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Influence of At-Bridge Nitro Groups on the Photophysics and Chiroptics of *helicoBODIPYs*: A Step Forward towards the Development of New Chiroptical Sensors †

César Ray [1], Carolina Díaz-Norambuena [2], Christopher Schad [1], Florencio Moreno [1], Antonia R. Agarrabeitia [1,3], María J. Ortiz [1], Teresa Arbeloa [2], Jorge Bañuelos [2], Beatriz L. Maroto [1,*] and Santiago de la Moya [1,*]

[1] Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain; cesarrayleiva@ucm.es (C.R.); cschad@ucm.es (C.S.); floren@ucm.es (F.M.); agarrabe@ucm.es (A.R.A.); mjortiz@ucm.es (M.J.O.)

[2] Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco-EHU, 48080 Bilbao, Spain; carolina.diaz@ehu.eus (C.D.-N.); teresa.arbeloa@ehu.eus (T.A.); jorge.banuelos@ehu.eus (J.B.)

[3] Sección Departamental de Química Orgánica, Facultad de Óptica y Optometría, Universidad Complutense de Madrid, 28037 Madrid, Spain

* Correspondence: belora@ucm.es (B.L.M.); santmoya@ucm.es (S.d.l.M.); Tel.: +34-913944716 (B.L.M.); +34-913945090 (S.d.l.M.)

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Abstract: A new helicoBODIPY (bisBODIPY with helical chirality) with nitro groups at the chiral bridge has been synthesized as a model to study the influence of the *at-bridge* substitution on the photophysics and chiroptics of the helicoBODIPY. This preliminary study reveals that *at-bridge* substitution can be a strategy for the development of chiroptical sensors based on helicoBODIPYs.

Keywords: organic dyes; BODIPY; stereoelectronic effects; photophysics; chiroptics

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1. Introduction

The discovery and exploration of chiroptical phenomena, such as circular dichroism (CD) and circularly polarized luminescence (CPL), has boosted the applicability of chiral systems and their interaction with light in the recent years [1–5], contributing to the development of chiroptics. Optical techniques based on chiroptics have major applications as CP-OLEDs, security inks, systems for the storage and processing of information, and CPL microscopy, among others [6–9].

One of the most interesting fields in which chiroptics has allowed to advance in science has been chemical analysis, with the so-called chiroptical sensing [10]. This type of sensing, based on CD or CPL specifically, enables analyses with greater sensitivity and resolution than traditional methods, due to the higher definition of circularly polarized light [10]. In addition, its applicability goes beyond the determination of configurations of chiral molecules, but it also covers important issues such as the determination of conformational arrangements of chiral molecules, detection of chiral or achiral species, as well as study of the self-assembly of supramolecular structures [11–13].

For the development and implantation of this novel tool it is necessary to have optically active chiral species that can act as sensors [3]. Unfortunately, there is no extensive collection of chiral chromophoric platforms available to date for the synthetic development of chiroptical sensors. The latter, together with the necessary technology and instrumentation, much of it yet to be developed, makes the exploitation of chiroptical sensing still in progress [14].

In this sense, de la Moya introduced in 2013 a new design based on a bis(BODIPY) with helical chirality provided by a chiral diamine or diol tether (*helicoBODIPY*, see (*R*,*R*)-**1** as an example in Figure 1) [15]. This design has characteristics with a great potential for the development of chiroptical sensors [15,16]. First, its chiroptical behavior: it shows a strongly bisignated signal in the CD spectrum and also CPL emission in the visible region, with luminescence dissimetry factor values (g_{lum}, [17]) which fall in the usual range for small organic molecules, and which can be modulated by structural changes in its chiral bridge [16]. This exceptional chiroptical behavior arises from the induction of a pseudo-helical conformation in solution, with a preferred configuration induced by the chiral bridge (see Figure 1), which allows an exciton coupling between the two chromophores. Second, its conformational flexibility, which enables the dye to adopt said helical conformation and provides the helicoBODIPY design with a great value as a platform for chiroptical sensing. And third, no less important, its straightforward synthetic accessibility, from easy-to-obtain *F*-BODIPYs and enantiopure C_2 symmetric diamines or diols [15,16].

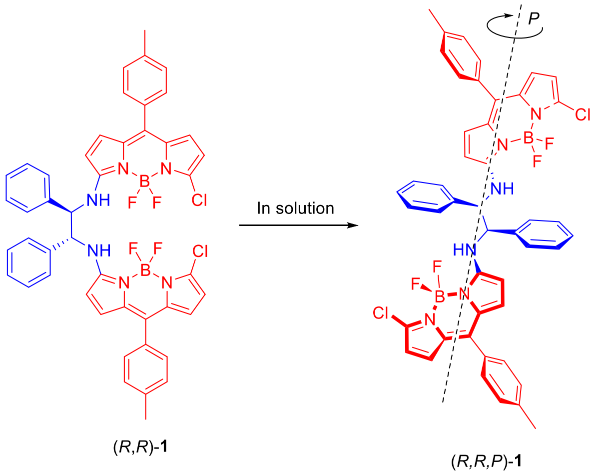
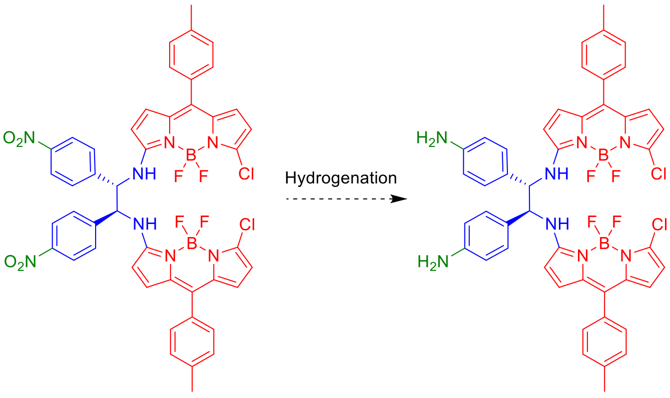


Figure 1. Example of the helicoBODIPY design introduced by de la Moya and its helical conformation with a preferred configuration in solution.

Therefore, we hypothesized that, as the flexible chiral bridge is responsible for providing the helicoBODIPY design with these exceptional chiroptical properties, modifications of the structure or the conformation of the bridge should lead to changes in the chiroptical behavior of the dye. It is precisely on this foundation on which the helicoBODIPY design would be based to carry out its function as a chiroptical sensor: the species to be detected being capable, through specific interactions with the spacer, of inducing changes in the original conformation of the sensor and, thus, leading to different chiroptical responses [18–20].

For this purpose, we decided to introduce in the bridge a functional group directed to the construction of chiroptical sensors. This group should be easily transformed into a group suitable for the recognition of analytes, keeping in mind that the introduction of this group should not interfere with the synthetic access to the dye, neither avoid the necessary helical arrangement. The nitro group was considered as a good option, due to its compatibility with the aromatic nucleophilic substitution ($S_{N}Ar$) reaction involved in the dye synthesis and also to the ease of derivatization to an amino group by simple hydrogenation (Scheme 1) [21,22]. The amino group has a well-known capability for the recognition of electron deficient analytes [23,24], as well as a rich chemistry that would allow numerous types of reactions directed to increase the applicability of the design.

In order to validate the at-bridge-substituted helicoBODIPY design for the future development of chiroptical sensors, it is necessary to study the influence of the nitro groups located at the bridge on the photophysics and chiroptics of the helicoBODIPY. This communication describes the preliminary results on this study, directed to get a closer knowledge on the key structural factors that govern the (chir)optical properties of the helicoBODIPY design, which could be of a great utility to consolidate this design for the development of chiroptical sensors.

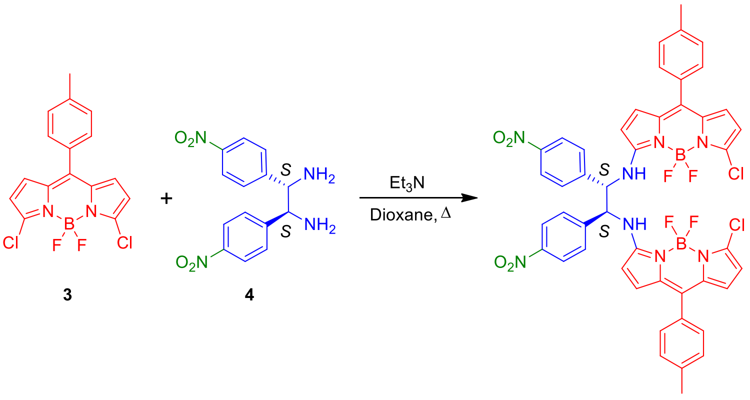


(*S*,*S*)-**2a** (*S*,*S*)-**2b**

Scheme 1. Rationalization of a new helicoBODIPY-based chiroptical sensor design.

2. Results and Discussion

The synthesis of helicoBODIPY (*S*,*S*)-**2a** was carried out following the methodology developed by us for the synthesis of **1**, this is, a double SNAr of chlorine in 3,5-dichloro-4,4-difluoro-8-(4-methylphenyl)BODIPY (**3**) [25], using (*S*,*S*)-*N*,*N*′-bis(4-nitrophenyl)ethane-1,2-diamine (**4**) as the nucleophile, in acetonitrile in the presence of triethylamine. However, the expected product (*S*,*S*)-**2a** was not obtained, not even at refluxing temperature, probably due to the lower nucleophilicity of the diamine when compared to the unsubstituted one in the synthesis of **1** (owing to the electron-withdrawing nitro groups). Fortunately, the application of more vigorous reaction conditions (refluxing dioxane) led to bis(BODIPY) (*S*,*S*)-**2a** in a satisfactory 44% yield (Scheme 2).



3 **4** (*S*,*S*)-**2a**
44%

Scheme 2. Synthesis of (*S*,*S*)-**2a**.

The study of the photophysical properties of new dye **2a** was done in comparison with its unsubstituted analogue **1** [15], in order to evaluate whether the introduction of substituents in the structure of the bridge could alter the photophysics of the helicoBODIPY. Fortunately, as it can be observed in Table 1, the photophysical signatures of both dyes do not differ much. The presence of the nitro groups in the diamine bridge of **2a** seems to induce a slight bathochromic shift of the spectral bands in relation to **1**, which could be related to changes in the probability of the vibrational transitions.

Regarding the fluorescence response, a similar behavior was observed for **2a** and **1**. The fluorescence quantum yield decreases when the polarity of the medium increases, for both dyes. This is an evidence of an intramolecular charge transfer (ICT) in the excited state, which has a higher probability in polar media [15]. As the nitro substituents are not π-conjugated with the nitrogens of the diamine, these groups do not have a significant influence on the ongoing ICT.

Table 1. Comparative spectroscopic data for **1** and **2a** in different solvents (*ca.* 10^{-6} M).

Dye	**Solvent**	λ_{ab} [a] **(nm)**	ε_{max} [b] **(10^4 M^{-1}cm^{-1})**	λ_{fl} [c] **(nm)**	φ [d]	τ [e] **(ns)**
1 [f]	*c*-hexane	529.0	12.4	544.0	0.17	1.15 (97%) 4.70 (3%)
	chloroform	525.5	8.3	544.5	0.14	0.23 (32%) 1.15 (68%)
	acetone	508.5 469.5	5.5 5.8	537.5	0.005	--
	methanol	511.0 469.5	5.4 5.5	535.5	0.001	--
2a	*c*-hexane	534.0 495.0	8.0 4.2	546.5	0.23	1.50 (96%) 5.03 (4%)
	chloroform	532.5 492.5	8.4 5.1	548.0	0.07	0.18 (42%) 0.75 (58%)
	acetone	512.0 473.5	5.0 5.4	537.5	0.003	--
	methanol	514.5 474.0	4.9 5.2	539.5	0.003	--

[a] Maximum absorption wavelength. [b] Maximum molar absorptivity. [c] Maximum fluorescence wavelength. [d] Fluorescence quantum yield. [e] Fluorescence lifetime. [f] Data from ref. [26].

The CD spectrum of the new dye (*S*,*S*)-**2a** is similar to that of its analogue (*S*,*S*)-**1** [15] (Figure 2). It provides a comparable bisignalized signal, with a positive Cotton effect, demonstrating the formation of a helical conformation in solution with a preferred *M* configuration. Therefore, the introduction of the *p*-nitro groups at the phenyl units of the bridge does not affect the induced axial stereochemistry of the dye in solution. However, it does induce a change in the degree of the differential absorption of circular polarized light, being the maximum absorption dissymmetry ratio, g_{abs} [27], for (*S*,*S*)-**2a** ($+3.8 \times 10^{-3}$, in chloroform) twice than for (*S*,*S*)-**1** ($+1.6 \times 10^{-3}$, in chloroform). This result shows that changes in the structure of the bridge can induce changes in the degree of the CD absorption, that is, changes in the chiroptical response of the dye, a behavior that is sought when developing chiroptical sensors.

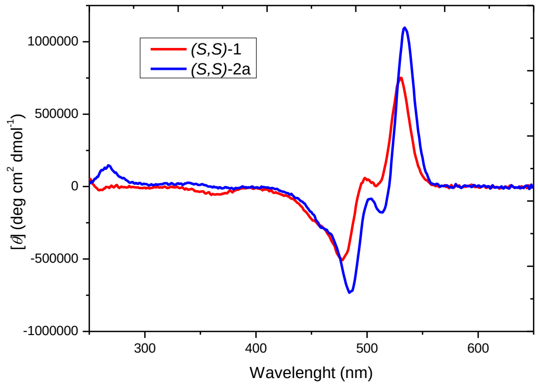


Figure 2. Circular dichroism spectra of (*S*,*S*)-**1** (red) and (*S*,*S*)-**2a** (blue) in chloroform (4×10^{-6} M).

3. Conclusions

A new helicoBODIPY (*S*,*S*)-**2a** has been designed and obtained. This helicoBODIPY is based on previously described (*S*,*S*)-**1** [15], but includes a chiral diamino bridge with nitro groups, for its future derivatization to amino groups, directed to the development of sensors. The new dye can be straightforwardly obtained following the previously described procedure for the synthesis of helicoBODIPYs and keeps the photophysical properties of parent **1**. It also provides a similar chiroptical response in CD, consequence of the formation of a helical conformation in solution, with the same preferred configuration than parent **1**, but with changes in the polarization degree, as detected by the measured g_{abs} value. The observed change in the g_{abs} value, caused by a change in the structure of the bridge, could be used for the development of chiroptical sensors based on CD.

4. Materials and Methods

4.1. Synthetic Procedures

General. Common solvents were dried and distilled by standard procedures. All starting materials and reagents were obtained commercially and used without further purifications. Elution flash chromatography was conducted on silica gel (230 to 400 mesh ASTM). Thin layer chromatography (TLC) was performed on silica gel plates (silica gel 60 F254, supported on aluminum). The NMR spectra were recorded at 20 °C. As internal standards, the residual solvent peaks were used in ^{1}H NMR ($CDCl_3$: δ 7.26 ppm) and ^{13}C NMR ($CDCl_3$: δ 77.16 ppm) and external standards were used in ^{11}B NMR (15% $BF_3{\cdot}OEt_2$ in $CDCl_3$: δ 0.00 pm) and in ^{19}F NMR (0.05% trifluorotoluene in $CDCl_3$: $\delta - 62.72$ ppm). The NMR signals are given in ppm. DEPT-135 NMR experiments were used for the assignation of the type of carbon nucleus (C, CH, CH_2 or CH_3). The FTIR spectra were recorded from neat samples using ATR technique and IR bands are given in cm^{-1}. The measurement of the optical rotations was performed in quartz cells of 1 dm length and 1mL capacity. For the specific rotation, $[\alpha]_D^t$ (where t is the temperature in °C and D refers to the sodium spectral line used, 589 nm), the concentration *c* (in g/100 mL) and the solvent are given. CD spectra were recorded on a Jasco (model J-715) spectropolarimeter using standard quartz cells of 1 cm optical-path length in chloroform solution, unless otherwise indicated, at a dye concentration of ca. 4×10^{-6} M.

Synthesis of (*S*,*S*)-2a: A mixture of 3,5-dichloro-4,4-difluoro-8-(4-methylphenyl)BODIPY (**3** [25]; 50 mg, 0.143 mmol), (*S*,*S*)-*N*,*N*′-bis(4-nitrophenyl)ethane-1,2-diamine (**4**; 25.5 mg, 0.068 mmol) and triethylamine (58 mg, 0.572 mmol) in dry dioxane (3 mL) was refluxed under argon for 3.5 h. After cooling down the reaction mixture to room temperature, CH_2Cl_2 (15 mL) and water (15 mL) were added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases were then washed with water (1 × 15 mL) and brine (1 × 15 mL) and dried over anhydrous Na_2SO_4. After filtration and solvent evaporation under reduced pressure, the obtained residue was purified by flash chromatography (CH_2Cl_2). **(*S*,*S*)-2a:** 29 mg (44%). Brown solid. R_f = 0.10 (hexane/CH_2Cl_2 1:1). $[\alpha]_D^{20}$ +6093.6 (*c* 0.104, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz) δ 8.12 (d, *J* = 8.4 Hz, 4H), 7.66 (br s, 2H), 7.28 (m, 4H), 7.12 (m, 8H), 6.63 (d, *J* = 4.9 Hz, 2H), 6.44 (d, *J* = 4.0 Hz, 2H), 6.26 (d, *J* = 4.0 Hz, 2H), 5.65 (d, *J* = 4.9 Hz, 2H), 5.20 (m, 2H), 2.41 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.2 (C), 148.3 (C), 144.4 (C), 139.9 (C), 135.6 (CH), 134.9 (C), 132.7 (C), 132.1 (C), 130.5 (C), 130.2 (br s, CH), 129.2 (CH), 128.8 (CH), 124.4 (CH), 122.7 (CH), 113.9 (CH), 110.1 (CH), 62.5 (CH), 21.5 (CH_3) ppm. ^{11}B NMR ($CDCl_3$, 160 MHz) δ 0.83 (s) ppm. ^{19}F NMR ($CDCl_3$, 471 MHz) δ −146.2 (br s), −148.1 (m) ppm. FTIR ν 1590, 1524, 1488, 1348, 1096 cm^{-1}.

4.2. Spectroscopic Measurements and Quantum Mechanic Calculations

The photophysical properties were registered using quartz cuvettes with optical pathways of 1 cm in diluted solutions (around 2×10^{-6} M), prepared by diluting the concentrated stock solution in acetone. Ultraviolet-visible (UV-vis) absorption and fluorescence spectra were recorded on a Varian model CARY 4E spectrophotometer and an Edinburgh Instruments spectrofluorimeter (model FLSP920), respectively. Fluorescence quantum yields (φ) were obtained using PM546 (Exciton, φ^r = 0.85), in ethanol as the reference. Radiative decay curves were registered with the time correlated single-photon counting technique, as implemented in the aforementioned spectrofluorimeter. Fluorescence emission was monitored at the maximum emission wavelength, by means a microchannel plate detector (Hamamatsu C4878) of picosecond time-resolution (20 ps), after excitation with a wavelength-tunable Fianium pulsed laser (time resolution of around 150 picoseconds). The fluorescence lifetime (τ) was obtained after the deconvolution of the instrumental response signal from the recorded decay curves by means of an iterative method. The goodness of the exponential fit was controlled by statistical parameters (chi-square) and the analysis of the residuals.

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