C–H Arylation

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Radical C–H Arylation of the BODIPY Core with Aryldiazonium Salts: Synthesis of Highly Fluorescent Red-Shifted Dyes**

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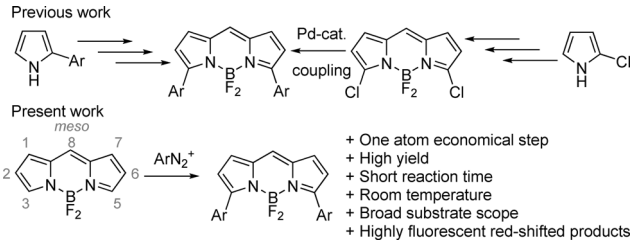
Abstract: *We describe herein the first radical C–H arylation of BODIPY dyes. This novel, general, one-step synthetic procedure uses ferrocene to generate aryl radical species from aryldiazonium salts and allows the straightforward synthesis of brightly fluorescent ($\Phi > 0.85$) 3,5-diarylated and 3-monoarylated boron dipyrrins in up to 86 % yield for a broad range of aryl substituents. In this way, new and complex dyes with red-shifted spectra can be easily prepared.*

Over the last two decades, BODIPY dyes (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacenes)[1,2] have become increasingly valuable fluorophores. The growing success of this class of compounds is attributed to their many excellent characteristics, including bright fluorescence and their vast potential for functionalization leading to sophisticated dyes with fine-tuned properties.[3] The numerous applications being reported for these dyes illustrate the importance of these interesting compounds.[4]

Most derivation strategies for synthesizing new boron dipyrrins either start from suitably functionalized pyrroles[5] or use reactive BODIPY dyes[6,7] (Scheme 1). However, these two methodologies tend to suffer from the use of unstable intermediates and/or the need for a long synthetic route. A more efficient method of introducing functional groups is by C–H functionalization reactions,[8,9] allowing the synthesis of new dyes in a single atom economical step. A few examples of such direct derivatization reactions for these fluorophores are currently known,[10,11] most of which require rather forcing reaction conditions to overcome the inertness of the C–H bond which limits the scope and the obtained yield.

In contrast, radical C–H functionalization can occur under mild conditions, owing to the high reactivity of radicals.[9,12] However, radical functionalization of boron dipyrromethenes is virtually unknown. Up to this point only one example, proposed to occur through an electrophilic radical species, has been reported in a low yield.[13] Until now, radical arylation of boron dipyrrins has not been described, despite the obviously desirable bathochromic spectral shift it



Scheme 1. Summary of synthetic pathways toward arylated BODIPY dyes.

can introduce. Aryldiazonium salts are one of the well-known sources of aryl radicals through a homolytic dediazoniation mechanism, mostly achieved by means of a reduction (Scheme S1, Supporting Information, SI).[14] Likewise, the use of aryldiazonium salts for the arylation of readily available *meso*-substituted BODIPY dyes **1** could prove to be an interesting alternative for synthesizing new derivatives of this fluorophore. Hence, we set out to investigate the feasibility of this novel radical reaction.

As an initial experiment 8-(2,6-dichlorophenyl)-BODIPY **1** was reacted with excess benzenediazonium tetrafluoroborate **2a** and one equivalent of copper(I) chloride at room temperature. After 25 h the desired diphenylated compound **3a** was obtained in a low yield of 13 % (Table S1, entry 2). Characterization of the formed products showed that the phenyl radicals reacted exclusively at the 3,5-positions of the boron dipyrromethene core. This selectivity can be compared with the exclusive 2-addition of radical species to electron-deficient alkenes, in which the electron-withdrawing group is stabilizing the newly formed radical species. In this case, after addition to the 3-position of one pyrrole moiety, and delocalization over several double bonds, the imine part of the adjacent pyrroline, aided by the complexed boron, is causing an increased stability of the formed radical (Scheme S1). Moreover, such a high selectivity in radical reactions is also known for protonated heteroaromatic bases.[12] This is accounted for by the strong increase in polarity of these heteroaromatic bases when protonated, causing polar effects to determine the outcome of the reaction. A similar reason can be used to rationalize the observed selectivity in the radical C–H arylation of the BODIPY core, because the BF_2 group can be seen as a strongly polarizing Lewis acid complexed with a dipyrromethene base.

The limited yield of the test reaction might be caused by the reductant used, because copper(I) chloride can react with diazonium salts in a Sandmeyer reaction.[15] To improve the yield, other common reducing agents were tried (Table S1, entries 1–11) and the most notable of these experiments was

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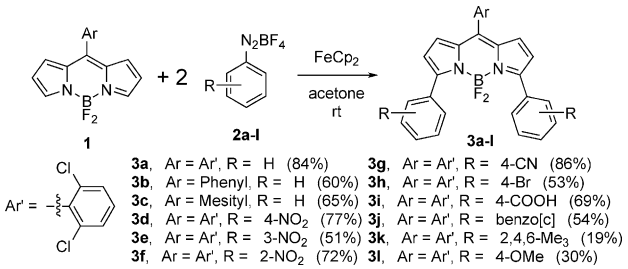
the use of ferrocene ($FeCp_2$), because it gave an immediate reaction although in a moderate yield. The yield in this case was limited due to a significant arylation of the formed ferricinium cation,[16] resulting in the formation of phenylferrocene and diphenylferrocene. To counter this, the ferrocene concentration has to be low (Table S1, entry 12). However, due to insufficient regeneration of the ferrocene catalyst (Table S1, entry 13), this can only be achieved by continuous addition of this reducing agent (Table S1, entries 14–17). The best result was obtained with an addition speed of 0.2 mmol h^{-1} providing the diphenylated product **3a** in less than an hour in an excellent yield of 84%. Further optimization tests afforded no improvement (Table S1, entries 18–25).

Using this optimized condition, the radical C–H arylation was executed with different BODIPY substrates and a range of aryldiazonium tetrafluoroborates (Scheme 2), illustrating the broad scope of this reaction. Different *meso*-substituted

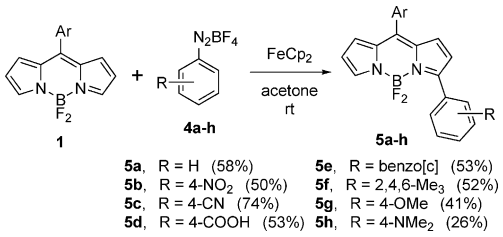


Scheme 2. Generality of the radical C–H diarylation of BODIPY dyes.

amino)benzenediazonium salt **2m** proved to be too electron-rich to be reduced by ferrocene. By using the more reducing decamethylferrocene, reaction did occur. However, after complete reaction only a trace amount of diarylated compound was formed and the monoarylated product **5h** was isolated instead in 35% yield.

These results demonstrate the vast improvement of the present radical C–H arylation compared to previous arylation protocols.[5,11] This new method provides easy access to new compounds in a much shorter reaction time, because most of these radical reactions are completed within one hour. Furthermore, our new procedure supplies compounds in a higher yield in one atom-economical step avoiding the use of multistep synthesis, high reaction temperatures, and unstable pyrrole intermediates.

The procedure developed for diarylation can be modified to allow radical C–H monoarylation (Scheme 3). This is achieved by using one equivalent of diazonium salt instead of

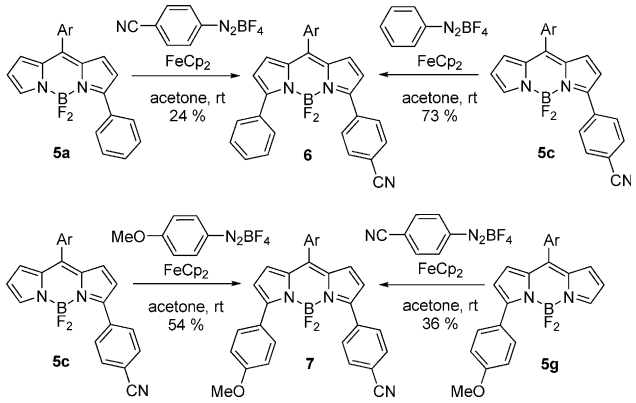


Scheme 3. Generality of the radical C–H monoarylation of BODIPY dyes (Ar = 2,6-dichlorophen-1-yl).

boron dipyrromethenes were reactive in this type of arylation providing the phenylated product **3a–c** in good to excellent yields. The three isomers of nitrobenzenediazonium tetrafluoroborate **2d–f** all yielded the desired compounds **3d–f**, with the directly conjugated 4-nitro and 2-nitro substituents resulting in higher yields in comparison to the cross-conjugated 3-nitro group. Other electron-poor diazonium salts **2g–i** were also reactive under these conditions and gave up to 86% yield. Of particular interest are the bromo **3h** and carboxy products **3i**, because both functionalities allow further derivatization through transition-metal-catalyzed cross-coupling and esterification/amidation reactions, respectively. Moreover, 3,5-bis(4′-carboxyphenyl)-BODIPY **3i** is a water-soluble fluorophore in its deprotonated form, highlighting the capabilities of this C–H arylation, because it provides easy access to water-soluble dyes with red-shifted UV/Vis absorption and emission spectra. Not only electron-poor diazonium salts can be used, because both the ring-fused naphthalene-2-diazonium tetrafluoroborate **2j** and the sterically hindered 2,4,6-trimethylbenzenediazonium tetrafluoroborate **2k** resulted in the 3,5-diarylated compounds **3j–k**. However, the steric hindrance of the latter made this reaction less effective. A three times longer reaction time was needed to give the product **3k** in a low yield of 19%. Lastly, 4-methoxybenzenediazonium salt **2l** gave product **3l** in a moderate yield. This lower yield was probably caused by a reduced reactivity of the more electron-rich monoarylated intermediate, hindering the second arylation step. The 4-(dimethyl-

an excess and simultaneously reducing the amount of ferrocene. In this way, the monoarylated product **5a**, formed by reaction between BODIPY **1** and benzenediazonium tetrafluoroborate **4a**, could be isolated in 58% yield. Similarly, electron-poor diazonium salts reacted in good yields, e.g., up to 74% in the case of 4-cyanobenzenediazonium tetrafluoroborate **4c**. Ring-fused and sterically hindered diazonium salts also resulted in the formation of the desired products with comparable yields. In the case of electron-rich diazonium salts, the resulting yields were unfortunately somewhat lower. Due to the identical reactivity of the 3- and the 5-hydrogens some overarylation occurs in all these examples, producing the diarylated compound **3** as a side product in an estimated yield between 5 and 15%, depending on the used diazonium salt.

Finally, to illustrate the potential of this novel reaction, two asymmetrically substituted dyes (**6** and **7**) were synthesized according to our developed methodology (Scheme 4). The 3-phenylBODIPY **5a** was reacted with excess 4-cyanobenzenediazonium tetrafluoroborate **4c**. Unfortunately, starting compound **5a** was insufficiently soluble in the reaction solvent, causing an incomplete reaction and hence a low yield. When the reaction order was reversed and 3-(4-cyanophenyl)-BODIPY **5c** was combined with benzenediazonium tetrafluoroborate **4a**, this problem was avoided. Thus, the desired 3-(4-cyanophenyl)-5-phenyl-BODIPY **6** was isolated in a good yield of 73%. Compound 3-(4-cyanophenyl)-BODIPY **5c** could also be used in the synthesis of 3-(4-



Scheme 4. Synthesis of asymmetrical 3,5-diarylated BODIPY dyes through radical C–H arylation (Ar = 2,6-dichlorophen-1-yl).

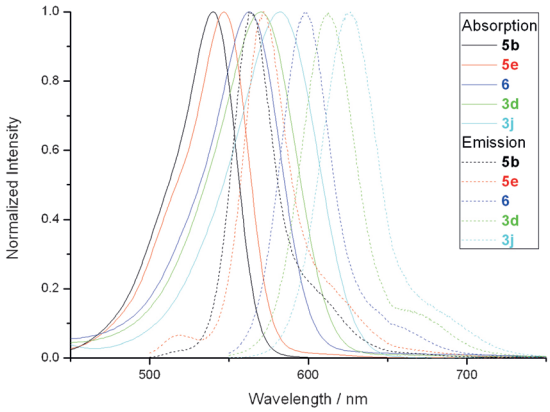


Figure 1. Normalized, visible absorption spectra and corresponding normalized fluorescence emission spectra of a selection of *meso*-(2,6-dichlorophenyl)-substituted BODIPY dyes (**5b**, **5e**, **6**, **3d**, **3j**) in MeCN.

cyanophenyl)-5-(4-methoxyphenyl)-BODIPY **7** through reaction with 4-methoxybenzenediazonium tetrafluoroborate **4g**. The separation of compound **7** from a small amount of starting material **5c** proved very tedious: thus 54% of the product was isolated as pure compound and the rest was lost as mixed column chromatography fractions. The same asymmetrical dye **7** was also prepared from 3-(4-methoxyphenyl)-BODIPY **5g**. However, in analogy with the synthesis of 3,5-di(4-methoxyphenyl)-BODIPY **3l**, compound **5g** was not reactive enough to give a complete conversion resulting in a lower yield. Both synthesized asymmetrical fluorophores described here are compounds that are a challenge to prepare with previously reported methodologies. Hence, the current radical C–H arylation allows the synthesis of sophisticated BODIPY dyes in a straightforward fashion.

BODIPY dyes are generally characterized by narrow absorption and emission bandwidths covering the entire visible spectral range[3,17] with high peak intensities, small Stokes shifts, and high fluorescence quantum yields Φ.[3,11b] The majority of the fluorophores synthesized for the present study show these properties. The versatility of the described radical C–H arylation is shown in its ability to create a library of compounds, which can greatly assist in creating a dye with fine-tuned spectroscopic and photophysical properties (Figure 1). The key spectroscopic and photophysical data of these BODIPY derivatives are compiled in Tables S4–S6.

For each dye, the absorption maxima are slightly bathochromically shifted with increasing solvent polarizability (from methanol/acetonitrile to toluene). The visible absorption band is assigned to the strong $S_1 \leftarrow S_0$ transition. An additional, much weaker, broad absorption band can be observed in the UV spectral range (see Figures S_1 and S_2), attributed to the $S_2 \leftarrow S_0$ transition. All the derivatives also show the typical emission features of boron dipyrrins: that is, a narrow, slightly Stokes-shifted band of mirror image shape, whose maximum λ_{em}(max) is somewhat red-shifted with increasing solvent polarizability. Although the shapes of the spectra of all the investigated difluoroboron dipyrrins are similar, their absorption and emission maxima [λ_{abs}(max), λ_{em}(max)], Stokes shifts ($\Delta\bar{\nu}$), absorption and emission bandwidths [measured by the full width at half-height of the maximum of the absorption (fwhm$_{abs}$) and the fluorescence emission (fwhm$_{em}$) bands], and fluorescence quantum yields (Φ) may vary considerably.

Most of the synthesized compounds have high Φ-values, an important exception to this is 8-phenyl BODIPY **3b**, due to the rotation of the 8-phenyl substituent being a major nonradiative deactivation pathway of the singlet excited state S_1. Rotation of the 8-(2,6-dichlorophenyl) group and 8-mesityl group (in **3a** and **3c**) is restricted by steric hindrance between the Cl atoms and methyl groups, respectively, and the 1,7-hydrogens of the BODIPY nucleus. The higher Φ-values of **3a** with a *meso*-2,6-dichlorophenyl group[11b] compared to those of **3c** with a *meso*-mesityl substituent indicate that the 2,6-dichlorophenyl group is the more efficient rotation-blocking group.

The symmetrically 3,5-disubstituted products **3** have bathochromically absorption and emission spectra compared to their asymmetrically 3-substituted counterparts **5** (Figure 1).[3a] These shifts reflect the better π-conjugation in the 3,5-diaryl dyes compared to their 3-aryl analogues and evidently to the starting material **1**. Introduction of one phenyl group at the 3-position (in **5a**) produces a bathochromic shift of approximately 29 nm in λ_{abs}(max) and ca. 35 nm in λ_{em}(max) compared to starting compound **1**, which serves as reference. Incorporating a second phenyl group (in **3a**) entails an additional red shift of approximately 27 nm in λ_{abs}(max) and ca. 40 nm in λ_{em}(max) relative to dye **5a**.[3a,11b]

Replacing the 3,5-phenyl (in **3a** and **5a**) substituents by the electron-donating *p*-anisyl groups (in **3l** and **5g**) results in a further red-shifted spectra for both the mono- and diarylated compound.[3a,11b] In contrast, the bulky mesityl group (in **3k** and **5f**) introduces only a small bathochromic shift, suggesting a severely restricted electronic coupling caused by steric hindrance twisting the mesityl group out of the BODIPY plane. Furthermore, 3,5-dimesityl dye **3k** has very small Stokes shifts ($\Delta\bar{\nu} \approx 600\ cm^{-1}$), combined with high Φ-values (up to 0.98), suggesting a very rigid structure. Compound 3-[4-(dimethylamino)phenyl]-BODIPY **5h** shows no fluorescence in the more polar solvents; it is quenched by the electron-rich 3-[4-(dimethylamino)-phenyl] substituent. Addition of acid (H^+) blocks the lone electron pair of the nitrogen donor and hence decreases the electron-donating

ability of the amine. This leads to inhibition of the quenching process, resulting in the "switching on" of the fluorescence, which renders this molecule an extremely sensitive probe for pH (Table S4).

BODIPY dyes with electron-withdrawing groups (4-nitrophenyl in **3d** and **5b**, 4-cyanophenyl in **3g** and **5c**, 4-bromophenyl in **3h**, and 4-carboxyphenyl in **3i** and **5d**) show smaller bathochromic spectral shifts compared to the phenyl derivatives (**3a** and **5a**), but the influence on the fluorescence quantum yields is minimal. The 3,5-di(4-nitrophenyl)-substituted **3d** shows rather small bathochromic shifts compared to the 3,5-di(3-nitrophenyl) derivative **3e**, but much larger red shifts compared to the 3,5-di(2-nitrophenyl) compound **3f**. The quantum yields and Stokes shifts of **3d** and **3e** are comparable, whereas the sterically hindered 2-nitro variant **3f** barely shows any fluorescence. Negligible fluorescence has previously also been observed for 8-(4-nitrophenyl)-3-phenylBODIPY and 8-(4-nitrophenyl)-3,5-diphenylBODIPY.[11b] Products **3i** and **5d**, containing two and one carboxylic acid groups, respectively, are soluble in slightly basic water. Combined with their moderate to good quantum yields Φ (up to 0.85), these compounds are promising candidates as the basis for constructing labeling dyes.

λ_{abs}(max) and λ_{em}(max) of **5e** and **3j**, with one and two 2-naphthyl groups, respectively, are bathochromically shifted compared to those of the corresponding phenyl-substituted analogues **5a** and **3a**, respectively. This reflects the improved π-conjugation in the 2-naphthyl-substituted derivatives relative to their phenyl counterparts.[3a]

The absorption and emission maxima of **6** and **7** correspond to the average between their corresponding symmetrical analogues. Likewise, λ_{abs}(max) and λ_{em}(max) of product **6** are the average between **3a** and **3g**, whereas those of product **7** are the average between **3l** and **3g**.

In conclusion, a versatile, general method for the synthesis of brightly fluorescent ($\Phi > 0.85$) 3,5-diarylated and 3-monoarylated BODIPY dyes with UV/Vis absorption and fluorescence emission spectra, which are bathochromically shifted compared to those of the starting boron dipyrrins, has been developed and investigated. The present radical C–H arylation, based on the ferrocene-catalyzed reduction of aryldiazonium salts, is a fast and high yielding reaction displaying a broad scope. In this way, new interesting fluorophores can be synthesized, such as asymmetrically substituted dyes, thus avoiding the tedious synthesis of substituted pyrrole building blocks and unstable intermediates.

Keywords: arylation · BODIPY · dyes · photophysics · radicals

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