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Dyes

Radical C–H Alkylation of BODIPY Dyes Using Potassium Trifluoroborates or Boronic Acids**

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Abstract: A one-step synthetic procedure for the radical C–H alkylation of BODIPY dyes has been developed. This new reaction generates alkyl radicals through the oxidation of boronic acids or potassium trifluoroborates and allows the synthesis of mono-, di-, tri-, and tetraalkylated fluorophores in a good to excellent yield for a broad range of organoboron compounds. Using this protocol, multiple bulky alkyl groups can be introduced onto the BODIPY core thus creating solid-state emissive BODIPY dyes.

Introduction

Among the known fluorophores, BODIPY dyes (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes, also known as boron dipyrromethenes or as boron dipyrrins)[1] have become an increasingly valuable class of compounds over the last two decades. Their growing success is mainly attributed to the many excellent characteristics they possess, such as a bright fluorescence in the visible spectral range and a good robustness towards light and chemicals.[2] The growing importance of these boron complexes is evident in the numerous applications being reported for these dyes. These applications include their use as chemosensors,[3] potential photosensitizers in photodynamic therapy,[4] laser dyes,[5] and photoactive materials in organic photovoltaic devices.[5,6]

The rich functionalization chemistry of these fluorophores is undoubtedly another major reason for the attractiveness of these boron-dipyrromethene (BODIPY) dyes. It allows a practically unlimited structural modification and hence leads to sophisticated dyes with fine-tuned chemical, optical, and (photo)-physical properties. The typical derivation strategy mostly starts from suitably functionalized pyrroles[7] or uses reactive BODIPY dyes, such as halogenated compounds[8] or derivatives containing a thioether as a pseudohalogen.[9] Although these two methodologies are well documented, they tend to suffer from the use of unstable intermediates and/or the need for a long synthetic route.

These two disadvantages can be avoided by introducing functional groups more efficiently onto the BODIPY core, for example, by using C–H functionalization reactions,[10–12] allowing the synthesis of new fluorophores in a single atom economical step. In the last few years, a handful of examples of such direct derivation reactions for boron dipyrrins have been described, namely, nucleophilic substitution of hydrogen[13] and palladium-catalyzed C–H arylation[14] at the 3,5-positions, and palladium-catalyzed C–H alkenylation[15] and C–H arylation[16] and iridium-catalyzed borylation[17] at the 2,6-positions. Most of these developed direct functionalization reactions are based on C–H activation and require rather forcing conditions to overcome the inertness of a C–H bond. Unfortunately, an appreciable amount of decomposition of the BODIPY substrate may occur under harsh reaction conditions, reducing the obtained yield, complicating purification, and limiting the substrate scope.

In contrast, because of the high reactivity of radical species as compared with the reagents used in C–H activation reactions, radical C–H functionalization can take place under mild conditions. In this way, the problems associated with C–H activation of boron dipyrromethenes can be avoided. Recently, our group had demonstrated this by developing a radical C–H arylation at the 3,5-positions, based on the ferrocene-catalyzed reduction of aryldiazonium salts.[18] This proved to be a versatile, general, high-yielding method for the synthesis of brightly fluorescent 3,5-diarylated and 3-monoarylated BODIPY dyes.

Most reactions to functionalize BODIPY fluorophores described so far are arylation, alkenylation, or alkynylation reactions. Up to this point, only three alkylation reactions have been described. The first two alkylation reactions are both nucleophilic substitutions of hydrogen using carbon nucleo-

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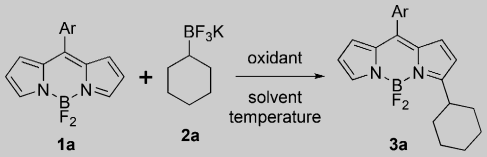
[**] *BODIPY = boron-dipyrromethene*

*Supporting information for this article (containing experimental procedures, characterization data (^{1}H and ^{13}C NMR spectra, absorption and emission spectra of all new compounds), a table with the solid state fluorescence properties of the powders of the cyclohexylated dyes **4**, **5** and **6a** and the crystallographic data of tetracyclohexyl-BODIPY **6a**) is available on the WWW under http://dx.doi.org/10.1002/chem.201500938.*

philes.[13] Although these methods use relatively mild conditions, the scope is rather limited because only enolates can react in this type of transformation. The last reported alkylation reaction uses a Negishi reaction between organozinc reagents and halogenated boron dipyrromethenes to introduce simple primary alkyl groups.[19] In the case of secondary alkyl groups, isomerization occurred to form a mixture of compounds. Further disadvantages of this alkylation method are the need for dry reaction conditions and the use of halogenated boron dipyrrins, which require extra steps and unstable halogenated pyrrole intermediates.

A more general and straightforward alkylation of BODIPY dyes could be possible with a radical C–H alkylation reaction.[11] Possible radical precursors for this transformation are boronic acids as well as potassium trifluoroborates. Both these compounds are known to decompose into radicals through a single-electron transfer in the presence of an oxidant.[12,20] Hence, oxidation of alkylboronic acids or potassium alkyltrifluoroborates can form alkyl radicals, and this could prove to be an interesting method to alkylate boron dipyrromethenes. Herein, we report our investigation on the use of stoichiometric alkylboronic acids and potassium alkyltrifluoroborates as radical precursors in a direct C–H alkylation of readily available *meso*-substituted BODIPY dyes **1**.

Table 1. Optimization of the radical C–H alkylation of 8-(2,6-dichlorophenyl)-BODIPY **1a** using potassium cyclohexyltrifluoroborate **2a**.[a,b]



Entry	Oxidant	Solvent	*T* [°C]	*t*	Yield [%][c]
1	$[Mn(OAc)_3]\cdot 2H_2O$	1,2-dichloroethane	50	45 h	52
2[d]	$[Mn(OAc)_3]\cdot 2H_2O$	DMF	50	23 h	77
3	$[Mn(OAc)_3]\cdot 2H_2O$	acetone	50	22.5 h	35
4	$[Mn(OAc)_3]\cdot 2H_2O$	DMSO	50	23 h	30
5	$[Mn(OAc)_3]\cdot 2H_2O$	MeOH	50	22 h	40
6	$[Mn(OAc)_3]\cdot 2H_2O$	toluene	50	19 h	18
7	$K_2Cr_2O_7$	DMF	50	4 d	28
8	$CuCl_2$	DMF	50	4 d	trace
9	$[Ce(NH_4)_4(SO_4)_4]\cdot 2H_2O$	DMF	50	4 d	trace
10	*p*-chloranil	DMF	50	19 h	–[e]
11[f]	$[Mn(OAc)_3]\cdot 2H_2O$	DMF	50	24.5 h	46
12	$[Mn(OAc)_3]\cdot 2H_2O$	DMF	RT	46 h	36
13	$[Mn(OAc)_3]\cdot 2H_2O$	DMF	80	4.5 h	68[g]

[a] Experimental conditions: 8-(2,6-dichlorophenyl)-BODIPY **1a** (0.1 mmol), potassium cyclohexyltrifluoroborate **2a** (1 equiv), oxidant (2.5 equiv), solvent (1 mL), stirring for the indicated time at the indicated temperature. [b] Ar is 2,6-dichlorophenyl. [c] Yields of the isolated product. [d] Highest yielding conditions. [e] No reaction occurred. [f] One equivalent of oxidant was used. [g] Dicyclohexylated side-product **4** (21%) was also isolated.

Results and Discussion

Optimization of the reaction

A well-known example of a single-electron oxidant in the field of radical chemistry is manganese(III) acetate.[21] Hence, this salt is often used for the oxidation of boronic acids and potassium trifluoroborates to generate radicals. This oxidant was consequently used for a trial reaction between 8-(2,6-dichlorophenyl)-BODIPY **1a** and cyclohexylboronic acid **2f**. Cyclohexylation was chosen due to the combination of commercial availability of the starting compound and ease of purification of the desired product. This reaction was carried out in 1,2-dichloroethane at 50 °C, but unfortunately only a trace amount of product was formed after two days. Perhaps oxidation of the boronic acid was inefficient under these conditions. On the other hand, the more electron-rich potassium cyclohexyltrifluoroborate **2a** (Table 1, entry 1) resulted in a more efficient formation of cyclohexyl radicals under the same reaction conditions. Hence, the desired cyclohexyl-BODIPY **3a** was, to our delight, formed in a good yield of 52% after reacting for 45 h at 50 °C.

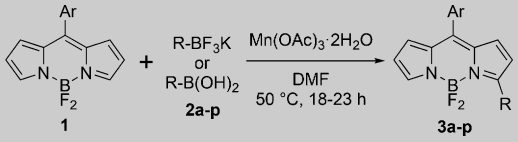
Characterization of the alkylated product **3a** of this reaction revealed that the cyclohexyl radical reacted exclusively at the 3-position of the BODIPY core. Such a high regioselectivity for radical reactions on boron dipyrromethenes has been demonstrated before with our previously published radical C–H arylation.[17] This was explained using the strongly polarizing effect the BF_2 group has on the dipyrromethene core. Furthermore, only a trace amount of the 3,5-dialkylated product **4** was formed during this radical alkylation, demonstrating the very good selectivity of mono- over difunctionalization of this radical C–H reaction.

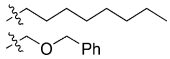
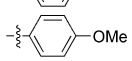
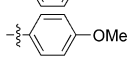
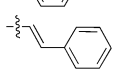
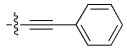
To further improve the yield, the alkylation reaction was tested in various solvents (Table 1, entries 1–6), using different oxidants (Table 1, entries 7–10) and using different amounts of oxidant (Table 1, entry 11). The reaction in DMF using 2.5 equivalents of manganese(III) acetate resulted in the highest yield, providing the desired 3-cyclohexyl-BODIPY **3a** in an excellent yield of 77% after 23 h. Using a slight excess of trifluoroborate resulted in an identical yield. The effect of temperature was also investigated. At room temperature, instead of 50 °C, the cyclohexyl-product **3a** was isolated in a lower yield after a longer reaction time (Table 1, entry 12). A substantial amount of starting material was still present in the crude mixture after 46 h. On the other hand, the reaction was completed in a few hours at 80 °C (Table 1, entry 13). However, dialkylation became significant at this higher temperature, providing 3,5-dicyclohexyl-BODIPY **4** in 21% yield as a side product, which reduced the monoalkylation yield.

Scope of the reaction

With the optimal conditions in hand, we investigated the scope of this radical C–H transformation by executing this reaction with different BODIPY substrates and a range of trifluoroborates (Table 2). Different *meso*-substituted boron dipyrromethenes **1a–e** could be cyclohexylated, providing the alkylated product **3a–e** in a good to excellent yield (Table 2, en-

Table 2. Scope of the radical C–H functionalization of BODIPY fluorophores using potassium trifluoroborates and boronic acids.[a]



Entry	Compound	Ar	R	*t* [h]	Yield [%][b]
1	**a**	2,6-dichlorophenyl		23	77
2	**b**	phenyl		19	60
3	**c**	mesityl		19.5	50
4	**d**	4-nitrophenyl		18.5	58
5	**e**	methylthio		18.5	44
6[c]	**f**	2,6-dichlorophenyl		20	67
7	**g**	2,6-dichlorophenyl		19	60
8	**h**	2,6-dichlorophenyl		19	76
9	**i**	2,6-dichlorophenyl		20	trace[d]
10	**j**	2,6-dichlorophenyl		18	–[e]
11	**k**	2,6-dichlorophenyl		20	51
12	**l**	2,6-dichlorophenyl		18.5	57
13	**m**	2,6-dichlorophenyl		22.5	42
14	**n**	2,6-dichlorophenyl		18	42
15[c]	**o**	2,6-dichlorophenyl		20	34
16	**p**	2,6-dichlorophenyl		19	20
17	**q**	2,6-dichlorophenyl		19	–[f]

[a] Experimental condition: BODIPY **1** (0.1 mmol), potassium alkyltrifluoroborate **2** (1 equiv), $[Mn(OAc)_3]\cdot 2H_2O$ (2.5 equiv), DMF (1 mL), stirring for the indicated time at 50 °C. [b] Yield of the isolated product. [c] Corresponding boronic acid was used instead of the potassium trifluoroborate. [d] Formation of alkylated product observed by using mass spectrometry (EI mode). [e] Product was formed, as detected by using mass spectrometry (EI mode), but was not stable under the reaction condition and decomposed. [f] No reaction occurred.

tries 1–5). The product formed from *meso*-(methylthio)-BODIPY **1e** is interesting, because its thioether substituent provides an opportunity to further functionalize this alkylated dye.[9] Not only cyclohexylation is possible, as both tertiary and acyclic secondary alkyltrifluoroborates were reactive under these conditions, producing 3-*tert*-butyl-BODIPY **3g** (Table 2, entry 7) and 3-*sec*-butyl-BODIPY **3h** (Table 2, entry 8) in a straightforward fashion in similar yields. Unfortunately, a primary organoboron compound, such as potassium octyltrifluoroborate **2i** (Table 2, entry 9), did not give the expected product under these conditions. Only a trace amount of the desired 3-octylboron dipyrrin **3i** was detected. Such a low reactivity of primary trifluoroborates in these type of reactions has been described before.[19b] This can be attributed to the more difficult oxidation of primary organoboron compounds as compared with secondary and tertiary derivatives. Hence, if an electron-donating group is present to increase the electron density of the α-carbon, such a limited formation of the alkyl radical through oxidation should not be a problem. Indeed, the use of potassium benzyloxymethyltrifluoroborate **2j** resulted in the formation of the expected 3-(benzyloxymethyl)-BODIPY dye **3j** (Table 2, entry 10). To our regret, this alkylated fluorophore proved to be unstable under the used reaction conditions and was lost during the reaction. The scope of this radical transformation is not limited to simple unfunctionalized alkyl groups: trifluoroborates bearing an ester group (**2k** and **2l**) reacted to form ester functionalized BODIPY dyes (**3k** and **3l**) in good yield (Table 2, entries 11 and 12). These experiments illustrate the generality of this radical C–H reaction. When we compared the results to other reported alkylation reactions of boron dipyrromethenes[13,18] it becomes apparent that this radical alkylation possess a significantly broader scope. Thus, a great variety of alkylated BODIPY fluorophores can be synthesized using a simple protocol without the need for reactive boron dipyrrin derivatives.

Potassium alkyltrifluoroborates are not the only known type of trifluoroborates: Aryl, alkenyl and alkynyl derivatives can also be prepared. Subsequently, we investigated the reactivity of these substrates under the optimized conditions. Using potassium aryltrifluoroborates **2m**–**n**, we synthesized the corresponding 3-aryl-BODIPYs **3m**–**n** in moderate yield (Table 2, entries 13 and 14). These yields are not competitive with those obtained by using our previously reported C–H arylation methodology,[18] although this reaction could still prove to be a useful alternative. Also, a reaction was observed in the case of potassium trans-β-styryltrifluoroborate **2p**. Unfortunately, because of the nature of the radical reaction, isomerization of the double bond takes place. Accordingly, a mixture of *cis*- and *trans*-3-styryl-BODIPY was isolated in 39% yield, with a *cis*/*trans* ratio of 16:84. After a crystallization of this mixture, pure *trans*-3-styryl-BODIPY **3p** was obtained in a yield of 20% (Table 2, entry 14). Thus, this is not a very effective reaction compared with the direct alkenylation procedure previously reported by our group.[13b] Lastly, the reactivity of potassium(phenylethynyl)trifluoroborate **2q** was tested, but regrettably no C–H alkynylation reaction took place (Table 2, entry 17).

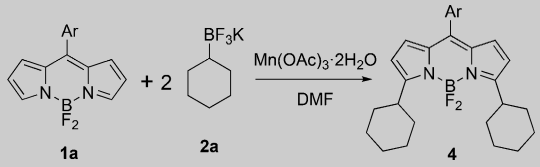
Because of the greater availability of boronic acids, we wanted to revisit their application under our optimized conditions. Hence, the use of boronic acids as the radical precursor for the functionalization of boron dipyrrins was tested once more. To our delight, the use of cyclohexylboronic acid **2f** under these conditions resulted in the formation of the desired 3-cyclohexyl-BODIPY **3f** in a good yield (Table 2, entry 6). How-

ever, the resulting yield was 10% lower than when potassium cyclohexyltrifluoroborate **2a** was used. This lower yield is presumably due to the less-efficient oxidation of a boronic acid as compared with a more electron-rich trifluoroborate, as described above. Similarly, using 4-methoxyphenylboronic acid **2o** the corresponding 4-methoxyphenyl-BODIPY **3o** could be synthesized in an 8% lower yield than the trifluoroborate example (Table 2, entry 14 and 15). Lastly, the pinacol ester of cyclohexylboronic acid was investigated as a radical source under our optimized condition, unfortunately after 42 h only a trace amount of the 3-cyclohexyl-BODIPY **3f** was formed.

Extension to di-, tri-, and tetraalkylation

When studying the effect of temperature on the radical monoalkylation reaction (see above), we observed that dialkylation became significant at a higher temperature. Consequently, the reaction was no longer selective for monoalkylation at this temperature. Accordingly, we investigated if this radical reaction could be modified to allow dialkylation using 2 equivalents of potassium cyclohexyltrifluoroborate **2a** to effectively synthesize 3,5-dicyclohexyl-BODIPY **4**. To this end, the C–H dialkylation reaction was executed at higher temperatures (Table 3). As the temperature increases, the reaction time decreases and the yield of the dicyclohexyl product **4** increases. The reaction is completed after 2 h at 80 °C, providing the 3,5-dicyclohexyl fluorophore **4** in an excellent yield of 92% (Table 3, entry 4). However, at even higher temperatures, decomposition of the starting compound **1a** became problematic, causing an in situ excess of trifluoroborate **2a** and hence a significant formation of tricyclohexyl-BODIPY **5**. This, combined with a rather difficult separation due to the extra side products being formed in this case, resulted in a drastically lower yield when the reaction was complete at 90 °C (Table 3, entry 5).

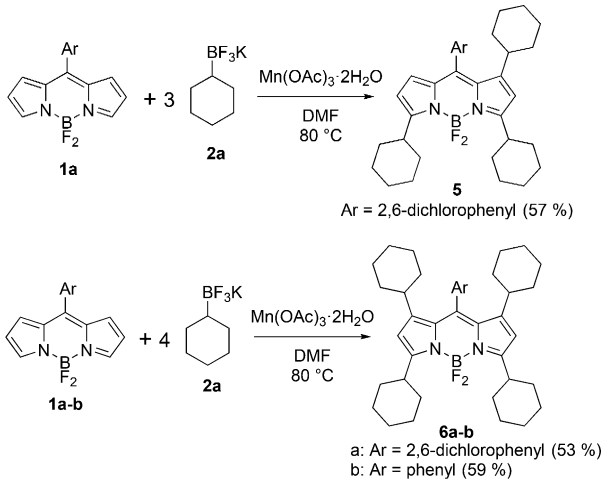
Table 3. Optimization of the radical C–H dialkylation of 8-(2,6-dichlorophenyl)-BODIPY **1a** using potassium cyclohexyltrifluoroborate **2a**.[a,b]



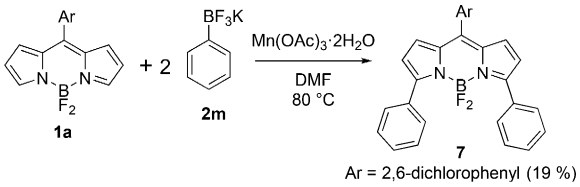
Entry	*T* [°C]	*t*	Dialkylation yield [%][c]
1	50	45 h	23
2	60	44 h	64
3	70	21 h	86
4[d]	80	2 h	92
5	90	45 min	14

[a] Experimental condition: 8-(2,6-dichlorophenyl)-BODIPY **1a** (0.1 mmol), potassium cyclohexyltrifluoroborate **2a** (2 equiv), $[Mn(OAc)_3]\cdot 2H_2O$ (5 equiv), DMF (1 mL), stirring for the indicated time at the indicated temperature. [b] Ar is 2,6-dichlorophenyl. [c] Yields of the isolated products. [d] Highest yielding conditions.

When the dialkylation reaction was complete at 80 °C (Table 3, entry 4), trace amounts of tricyclohexyl-BODIPY **5** and tetracyclohexyl-BODIPY **6a** were formed as well as the main dicyclohexyl product **4**. At 90 °C, an even higher amount of tri- and tetracyclohexylated dyes were formed. However, because of the increased decomposition and side-product formation in this case, the complete purification of these products was not possible. Still, by using a higher amount of potassium cyclohexyltrifluoroborate **2a**, the reaction at 80 °C could be modified to allow further alkylation of the boron dipyrromethene core (Scheme 1). Thus, treatment of 8-(2,6-dichlorophenyl)-BODIPY **1a** with 3 equivalents of the organoboron compound **2a** resulted in the formation of 1,3,5-tricyclohexyl-BODIPY **5** in a yield of 57%. On the other hand, using 4.5 equivalents of the same trifluoroborate **2a** gave 53% of 1,3,5,7-tetracyclohexyl-BODIPY **6a**. Similarly, 8-phenyl-BODIPY **1b** could be tetraalkylated in a comparable yield. It should be mentioned that the tetracyclohexylation of 8-phenyl-BODIPY **1b** was significantly faster than the reaction of the more sterically hindered 8-(2,6-dichlorophenyl) derivative **1a**, with the reaction being completed in 3.5 h for the 8-phenyl dye **1b** and in 19.5 h for the dichlorophenyl dye **1a**. Hence, this radical transformation allows the synthesis of boron dipyrrin dyes with multiple *sec*-alkyl substituents, such as 1,3,5,7-tetracyclohexyl-BODIPYs **6**. The synthesis for these compounds has not been described previously. Characterization of the formed 1,3,5,7-tetracyclohexyl-BODIPY **6a** using X-ray diffraction (see below) showed that the cyclohexyl radical reacted exclusively at the 1,7-positions once the 3,5-positions were occupied. To investigate if the 2,6- or 8-positions are at all reactive towards radicals, the less sterically hindered 1,3,5,7-tetramethyl-BODIPY was subjected to the developed radical alkylation condition with potassium cyclohexyltrifluoroborate **2a**. Despite that the 2,6- and 8-positions are unsubstituted in this molecule, no reaction was observed and the starting material was recovered. This once more illustrates the high selectivity of these radical reactions.



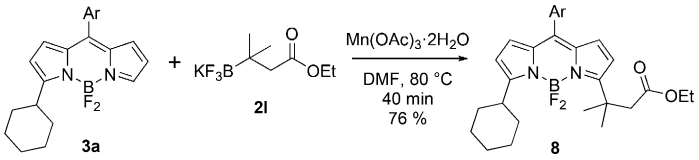
Scheme 1. Tri- and tetraalkylation of *meso*-substituted BODIPY dyes **1** using an excess of potassium cyclohexyltrifluoroborate **2a** at higher temperatures.



Scheme 2. Diarylation of 8-(2,6-dichlorophenyl)-BODIPY **1a** using an excess of potassium phenyltrifluoroborates **2m**.

Difunctionalization at higher temperatures could also be applied for the radical C–H arylation using 2 equivalents of potassium phenyltrifluoroborates **2m** at 80 °C. In this way, 3,5-diphenyl-BODIPY **7** was synthesized in an admittedly low yield (Scheme 2). This once more indicates the superiority of our previously reported radical arylation method, at least in the case of direct arylation.[18] Using an excess of 4.5 equivalents of organoboron compound **2m** did not improve the yield of fluorophore **7**, and the formation of tri- or tetraarylated dyes was not detected.

Lastly, the increased reactivity at higher temperatures can also be exploited to allow the synthesis of an asymmetric dye bearing two different alkyl groups. When 3-cyclohexyl-BODIPY **3a** was treated with 1 equivalent of ester functionalized trifluoroborate **2l** at 80 °C for 40 min, the desired asymmetrically substituted fluorophore **8** was isolated in an excellent yield of 76% (Scheme 3). The synthesis of such an asymmetrically dialkylated derivative bearing a functional group would be rather



Scheme 3. Synthesis of an asymmetrically alkylated BODIPY fluorophore (Ar = 2,6-dichlorophenyl).

difficult with previously reported methodologies. Hence, this example illustrates the potential of this new radical C–H alkylation reaction, because it allows the synthesis of sophisticated dyes using a simple, straightforward procedure.

Crystal structure determination of 1,3,5,7-tetracyclohexyl-BODIPY 6a

The tetracyclohexyl compound **6a** crystallizes in the non-centrosymmetric space group $P2_12_12_1$ with one molecule and one dichloromethane solvent molecule in the asymmetric unit. The cyclohexyl groups are located at the 1,3,5- and 7-positions of the BODIPY core (Figure 1). Inside the crystal packing, dichloromethane is located in a void of 17.8 Å^3, between four BODIPY molecules. It interacts with one molecule, by non-classical hydrogen bonding with the fluorine atoms located on the boron, with donor–acceptor distances of C40···F1: 3.474(4) and C40···F2: 3.108(4) Å, respectively. C–H···Cl interactions are observed, with carbon–chloride distances ranging between

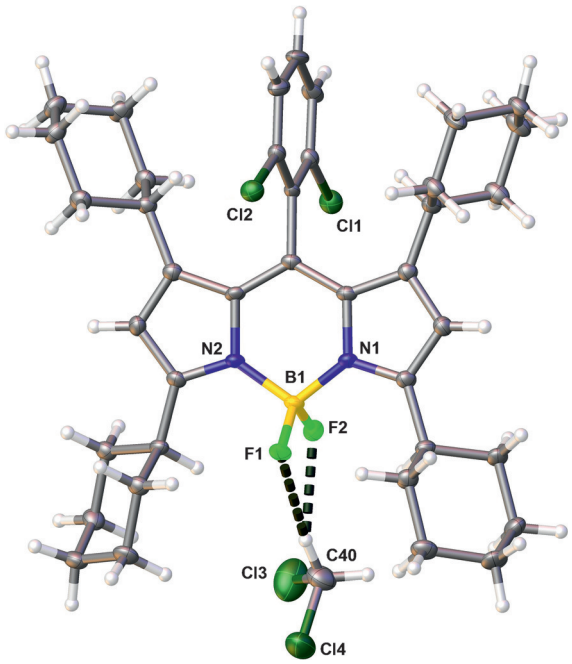


Figure 1. The molecular structure of 1,3,5,7-tetracyclohexyl-BODIPY **6a** as determined by X-ray diffraction.

3.585(3) and 3.633(3) Å. Two intermolecular interactions between the different BODIPY compounds are observed between Cl2 and hydrogens of the cyclohexane ring, with carbon–chloride distances of Cl2···C13: 2.695(3) and Cl2···C20: 3.675(3) Å. The particular location of the dichloromethane and the effect of the bulky cyclohexyl substituents make it impossible for these BODIPY molecules to form π-stacking interactions between each other, thus limiting aggregation-induced fluorescence quenching. This explains the fluorescent behavior of this compound **6a** in the solid state (see below). In contrast, π-stacking is clearly observed in boron dipyrromethenes lacking bulky substituents, resulting in a quenching of the solid-state fluorescence.[22]

UV/Vis Spectroscopic properties

Spectroscopic properties of newly synthesized compounds were studied in five solvents and overall typical BODIPY features were observed (Table 4). In the absorption spectra, regardless of solvent polarity and alkylation pattern, it was possible to observe a very sharp main absorption band usually centered between 500 and 525 nm attributed to $S_1 \leftarrow S_0$ transition. A secondary, broader and less intense band around 300 and 400 nm from the $S_2 \leftarrow S_0$ transition was also observed. Regarding fluorescence, emission peaks were around 520 and 540 nm, resulting in rather small Stokes shifts between 230 and 1170 cm^{-1}.

Overall, absorption and emission of *meso*-dichlorophenyl- and *meso*-nitrophenyl-BODIPYs were some 10 nm redshifted as compared with the more electron-rich *meso*-mesityl and *meso*-phenyl derivatives. Relevant bathochromism in absorption and

Table 4. Photophysical properties of new compounds.

Compound	Solvent[a]	λ [nm]		Stokes	fwhm [cm^{-1}]		Φ_{fl}[b]	Compound	Solvent[a]	λ [nm]		Stokes	fwhm [cm^{-1}]		Φ_{fl}[b]
		Abs.	Emis.		Abs.	Emis.				Abs.	Emis.		Abs.	Emis.	
3a	MeOH	512	524	447	887	955	0.79	**3k**	MeOH	512	524	447	854	948	0.86
	MeCN	511	525	521	908	936	0.80		MeCN	511	524	485	899	952	0.89
	EtOAc	514	526	443	837	954	0.82		EtOAc	513	526	482	865	963	0.73
	THF	515	528	478	855	955	0.84		THF	515	528	478	874	967	0.84
	toluene	518	531	477	817	970	0.84		toluene	518	532	508	842	988	0.75
3b	MeOH	502	517	578	951	1048	0.03	**3l**	MeOH	513	527	517	840	1016	0.85
	MeCN	501	516	580	989	1065	0.02		MeCN	512	525	484	912	1001	0.84
	EtOAc	503	519	613	888	956	0.04		EtOAc	514	527	480	831	1016	0.87
	THF	504	520	610	976	1138	0.04		THF	516	530	412	872	1014	0.67
	toluene	507	522	567	881	1077	0.08		toluene	518	532	508	833	1061	0.82
3c	MeOH	502	512	389	847	868	0.99	**4**	MeOH	523	533	359	689	834	0.72
	MeCN	502	513	427	895	856	0.99		MeCN	522	534	430	672	810	0.76
	EtOAc	503	514	425	826	865	0.78		EtOAc	524	536	427	660	825	0.66
	THF	505	515	384	854	883	0.84		THF	525	536	391	683	853	0.71
	toluene	507	518	419	810	860	0.93		toluene	528	538	352	641	839	0.99
3d	MeOH	508	535	976	1456	1699	0.00	**5**	MeOH	520	529	327	703	840	0.75
	MeCN	508	539	1115	1335	1557	0.00		MeCN	519	528	328	710	830	0.85
	EtOAc	509	541	1162	1283	1447	0.01		EtOAc	521	530	326	697	845	0.88
	THF	511	535	878	1273	1322	0.01		THF	522	532	360	691	889	0.65
	toluene	515	547	1136	1177	1452	0.01		toluene	524	533	322	652	869	0.78
3e	MeOH	501	532	1163	2021	949	0.46	**6a**	MeOH	519	528	328	642	799	0.81
	MeCN	500	531	1168	1799	983	0.44		MeCN	518	526	294	663	793	0.83
	EtOAc	502	532	1123	1888	912	0.56		EtOAc	518	530	437	640	800	0.88
	THF	504	534	1097	1873	939	0.54		THF	521	529	290	663	815	0.79
	toluene	509	538	1042	1864	957	0.60		toluene	523	531	288	618	798	0.99
3g	MeOH	512	523	411	846	1025	0.92	**6b**	MeOH	506	513	270	691	790	0.65
	MeCN	511	525	522	867	1025	0.96		MeCN	505	512	271	694	796	0.65
	EtOAc	513	526	482	817	1031	0.95		EtOAc	506	513	270	678	768	0.69
	THF	515	529	514	845	1035	0.79		THF	508	514	230	662	789	0.59
	toluene	517	530	474	810	1029	0.73		toluene	510	517	265	648	769	0.71
3h	MeOH	511	523	449	948	968	0.82	**8**	MeOH	521	532	397	700	1016	0.83
	MeCN	510	523	487	961	968	0.98		MeCN	521	530	326	717	999	0.84
	EtOAc	512	524	447	852	983	0.94		EtOAc	523	533	358	702	1016	0.91
	THF	514	527	480	902	976	0.76		THF	523	534	394	735	1015	0.74
	toluene	517	528	403	882	989	0.63		toluene	526	536	355	698	1059	0.69

[a] Solvents are listed in descending order of ionizing power according to the Dimroth–Reichardt index. [b] Φ Determined versus fluorescein in 0.1 M NaOH(aq) ($\Phi = 0.90$, $\lambda_{exc} = 488$ nm) as a reference.

emission spectra of styryl and aryl-substituted BODIPYs **3m**, **3n**, **3p**, and **7** was previously reported.[13b,23] On the other hand, no significant spectral shift was observed for the new alkylated BODIPYs. Depending on the solvent, a small variation of 5–8 nm of both absorption and emission peaks was observed, with apolar solvents resulting in a slightly larger red-shift.

As expected, the fluorescence efficiency was highly influenced by the substituent at the *meso* position, as higher quantum yields were observed for 2,6 dichlorophenyl- (**3a**) and mesityl- (**3c**) substituted dyes as compared with *meso*-phenyl (**3b**) and *meso*-nitrophenyl (**3d**) dyes. The free rotation of the phenyl and the nitrophenyl group results in a non-radiative decay of the excited state,[24] whereas such rotation is sterically hindered by chlorine atoms in **3a** and methyl groups in **3c**. A particularly interesting observation is the fluorescence quantum yield of the tetracyclohexylated compound **6b**, which was roughly 10 to 30 times higher than the one observed for the unsubstituted dye **3b**. The bulky cyclohexyl groups added at positions 1 and 7 of the BODIPY core, in fluorophore **6b**, hamper the free rotation of the phenyl ring and consequently diminish the rate of non-radiative decay. Hence, introduction of these bulky groups is an interesting strategy to increase the fluorescence quantum yield of boron dipyrrins at a later stage of their synthesis. Excluding this aforementioned exception, the effect of alkylations on the quantum yield was rather limited and, in general, the usually desired high fluorescence quantum yields were maintained.

Fluorescence of boron dipyrrins in diluted solution is a well-known phenomenon. Solid-state emissive BODIPYs, on the

other hand, are far less commonly reported.[25] Nevertheless, such solid-state emissive dyes are interesting compounds with several applications in the field of optoelectronics, including organic light-emitting diodes[26] and organic photovoltaic devices.[5,6] The scarcity of solid-state emissive BODIPY dyes is due to the typical planarity of these fluorophores favoring intermolecular π–π interactions resulting in non-fluorescent aggregates.[23] In this regard, the introduction of bulky substituents onto the BODIPY structure can be used to weaken the intermolecular π-stacking forces (see above), consequently diminishing aggregation-induced fluorescence quenching and thus enabling solid-state fluorescence.[23,27]

Because of the bulky character of a cyclohexyl substituent, insertion of this large moiety is a feasible approach for the formation of solid-state emissive BODIPYs. Hence, the emission spectra in the solid state of the powders of the cyclohexylated compounds **3a**, **4**, **5**, and **6a**, with one, two, three, and four bulky alkyl groups, respectively, were studied (Figure 2). The results show that whereas a BODIPY dye bearing only one cyclohexyl group (**3a**) was virtually non-fluorescent in the solid state, introduction of extra cyclohexyl substituents onto the boron dipyrromethene core (in compounds **4**, **5**, and **6a**) resulted in solid-state emission. The emission spectra of compounds **5** and **6a** show that the solid-state emission is roughly 60 nm redshifted compared with the emission in solution, whereas for the dicyclohexyl compound **4** this shift is about 70 nm (the Supporting Information, Table S1). This indicates at a less efficient prevention of π-stacking in the dicyclohexyl dye **4** as compared with the tri- and tetracyclohexyl derivatives. The absolute quantum yields of these powders were determined to be 0.14, 0.10, and 0.11 for compounds **4**, **5**, and **6a**, respectively (the Supporting Information, Table S1). The above results clearly highlight the utility of the described radical alkylation method, as it readily gives access to solid-state emissive dyes by introducing multiple bulky alkyl substituents onto the BODIPY core in one reaction step. In contrast, preparation of the few solid-state emissive boron dipyrrins currently described in literature require a longer synthetic route.[25]

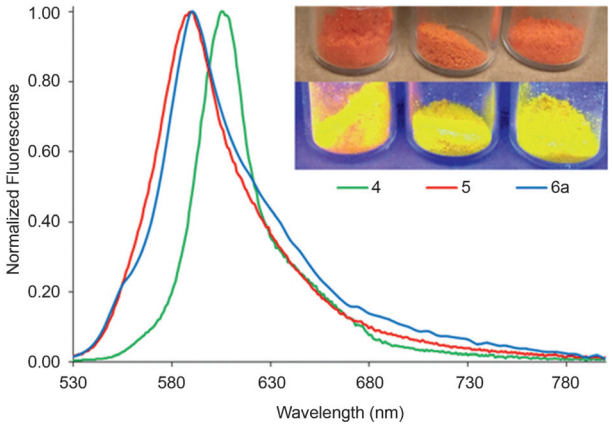


Figure 2. Normalized emission spectra of cyclohexylated compounds **4**, **5**, and **6a** in powder form. The inset shows the photograph of the powders of compounds **4** (left), **5** (middle), and **6a** (right) without UV irradiation (above) and with UV irradiation at 360 nm (below).

Conclusion

A versatile, straightforward, and general method for the radical C–H functionalization of BODIPY dyes, based on the oxidation of boronic acids and potassium trifluoroborates with manganese(III) acetate, has been developed and investigated. This reaction proved to be a powerful tool for the alkylation of these fluorophores, allowing a broad range of alkyl groups to be introduced onto the boron dipyrromethene core. This transformation also shows limited applicability for the arylation and alkenylation of these dyes. Furthermore, this method can be modified to synthesize previously unavailable, tri-, and tetraalkylated BODIPY fluorophores as well as asymmetrically alkylated derivatives. In this way, multiple bulky cycloalkyl groups can be introduced onto the core structure, which was shown to be an interesting approach to obtain solid-state emissive BODIPY dyes in one reaction step. In other words, this new radical reaction opens up new possibilities for the synthesis of new and sophisticated dyes, while avoiding a tedious synthesis of substituted pyrrole building blocks as well as preventing unstable intermediates.

Experimental Section

Chemicals were purchased from Acros Organics and Sigma Aldrich, and used as received. 8-Arylated BODIPY dyes were prepared according to published literature procedures, through a water-based dipyrromethane synthesis followed by oxidation and condensation.[13b] Non-commercial potassium trifluoroborates were synthesized by literature procedures.[19a,28] 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. All reactions were carried out under a nitrogen atmosphere.

^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance 300 instrument operating at a frequency of 300 MHz for ^{1}H and 75 MHz for ^{13}C. In the case of ambiguous assignments, spectra were run on a Bruker 400 or Bruker 600. ^{1}H NMR spectra in $CDCl_3$ and [D_6]DMSO were referenced to tetramethylsilane ($\delta = 0.00$ ppm) as an internal standard. ^{13}C NMR spectra in $CDCl_3$ were referenced to the $CDCl_3$ ($\delta = 77.16$ ppm) signal. ^{13}C NMR spectra in [D_6]DMSO were referenced to the [D_6]DMSO ($\delta = 39.52$ ppm) signal. ^{19}F NMR spectra were referenced to external $CFCl_3$ ($\delta = 0.00$ ppm). ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$ ($\delta = 0.00$ ppm) with a negative sign indicating an upfield shift. Because of the small coupling constants in pyrroles and pyrrolic dyes, the multiplicity of the signals is often unclear. In these cases, NMR signals often appear as singlets, which they are not. Mass spectra were recorded on a Hewlett–Packard 5989 A mass spectrometer (EI mode and CI mode). High-resolution mass data were obtained with a Kratos MS50TC instrument. Melting points were taken on a Reichert Thermovar and are uncorrected.

Single crystals of tetracyclohexyl-BODIPY **6a**, suitable for X-ray diffraction were obtained by slow diffusion of methanol into a dichloromethane solution of the compound at room temperature over a one week period. X-ray intensity data were collected at 100 K on an Agilent Supernova diffractometer, equipped with an Atlas CCD detector, using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The

images were interpreted and integrated with the CrysAlisPro software from Agilent Technologies.[29] Using Olex2,[30] the structure was solved with the ShelxS[31] structure solution program using Direct Methods and refined with the ShelxL[30] refinement package using full-matrix least squares minimization on F^2. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors were fixed at 1.2 times U_{eq} of the parent atoms (1.5 for methyl groups). CCDC-1051771 (**6a**) 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.

Absorption spectroscopy was performed in a PerkinElmer Lambda 40 UV/Vis spectrophotometer and fluorescence emission spectra were obtained in a SPEX Fluorolog fluorimeter with excitation in 488 nm. Relative fluorescence quantum yields were calculated using diluted samples and a fluorescein standard (fluorescein in 0.1 M NaOH(aq): $\Phi = 0.90$, $\lambda_{exc} = 488$ nm). The quantum yield of the tested compound (Φ_x) was calculated using Equation (1), in which Φ_{st} is the quantum yield of the standard, F_x and F_{st} are integrated fluorescence of the test compound and the standard ($\lambda_{exc} =$ 488 nm), A_x and A_{st} are the absorbance of the test compound and the standard at 488 nm, and n_x and n_{st} are the refractive indexes of the solvents in which the test compound and standard were diluted in.

$$\Phi_x = \Phi_{st}\left[\frac{F_x/A_x}{F_{st}/A_{st}}\right]\left[\frac{n_x}{n_{st}}\right]^2 \quad (1)$$

Solid-state fluorescence spectroscopy of the powders was performed in an Edinburgh FLS980 fluorescence spectrometer with excitation in 485 nm and absolute fluorescence quantum yields were obtained with the same equipment using the integrating sphere accessory.

General radical C–H monofunctionalization procedure

BODIPY **1** (0.1 mmol), the organoboron compound **2a–p** (0.1 mmol, 1 equiv) and $[Mn(OAc)_3]\cdot 2H_2O$ (0.25 mmol, 2.5 equiv) were dissolved in DMF (1 mL). The reaction mixture was heated at 50 °C and stirred for the indicated time. Upon completion, this was cooled to room temperature. Subsequently, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified chromatographically.

General radical C–H difunctionalization procedure

BODIPY **1** (0.1 mmol), the organoboron compound **2a** or **2m** (0.2 mmol, 2 equiv) and $[Mn(OAc)_3]\cdot 2H_2O$ (0.5 mmol, 5 equiv) were dissolved in DMF (1 mL). The reaction mixture was heated at 80 °C and stirred for the indicated time. Upon completion, this was cooled to room temperature. Subsequently, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified chromatographically.

General radical C–H trialkylation procedure

BODIPY **1** (0.1 mmol), the organoboron compound **2a** (0.3 mmol, 3 equiv) and $[Mn(OAc)_3]\cdot 2H_2O$ (0.75 mmol, 7.5 equiv) were dissolved in DMF (1 mL). The reaction mixture was heated at 80 °C and stirred for the indicated time. Upon completion, the mixture was cooled to room temperature. Subsequently, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified chromatographically.

General radical C–H tetraalkylation procedure

BODIPY **1** (0.1 mmol), the organoboron compound **2a** (0.45 mmol, 4.5 equiv) and $[Mn(OAc)_3]\cdot 2H_2O$ (1.1 mmol, 11 equiv) were dissolved in DMF (2 mL). The reaction mixture was heated at 80 °C and stirred for the indicated time. Upon completion, this was cooled to room temperature. Subsequently, the crude mixture was poured in diethyl ether (100 mL), washed three times with water (100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified chromatographically.

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Keywords: alkylation · boron · dyes · photophysics · radicals

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