

# Circularly Polarized Luminescence by Visible-Light Absorption in a Chiral O-BODIPY Dye: Unprecedented Design of CPL Organic Molecules from Achiral Chromophores

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## S Supporting Information

**ABSTRACT:** Circularly polarized luminescence (CPL) in simple (small, nonaggregated, nonpolymeric) O-BODIPYs (*R*)-1 and (*S*)-1 by irradiation with visible light is first detected as proof of the ability of a new structural design to achieve CPL from inherently achiral monochromophore systems in simple organic molecules. The measured level of CPL ( $|g_{lum}|$ ) in solution falls into the usual range of that obtained from other simple organic molecules ( $10^{-5}$ – $10^{-2}$  range), but the latter having more complex architectures since axially chiral chromophores or multichromophore systems are usually required. The new design is based on chirally perturbing the acting achiral chromophore by orthogonally tethering a single axially chiral 1,1'-binaphthyl moiety to it. The latter does not participate as a chromophore in the light-absorption/emission phenomenon. This simple design opens up new perspectives for the future development of new small-sized CPL organic dyes (e.g., those based on other highly luminescent achiral chromophores and/or chirally perturbing moieties), as well as for the improvement of the CPL properties of the organic molecules spanning their use in photonic applications.

The interest in circularly polarized luminescence (CPL), which is the differential emission of right- and left-circularly polarized light by chiral luminescence systems (molecules, polymers, supramolecular aggregates, etc.),<sup>1</sup> has experienced noticeable growth in recent years. This fact is due to not only the valuable use of CPL as a source of information on the structure of the involved excited states but also its application in the improvement and potential development of multiple photonic tools, such as display devices including 3D optical displays,<sup>2</sup> optical storage and processing systems,<sup>3</sup> spintronics-based devices,<sup>4</sup> biological probes and signatures,<sup>5</sup> security tags,<sup>5b</sup> CPL lasers,<sup>6</sup> enantioselective CPL sensors,<sup>7</sup> or light-emission systems for asymmetric photosynthesis.<sup>8</sup> Additionally, the omnipresence of chirality in the world around us (especially in the living world) makes CPL a valuable source of information on chiral environments to be exploited, e.g., by the future development of CPL microscopes.<sup>5c,9</sup>

Despite the well-known interest in organic molecules for the development of photonic materials (mainly due to easy photonic-property modulation by accessible structural variations based on workable organic-chemistry transformations, as well as to material processability factors derived from their organic nature), the highest values of CPL, measured in absolute terms of  $|g_{lum}|$ ,<sup>1,10</sup> are mainly achieved from chiral lanthanide complexes instead,<sup>1c,5</sup> which typically exhibit  $|g_{lum}|$  values in the range 0.1–0.5 (a value of *ca.* 1.4 has been exceptionally reported for a Eu(III) complex).<sup>11</sup> In contrast, smaller CPL levels can be found for some purely organic molecules when they are hierarchically self-organized into axially chiral helical polymers or aggregates.<sup>12</sup> In this line, some chirally superorganized polymeric cholesteric crystals (PCC) can exhibit impressive levels of CPL. Thus, an interesting wide-band CPL with a  $|g_{lum}|$  value of *ca.* 1.6 has been reported for a light-emitting organic diode with a three-layered PCC reflector.<sup>13</sup> However, simple (small, nonaggregated, nonpolymeric) chiral organic molecules enabling CPL are rare and exhibit much smaller levels of CPL (typical  $|g_{lum}| = 10^{-5}$ – $10^{-2}$ ).<sup>14,15</sup> On the other hand, the structural diversity of the acting chromophores in these simple organic molecules is very poor, being practically restricted to chiral helicenes and 1,1'-binaphthyls (axially chiral chromophores),<sup>14</sup> as well as to achiral perylenes arranged in a molecular chiral helix (two identical chromophores are disposed in a rotated arrangement by attaching them to the ends of an axially chiral spacer).<sup>15</sup> Therefore, research guidelines directed toward expansion of the structural diversity of simple organic molecules enabling CPL are needed in order to develop usable, smarter, and better CPL dyes based on these compounds.

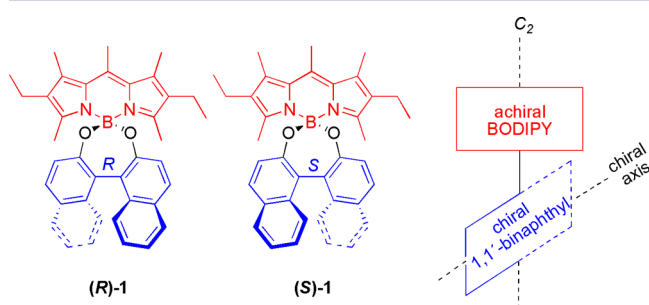
Boron dipyrromethene (BODIPY) dyes constitute one of the most important families of simple organic luminophores due to their special absorption and emission properties, which can be easily modulated by straightforward functionalizations of the rich BODIPY chemistry, as well as to their valuable processability properties derived from noticeably high solubility and stability in many solvent systems.<sup>16</sup> The strong absorption and emission of the  $\pi$ -conjugated BODIPY system in the visible (vis) and near-infrared (NIR) region of the electromagnetic

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spectrum makes this system highly interesting for the development of valuable technological applications, such as chemosensors and probes, biological labels, laser dyes, photodynamic therapy agents, and a plethora of photonic devices, including solar-light harvesting antennas or solar cells.<sup>17</sup> Despite the important role that CPL can play in all of these technologies (e.g., CPL-based sensing),<sup>18,14d,19</sup> chiral BODIPYs are still scarce<sup>20</sup> and are practically unknown in systems enabling CPL activities. Thus, to date, the only case of CPL in BODIPYs has been reported for a complex multi-chromophore urobilin-based *F*-BODIPY by irradiation with ultraviolet light (two identical absorbing chiral urobilinoid chromophores are covalently tethered to an emitting central achiral *F*-BODIPY chromophore;  $|g_{lum}|$  ca.  $10^{-3}$ ).<sup>20f</sup>

Herein we report the synthesis and chiroptical properties (electronic circular dichroism (ECD) and CPL) of the enantiomeric *O*-BODIPYs (**R**)-**1** and (**S**)-**1** (Figure 1), as

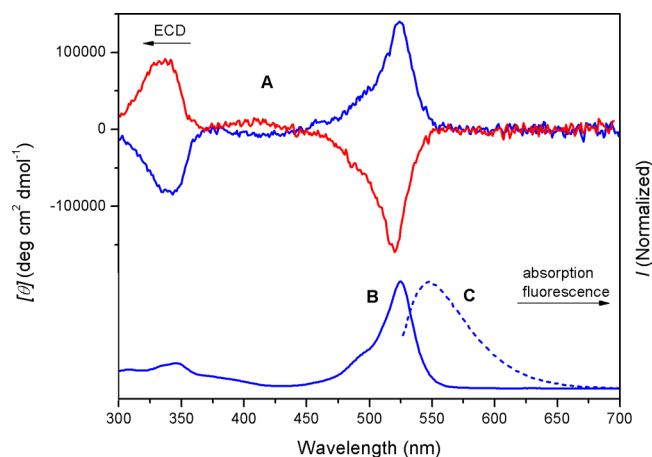


**Figure 1.** Studied chiral spiroBODIPYs. Structural design to chirally perturb the BODIPY chromophore.

evidence of the workability of a new simple structural design for developing small organic molecules enabling CPL from inherently achiral chromophores (BODIPY in our case), and thus allowing the first example of a chiral BODIPY dye enabling CPL upon direct absorption of vis light by the BODIPY chromophore itself.

The spiranic structure of *O*-BODIPYs **1** was chosen with the aim to achieve the required chiral perturbation of the inherently achiral BODIPY chromophore. In this axially chiral  $C_2$  structure, the luminescent BODIPY chromophore is orthogonally attached to an axially chiral 1,1'-binaphthyl unit. This structural design for simple CPL organic molecules based on inherently achiral chromophores is new, to the best of our knowledge, and it only requires the participation of a single acting chromophore (i.e., both light absorption and emission are produced by the same chromophore).

*O*-BODIPYs (**R**)-**1** and (**S**)-**1** (Figure 1) were straightforwardly obtained from highly luminescent and commercially available 1,3,5,7,8-pentamethyl-2,6-diethyl-*F*-BODIPY (PM567), by nucleophilic substitution with commercial (*R*)- and (*S*)-1,1'-bi(2-naphthol) (BINOL), respectively, and according to a slight modification of the methodology described by Mély and Bonnet<sup>21</sup> for a related compound (see Experimental Section and Figure S1 in Supporting Information (SI)). The absorption and emission spectra of **1** (B and C in Figure 2 for (*S*)-**1**) were expected from its BINOL-based structure.<sup>21</sup> Also as expected,<sup>21</sup> the fluorescence quantum yield ( $\phi$ ) of **1** (46.1 and 44.3% for (*R*)-**1** and (*S*)-**1**, respectively, in chloroform solution upon excitation at the maximum absorption wavelength; see SI), was lower than that exhibited by the starting *F*-BODIPY PM567.



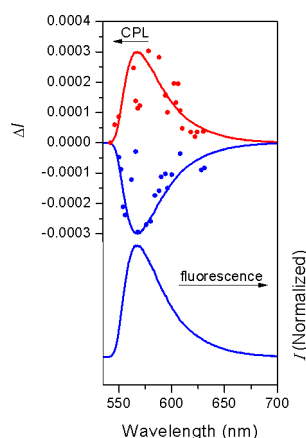
**Figure 2.** ECD (A), UV-vis absorption (B), and fluorescence (C) spectra for (**R**)-**1** (in red) and for (**S**)-**1** (in blue) in  $CHCl_3$  solution (ca.  $5.7 \times 10^{-6}$  M). C upon excitation at 525 nm.

<sup>1</sup>H NMR spectroscopy shows a clear diastereotopicity for the protons of the isochronous methylene groups of **1** ( $ABX_3$  spin system; see spectrum and corresponding spin-system simulation in SI). This diastereotopicity first indicates that the projected chiral perturbation is acting at least on the magnetic properties of the mentioned proton nucleus (note that the <sup>1</sup>H NMR spectrum of the starting achiral PM567 exhibits instead the expected methylene signal for their isochronous  $A_2X_3$  spin systems; see SI). Moreover, enantiomeric *O*-BODIPYs (**R**)-**1** and (**S**)-**1** exhibit mirror ECDs with a maximum dichroic signal matching the maximum vis absorption of the BODIPY chromophore ( $\lambda$  ca. 525 nm; cf., A and B in Figure 2). The maximum level of vis ECD measured in terms of  $g_{abs}$ <sup>22</sup> was +0.00074 for (*S*)-**1** and −0.00093 for (*R*)-**1**, as determined at the maximum absorption wavelength.

The strong Cotton effect observed for **1** in the vis region of the electromagnetic spectrum (see the ECD spectra in Figure 2) demonstrates that the designed chiral perturbation is acting on the BODIPY chromophore, at least in its ground state, and therefore, it could also act on the involved BODIPY-chromophore excited states, making the emission of circularly polarized light possible.<sup>23</sup>

Indeed, CPL was satisfactorily detected for (**R**)-**1** and (**S**)-**1** by absorption of vis light. The recorded CPL spectra (Figure 3) are virtually mirror images, showing maxima matching the maximum vis emission of the BODIPY chromophore ( $\lambda$  ca. 570 nm; see Figure 3). The solid lines in the CPL plot of Figure 3 are presented to show the luminescence spectral line shape, as it is common for most chiral organic and transition-metal chromophores (note that the usual small values for the CPL activity, mainly for organic chromophores, make the CPL plots highly noisy in most of the cases).<sup>1–4,14f,g,24</sup>

Although the  $|g_{lum}|$  values to be determined were very small (ca. 0.001 at the maximum emission wavelength of **1**, which corresponds to light that is only ca 0.1% circularly polarized), almost opposite CPL signals (see Figure 3) and  $g_{lum}$  values (+0.00071 for (*R*)-**1** and −0.00085 for (*S*)-**1**) were measured for each enantiomer, respectively. These results confirm that the constructed simple organic architecture is really able to produce the searched luminescent phenomenon in solution, since the emitted light is equally polarized in opposite directions by each enantiomer, and, more important, that the



**Figure 3.** CPL (upper curves) and total luminescence (lower curve) spectra for (*R*)-1 (in red) and for (*S*)-1 (in blue) in degassed  $\text{CHCl}_3$  solution (ca.  $10^{-3}$  M) at 295 K, upon excitation at 529 nm.

new structural design used to achieve CPL from the inherently achiral BODIPY chromophore works.

In summary, we report the first example of a new structural design to achieve CPL from an inherently achiral organic chromophore. In this simple design only two systems are required: the acting chromophore and the chirally perturbing moiety. Both systems are arranged closely and orthogonally to each other. The workability of this design has been evidenced by the opposite vis CPL activity of the *O*-BODIPYs (*R*)-1 and (*S*)-1, which were built up on the basis of the mentioned design. The report of this activity is, additionally, the first example of chiral BODIPYs enabling CPL by direct absorption of vis light. Although the reached  $g_{\text{lum}}$  values are in the typical range for simple organic molecules (typical  $|g_{\text{lum}}| = 10^{-5} - 10^{-2}$ ), the incorporation of a new chromophore type to the still scarce but highly interesting family of the CPL organic molecules, the straightforward synthetic access from *F*-BODIPYs, the inherent interest of BODIPY dyes in a plethora of photonic applications, and the easy modulation of their properties by known straightforward BODIPY functionalizations augur a promising future for the CPL BODIPYs.

We are convinced that the herein communicated new structural design to achieve CPL has great potential as a starting point to expand the valuable family of simple (small, nonaggregated, nonpolymeric) organic molecules enabling CPL, as well as to develop smarter and better CPL dyes, due to the special structural characteristics of these molecules, such as small molecular sizes allowing high solubilities or good diffusion processes, which can be interesting for some CPL applications (e.g., biomolecular CPL sensing into cells). Thus, further experimental and computational studies are now in progress, directed toward discovering the key structural factors ruling the CPL level in small organic molecules constructed on the basis of the new design (not only in BODIPY dyes and BINOL derivatives). These studies should allow the future development of simple organic dyes with usable levels of CPL. Some of the key factors to be studied are the conformational flexibility of the organic molecule (mainly around the linking region between the acting chromophore and the chirally perturbing system), the linkage positions, the type of chromophore and its substitution (e.g., presence of key functional groups in key positions), the type of chirally perturbing system (e.g., center vs axial chirality), etc.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental details, as well as characterization data and spectra of compounds (*R*)-1 and (*S*)-1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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