

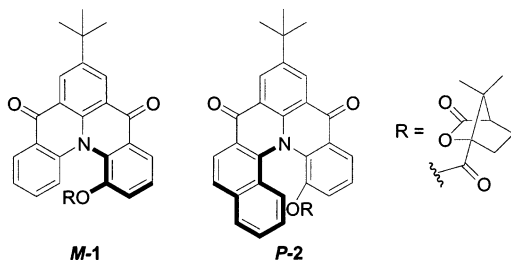
## Circularly Polarized Luminescence from Bridged Triarylamine Helicenes

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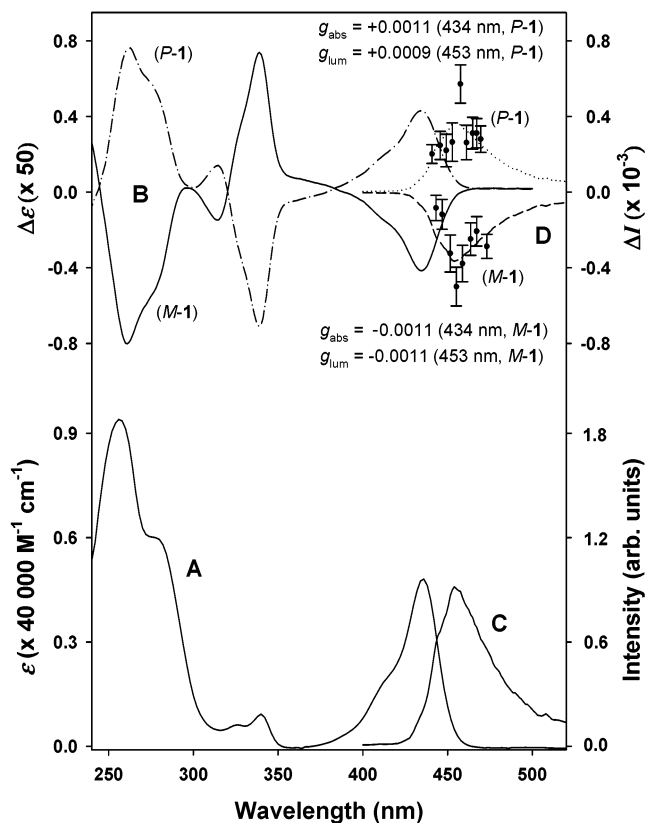
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Circularly polarized luminescence (CPL) is the differential emission of right-circularly polarized light versus left-circularly polarized light by chiral molecular systems. Applications of CPL have primarily been used to obtain structural information about molecular excited states, and the field has thus far been dominated by studies involving chiral lanthanide complexes.<sup>1</sup> In recent years, there has been a growing interest in developing organic molecules that are capable of emitting circularly polarized light because of their potential applications in display devices,<sup>2</sup> optical storage devices,<sup>3</sup> and in asymmetric photochemical synthesis.<sup>4</sup> Although all luminescent organic molecules that are chiral will display some CPL, the extent of circular polarization is almost always less than 0.1%.<sup>1</sup> Recent strategies that have been explored to increase the circular polarization include attaching chiral side chains to conjugated polymers,<sup>5</sup> embedding organic chromophores in a chiral matrix,<sup>3</sup> and the aggregation of chromophores.<sup>6</sup> Here, we report the first examples of CPL from two chiral heterohelicenes, **1** and **2**, based on triarylamines—a moiety that has been widely exploited in the OLED industry due to its electronic, photochemical, and physical properties.



We have recently reported the synthesis and properties of a series of racemic bridged triarylamine helicenes.<sup>7</sup> To study the properties arising from the inherent chirality of these molecules, it was necessary to separate them into their respective *P*- and *M*-atropisomers. Recent work by Thongpanchang et al.<sup>8</sup> has shown that (1*S*)-camphanates are excellent resolving agents for functionalized carbocyclic helicenes. We thus synthesized the camphanate derivatives, **1** and **2**, and were then able to separate the diastereomeric mixtures into their constituent *P*- and *M*-isomers using standard column chromatography. Previous work<sup>8</sup> suggests that the difference in polarity arises from the preferred conformation of the camphanate with respect to the helicene. Assuming that this holds true for the present system, assignments can be made for the more polar *P*-isomer (lower  $R_f$ ) and the less polar *M*-isomer (higher  $R_f$ ). These assignments are also supported by NMR spectra (see Supporting Information). The two constituent atropdiastereomers of **1** (*M-1* and *P-1*) give identical absorption spectra (Figure 1) in the UV–vis region with the absorption maxima occurring at 434 nm ( $\epsilon = 19 \times$



**Figure 1.** UV–vis electronic spectra of *M-1* and *P-1* in  $\text{CHCl}_3$ . (A) Absorption; (B) CD; (C) total luminescence; (D) CPL.

$10^3 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ). Similarly, *M-2* and *P-2* give identical absorption spectra with maxima at 442 nm ( $\epsilon = 12 \times 10^3 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ). Further evidence for the separation of the diastereomers is given by the circular dichroism (CD) spectra of **1** (Figure 1, top left). The preferential absorptions of left and right circularly polarized light are identical in magnitude and opposite in sign for the two species, indicative of chromophores with opposite chirality. Since the chirality of the (1*S*)-camphanate is the same on each diastereomer, the difference in the signs of the spectra can be attributed to the intrinsic chirality of the helicene chromophore. As displayed in Figure 2, the separated diastereomers of helicene **2** show CD spectra similar to those observed for **1**.

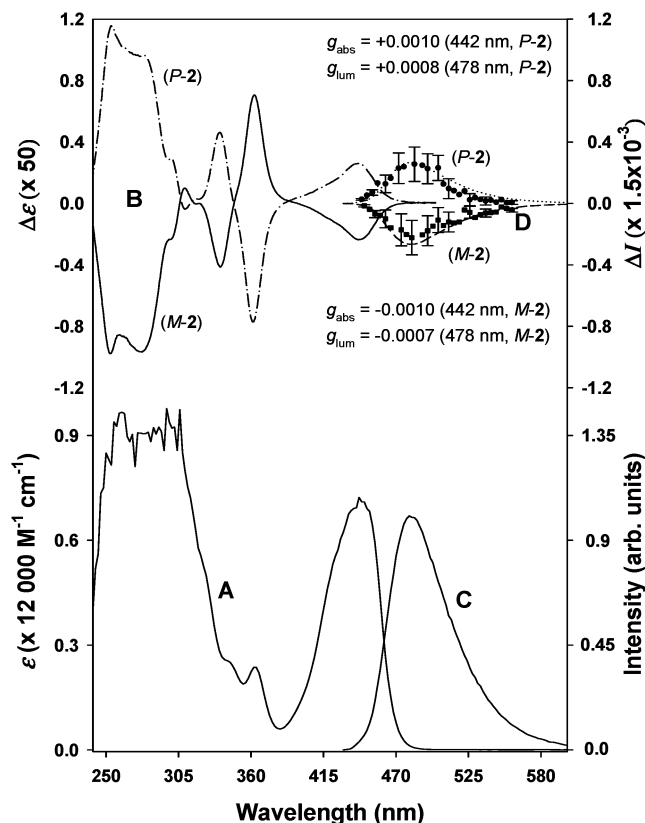
The degree of circular polarization in the absorption is usually expressed in terms of the absorption dissymmetry factor,  $g_{\text{abs}}$ , which is defined as

$$g_{\text{abs}} = \frac{\Delta\epsilon}{\epsilon} = \frac{\epsilon_L - \epsilon_R}{(1/2)(\epsilon_L + \epsilon_R)} \quad (1)$$

where  $\Delta\epsilon$  is the difference in the molar absorptivity of left and

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**Figure 2.** UV-vis electronic spectra of *M-2* and *P-2* in  $\text{CHCl}_3$ . (A) Absorption; (B) CD; (C) total luminescence; (D) CPL.

right circularly polarized light and  $\epsilon$  is defined as the average molar absorptivity. Also plotted in Figures 1 and 2 are the total luminescence spectrum ( $I$ ) and the circularly polarized luminescence spectra ( $\Delta I$ ) for the diastereomers of **1** and **2**. As expected, the total emission spectra of *M-1* and *P-1* are virtually identical, as are *M-2* and *P-2*, and, therefore, only one is plotted. The emission maximum occurs at 453 nm for helicene **1** and 478 nm for helicene **2**.

In analogy with eq 1, the degree of circularly polarized luminescence is given by the luminescence dissymmetry ratio

$$g_{\text{lum}} = \frac{\Delta I}{(1/2)I} = \frac{I_L - I_R}{(1/2)(I_L + I_R)} \quad (2)$$

where  $\Delta I$  is the difference in the intensities of left and right circularly polarized emissions and  $I$  is the total emission intensity. In Figures 1 and 2, we plot  $\Delta I$  at various wavelengths through the luminescence transition. In Figure 1 each point is plotted with a standard error bar, and in Figure 2 representative error bars are given. The dashed lines in the CPL plot are presented to show the luminescence spectral line shape. As can be seen in these figures, for the same transition,  $g_{\text{abs}}$  and  $g_{\text{lum}}$  have essentially the same value for both helicenes. This is the result one expects in situations where there is no significant geometry change upon population of the emitting state. This is further corroborated by the small Stokes shifts of the emission maxima. The dissymmetry factors at the peak maxima for **1** and **2** are  $|0.001|$  and  $|0.0008|$ , respectively.

It should be noted that the results obtained show that even for these very strained systems that the chiral discrimination in absorption or the net circular polarization in emission is quite small. A value of  $g_{\text{lum}}$  equal to 0.001 corresponds to light that is only

0.1% circularly polarized. It is somewhat surprising that the measured dissymmetry factors for *P-2* and *M-2* are approximately the same or even slightly less than that determined for **1**. We had anticipated that the increased helical overlap introduced by the additional aromatic ring might lead to an increase in circular polarization in the luminescence. It is well-known that interacting independent chromophores exhibit maximum chirality when the angle between the transition dipole directions is equal to  $90^\circ$ . Although the additional aromatic ring in **2** increases the helical twist, it must be the case that the net chirality is an inherently complex function of the electronic structure of the twisted chromophore. Previous studies on the CD of *n*-helicenes have also shown that the prediction of net chirality of the observed transitions is not a simple function of molecular geometry.<sup>9</sup>

It is important to compare the results presented here with previous work by Phillips et al.<sup>6</sup> In this study a 10-fold increase in the luminescence dissymmetry ratio was observed ( $g_{\text{lum}} = 0.01$ ) for a system of aggregating helicenes. However, the increased ordering of these aggregates also results in a large degree of linear polarization ( $P = 0.39$ ) which can greatly affect the CPL measurement.<sup>10</sup> In the measurements presented here, precautions have been taken to ensure the complete removal of linearly polarized emission in the direction of emission detection (see Supporting Information).

In summary, we have reported the first triarylamine-based helicenes capable of preferentially absorbing and emitting circularly polarized light. We believe that these systems are amenable to device application, and we are thus pursuing derivatives of these molecules to attain an increased CPL response that would allow for the development of practical polarized organic light-emitting diodes (POLEDs).

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**Supporting Information Available:** Synthetic procedures and characterization data for all compounds, and experimental procedures for the CPL measurements (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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