

## Modulating ICT emission: A new strategy to manipulate the CPL sign in chiral emitters†

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**A new strategy to manipulate the circularly polarized luminescence (CPL) handedness in chiral emitters, based on modulating the population of an emissive ICT state, is proposed. Such a strategy is particularly interesting for conformationally-rigid and non-aggregating chiral organic emitters, opening up new perspectives for the development of CPL applications based on organic molecules.**

Circularly polarized luminescence (CPL) is the differential emission of right and left circularly polarized light by non-racemic chiral luminescent systems (molecules, polymers, ionic pairs, supramolecular aggregates, etc.) or achiral ones in non-racemic chiral environments (*e.g.*, chiral crystals, solvents, etc.).<sup>1</sup> Research on this chiroptical phenomenon has experienced a noticeable growth in the last decade, mainly in that related to the development of efficient CPL emitters based on simple (small-sized, non-polymeric and non-aggregated) organic molecules (SOMs).<sup>2</sup> The interest of CPL roots in the higher resolution provided by the circular polarization of the light, which is key for the development and improvement of smarter photonic tools, such as 3D displays,<sup>3</sup> data storage, enciphering and processing devices (quantum information technology),<sup>4</sup> chemosensors and bioprobes,<sup>5</sup> or ellipsometry-based tomographers.<sup>6</sup> On the other hand, resolution and differential interaction with chiral matter makes CPL an unavoidable source of information to study chirality at excited states (CPL spectroscopy),<sup>7</sup> but also to discern and quantify chiral enantiomers (CPL chiral sensing).<sup>8</sup> Moreover, CPL has been successfully used to promote asymmetric reactions,<sup>9</sup> as well as to control chiral morphologies in nanomaterials.<sup>10</sup>

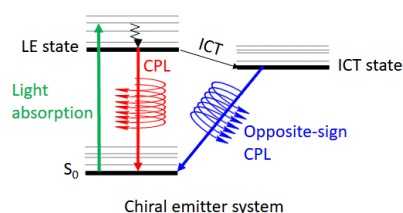
The level of CPL is quantified by the luminescence dissymmetry factor,  $g_{lum}$ , whose values stand between  $-2$  and  $+2$  (full right and left polarized emission, respectively).<sup>11</sup> Reversal of the CPL handedness ( $g_{lum}$  sign; CPL sign) has been highlighted as a useful phenomenon with huge potential for the development of sophisticated optical materials and devices.<sup>12</sup> However, changing the CPL sign in a chiral emitter, without changing its absolute configuration, is rare and it has been generally achieved only by two general strategies: (1) modifying the 3D geometry in flexible chromophoric systems;<sup>12a,13</sup> (2) promoting excimer emission,<sup>12b,14</sup> since key CPL differences (sign and level) are possible when such species are at play (note that emission from excimers should involve states with very different geometries, as they only exists at the excited state). Therefore, research directed to expand the strategies to manipulate the CPL sign, especially in conformationally-rigid emitters or without capability to interact, intra or intermolecularly, promoting excimer emission, is needed to advance in the development of smarter photonic applications based on CPL. Boron dipyrromethenes (BODIPY dyes) have emerged as interesting CPL-enabling SOMs.<sup>12c,15,16</sup> This is due to the possibility of combining CPL with the outstanding physical and chemical properties of the BODIPY dyes, such as good solubility in many different solvents, low aggregation capability, high chemical robustness and photostability, large both light-absorption coefficients and fluorescence quantum yields, and workable chemistry allowing ample structural diversity.<sup>17</sup> Moreover, CPL BODIPYs exhibit a good linear correlation between their absolute  $g_{lum}$  and  $g_{abs}$  values, the latter being the absorbance dissymmetry ratio,<sup>18</sup> availing the potential of the BODIPY dyes as useful SOMs to develop CPL applications. However, although BODIPY chemistry allows finely modulating different photonic properties,<sup>19</sup> it has been marginally explored with the aim of manipulating the CPL sign.<sup>16b</sup> Herein we have investigated a new strategy to change the CPL sign. We have used a family of CPL-enabling *O*-BODIPY dyes for this purpose. The herein introduced strategy could be expanded to other chiral emitters and is particularly interesting for

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† Electronic Supplementary Information (ESI) available: Experimental details, supplementary tables and figures, as well as synthetic procedures and characterization data for new compounds. See DOI: 10.1039/x0xx00000x



**Fig. 1.** Jablonsky diagram explaining the change of the CPL handedness by promoting the population of an ICT state enabling CPL with opposite sign to that from the LE state.

manipulating the CPL sign in conformationally-rigid and non-aggregating emitting systems.

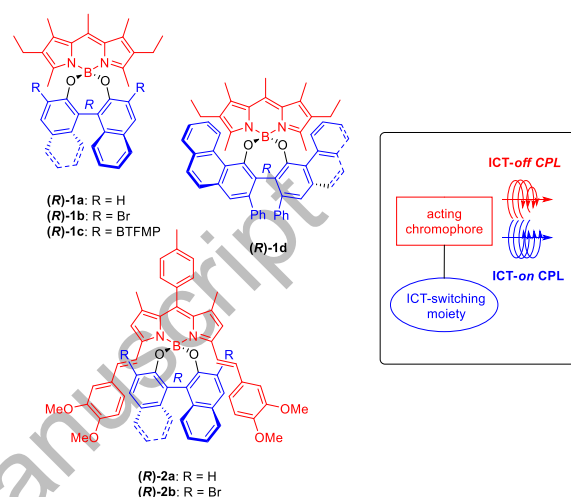
Our research is based on the following hypothesis: promoting the population of an intramolecular charge-transfer (ICT) state enabling CPL with opposite sign to that obtained from the locally-excited (LE) state should serve to manipulate the CPL sign, since such an emission should provide a larger  $|g_{lum}|$  value than that from the LE state (note the weaker character of the ICT transition; see Fig. 1).<sup>1,2a</sup> It should be also noted that the subtle structural change caused by the ICT could be enough to induce a change in the potential energy surface and the vibrational frequency and spacing,<sup>2b</sup> as significant as to reverse the ICT-CPL handedness when compared to the LE-CPL one in some cases.

As a hypothesis-confirming bias, we realized from previous data reported by us that related, conformationally-rigid, non-aggregating and chiral *O*-BODIPY dyes (*R*)-**1a** and (*R*)-**1b** (see Fig. 2) exhibit CPL with opposite signs upon visible (vis) irradiation (*i.e.*, BODIPY-chromophore excitation) in chloroform solution under identical experimental conditions (maximum  $g_{lum}$ (568 nm) =  $+0.7 \cdot 10^{-3}$  for (*R*)-**1a** and  $g_{lum}$ (589 nm) =  $-0.6 \cdot 10^{-3}$  for (*R*)-**1b**; see Fig. 3).<sup>16a,c</sup> This fact seems striking, since both dyes involve very similar BODIPY chromophores. In fact, (*R*)-**1a** and (*R*)-**1b** show similar vis electronic circular dichroism (ECD) spectra, with the same negative sign, under identical conditions (maximum  $g_{abs}$ (ca. 525 nm) =  $-0.9 \cdot 10^{-3}$  for both dyes in chloroform solution; see Fig. 3, and Table S1 in ESI†).<sup>16a,c</sup> However, both dyes are also known to show very different capability to populate emissive ICT states: higher for BINOL-based **1a**; undetectable for 3,3'-dibromoBINOL-based **1b**.<sup>19</sup> Thus, the luminescent ICT state of **1a**, originated by charge transfer from the electron-rich BINOL moiety to the electron-poor BODIPY core,<sup>19</sup> must be responsible for the observed change in the CPL sign.

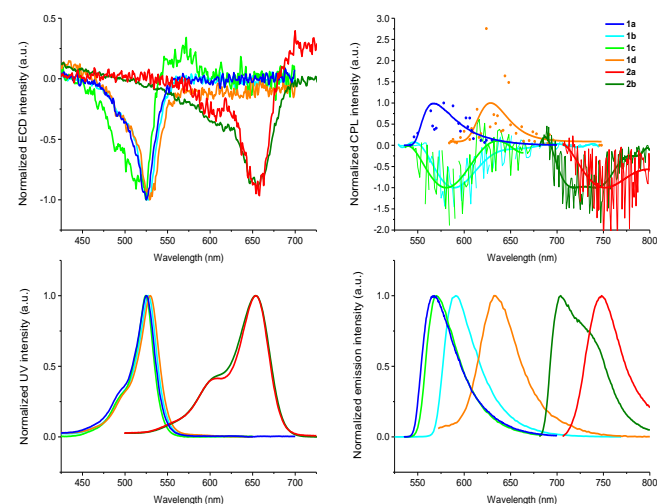
To confirm this hypothesis, we decided to chirally study (*R*)-**1c** and (*R*)-**1d** in comparison to related (*R*)-**1a** and (*R*)-**1b** (Fig. 2). Thus, the known high capability of the VAPOL (2,2'-diphenyl-3,3'-biphenanthr-4-ol) moiety of (*R*)-**1d** to promote ICT in such a dye upon its vis excitation<sup>19</sup> could induce a change in the sign of the observed vis CPL when compared to that of the corresponding vis ECD (*i.e.*, opposite signs for the corresponding  $g_{lum}$  and  $g_{abs}$  values), as it occurs in ICT-enabling BINOL-based (*R*)-**1a**. Oppositely, the demonstrated incapability of the 3,3'-bis[(3,5-trifluoromethyl)phenyl]BINOL moiety of (*R*)-**1c** to promote ICT in this dye<sup>19</sup> should keep the CPL sign in agreement with that of the ECD spectrum, as it happens in 3,3'-dibromoBINOL-based (*R*)-**1b**.

(*R*)-**1c** and (*R*)-**1d** were straightforwardly prepared from commercial (*R*)-3,3'-bis[(3,5-trifluoromethyl)phenyl]BINOL and

(*R*)-VAPOL, respectively, following the same procedure described by us for the corresponding racemates.<sup>19</sup> Similarly to that occurring in  $C_2$ -symmetric (*R*)-**1a** and (*R*)-**1b**, (*R*)-**1c** and (*R*)-**1d** enable huge specific optical rotations ( $[\alpha]_D^{20}$ ) in solution (see Table S1 in Electronic Supporting Information, ESI†), as well as similar negative vis ECD signals upon vis irradiation under the same experimental conditions (see Fig. 3, and Table S1 in ESI†). However, whereas (*R*)-**1c** exhibits a CPL spectrum with a vis negative band in chloroform solution, (*R*)-**1d** does it with a positive vis band (see Fig. 3, and Table S1 in ESI†). This result shows that is possible to control the CPL handedness by way of



**Fig. 2.** Studied CPL-enabling dyes and strategy to manipulate chemically the CPL sign. The acting BODIPY chromophore is highlighted in red, whereas the ICT-modulating bipolyarene moiety (based on BINOL for **1a** and **2a**, 3,3'-dibromoBINOL for **1b** and **2b**, 3,3'-(BTFMP)BINOL for **1c**, and VAPOL for **1d**) is highlighted in blue. BTFMP: bis(3,5-trifluoromethyl)phenyl.



**Fig. 3.** ECD (top, left) and UV-vis absorption (bottom, left), CPL (top, right) and total luminescence (bottom, right) spectra for (*R*)-**1a-d** and (*R*)-**2a-b** in solution (concentration ca.  $3.5 \cdot 10^{-6}$  M for UV-vis absorption and ECD and ca.  $2.0 \cdot 10^{-3}$  M for CPL and total luminescence). Chloroform solution was used in all cases, with the exception of the CPL and total luminescence spectra of (*R*)-**2a** (recorded in acetone; see text). For additional experimental details, see ESI.† Regarding spectral-shifting, plotting and noise issues, see text.

modulating the ICT emission, which can be done chemically by modifying the electron richness of the bipolyarene moiety.

It should be noted that the selected *O*-BODIPYs dyes have some important characteristics availing their properness for supporting our hypothesis on changing the CPL sign by modulating CPL from ICT: (1) their capability to populate luminescent ICT states; (2) the conformational rigidity of the acting BODIPY chromophore, discarding changes in the CPL sign due to differences in the 3D geometry of the chromophore when comparing related dyes; (3) their peculiar spiranic structure, avoiding aggregation and excimer formation and, therefore, discarding changes in the CPL sign due to differential excimer emission by differential behaviour in related dyes. Besides, it must be also noted that spectral shifting in CPL spectra, when compared to each other and to ECD spectra, is associated to the specific conditions used for recording the CPL spectra (*i.e.*, excitation energy and dye concentration; see in General methods, instrumentation and techniques in ESI<sup>†</sup>), as well as to differential participation of the ICT state in such spectra. On the other hand, the method used for plotting the CPL spectra of (*R*)-**1a** and (*R*)-**1d** was different to that used for the other dyes (Fig. 3). This is because two different methods were used to record the spectra. Thus, due to the observed high sensitivity of (*R*)-**1a** and (*R*)-**1d** to the excitation source (see in General methods, instrumentation and techniques in ESI<sup>†</sup>), it was not possible to record CPL spectra by using a single sample-solution badge, but a set of solution badges was used instead to record single  $g_{lum}$  values for each given wavelength. The said sample sensitivity explains also the significant noise of the CPL spectra of (*R*)-**1a** and (*R*)-**1d** (Fig. 3).

As a proof of concept, we have studied two additional spiranic *O*-BODIPY dyes: the couple formed by (*R*)-**2a** and (*R*)-**2b**, which are based on BINOL and 3,3'-dibromoBINOL, respectively (see Fig. 2). Despite (*R*)-**2a** being based on BINOL, this dye is expected to have no capability for ongoing from-BINOL-to-BODIPY ICT, due to the electron-rich character of the involved BODIPY chromophore (note the electron-donating methoxyl groups attached to the  $\pi$ -extended BODIPY chromophore; see Fig. 2).<sup>19</sup> Therefore, this new couple of related dyes should exhibit the same ECD sign and, additionally, the same CPL sign. (*R*)-**2a** and (*R*)-**2b** were straightforwardly prepared by the same methodology used for obtaining the previous dyes (see Fig. S1 and synthetic details in ESI<sup>†</sup>). As expected, the new  $C_2$ -symmetric *O*-BODIPY dyes enable huge specific optical rotations in solution, as well as notable fluorescence and CPL efficiencies in solution, too (see Table S1 and Fig. S2 in ESI<sup>†</sup>). Noticeably, ICT is not detected in 3,3'-dibromoBINOL-based (*R*)-**2b**, neither in BINOL-based (*R*)-**2a**, as shown by the lack of significant dependency of the fluorescence efficiency on the solvent polarity (see Table S2 and Fig. S3 in ESI<sup>†</sup>). To our satisfaction, (*R*)-**2a** and (*R*)-**2b** exhibit not only vis ECD with the same sign (negative), but also vis CPL with the same negative sign (see Fig. 3, and Table S1 in ESI<sup>†</sup>), supporting our hypothesis.

It must be noted here that the CPL spectrum of (*R*)-**2a** could not be recorded in chloroform solution due to rapid and full photodegradation of the dye. This differential behaviour is attributed to the higher instability of the boron chelate involved

in **2a**, due to both steric and electronic factors, combined with the significant acidity of chloroform. Thus, acetone was used as an alternative polar enough solvent (see Fig. 3). Nonetheless, to discard differential effects affecting the CPL sign, additional polar solvents were also tested (*e.g.*, dichloromethane) giving place to CPL spectra with negative maxima in all cases.

In summary, we report the first examples on the control of the CPL handedness (sign of observed circularly emission) by chemically modulating ICT emission competing with that from the LE state. Although chiral BODIPYs were selected to exemplify this control, it could be easily applied to other chiral emitters, too. To apply such a control, it is not necessary that the emission from the ICT state surpasses the one from the LE one, since the ICT emission is expected to involve larger circular polarization. However, both circularly polarized emissions do need to show opposite handedness. This is an unprecedented strategy to manipulate the CPL sign in chiral emitters without changing absolute configurations, being specifically useful for rigid emitters and emitters without capability to promote excimer emission. This makes the new strategy especially valuable for manipulating CPL sign in simple organic molecules (SOMs), since SOMs fulfilling those characteristics, conformational rigidity and inability to aggregate, are expected to exhibit high fluorescence in solution, being interesting for the development of specific photonic applications.<sup>2a</sup> However, general alternative ways to change the CPL sign in SOMs were not available beyond changing absolute configurations. Moreover, the new strategy paves the way to expand the use of such SOMs to applications based on switching the CPL sign, since the key sign-controlling ICT should be dynamically modulated by external stimuli, such a temperature or solvent polarity. Moreover, since only the CPL sign, but not the ECD one, is changed, the strategy could be also interesting for the development of sophisticated applications based on differential ECD vs. CPL behaviour (*e.g.*, cryptochirality).<sup>20</sup> Further studies are in progress to exploit this possibility by developing advanced ICT-switching dyes based on rigid and non-aggregating CPL-enabling SOMs, as well as to predict computationally the reversal of the CPL from ICT when compared to the CPL from LE (necessary condition to apply the reported CPL-sign control). Financial support from Ministerio de Ciencia, Innovación y Universidades de España (MAT2017-83856-C3-2-P and MAT2017-83856-C3-3-P) and Gobierno Vasco (IT912-16) is gratefully acknowledged. G.M. thanks the NIH, Minority Biomedical Research Support (1 SC3 GM089589-08) and the Henry Dreyfus Teacher-Scholar Award for financial support. J.J. thanks Comunidad de Madrid - UCM for a research contract.

## Conflicts of interest

There are no conflicts to declare.

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