solid in near-quantitative yield (46 mg): mp 188−191 °C; ^{1}H NMR δ 7.34 (s, 1H), 7.25−7.19 (m, 4H), 7.14−7.11 (m, 6H), 2.56 (s, 6H), 1.92 (s, 6H) ppm; ^{13}C NMR δ 156.3, 136.3, 135.6, 132.1, 131.5, 129.2, 127.9, 126.2, 121.2, 13.2, 10.1 ppm; MS (EI, 70 eV; *m*/*z*) 464; HRMS (*m*/*z*) calcd for $C_{25}H_{23}BF_2N_2S_2$ 464.136 38, found 464.134 54.

1,7-Dichloro-2,3,5,6-bis(dihydronaphthyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (11a). Obtained by following General Procedure for the Decarbonylative Condensation of pyrrolic aldehydes to symmetric BODIPY dyes, as a deep blue, metallic solid (111 mg, 48%): mp >300 °C; ^{1}H NMR δ 8.70 (d, 2H, J = 7.92 Hz), 7.46−7.24 (m, 7H), 2.94 (, 4H, J = 6.39 Hz), 2.73 (, 4H, J = 3.69 Hz) ppm; ^{13}C NMR δ 151.8, 140.8, 133.3, 130.6, 129.8, 128.6, 128.5, 128.3, 127.7, 127.6, 117.6, 34.2, 20.2 ppm; LRMS (EI, 70 eV; m/z): 464; HRMS (m/z) calcd for $C_{25}H_{17}BCl_2F_2N_2$ 464.082 99, found 464.0765.

1,7-Dibromo-2,3,5,6-bis(dihydronaphthyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (11b). Obtained by following the General Procedure for the Decarbonylative Condensation of pyrrolic aldehydes to symmetric BODIPY dyes, as a bronze metallic solid (153 mg, 55%): mp 282−283 °C; ^{1}H NMR δ 8.70 (d, 2H, J = 7.71 Hz), 7.45−7.24 (m, 7H), 2.95 (t, 4H, J = 6.39 Hz), 2.72 (t, 4H, J = 5.67 Hz) ppm; ^{13}C NMR δ 152.4, 141.5, 135.1, 133.2, 131.0, 129.0, 128.7, 128.5, 128.4, 127.7, 127.7, 120.3, 117.0, 30.1, 21.7 ppm; LRMS (EI, 70 eV; m/z): 556; HRMS (m/z) calcd for $C_{25}H_{17}BBr_2F_2N_2$ 553.979 92, found 553.982 03.

1,7-Bis(2-thienyl)-2,3,5,6-bis(dihydronaphthyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (12). Obtained from General Procedure for Stille Coupling, as a blue metallic solid (36 mg, 64%): mp >300 °C; ^{1}H NMR δ 8.30 (d, 2H), 7.77 (s, 1H), 7.48 (m, 4H), 7.34−7.16 (m, 8H), 2.95-.289 (m, 8H) ppm; ^{13}C NMR δ 140.6, 133.9, 130.1, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 127.3, 31.0, 21.5 ppm; LRMS (EI, 70 eV; m/z): 560; HRMS (m/z) calcd for $C_{33}H_{23}BF_2N_2S_2$ 560.136 38, found 560.139 48.

1,7-Bis(phenylsulfenyl)-2,3,5,6-bis(dihydronaphthyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (13). Obtained from Nucleophilic Substitution Procedure with triethylamine as base and 4 equiv of thiophenol, as a golden metallic solid (22 mg, 36%): mp 214 °C dec; ^{1}H NMR δ 8.76 (d, 2H, J = 7.92 Hz), 7.58 (s, 1H), 7.43 (t, 2H, J = 7.53 Hz), 7.36−7.13 (m, 14H), 2.87 (t, 4H, J = 6.57 Hz), 2.58 (t, 4H, J = 7.53 Hz) ppm; ^{13}C NMR δ 152.5, 140.9, 138.4, 136.7, 136.1, 130.4, 129.3, 128.9, 128.5, 128.0, 127.9, 127.7, 126.3, 123.1, 120.0, 30.0, 21.3 ppm; HRMS (m/z) calcd for $C_{37}H_{27}BF_2N_2S_2$ 612.167 68, found 612.168 62.

■ ASSOCIATED CONTENT

Supporting Information. Figures giving additional spectroscopic data and NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: Wim.Dehaen@chem.kuleuven.be.

■ ACKNOWLEDGMENT

The continuing support from the KU Leuven, the "Fonds voor Wetenschappelijk Onderzoek" (FWO), and the "Ministerie voor Wetenschapsbeleid (Belgium)" is gratefully acknowledged. V.L. thanks the "Instituut voor de aanmoediging van innovatie door Wetenschap en Technologie in Vlaanderen" (IWT) for a doctoral grant. A.F. and J.M.N. are grateful for financial support through GOA 2006-2 and IAP 6/27.

■ REFERENCES

(1) (a) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891. (b) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1184.

(2) (a) Kim, T. G.; Castro, J. C.; Loudet, A.; Jiao, J. G.-S.; Hochstrasser, R. M.; Burgess, K.; Topp, M. R. *J. Phys. Chem. A* **2006**, *110*, 20. (b) Cakmak, Y.; Akkaya, E. U. *Org. Lett.* **2009**, *11*, 85.

(3) (a) Thivierge, C.; Bandichhor, R.; Burgess, K. *Org. Lett.* **2007**, *9*, 2135. (b) Chen, J.; Mizumura, M.; Shinokubo, H.; Osuka, A. *Chem. Eur. J.* **2009**, *15*, 5942.

(4) (a) Goud, T. V.; Tutar, A.; Biellmann, J.-F. *Tetrahedron* **2006**, *62*, 5084.(b) Peña-Cabrera, E.; Aguilar-Aguilar, A.; González-Domínguez, M.; Lager, E.; Zamudio-Vázquez, R.; Godoy-Vargas, J.; Villanueva-García, F. *Org. Lett.* **2007**, *9*, 3985.

(5) (a) Baruah, M.; Qin, W.; Basarić, N.; De Borggraeve, W. M.; Boens, N. *J. Org. Chem.* **2005**, *70*, 4152. (b) Baruah, M.; Qin, W.; Vallée, R. A. L.; Beljonne, D.; Rohand, T.; Dehaen, W.; Boens, N. *Org. Lett.* **2005**, *7*, 4377. (c) Rohand, T.; Baruah, M.; Qin, W.; Boens, N.; Dehaen, W. *Chem. Commun.* **2006**, 266. (d) Rohand, T.; Qin, W.; Boens, N.; Dehaen, W. *Eur. J. Org. Chem.* **2006**, 4658. (e) Leen, V.; Braeken, E.; Luckermans, K.; Jackers, C.; Van der Auweraer, M.; Boens, N.; Dehaen, W. *Chem. Commun.* **2009**, *30*, 4515. (f) Jiao, L.; Yu, C.; Uppal, T.; Liu, M.; Li, Y.; Zhou, Y.; Hao, E.; Hu, X.; Vicente, M. G. H. *Org. Biomol. Chem.* **2010**, *8*, 2517. (g) Rao, M. R.; Kumar, K. V. P.; Ravikanth, M. *J. Organomet. Chem.* **2010**, *695*, 863. (h) Ziessel, R.; Rihn, S.; Harriman, A. *Chem. Eur. J.* **2010**, *16*, 11942.

(6) (a) Leen, V.; Zaragozí Gonzalvo, V.; De Borggraeve, W. M.; Boens, N.; Dehaen, W. *Chem. Commun.* **2010**, *46*, 4908. (b) Leen, V.; Van der Auweraer, M.; Boens, N.; Dehaen, W. *Org. Lett.* **2011**, *13*, 1470.

(7) (a) Gabe, Y.; Ueno, T.; Urano, Y.; Kojima, H.; Nagano, T. *Anal. Bioanal. Chem.* **2006**, *386*, 621. (b) Tahtaoui, C.; Thomas, C.; Rohmer, F.; Klotz, P.; Duportail, G.; Mély, Y.; Bonnet, D.; Hibert, M. *J. Org. Chem.* **2007**, *72*, 269. (c) Didier, P.; Ulrich, G.; Mély, Y.; Ziessel, R. *Org. Biomol. Chem.* **2009**, *7*, 3639. (d) Goze, C.; Ulrich, G.; Mallon, L. J.; Allen, B. D.; Harriman, A.; Ziessel, R. *J. Am. Chem. Soc.* **2006**, *128*, 10231.

(8) Coskun, A.; Yilmaz, M. D.; Akkaya, E. U. *Org. Lett.* **2007**, *9*, 607.

(9) Wu, L.; Burgess, K. *Chem. Commun.* **2008**, 4933.

(10) Schmidt, E. Y.; Mikhaleva, A. I.; Vasil'tsov, A. M.; Zaitsev, A. B.; Zorina, N. V. *ARKIVOC* **2005**, *7*, 11.

(11) Qin, W.; Rohand, T.; Dehaen, W.; Clifford, J. N.; Driesen, K.; Beljonne, D.; Van Averbeke, B.; Van der Auweraer, M.; Boens, N. *J. Phys. Chem. A* **2007**, *111*, 8588.

(12) Rihn, S.; Retailleau, P.; Bugsaliewicz, N.; De Nicola, A.; Ziessel, R. *Tetrahedron Lett.* **2009**, *50*, 7008.

(13) (a) Rurack, K.; Kollmannsberger, M.; Daub, J. *New J. Chem.* **2001**, *25*, 289. (b) Atilgan, S.; Kutuk, I.; Ozdemir, T. *Tetrahedron Lett.* **2010**, *51*, 892.

(14) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1991; p 71.

(15) Bässler, H. In *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 418−419.

(16) Fron, E.; Coutiño-Gonzalez, E.; Pandey, L.; Sliwa, M.; Van der Auweraer, M.; De Schryver, F. C.; Thomas, J.; Dong, Z.; Leen, V.; Smet, M.; Dehaen, W.; Vosch, T. *New J. Chem.* **2009**, *33*, 1490.

(17) (a) Qin, W.; Baruah, M.; Van der Auweraer, M.; De Schryver, F. C.; Boens, N. *J. Phys. Chem. A* **2005**, *109*, 7371. (b) Qin, W.; Rohand, T.; Baruah, M.; Stefan, A.; Van der Auweraer, M.; Dehaen, W.; Boens, N. *Chem. Phys. Lett.* **2005**, *420*, 562. (c) Qin, W.; Baruah, M.; Stefan, A.; Van der Auweraer, M.; Boens, N. *ChemPhysChem* **2005**, *6*, 2343.

(18) (a) Chen, J.; Burghart, A.; Derecskei-Kovacs, A.; Burgess, K. *J. Org. Chem.* **2000**, *65*, 2900. (b) Shen, Z.; Röhr, H.; Rurack, K.; Uno, H.; Spieles, M.; Schulz, B.; Reck, G.; Ono, N. *Chem. Eur. J.* **2004**, *10*, 4853. (c) Goeb, S.; Ziessel, R. *Org. Lett.* **2007**, *9*, 737. (d) Umezawa, K.; Nakamura, Y.; Makino, H.; Citterio, D.; Suzuki, K. *J. Am. Chem. Soc.* **2008**, *130*, 1550. (e) Umezawa, K.; Matsui, A.; Nakamura, Y.; Citterio, D.; Suzuki, K. *Chem. Eur. J.* **2009**, *15*, 1096. (f) Wang, Y.-W.; Descalzo, A. B.; Shen, Z.; You, X.-Z.; Rurack, K. *Chem. Eur. J.* **2010**, *16*, 2887. (g) Leen, V.; Qin, W.; Yang, W.; Cui, J.; Xu, C.; Tang, X.; Liu, W.; Robeyns, K.; Van Meervelt, L.;

Beljonne, D.; Lazzaroni, R.; Tonnelé, C.; Boens, N.; W. Dehaen, W. *Chem. Asian J.* **2010**, *5*, 2016.
(19) Braslavsky, S. E. *Pure Appl. Chem.* **2007**, *79*, 293.
(20) Boens, N.; Leen, V.; Dehaen, W. *Chem. Soc. Rev.* **2011**, DOI: 10.1039/c1cs15132k.