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## ARTICLE

# Enhancing circularly polarised luminescence by extending the $\pi$ -conjugation of axially chiral compounds

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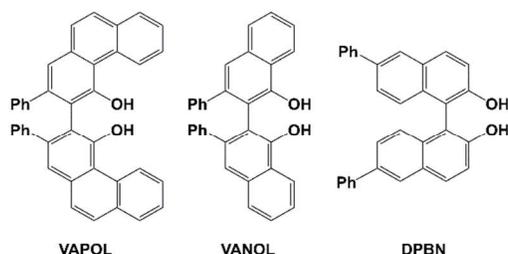
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Circularly polarised luminescence (CPL) and photoluminescence (PL) properties of  $\pi$ -conjugated (*R*)- and (*S*)-2,2'-diphenyl-4-biphenanthrol (VAPOL) exhibited an efficient CPL ( $\sim 1.3 \times 10^{-3}$ ) with a quantum yield ( $\Phi_F$ ) of 0.20 at 376 nm. By comparison, (*R*)- and (*S*)-3,3'-diphenyl-2,2'-bi-1-naphthol (VANOL) exhibited no CPL or PL.

## Introduction

Chiral organic fluorophores have attracted great attention in recent (chir)optoelectronics for use in potential applications, such as elaborative electroluminescence (EL) devices and optical sensors.<sup>1</sup> Few organic fluorophores, however, are known to exhibit circularly polarised luminescence (CPL) with an efficient quantum yield and a high dissymmetry ratio.<sup>2</sup> To rationally design a chiral fluorophore with high-performance CPL characteristics, further systematic study of the relationship between the chiral chromophores and their photophysical properties in the ground and photoexcited states is needed. Recently, we reported several binaphthyl derivatives that exhibit CPL properties under unpolarised photoexcitation in fluid solutions and in solid polymeric and inorganic matrices.<sup>3,4</sup> Herein, we found a marked difference in CPL properties between 2,2'-diphenyl-4-biphenanthrol (VAPOL) and 3,3'-diphenyl-2,2'-bi-1-naphthol (VANOL) (Fig. 1). A novel molecular design for increase of CPL capability was suggested.

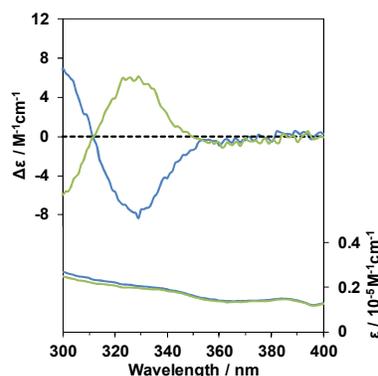


**Fig. 1** The chemical structures of three axially chiral biaryl compounds. 2,2'-diphenyl-4-biphenanthrol (VAPOL), 3,3'-diphenyl-2,2'-bi-1-naphthol (VANOL) and 6,6'-diphenyl-1,1'-bi-2-naphthol (DPBN).

## Results and discussion

First, we compared the circular dichroism (CD) and unpolarised UV-vis absorption spectra of the respective (*R*)-VANOL and

(*R*)-VAPOL in the ground state in a dilute chloroform ( $\text{CHCl}_3$ ) solution ( $10^{-5}$  M); the results are shown in Figs. 2 and 3 (blue lines).

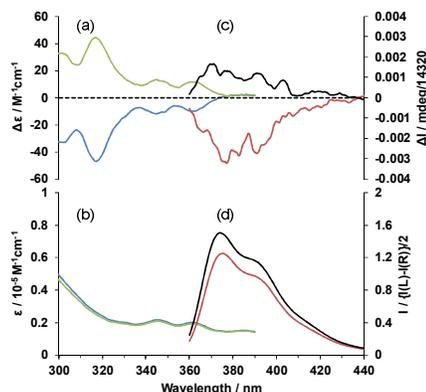


**Fig. 2** CD (upper panel) and UV-vis (lower panel) spectra of (*R*)-VANOL (blue lines) and (*S*)-VANOL (green lines) in  $\text{CHCl}_3$  ( $1.0 \times 10^{-5}$  M).

From Fig. 2 (lower panel, blue line), (*R*)-VANOL has several  $\pi \rightarrow \pi^*$  transitions in the range of 310–350 nm, characteristic of the binaphthyl group. Evidently, (*R*)-VANOL has a split-type Cotton CD band at 329 nm, which originates from the exciton coupling of the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO)  $\pi \rightarrow \pi^*$  electronic transitions between the two naphthalene rings.

From Figs. 3(a) and 3(b) (lower left panel, blue line), the UV-vis absorption band of (*R*)-VAPOL is markedly red-shifted by  $\approx 30$  nm compared to that of (*R*)-VANOL because of the extension of the  $\pi$ -conjugation. (*R*)-VAPOL also has several  $\pi \rightarrow \pi^*$  transitions in the range of 310–380 nm, characteristic of the biphenanthryl group. However, a split-type Cotton CD band in this range cannot be observed. For comparison, CD and UV-vis spectra of (*S*)-VANOL and (*S*)-VAPOL are shown in Figs.

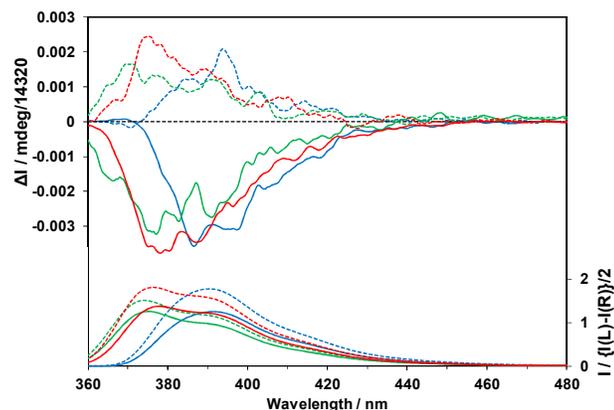
2, 3(a) and 3(b) (green lines), respectively. These two CD spectra are mirror images of the corresponding (*R*)-isomers.



**Fig. 3** (a) CD, (b) UV-vis, (c) CPL, and (d) PL spectra of (*R*)-VAPOL (blue and red lines) and (*S*)-VAPOL (green and black lines) in  $\text{CHCl}_3$  ( $1.0 \times 10^{-5}$  M).  $\lambda_{\text{ex}} = 282$  nm.

To quantitatively evaluate the absolute chiroptical magnitude in the ground state, the dimensionless Kuhn's anisotropy of CD, defined as  $|g_{\text{CD}}| = |\Delta\text{OD}/\text{OD}|$ , is used. From the first Cotton CD bands of VAPOL and VANOL in  $\text{CHCl}_3$ , the  $|g_{\text{CD}}|$  values are  $\sim 5.5 \times 10^{-4}$  at 361 nm ( $\lambda_{\text{CD}}$ ) and  $\sim 4.4 \times 10^{-4}$  at 329 nm ( $\lambda_{\text{CD}}$ ), respectively.

The PL and CPL spectra of (*R*)-VAPOL in  $\text{CHCl}_3$  clearly show the effect of the solution concentration, as shown in Fig. 4 (indicated by the solid lines). Subtle differences in the CPL signals of (*R*)-VAPOL and (*S*)-VAPOL (dotted lines) were observed. Although the reason for this difference is unclear at this time, clearly, the CPL spectra of (*R*)- and (*S*)-VAPOL display an almost mirror-image relationship.

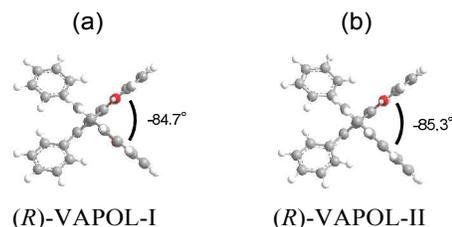


**Fig. 4** Concentration dependent CPL (upper panel) and PL (lower panel) spectra for (*R*)-VAPOL (solid lines) and (*S*)-VAPOL (dotted lines) in  $\text{CHCl}_3$ . Green, red, and blue lines are  $1.0 \times 10^{-5}$  M,  $1.0 \times 10^{-4}$  M, and  $1.0 \times 10^{-3}$  M, respectively.  $\lambda_{\text{ex}} = 282$  nm ( $1.0 \times 10^{-5}$  M), 289 nm ( $1.0 \times 10^{-4}$  M), and 320 nm ( $1.0 \times 10^{-3}$  M).

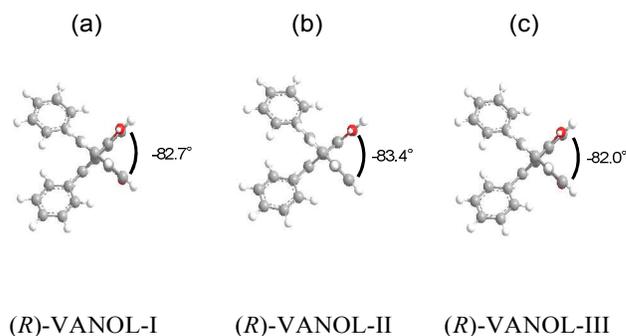
Interestingly, the  $\lambda_{\text{em}}$  value of (*R*)-VAPOL was greatly red-shifted as the concentration increased, with values of 376 nm ( $1.0 \times 10^{-5}$  M) < 378 nm ( $1.0 \times 10^{-4}$  M) < 391 nm ( $1.0 \times 10^{-3}$  M). Conversely, the PL quantum yield ( $\Phi_{\text{F}}$ ) of (*R*)-VAPOL slightly decreased when the concentration increased, with values of

0.20 ( $1.0 \times 10^{-5}$  M) > 0.16 ( $1.0 \times 10^{-4}$  M) > 0.13 ( $1.0 \times 10^{-3}$  M). Note that the  $|g_{\text{em}}|$  values of (*R*)-VAPOL remain approximately constant in the dilute and concentrated samples ( $1.3 \times 10^{-3}$  ( $1.0 \times 10^{-5}$  M) and  $1.1 \times 10^{-3}$  ( $1.0 \times 10^{-3}$  M)). This red-shift may be caused by the excimer luminescence derived from intermolecular phenanthryl interactions.

We previously reported that the CPL properties of the chiral binaphthyl fluorophore were controlled by changing the dihedral angle of the binaphthyl unit rather than the chirality of the binaphthyl unit.<sup>4</sup> Therefore, to extend the effect of the  $\pi$ -conjugation that is responsible for the CPL of VAPOL, several stable conformations of (*R*)-VAPOL and (*R*)-VANOL in  $\text{CHCl}_3$  were obtained. The optimized conformers are displayed in Figs. 5 and 6, respectively. These structures were generated using a conformation search method (Conflex7, rev.A)<sup>5,6</sup> followed by DFT B3LYP/6-31G(d) optimization with IEFPCM (chloroform).<sup>7</sup> The most and second-most stable conformations of VAPOL are called (*R*)-VAPOL-I and (*R*)-VAPOL-II, respectively. The three most stable conformations of VANOL are called, in order of stability, (*R*)-VANOL-I, (*R*)-VANOL-II, and (*R*)-VANOL-III. Two of the possible conformational isomers of (*R*)-VAPOL commonly hold  $\theta$  ((O)C-C-C(O)) of  $-84.7^\circ$  for (*R*)-VAPOL-I and  $-85.3^\circ$  for (*R*)-VAPOL-II. Similarly, all three possible conformational isomers of (*R*)-VANOL adopt a similar equilibrium dihedral angle  $\theta$  ((O)C-C-C(O)) of  $-82.7^\circ$  for (*R*)-VANOL-I,  $-83.4^\circ$  for (*R*)-VANOL-II and  $-82.0^\circ$  for (*R*)-VANOL-III. No marked differences in the  $\theta$  angles between (*R*)-VAPOL and (*R*)-VANOL are obtained theoretically.



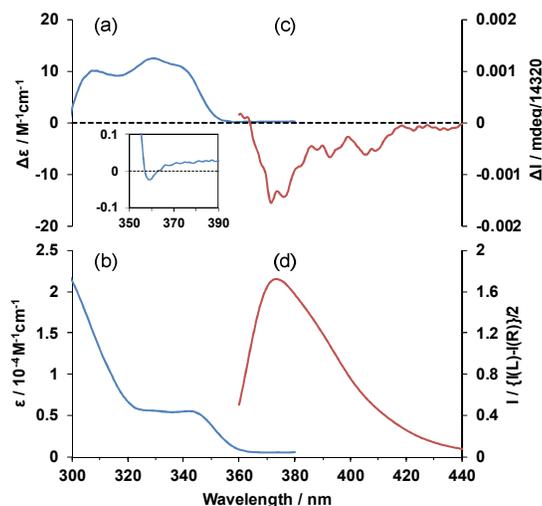
**Fig. 5** Two optimized conformers of (*R*)-VAPOL. (a) The most stable (*R*)-VAPOL-I and (b) the metastable (*R*)-VAPOL-II.



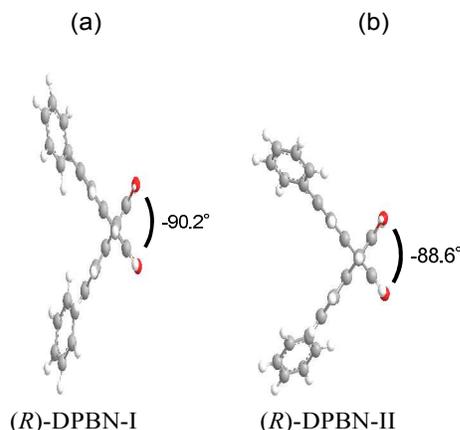
**Fig. 6** Three optimized conformers of (*R*)-VANOL. (a) The most stable (*R*)-VANOL-I, (b) the metastable (*R*)-VANOL-II, and (c) the metastable (*R*)-VANOL-III.

The PL and CPL spectra of (*R*)-6,6'-diphenyl-1,1'-bi-2-naphthol, (*R*)-DPBN, which have twisted binaphthyl moieties in  $\text{CHCl}_3$ , are shown in Fig. 7. (*R*)-DPBN exhibited a PL ( $\Phi_{\text{F}} = 0.05$ ) at  $\lambda_{\text{em}} = 373$  nm although it was weak, and the resulting  $|g_{\text{em}}|$  value is  $\sim 7.8 \times 10^{-4}$ . The major differences between

VANOL and DPBN are that the OH groups are located at the 1- and 2-positions of the naphthol, respectively, and that the linkage of the naphthyl rings are at the 2,2- and 1,1-positions, respectively. Two possible conformational isomers of (*R*)-DPBN commonly hold  $\theta$  ( $(O)C-C-C(O)$ ) of  $-90.2^\circ$  for (*R*)-DPBN-I and  $-88.6^\circ$  for (*R*)-DPBN-II (Fig. 8). These results suggest that the different direction and angle of the dipole moments of the chiral binaphthyl units in VANOL and DPBN may drive their different PL and CPL capabilities.



**Fig. 7** (a) CD (inset  $1.0 \times 10^{-3}$  M), (b) UV-vis, (c) CPL and (d) PL spectra of (*R*)-DPBN (blue and red lines) in  $\text{CHCl}_3$  ( $1.0 \times 10^{-4}$  M).  $\lambda_{\text{ex}} = 320$  nm.

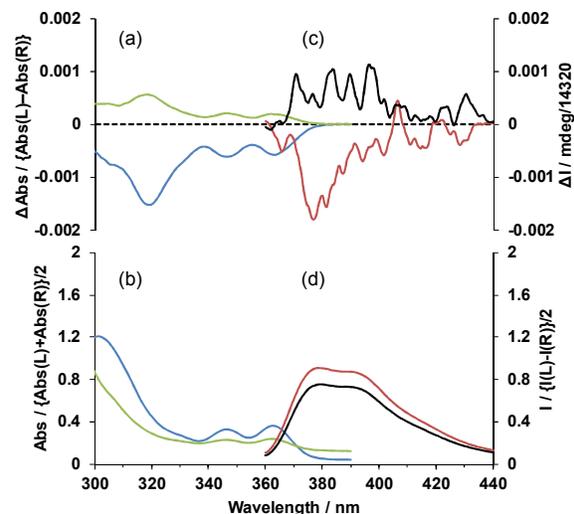


**Fig. 8** Two optimized conformers of (*R*)-DPBN: (a) the most stable (*R*)-DPBN-I and (b) the metastable (*R*)-DPBN-II.

This enhancement of the PL and CPL properties of VAPOL by extending the  $\pi$ -conjugation of VANOL suggests the novel molecular design to increase the PL and CPL capabilities. By extending the  $\pi$ -conjugation, preferred direction and angle of the dipole moments of the chiral biaryl units may change in the ground and photoexcited states. As a result, CPL capability appeared and increased.

In a recent paper, we observed a marked enhancement of the  $\Phi_F$  values compared to fluid solutions for several chiral fluorophores by doping a poly(methyl methacrylate) (PMMA) solid matrix with the compounds.<sup>8</sup> To test whether

this behaviour is applicable to VAPOL and VANOL, CPL spectra of (*R*)- and (*S*)-VAPOL and (*R*)- and (*S*)-VANOL dispersed in spin-coated PMMA films are employed, respectively. (*R*)- and (*S*)-VAPOL in PMMA films exhibit similar PL and CPL performance to the corresponding  $\text{CHCl}_3$  solutions, as shown in Figs. 9(c) and 9(d) (red and black lines), respectively.



**Fig. 9** (a) CD, (b) UV-vis, (c) CPL, and (d) PL spectra of (*R*)-VAPOL (blue and red lines) and (*S*)-VAPOL (green and black lines) dispersed in PMMA film.  $\lambda_{\text{ex}} = 348$  nm.

## Conclusions

We demonstrated the CPL properties of axially chiral biaryl chromophores by varying the degree of  $\pi$ -conjugation with different backbones (VAPOL and VANOL) to systematically study their chiroptical properties in the photoexcited states. VANOL with a binaphthyl backbone exhibited no PL or CPL in a  $\text{CHCl}_3$  solution and no CPL in a PMMA film. On the other hand, by extending the  $\pi$ -conjugation of VANOL, VAPOL exhibited efficient CPL properties ( $|g_{\text{eml}}| \approx 1.1\text{--}1.3 \times 10^{-3}$ ) in both  $\text{CHCl}_3$  solutions and PMMA solid films. CPL wavelength of VAPOL was slightly red-shifted by the increase in concentration. These knowledge led to the idea that efficient CPL is possible by extending the  $\pi$ -conjugation of a chiral biaryl unit, possibly, due to the suitable directions and angles of the dipole moments of the axially chiral biaryl units. Our results should provide significant insight into the rational design of chiral, biaryl-based fluorophores with high  $|g_{\text{eml}}|$  and  $\Phi_F$  values.

## Experimental section

### General methods

Chloroform ( $\text{CHCl}_3$ ), purchased from Wako Pure Chemical (Osaka, Japan), was used for crystallization and optical measurements. Compounds (*R*)- and (*S*)-VANOL and (*R*)- and (*S*)-VAPOL were purchased from Sigma-Aldrich Japan (Tokyo, Japan). The compound (*R*)-DPBN was purchased from Kankyo Kagaku Center (Tokyo, Japan).

### Measurement of fluorescence spectra

Fluorescence spectra and absolute photoluminescence quantum yields of the chloroform solutions and PMMA films were measured using an absolute PL quantum yield measurement system (Hamamatsu Photonics C9920-02, Hamamatsu, Japan) under an atmosphere of air at room temperature. PMMA films doped with biaryls were prepared using a spin coater at 3000 rpm (Opticoat MS-A100, Mikasa, Tokyo, Japan). VANOL in a PMMA film was excited at 296 nm. VAPOL at a concentration of  $1.0 \times 10^{-5}$  M in a  $\text{CHCl}_3$  solution was excited at 282 nm. The excitation was changed to 289 nm for a  $1.0 \times 10^{-4}$  M solution and 320 nm for a  $1.0 \times 10^{-3}$  M solution. In the PMMA film, an excitation of 348 nm was used. (R)-DPBN in  $\text{CHCl}_3$  solution was excited at 320 nm.

The CPL spectra in  $\text{CHCl}_3$  solutions and PMMA films were measured using a JASCO CPL-200 spectrofluoropolarimeter (Tokyo, Japan) at room temperature. The instrument used a scattering angle of  $0^\circ$  from the excitation of unpolarised, monochromated incident light with a bandwidth of 10 nm. The specimens in PMMA films were prepared analogously to the samples used for the solid-state fluorescence spectra. VAPOL molecules were excited at 282 nm for the  $1.0 \times 10^{-5}$  M solution, 289 nm for the  $1.0 \times 10^{-4}$  M solution, 320 nm for the  $1.0 \times 10^{-3}$  M solution (all in  $\text{CHCl}_3$ ), and 348 nm for PMMA film. (R)-DPBN in  $\text{CHCl}_3$  solution was excited at 320 nm. The CPL spectra were approximated using the simple moving average (SMA) method.

### Measurement of the CD and UV-vis absorption spectra

CD and UV-vis absorption spectra in chloroform solution and the PMMA film were measured using a JASCO J-820 spectropolarimeter at room temperature. PMMA films containing biaryls were prepared analogously to the aforementioned samples for the solid-state fluorescence spectra. CD spectra were approximated using the SMA method.

### Theoretical calculations

To obtain optimized conformations, a conformation search (Conflex7, rev.A)<sup>5,6</sup>, optimization of structure using density functional theory (DFT) (Gaussian03, rev.E)<sup>7</sup> and energy calculation using TD-DFT (Gaussian03, revision E) were carried out in the following order: First, a conformation search was employed to obtain several stable conformers for (R)-VAPOL, (R)-VANOL and (R)-DPBN. The conformation search was performed using MMFF94S as a force field (Conflex Inc., Japan) setting and applying SEL and dielectric constant values of 1.0 kcal/mol and 4.806, respectively. Next, the conformation of each chemical was sequentially optimized using DFT B3LYP/6-31G(d) and DFT B3LYP/6-31G(d) with IEFPCM (chloroform). Finally, an energy calculation using TD-DFT B3LYP/6-31G(d) with IEFPCM (chloroform) was carried out for the optimized structures, calculating singlet states only (number of excited states = 20).

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### Notes and references

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