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Introducing chiral *N*-BODIPYs: Promising dyes for chiroptical applications

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Abstract: *N*-BODIPYs (diaminoborondipyrromethenes) were recently described by us for the first time as a new family of BODIPY dyes with huge technological potential. We present now a series of unprecedented chiral *N*-BODIPYs, which have been straightforwardly synthesized in a simple one-pot procedure starting from parent *F*-BODIPYs and chiral sulfonamides. The circular dichroism (CD) of the new chiral dyes has been measured with the aim of studying the possibility of modulating the CD signal in chiral BODIPYs by simple chemical functionalization.

Keywords: Organic Dyes, BODIPYs, Chiroptics, Circular dichroism.

1. Introduction

BODIPYs (boron dipyrromethenes; 4-bora-3a,4a-diaza-*s*-indacenes) constitute one of the most valuable families of technological dyes [1-10]. Nowadays, there is a plethora of available synthetic procedures for their direct functionalization, focused on appropriate modulation of key physical (mainly photophysical) properties. This ample reactivity allows the derivatization of BODIPYs at their dipyrrin moiety with a great variety of pendant functional groups (blue in Figure 1) [3,8,11-20]. However, less synthetic diversity is found when directly functionalizing BODIPYs at boron (red in Figure 1) [21-36]. This boron functionalization, virtually restricted to *O*- and *C*-BODIPYs until recently, has allowed the facile preparation of dyes with enhanced photostability for lasing [21-24], with improved water solubility for biological applications [25-27], with boosted energy-transfer processes for efficient light collection [19,28-32] or with enhanced chiral perturbation enabling circularly polarized luminescence (CPL) [33-36], among other valuable properties.

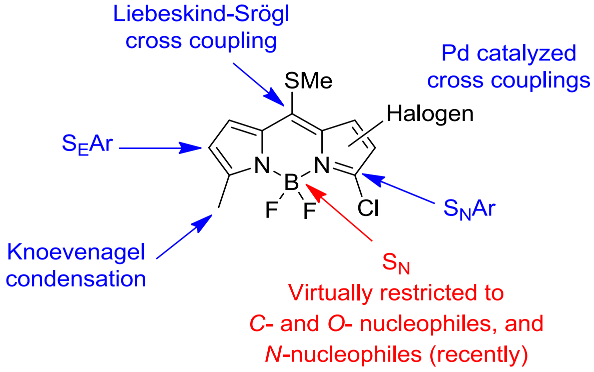


Figure 1. Some useful chemical transformations in BODIPYs.

Recently, de la Moya group has reported a protocol to directly functionalize BODIPYs at boron with two nitrogen moieties thus obtaining the first *N*-BODIPYs (e.g. **1**, Figure 2) [37]. Nitrogens with electron withdrawing groups (alkyl- or arylsulfonyl) and electron rich dipyrrins (peralkylated) were used to stabilize the corresponding diaminoboron-dipyrrin complex. This combination gave place to highly stable *N*-BODIPYs, which additionally turned out to be highly fluorescent [37].

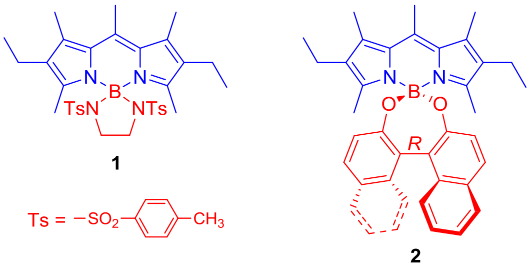


Figure 2. First *N*-BODIPY (**1**) and spiranic chiral *O*-BODIPY (**2**) enabling CPL described by de la Moya.

The new *N*-BODIPYs show great versatility for chemically functionalizing BODIPYs. Thus, the distinct key bonding features of nitrogen compared with those of oxygen (enhanced bond valence and different bond directionality) should open up new possibilities for functionalizing BODIPY dyes, allowing an increase in the number of pendant moieties near the BODIPY chromophore (from two in *O*-BODIPYs, up to four different residues in *N*-BODIPYs) [37]. Such versatile and multiple functionalization is of great interest for achieving a smarter modulation of the BODIPY photophysics, which should increase the applicability of these dyes as advanced photonic platforms, for example in chiroptical applications, a field that has experienced an exponential growth in the last years. Thus, circular dichroism (CD) or circularly polarized luminescence (CPL) have found application in the improvement and potential development of multiple photonic tools as display devices including 3D optical displays, optical storage and processing systems, spintronics-based devices, biological probes and signatures, security tags, CPL lasers and enantioselective CPL sensors, among others [38-46]. In this chiroptical context, our group described a new simple structural design for developing small organic molecules (SOM) enabling CD and CPL from inherently achiral chromophores [33]. This strategy is based on a spiranic *O*-BODIPY, which is chirally perturbed by a 1,1′-binaphtyl unit orthogonally tethered to it in a spiranic fashion, providing CPL levels (|g_{lum}|) [47] in solution falling into the usual range (10^{-5} to 10^{-2}) of that obtained from other SOMs (**2**, Figure 2).

On the basis of the said new design for CPL-SOMs based on BODIPY, exemplified by **2**, and taking advantage of the easiness of preparation and high stability, fluorescence and chemical versatility of the newly discovered *N*-BODIPYs [37], we decided to prepare a battery of chiral *N*-BODIPYs and carry out a study on the variation of their chiroptical properties with the structural factors. In this preliminary study, the synthesis and measurement of CD is accomplished.

2. Results and discussion

Three different modulation strategies will be followed to study the influence of the structure on the chiroptical properties of chiral *N*-BODIPYs: (1) the generation of a chiral center at the boron atom itself, (2) the use of a diamine moiety with stereogenic carbons attached to the nitrogens and (3) the use of a sulfonamide moiety with a conformationally-mobile pending chiral fragment. Additionally, the designed structures will present either C_1 or C_2 symmetry. These variations will make possible to carry out a preliminary study on the effect of different factors (distance of the stereogenic elements to the chromophore, molecular symmetry, conformational flexibility of stereogenic moieties, etc.) on the CD properties of chiral *N*-BODIPYs.

The selected library of easily accessible chiral *N*-BODIPYs shown in Figure 3 was chosen to comprise the above mentioned structural factors. Thus, for example, **3a**-**c** are C_2-symmetric structures, which, in principle, is a good structural motif to achieve CD [48]. In **3c** the chirality has been introduced in the sulfonamide moiety, whereas in **3a** and **b**, the chiral center is attached to the nitrogen and thus closer to the central boron atom. On the other hand, an asymmetric dipyrrin has been selected to see the influence of a stereogenic boron atom (diastereomeric couple **4d**).

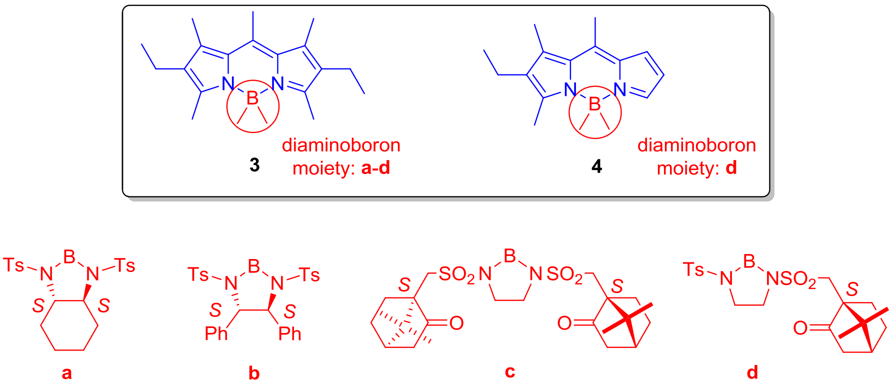
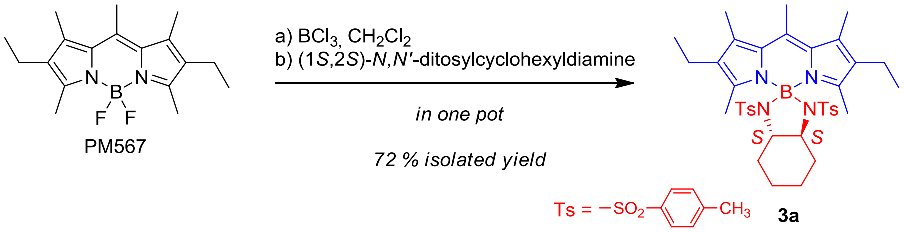


Figure 2. Developed library of chiral *N*-BODIPYs. Ts = *p*-toluenesulfonyl (tosyl).

The selected chiral *N*-BODIPYs were straightforwardly prepared using the procedure described by de la Moya [37] (Scheme 1), starting from the corresponding parent *F*-BODIPY and a chiral disulfonamide. The reaction of formation of the *N*-BODIPY is a simple one-pot nucleophilic substitution of fluorine by nitrogen promoted by boron trichloride (Scheme 1).



Scheme 1. Synthesis of chiral *N*-BODIPYs, exemplified for **3a.**

On the one hand, C_2-symmetric *N*-BODIPYs **3a**-**c** were made from a symmetric *F*-BODIPY (commercially available 2,6-diethyl-1,3,5,7,8-pentamethyl-*F*-BODIPY, PM567, Figure 4) and a symmetric chiral disulfonamide. These sulfonamides were in turn made either by reacting a chiral diamine ((1*S*,2*S*)-cyclohexane-1,2-diamine for **a** or (1*S*,2*S*)-1,2-diphenylethane-1,2-diamine for **b**) with *p*-toluenesulfonyl chloride, or achiral ethane-1,2-diamine with (1*S*)-camphorsulfonyl chloride, for **c**.

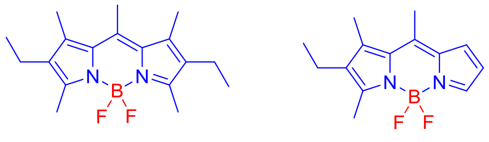
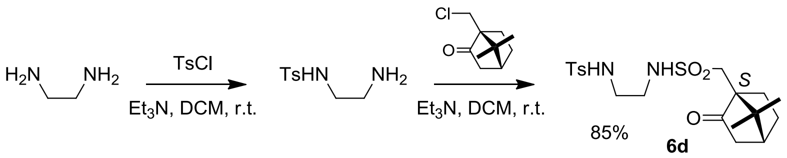


Figure 4. Starting *F*-BODIPYs.

On the other hand, C_1-symmetric *N*-BODIPYs **3d** and **4d** were made using either an asymmetric *F*-BODIPY or an asymmetric disulfonamide or both. As starting asymmetric *F*-BODIPY, easily accessible 2-ethyl-1,3,8-trimethyl-*F*-BODIPY [49] (**5**, Figure 4) was used. For the asymmetric disulfonamide (**6d**, Scheme 2), ethane-1,2-diamine was reacted in two steps, first with one equivalent of *p*-toluenesulfonyl chloride and then with one equivalent of (1*S*)-camphorsulfonyl chloride, giving place to **6d** in 85% yield.



Scheme 2. Synthesis of asymmetric disulfonamide **6d**.

The CD spectra of the obtained chiral *N*-BODIPYs were recorded in diluted chloroform solution and the corresponding g_{abs} [50] calculated. Except for **3c**, all synthesized chiral *N*-BODIPYs were CD-active (see Table 1). Also noteworthy is the high fluorescence of all species, something of a great interest, as it is critical to the development of CPL-SOMs. However, no clear conclusions on the relationship between the dye structure and the CD properties can be extracted from this preliminary series.

Table 1. Kuhn´s disymmetry ratio (g_{abs}) for studied *N*-BODIPYs (10^{-6} M $CHCl_3$ solution).

***N*-BODIPY**	**$10^3 \cdot g_{abs}$**
3a	+0,53
3b	+0,13
3c	0
3d	−0,08
4d	+1,40
4d′	−0,15

Thus, **3a** and **3b**, both coming from chiral diamines with α-stereogenic carbons, are CD-active, demonstrating that using easily-available chiral diamines is a good strategy for achieving CD in *N*-BODIPYs. However, the g_{abs} values reached by them are significantly different (Table 1), which could be due to key differential conformational and/or steric factors.

From the CD results for camphor-derived **3c** and **3d**, it seems that introducing this chiral element in the sulfonamide moiety is not a good strategy for achieving CD. Neither when the resulting structure has C_1-symmetry, nor when it has C_2-symmetry. However, the camphor moiety does clearly have an influence on the CD of the dye, since diastereomeric **4d** and **4d′** show very different values of g_{abs} (Table 1).

At first, the highest value of g_{abs} for **4d** (+1.40) seems to indicate that asymmetric boron is the best structural motif for a CD-active *N*-BODIPY. However, as above-mentioned, there has to be another effect playing, since both diastereomers show completely different g_{abs} values.

3. Conclusion

A series of unprecedented chiral *N*-BODIPYs have been straightforwardly synthesized. The measurement of the CD signalization of these new dyes shows that they can be CD-active, exhibiting g_{abs} values in the typical range of most of the CD-active dyes based on SOM. The interest of this chiroptical property (*e.g.*, in high-resolution and chiral sensing), joined to excellent absorption/emission signatures and synthetic accessibility, make chiral *N*-BODIPYs to be potentially interesting for Chiroptics. Nonetheless, further investigation related with assessing the influence of the *N*-BODIPY structure in the dichroic signalization (level and sign) is needed to make possible the rational design of future chiral *N*-BODIPYs with improved properties for chiroptics. Is this line, research is being conducted by synthesizing and chiroptically studying (CD and CPL) new series of chiral *N*-BODIPYs.

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Conflicts of Interest: The authors declare no conflict of interest.

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50. The degree of CD is given by the *Kunh dissymmetry ratio, or* absorption dissymmetry factor $g_{abs}(\lambda) = 2(\varepsilon_L - \varepsilon_R)/(\varepsilon_L + \varepsilon_R)$, where ε_L and ε_R are the molar absorption coefficients for left and right circularly polarized light, respectively.