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Josué Jiménez, *Universidad Complutense de Madrid*

Luis Cerdán, *Instituto de Química Física "Rocasolano"*

Florencio Moreno, *Universidad Complutense de Madrid*

Beatriz L. Maroto, *Universidad Complutense de Madrid*

Inmaculada García-Moreno, *Instituto de Química Física "Rocasolano"*, et al.

# Chiral Organic Dyes Endowed with Circularly Polarized Laser Emission

Josué Jiménez,<sup>†</sup> Luis Cerdán,<sup>\*,†,‡,§</sup> Florencio Moreno,<sup>†</sup> Beatriz L. Maroto,<sup>†</sup> Inmaculada García-Moreno,<sup>‡</sup> Jamie L. Lunkley,<sup>§</sup> Gilles Muller,<sup>§</sup> and Santiago de la Moya<sup>\*,†,§</sup>

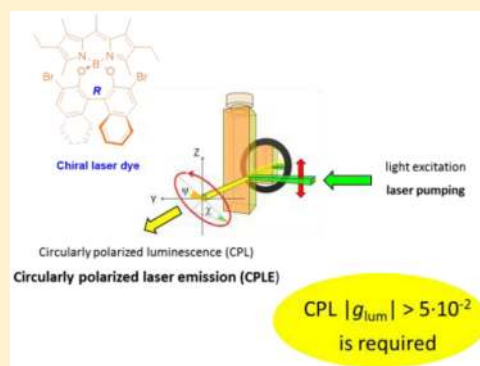
<sup>†</sup>Departamento de Química Orgánica I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040, Madrid, Spain

<sup>‡</sup>Instituto de Química Física "Rocasolano" (IQFR), Consejo Superior de Investigaciones Científicas (CSIC), C/Serrano 119, 28006, Madrid, Spain

<sup>§</sup>Department of Chemistry, San José State University, San José, California 95192-0101, United States

## S Supporting Information

**ABSTRACT:** The direct generation of efficient, tunable, and switchable circularly polarized laser emission (CPLE) would have far-reaching implications in photonics and material sciences. In this paper, we describe the first chiral simple organic molecules (SOMs) capable of simultaneously sustaining significant chemical robustness, high fluorescence quantum yields, and circularly polarized luminescence (CPL) ellipticity levels ( $|g_{lum}|$ ) comparable to those of similar CPL-SOMs. All these parameters altogether enable efficient laser emission and CPLE with ellipticity levels 2 orders of magnitude stronger than the intrinsic CPL ones.



## INTRODUCTION

Circularly polarized luminescence (CPL) accounts for the differential emission of left-handed and right-handed circularly polarized (CP) light.<sup>1–6</sup> The interest in this phenomenon lies in the higher resolution that CP light brings to the applications where it is used, leading to the development of smarter photonic materials for advanced technologies, such as three-dimensional (3D) displaying,<sup>7</sup> information storage and processing,<sup>8,9</sup> communication of spin information (spintronics-based devices),<sup>10</sup> or ellipsometry-based tomography.<sup>11,12</sup> Going one step beyond, the virtually unexplored direct emission of circularly polarized laser light (CPLE) has a huge potential in the improvement of many of these applications<sup>13,14</sup> as well as in other advanced fields such as the accurate study of biological processes involving chiral products;<sup>15,16</sup> the efficient promotion of light-induced asymmetric processes in confined systems, such as zeolites,<sup>17,18</sup> nanostructured surfaces,<sup>19</sup> or polymeric matrixes;<sup>20–23</sup> or the control of chiral morphologies in nanostructures.<sup>24</sup> Therefore, the development of new materials enabling CPLE should be a top priority objective in materials science research.

Currently, organic lasers directly generating visible (vis), tunable, and circularly polarized laser radiation are scarce and rely on intracavity conversion to CPLE by means of optical retardation. This effect has been achieved so far by using either chiral liquid crystals as hosts for the chromophores<sup>13,25–28</sup> or dynamic chiral gratings induced by interference of circularly

polarized beams.<sup>29</sup> Besides, it has been demonstrated that it is possible to generate CPLE in achiral solutions in random lasers<sup>30</sup> or by means of pump-induced birefringence in transversely pumped Fabry–Perot cavities.<sup>31</sup> In this last case, it was studied how the pump polarization influenced the polarization state of the generated laser light. The strong and polarized pump light excites preferentially the molecules whose absorption dipole moments are properly aligned with the pump electric field. This excitation selectivity leads to a ground and excited state molecular orientation anisotropy, i.e., to an absorption and emission anisotropy. The presence of an absorption orientation anisotropy is causally translated into a refractive index orientation anisotropy; i.e., an optical birefringence is induced. This birefringence exerts a phase delay between the two transverse cavity modes, providing the generated laser beam with elliptical polarization. Depending on the chosen pump polarization, the birefringence can be made stronger, weaker, or even to disappear.

In the development of smart optical materials endowed with vis, tunable, and efficient CPL emission, chiral organic laser dyes arise as very attractive candidates, mainly owing to the properties associated with their strong absorption and efficient emission in the vis spectral region, small size, and excellent

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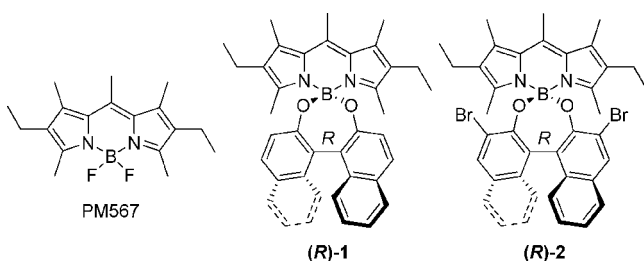
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organic-solvent solubility.<sup>32–39</sup> These characteristics confer on them unique capability for the direct generation of CPL in solution and in confined systems.

Considering their huge potential, it is noticeable that chiral organic dyes enabling intrinsic CPL are unknown to date. It is in this context that we demonstrate for the first time laser emission from a CPL compound and run the first study on the CPL properties of a newly and specifically designed enantiomeric couple of model simple organic dyes, assessing the possible transfer of their fluorescent CPL ability into circular (or elliptical) polarized laser light emission (free of optical retardation artifacts) with controlled handedness.

## RESULTS AND DISCUSSION

An enantiomeric couple of organic dyes showing high fluorescence quantum yields, enabling CPL, and sustaining efficient laser emission was necessary for this study. Thus, we took our recently reported new design for CPL-SOMs (simple organic molecules) as a starting point (see BODIPY (*R*)-1 in Figure 1).<sup>40</sup> As we reported, this molecule shows CPL levels



**Figure 1.** Dyes synthesized for this study (**2**), based on previously described CPL-SOMs **1** and parent achiral dye (PM567). Only the *R* enantiomers are shown.

falling in the same range as most CPL-SOMs. However, we had found a decrease in the fluorescence of this chiral *O*-BODIPY dye when compared with the corresponding parent *F*-BODIPY PM567 (0.45 vs 0.80 in CHCl<sub>3</sub>, see Figure 1). On the other hand, we had also observed that, in the case of *O*-BODIPYs involving carboxyl units attached to the boron, those having electron-withdrawing (EW) substituted carboxyls showed higher fluorescence quantum yields.<sup>41</sup> Therefore, we decided to introduce EW bromine groups in the BINOL moiety of (*R*)-1 and (*S*)-1 to generate new chiral dyes (*R*)-2 and (*S*)-2 (Figure 1). The introduced bromines are expected to have a triple effect on the dye properties. First, they should increase the chemical stability of the boron-chelate-based BODIPY chromophore, by enhancing the electrophilic character of the dioxyboron rest by means of negative electronic inductive effect (as we have observed for other *O*-BODIPY dyes), which is essential for laser dyes. Second, they should improve the fluorescence quantum yield of the dyes,<sup>41</sup> which is necessary for an efficient laser emission. Third, the large volume of the bromine atoms would amplify the chiral perturbation that the BINOL moiety exerts over the BODIPY chromophore.<sup>40</sup> It is expected that this effect would enhance the chiroptical properties of the dye, in both absorption and emission of circularly polarized light (circular dichroism and CPL, respectively).

**Synthesis and Photophysics.** The synthesis of (*R*)-2 and (*S*)-2 was carried out following the same procedure described for the synthesis of related (*R*)-1 and (*S*)-1,<sup>40</sup> using the

corresponding enantiopure 3,3'-dibromo-1,1'-bi(2-naphthol) (3,3'-dibromoBINOL, see Supporting Information (SI) for details) in yields comparable to those reached for enantiomers **1** (60% for (*R*)-2 and 64% for (*S*)-2). The handling of the new dyes showed them to be more chemically stable than their counterparts **1**. As a matter of fact, enantiomers **2** are robust enough to be purified by flash chromatography on silica gel without significant decomposition. This is not the case for enantiomers **1**, which require less reactive neutral alumina as the chromatographic stationary phase.<sup>40</sup> Besides, as it was the case for **1**, the <sup>1</sup>H NMR spectrum of **2** shows clear diastereotopicity for the protons of the isochronous methylene groups (ABX<sub>3</sub> spin system, see SI). This diastereotopicity is indicative of the expected chiral perturbation of the BODIPY moiety, at least on the magnetic properties of the mentioned proton nuclei.

Regarding the photophysical properties of the new dyes **2**, conventional steady-state UV–vis photophysical measurements (see SI) revealed identical parameters for both enantiomers (*R*)-2 and (*S*)-2, as it was otherwise expected (Table S1 in the SI). Compared to the nonbrominated counterpart **1**, the absorption and fluorescence peak wavelengths of **2** remained almost unchanged (527 and 547 nm, respectively), whereas the quantum yield significantly increased from 0.45 to 0.69 (chloroform as solvent; see SI for experimental details). This result confirms, once again, the positive influence of EW groups attached to the *O*-moiety over the fluorescence of the *O*-BODIPY.<sup>41</sup>

**Chiroptical Properties.** Optical rotation and, mostly, circular dichroism (CD) are important sources of information about the existence of helical (or pseudohelical) structures in solution. Thus, high optical rotation values and, especially, high Cotton effects in CD are usually indicative of a high helical character. In turn, a high helical character is an essential feature when it comes to reaching high CPL values.<sup>42</sup> Therefore, both optical rotation and CD were measured for new dyes **2** before studying their CPL behavior.

Analogously to dyes **1** { $[\alpha]_D^{20}$  ca. 5000 (*c* 0.1, CHCl<sub>3</sub>)},<sup>40</sup> enantiomers **2** showed huge specific optical rotation values { $[\alpha]_D^{20}$  ca. 4000 (*c* 0.1, CHCl<sub>3</sub>)} (see the SI). On the one hand, these values are in agreement with the expected high pseudohelical character of the dye, imposed by the conformationally restricted C<sub>2</sub>-symmetric BINOL moiety. On the other hand, the fact that the optical rotation remains unaltered over the concentration (see the SI) demonstrates that there are no aggregates in solution, which is a crucial factor for their use as laser dyes.

The CD spectra of **2** show strong dichroic signals in the vis region, with maxima at the maximum absorption wavelength of the BODIPY chromophore, as occurred in the case of **1** (Figure 2). This dichroic signalization has been quantified in terms of the absorption anisotropy factor (Kuhn dissymmetry ratio)  $g_{\text{abs}}(\lambda) = 2\Delta\epsilon/\epsilon = 2((\epsilon_L - \epsilon_R)/(\epsilon_L + \epsilon_R)) = (\theta)/(3298\epsilon)$ , where  $\epsilon_L$  and  $\epsilon_R$  refer, respectively, to the molar extinction coefficients of left and right circularly polarized light, ( $\theta$ ) is the molar ellipticity in deg·cm<sup>2</sup>·mmol<sup>-1</sup>, and  $\epsilon$  is the global molar extinction coefficient. Contrary to what we had predicted, we have not observed any improvement in the maximum  $g_{\text{abs}}$  values in relation to **1**, nor any significant decrease ( $-8.6 \times 10^{-4}$  for (*R*)-2 vs  $-9.4 \times 10^{-4}$  for (*R*)-1, and  $+8.8 \times 10^{-4}$  for (*S*)-2 vs  $+7.4 \times 10^{-4}$  for (*S*)-1, see Table S2 in SI). As was the case for **1**, the detected strong Cotton effect demonstrates that the achiral BODIPY chromophore is chirally perturbed by the

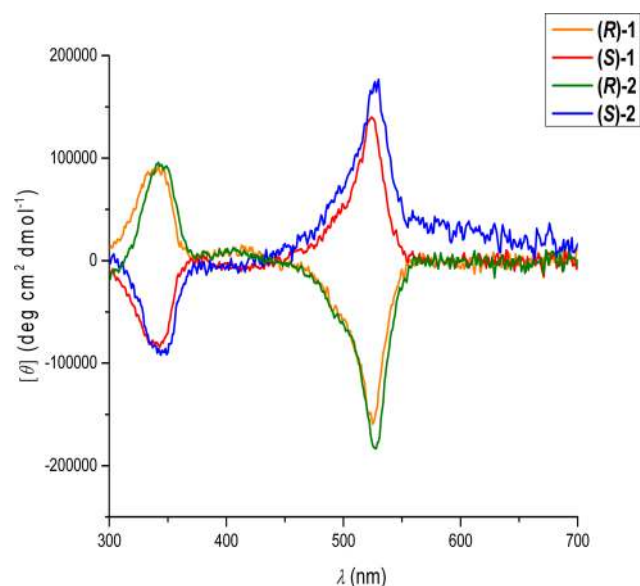


Figure 2. CD spectra of **1** and **2** in chloroform solution (ca.  $10^{-6}$  M).

BINOL moiety, at least at its ground state. Therefore, an analogous perturbation can be expected for the excited state, which would lead to CPL from enantiomers **2**.

Analogously to  $g_{\text{abs}}$  for CD, the degree of CPL is given by the dissymmetry factor,  $g_{\text{lum}}(\lambda) = 2\Delta I/I = 2(I_L - I_R)/(I_L + I_R)$ , where  $I_L$  and  $I_R$  refer, respectively, to the intensities of left and right circularly polarized emissions.<sup>44</sup> Indeed, as expected from the results obtained for the optical rotation and CD, together with the fact that dyes **2** follow the CPL-SOM design exemplified by **1**,<sup>40</sup> almost mirrored spectra with opposite maximum  $g_{\text{lum}}$  values ( $-0.6 \times 10^{-3}$  for (R)-**2** and  $+0.8 \times 10^{-3}$  for (S)-**2**) were obtained (Figure 3, see Table S3 in SI). These values are similar to those from the nonbrominated counterparts **1** ( $|g_{\text{lum}}|$  ca.  $0.7 \times 10^{-3}$ ),<sup>40</sup> being in the range of other CPL-SOMs.<sup>32</sup> These all-in-one characteristics of enantiomers **2** when compared to **1** (improved chemical stability, similar and acceptable CPL activity, and, especially, enhanced fluorescence) make them suitable candidates for analyzing their CPLE behavior.

**Circularly Polarized Laser Study.** The previous photo-physical results suggest that BODIPYs **2** should be capable of sustaining efficient laser emission. In a transversally pumped cavity configuration (Figure 4a) and at an optimized dye concentration of 1 mM, ethyl acetate solutions of the new dyes emit laser light at 575 nm with efficiency (output/input energy ratio) as high as 68%. These results represent the first demonstration of coherent radiation from any CPL compound so far, becoming a most relevant result of this paper. This efficiency is slightly higher than that of the parent dye PMS67. This enhancement, which ultimately comes from an improvement in the chromophore planarity and aromaticity,<sup>41</sup> is expected for BODIPY dyes whose fluorine atoms have been substituted by oxygen pendant groups (i.e., O-BODIPYs instead of F-BODIPYs), such as the carboxyl groups reported in ref 41 or the 3,3'-dibromobINOL groups in the present work.

To check whether the CPL shown by enantiomers **2**, both in strength and in sign, was translated into CPLE, we performed a complete polarimetric study of their laser emission with a homemade polarimeter<sup>31</sup> (see Figure S1 in the SI for full details

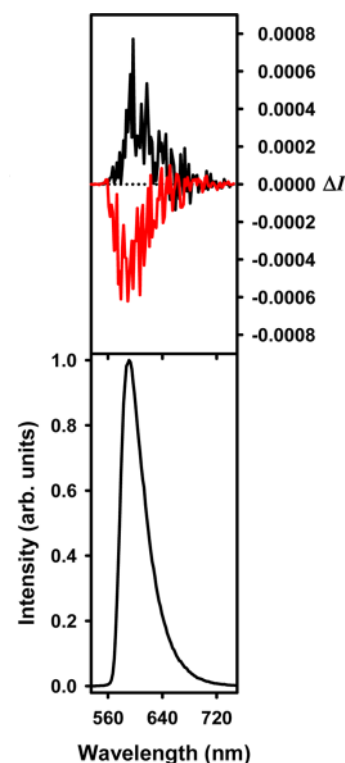
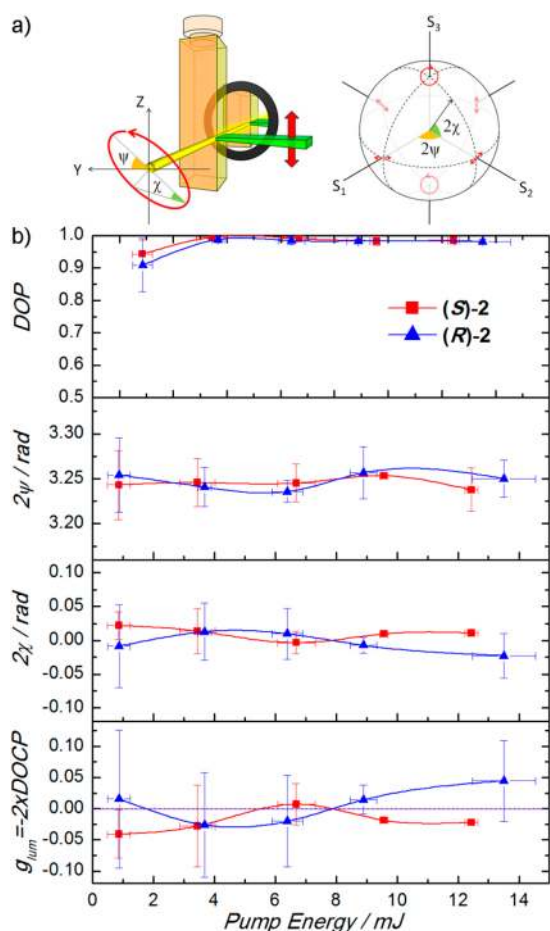


Figure 3. CPL (upper curves; S enantiomer in black, R in red) and total luminescence (lower curves) spectra of **2** in degassed chloroform solutions (ca.  $10^{-3}$  M) at 295 K, upon excitation at 445 nm.

on the experimental setup and methodology). In order to detect intrinsic (free of anisotropy artifacts) CPLE with the current pump and cavity configuration (Figure 4a), one should ideally reduce as much as possible the contribution from the laser-induced birefringence.<sup>31</sup> In our previous work, we showed that this happens when the solution is excited with light polarized in the excitation/detection plane (horizontal linear polarization in our case).<sup>31</sup> However, under these conditions the emission is highly unpolarized, and the polarimetry formalism that we use to retrieve the polarization state struggles to find realistic and reliable solutions.<sup>31</sup> To avoid this uncertainty, one could run many experiments to get as better statistics as possible, but it would be extremely time-consuming and the solution would be probably photodegraded before the experiment is finished due to the intense excitation. On the other hand, our method works very well when the signals are partially or fully polarized (pump polarization other than horizontal), and we rely on this accuracy to detect changes in the overall CPLE (birefringence effect + intrinsic CPL) due to the intrinsic contribution of CPL. In any case, the accuracy in measuring  $|g_{\text{lum}}|$  values in our current setup is  $\sim 0.05$ . Hence,  $|g_{\text{lum}}|$  below this value cannot be confidently discerned. In this sense, our methodology is useful for measuring CPLE levels (intrinsic or influenced by light-induced birefringence) under laser pumping and would be complementary to, but never substitutive for, that used for measuring CPL signals.<sup>3,4</sup>

The global polarization state of a given arbitrary beam can be described in terms of the Stokes parameters  $S_i$  ( $i = 0, 1, 2, 3$ ),<sup>43</sup> but it is more physically insightful to express it with the related parameters beam energy ( $E_{\text{out}}$ ), degree of polarization (DOP), degree of circular polarization (DOCP), and orientation ( $\psi$ ) and ellipticity ( $\chi$ ) of the polarization ellipse (Figure 4a). Note that the DOCP calculated with this method, which in turn is



**Figure 4.** (a) Sketch of cavity and pump configuration and polarization ellipse, and Poincaré sphere with representative polarization states. (b) Laser emission polarization state parameters of **2** as a function of pump energy for a linear vertical pump polarization. Each point and error bar in (b) represent the average and standard deviation, respectively, of the fitting parameters obtained over five sets of measurements. Lines are guides to the eye. The dashed lines in the bottom plot mark the values of CPL  $g_{\text{lum}}$  for each dye.

related to  $\chi$ , equals minus half the  $g_{\text{lum}}$  defined for CPL.<sup>31</sup> However, care must be exercised in comparing CPL  $g_{\text{lum}}$  with CPLE  $g_{\text{lum}}$  (or DOCP), as they may be radically different. In fact, the laser  $g_{\text{lum}}$  for PM567 amounted to  $-0.1$  for a CPL  $g_{\text{lum}}$  of  $0$ .<sup>31</sup>

The laser light polarization state parameters for solutions of (R)-**2** and (S)-**2** were evaluated as a function of the pump energy and polarization. Figure 4b shows the results corresponding to a linear vertical pump polarization (those corresponding to a linear  $45^\circ$  pump polarization can be found in Figure S2 of the SI). Both the DOP and the polarization ellipse orientation  $2\psi$  follow the expected behavior for laser dyes with nearly parallel absorption and emission transition dipole moments;<sup>31</sup> i.e., the emission is highly polarized and vertically oriented. Analogous results are obtained for a linear  $45^\circ$  polarized pump (Figure S2 of the SI). As explained elsewhere, this arises from the orientation anisotropy of the excited state dipole moments induced by the polarized pump.<sup>31</sup> Note here that both chiral dyes present a laser emission which is more polarized than that of the parent dye PM567.<sup>31</sup> The rationale of this increment can be found in the bulkier nature of the chiral dyes, nearly doubling the size of the parent PM567.

In this sense, the rotational relaxation rate should be smaller, preventing the molecules from randomizing their orientation before the photons were emitted. Time-resolved fluorescence anisotropy measurements rendered rotational relaxation lifetimes for PM567 and (R)-**2** ((S)-**2** is expected to show the same lifetime) of  $130 \pm 10$  and  $160 \pm 10$  ps, respectively. In other words, the chiral dyes need more time to randomize their orientation, thus confirming our reasoning. The very same DOP enhancement has been observed in chromophores dissolved in viscous solvents, where rotational relaxation is greatly hindered.<sup>31</sup>

The laser emission from both dyes showed signatures of polarization ellipticity ( $2\chi \neq 0$  or  $g_{\text{lum}} \neq 0$ ), with values that oscillate as the pump intensity increases (Figure 4b). Analogous results are obtained for linear  $45^\circ$  polarized pump (Figure S2 of the SI). In our previous publication<sup>31</sup> we showed that the origin of this ellipticity arises from the dynamic birefringence induced in the dye solution by the strong and polarized laser pumping and the subsequent orientation anisotropy of the excited molecular dipoles. In other words, the pumping process turns the active medium into a wave retarder. Once the pulse is over, the solution recovers its isotropy. The induced anisotropy has a complex nonlinear dependence on the pump energy, position, and time, thus the characteristic oscillating behavior shown by  $2\psi$  and  $2\chi$ .<sup>31</sup> For (R)-**2** and (S)-**2**,  $2\chi$  oscillates from positive (right-handed) to negative (left-handed), reaching CPLE  $|g_{\text{lum}}|$  values up to  $5 \times 10^{-2}$ , 2 orders of magnitude higher than the CPL  $g_{\text{lum}}$  (dashed lines in bottom plot, Figure 4b).

These results show that the laser polarization ellipticity originated by the chiral dyes is of the same magnitude as that originated by the achiral dye.<sup>31</sup> Nevertheless, there is no strong evidence that the enantiomers show a clear and opposite handedness in CPLE (within experimental errors). This is not surprising, since even if one could remove the birefringence contribution, there is no reason by which one should obtain a relevant difference in magnitude between the CPL and intrinsic CPLE  $|g_{\text{lum}}|$  values. Hence, the contribution to the polarization ellipticity of the pump-induced dynamic birefringence, which has its origin in the anisotropy of the excited state dipole moments, but not in the intrinsic chirality of the dyes, screens the CPLE ellipticity contributed by the intrinsic CPL (maximum  $|g_{\text{lum}}| \sim 10^{-3}$ ).

Thus, in terms of detecting intrinsic CPLE (i.e., amplification of CPL), both chiral dyes **1** and **2** could be catalogued as nonsuitable. In terms of extrinsic CPLE (i.e., due to laser-induced birefringence), they could be seen “as good as an achiral dye”. In this sense, the dissymmetry factor  $|g_{\text{lum}}|$  due to the pump-induced effects has an upper value of  $(5-9) \times 10^{-2}$ . Therefore, it would be possible to detect, even in the presence of birefringence “artifacts”, intrinsic CPLE with a definite handedness from a chiral dye, provided that its CPL dissymmetry factor  $|g_{\text{lum}}|$  was higher than  $5 \times 10^{-2}$ . Work in progress is directed to design new enantiomeric organic laser dyes with stronger CPL levels by further increasing, for instance, their helical (or pseudohelical) character.<sup>32</sup>

## CONCLUSIONS

We have generated for the first time laser emission from a CPL molecular system, and have presented a proof of concept to lay the foundations for the development of simple organic molecules capable of emitting circularly polarized laser light. We have demonstrated that, on the one hand, the described chiral organic dyes **2** are capable of emitting circularly polarized

luminescence ( $I_{\text{glum}}$  in the range of other CPL-SOMs) and, on the other hand, they sustain efficient elliptically polarized laser emission.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b00654.

Experimental details (synthetic procedure, structural characterization data, NMR spectra, photophysical and chiroptical characterization data, and laser measurements including experimental setup); Tables S1–S4; Figures S1 and S2 (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: lcerdan@iqfr.csic.es (L.C.).

\*E-mail: santmoya@ucm.es (S.M.).

### ORCID

Luis Cerdán: 0000-0002-7174-2453

Santiago de la Moya: 0000-0002-7406-909X

### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Riehl, J. P.; Richardson, F. S. Circularly Polarized Luminescence Spectroscopy. *Chem. Rev.* **1986**, *86*, 1–16.
- (2) Brittain, H. G. Excited-State Optical Activity, 1987–1995. *Chirality* **1996**, *8*, 357–363.
- (3) *Comprehensive Chiroptical Spectroscopy Vol. 1. Instrumentation, Methodologies, and Theoretical Simulations*; Berova, N., Polavarapu, P. L., Nakanishi, K., Woody, R. W., Eds.; John Wiley and Sons: Hoboken, NJ, USA, 2012.
- (4) *Luminescence of Lanthanide Ions in Coordination Compounds and Nanomaterials*; de Bettencourt-Dias, A., Ed.; John Wiley and Sons: Chichester, U.K., 2014.
- (5) Zinna, F.; Di Bari, L. Lanthanide Circularly Polarized Luminescence: Bases and Applications. *Chirality* **2015**, *27*, 1–13.
- (6) Wu, T.; You, X.-Z.; Bour, P. Applications of Chiroptical Spectroscopy to Coordination Compounds. *Coord. Chem. Rev.* **2015**, *284*, 1–18.
- (7) Schadt, M. Liquid Crystal Materials and Liquid Crystal Displays. *Annu. Rev. Mater. Sci.* **1997**, *27*, 305–379.
- (8) Sherson, J. F.; Krauter, H.; Olsson, R. K.; Julsgaard, B.; Hammerer, K.; Cirac, I.; Polzik, E. S. Quantum Teleportation between Light and Matter. *Nature* **2006**, *443*, 557–560.
- (9) Wagenknecht, C.; Li, C.-M.; Reingruber, A.; Bao, X.-H.; Goebel, A.; Chen, Y.-A. Q.; Zhang, Chen, K.; Pan, J.-W. Experimental Demonstration of a Heralded Entanglement Source. *Nat. Photonics* **2010**, *4*, 549–552.
- (10) Farshchi, R.; Ramsteiner, M.; Herfort, J.; Tahraoui, A.; Grahm, H. T. Optical Communication of Spin Information between Light Emitting Diodes. *Appl. Phys. Lett.* **2011**, *98*, 162508.
- (11) Yu, C. J.; Lin, C. E.; Yu, L. P.; Chou, C. Paired Circularly Polarized Heterodyne Ellipsometer. *Appl. Opt.* **2009**, *48*, 758–764.
- (12) Jan, C. M.; Lee, Y.-H.; Wu, K.-C.; Lee, C.-K. Integrating Fault Tolerance Algorithm and Circularly Polarized Ellipsometer for Point-of-Care Applications. *Opt. Express* **2011**, *19*, 5431–5441.
- (13) Furumi, S. Recent Progress in Chiral Photonic Band-Gap Liquid Crystals for Laser Applications. *Chem. Rec.* **2010**, *10*, 394–408.
- (14) Topf, R. D. M.; McCall, M. W. Modes of Structurally Chiral Lasers. *Phys. Rev. A: At., Mol., Opt. Phys.* **2014**, *90*, 053824.
- (15) Jorissen, A.; Cerf, C. Asymmetric Photoreactions as the Origin of Biomolecular Homochirality: A Critical Review. *Origins Life Evol. Biospheres* **2002**, *32*, 129–142.
- (16) Pavlov, V. A.; Klabunovskii, E. I. Homochirality Origin in Nature: Possible Versions. *Curr. Org. Chem.* **2014**, *18*, 93–114.
- (17) Sivaguru, J.; Natarajan, A.; Kaanumalle, L. S.; Shailaja, J.; Uppili, S.; Joy, A.; Ramamurthy, V. Asymmetric Photoreactions within Zeolites: Role of Confinement and Alkali Metal Ions. *Acc. Chem. Res.* **2003**, *36*, 509–521.
- (18) Joy, A.; Kaanumalle, L. S.; Ramamurthy, V. Role of Cations and Confinement in Asymmetric Photochemistry: Enantio- and Diastereo-Selective Photocyclization of Tropolone Derivatives within Zeolites. *Org. Biomol. Chem.* **2005**, *3*, 3045–3053.
- (19) Kampling, M.; Al-Shamery, K.; Freund, H.-J.; Wilde, M.; Fukutani, K.; Murata, Y. Surface Photochemistry on Confined Systems: UV-Laser-Induced Photodesorption of NO from Pd-Nanostructures on Al<sub>2</sub>O<sub>3</sub>. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2629–2637.
- (20) Brunet, E. Asymmetric Induction under Confinement. *Chirality* **2002**, *14*, 135–143.
- (21) Pagni, R. M.; Compton, R. N. Is Circularly Polarized Light an Effective Reagent for Asymmetric Synthesis? *Mini-Rev. Org. Chem.* **2005**, *2*, 203–209.
- (22) Cave, R. J. Inducing Chirality with Circularly Polarized Light. *Science* **2009**, *323*, 1435–1436.
- (23) Meinert, C.; Hoffmann, S. V.; Cassam-Chenaï, P.; Evans, A. C.; Giri, C.; Nahon, L.; Meierhenrich, U. J. Photonenergy-Controlled Symmetry Breaking with Circularly Polarized Light. *Angew. Chem., Int. Ed.* **2014**, *53*, 210–214.
- (24) Yeom, J.; Yeom, B.; Chan, H.; Smith, K. W.; Dominguez-Medina, S.; Bahng, J. H.; Zhao, G.; Chang, W.-S.; Chang, S.-J.; Chuvilin, A.; Melnikau, D.; Rogach, A. L.; Zhang, P.; Link, S.; Král, P.; Kotov, N. A. Chiral Templating of Self-Assembling Nanostructures by Circularly Polarized Light. *Nat. Mater.* **2015**, *14*, 66–72.
- (25) Morris, S. M.; Hands, P. J. W.; Findeisen-Tandel, S.; Cole, R. H.; Wilkinson, T. D.; Coles, H. J. Polychromatic Liquid Crystal Laser Arrays towards Display Applications. *Opt. Express* **2008**, *16*, 18827–18837.
- (26) Hands, P. J. W.; Morris, S. M.; Wilkinson, T. D.; Coles, H. J. Two-Dimensional Liquid Crystal Laser Array. *Opt. Lett.* **2008**, *33*, 515–517.
- (27) Gardiner, D. J.; Morris, S. M.; Hands, P. J.; Mowatt, C.; Rutledge, R.; Wilkinson, T. D.; Coles, H. J. Paintable Band-Edge Liquid Crystal Lasers. *Opt. Express* **2011**, *19*, 2432–2439.
- (28) Gardiner, D. J.; Hsiao, W.-K.; Morris, S. M.; Hands, P. J. W.; Wilkinson, T. D.; Hutchings, I. M.; Coles, H. J. Printed Photonic Arrays from Self-Organized Chiral Nematic Liquid Crystals. *Soft Matter* **2012**, *8*, 9977–9980.
- (29) Chen, F.; Gindre, D.; Nunzi, J.-M. Tunable Circularly Polarized Lasing Emission in Reflection Distributed Feedback Dye Lasers. *Opt. Express* **2008**, *16*, 16746–16753.
- (30) Knitter, S.; Kues, M.; Fallnich, C. Emission Polarization of Random Lasers in Organic Dye Solutions. *Opt. Lett.* **2012**, *37*, 3621–3623.
- (31) Cerdán, L.; García-Moreno, S.; Costela, A.; García-Moreno, I.; de la Moya, S. Circularly Polarized Laser Emission Induced in Isotropic and Achiral Dye Systems. *Sci. Rep.* **2016**, *6*, 28740.
- (32) Sánchez-Carnerero, E. M.; Agarrabeitia, A. R.; Moreno, F.; Maroto, B. L.; Muller, G.; Ortiz, M. J.; de la Moya, S. Circularly

Polarized Luminescence from Simple Organic Molecules. *Chem. - Eur. J.* **2015**, *21*, 13488–13500.

(33) Kumar, J.; Nakashima, T.; Kawai, T. Circularly Polarized Luminescence in Chiral Molecules and Supramolecular Assemblies. *J. Phys. Chem. Lett.* **2015**, *6*, 3445–3452.

(34) Gon, M.; Morisaki, Y.; Chujo, Y. Highly Emissive Optically Active Conjugated Dimers Consisting of a Planar Chiral [2.2]-Paracyclophane Showing Circularly Polarized Luminescence. *Eur. J. Org. Chem.* **2015**, *2015*, 7756–7762.

(35) Sakai, H.; Shinto, S.; Kumar, J.; Araki, Y.; Sakanoue, T.; Takenobu, T.; Wada, T.; Kawai, T.; Hasobe, T. Highly Fluorescent [7]Carbohelicene Fused by Asymmetric 1,2-Dialkyl-Substituted Quinoxaline for Circularly Polarized Luminescence and Electroluminescence. *J. Phys. Chem. C* **2015**, *119*, 13937–13947.

(36) Nakabayashi, K.; Kitamura, S.; Suzuki, N.; Guo, S.; Fujiki, M.; Imai, Y. Non-Classically Controlled Signs in a Circularly Polarised Luminescent Molecular Puppet: The Importance of the Wire Structure Connecting Binaphthyl and Two Pyrenes. *Eur. J. Org. Chem.* **2016**, *2016*, 64–69.

(37) Gon, M.; Morisaki, Y.; Sawada, R.; Chujo, Y. Synthesis of Optically Active, X-Shaped, Conjugated Compounds and Dendrimers Based on Planar Chiral [2.2]Paracyclophane, Leading to Highly Emissive Circularly Polarized Luminescence. *Chem. - Eur. J.* **2016**, *22*, 2291–2298.

(38) Alnoman, R. B.; Rihn, S.; O'Connor, D. C.; Black, A.; Costello, B.; Waddell, P. G.; Clegg, W.; Peacock, R. D.; Herrebout, W.; Knight, J. G.; Hall, M. J. Circularly Polarized Luminescence from Helically Chiral *N,N,O,O*-Boron-Chelated Dipyrromethenes. *Chem. - Eur. J.* **2016**, *22*, 93–96.

(39) Longhi, G.; Castiglioni, E.; Villani, C.; Sabia, R.; Menichetti, S.; Vigliani, C.; Devlin, F.; Abbate, S. Chiroptical Properties of the Ground and Excited States of Two Thia-Bridged Triarylamine Heterohelicenes. *J. Photochem. Photobiol., A* **2016**, *331*, 138–145.

(40) Sánchez-Carnerero, E. M.; Moreno, F.; Maroto, B. L.; Agarrabeitia, A. R.; Ortiz, M. J.; Vo, B. G.; Muller, G.; de la Moya, S. Circularly Polarized Luminescence by Visible-Light Absorption in a Chiral O-BODIPY Dye: Unprecedented Design of CPL Organic Molecules from Achiral Chromophores. *J. Am. Chem. Soc.* **2014**, *136*, 3346–3349.

(41) Durán-Sampedro, G.; Agarrabeitia, A. R.; Cerdán, L.; Pérez-Ojeda, M. E.; Costela, A.; García-Moreno, I.; Esnal, I.; Bañuelos, J.; López Arbeloa, I.; Ortiz, M. J. Carboxylates versus Fluorines: Boosting the Emission Properties of Commercial BODIPYs in Liquid and Solid Media. *Adv. Funct. Mater.* **2013**, *23*, 4195–4205.

(42) Ray, C.; Sánchez-Carnerero, E. M.; Moreno, F.; Maroto, B. L.; Agarrabeitia, A. R.; Ortiz, M. J.; López-Arbeloa, I.; Bañuelos, J.; Cohovi, K. D.; Lunkley, J. L.; Muller, G.; de la Moya, S. Bis(haloBODIPYs) with Labile Helicity: Valuable Simple Organic Molecules that Enable Circularly Polarized Luminescence. *Chem. - Eur. J.* **2016**, *22*, 8805–8808.

(43) *Principles of Optics*, 5th ed.; Born, M., Wolf, E., Eds.; Pergamon Press: Oxford, U.K., 1975.

(44) Riehl, J. P.; Muller, G. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Bünzli, J.-C. G., Pecharsky, V. K., Eds.; North-Holland Publishing Co.: Amsterdam, Netherlands, 2005; Vol. 34, Chapter 220, pp 289–357, and references therein.