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Circularly polarized emission from a narrow bandwidth dye doped into a chiral nematic liquid crystal

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We report on circularly polarized light emitted from a chiral nematic liquid crystal doped with a luminescent organolanthanide dye. The organolanthanide emission displays an extremely narrow spectral bandwidth of $\Delta\lambda_E \approx 8$ nm. This is considerably narrower than the CNLC selective reflection bandwidth $\Delta\lambda_R \approx 60$ nm. When conventional dyes with broader emission bandwidths are dissolved into CNLCs, the average degree of circular polarization g of emitted light is reduced from the maximum degree g_{MAX}; this is due to the overlap of the emission band with the reflection band edges, and spectral regions outside the reflection band. Here, however, we can place the entire emission band inside the reflection band and achieve $g \approx g_{MAX} = 1.27$. Furthermore, a high degree of circular polarization is maintained under off-axis viewing up to a viewing angle of ≈ 30° to the normal.

1. Introduction

Over the last few years, the study of chiral nematic liquid crystals (CNLCs) doped with emissive dyes has seen a remarkable revival. The key conceptual development that sets apart the recent work from older investigations is the choice of the pitch length p of the CNLC with respect to the emission wavelength of the dye, λ_E. λ_E is typically in the visible range; $\lambda_E \approx 400$–700 nm. The classic study by Pollmann *et al.* [1], dating from 1976, addressed dye-doped CNLCs in the so-called Mauguin limit [2] with $p \gg \lambda_E$. This is also the regime in which conventional, twisted nematic liquid crystal displays operate [3]. Pollmann *et al.* observed that the dye fluorescence in CNLC solution may display a certain degree of circular polarization (CP), and developed a quantitative theory of CP based on the guest–host alignment of the fluorescent dye in the CNLC.

The common feature of the more recent work in the field [4–8] is that it instead uses CNLCs with p close to the visible regime. Short-pitch CNLCs display a chiroselective optical reflection band centred at $\lambda_R = \bar{n}p$, with $\bar{n}$ the CNLCs' average refractive index, and bandwidth $\Delta\lambda/\lambda_R \approx \Delta n/\bar{n}$, with Δn the CNLCs' birefringence. Within that band, light with circular polarization equal to the sense of chirality of the supramolecular helix is reflected. When a luminescent dye with $\lambda_E \approx \lambda_R$ is doped into a CNLC, one observes that in the centre of the selective reflection band, dye emission CP is of the same sense as it would be for light transmitted through the CNLC from an external source. At the edges of the reflection band, however, the sense of CP is reversed [8]. This behaviour is now understood within the framework of photonic crystal theory as the result of the divergence of the density of states (DOS) at the edges of a one-dimensional stopband [6–8].

Work with dye-doped CNLCs in the 'resonance regime' $\lambda_R \approx \lambda_E$ has targeted two main applications: firstly, the manufacture of circularly polarized light sources [4, 5], and secondly, the manufacture of low threshold lasers [6, 7]. While lasing applications exploit the band-edge DOS divergence [6, 7], the resulting CP reversal at the stopband edges represents a serious problem for the design of circularly polarized light sources. The emission bandwidth (FWHM) of typical organic dyes is of the same order or larger than the typical reflection bandwidth of practical CNLCs ($\Delta\lambda_R \approx 60$ nm). Therefore, a considerable fraction of dye emission will be in the spectral region outside the reflection band, where it is not circularly polarized, or at the stopband edges, where CP is reversed. Consequently, rather high degrees of CP may be achieved in the reflection band centre, with $g_{MAX} \geqslant 1.5$ [8], wherein the degree of CP $g(\lambda)$ is defined as:

$$g(\lambda) = 2\frac{I_L(\lambda) - I_R(\lambda)}{I_L(\lambda) + I_R(\lambda)} = 2\frac{r(\lambda) - 1}{r(\lambda) + 1} \tag{1}$$

where $I_{L/R}$ is the intensity of left/right handed light and $r = I_L/I_R$ the CP ratio. However, when $g(\lambda)$ is averaged over the full emission band, g is severely reduced compared with g_{MAX}. A second problem for the application

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of dye-doped CNLCs as circularly polarized light sources is that their reflection band shifts to shorter wavelengths with increasing viewing angle [9]:

$$\lambda_R(\theta) = \lambda_R(0)\cos\theta \qquad (2)$$

where θ stands for the internal angle of propagation with respect to the cell normal, which is related but not identical to the external viewing angle. Hence, when a dye-doped CNLC cell is viewed under non-normal angle, the reflection band centre shifts to shorter wavelengths, while the dye emission maximum remains fixed. Consequently, emission is no longer centred at the middle of the reflection band. This further compromises g.

Katsis *et al.* [5] have addressed the first of these problems by using a 'chirped' CNLC with a much broadened reflection band ($\Delta\lambda_R \approx 200$ nm). The 'chirp' or pitch gradient was established with the help of CNLC reactive mesogens undergoing an elaborate crosslinking procedure, as first described by Broer *et al.* [10]. While the results of Katsis *et al.* show the absence of a marked edge-of-reflection band CP reversal, their g_{MAX} is considerably lower than for dyes dissolved in conventional CNLCs ($|g_{MAX}| < 1$ vs. $|g_{MAX}| \approx 1.5$ in their previous work [4]). No off-axis viewing results were reported.

In this report, we propose an alternative approach to resolve the described problems with dye-doped CNLC circularly polarized light sources. We use a luminescent dye of unusually narrow emission bandwidth $\Delta\lambda_E \approx$ 8 nm (FWHM). Figure 1 shows our dye 'ADS053RE'. ADS053RE is a member of the 'organolanthanide' family of luminescent dyes, which have recently received considerable attention from the organic electroluminescence community [11]. This is due to their ability to emit light from all electrically generated excitons (singlets and triplets) via an intramolecular transfer of excitation from the organic ligands to an excited state of the central lanthanide atom, and subsequent emission by a weakly allowed (dipole-forbidden) atomic transition of the lanthanide. Therefore, these dyes show high electroluminescence quantum yields. Also, since atomic transition bandwidths are much narrower than typical organic dye emission bands, organolanthanides emit spectrally pure colours, and are therefore particularly well suited for use in full-colour displays.

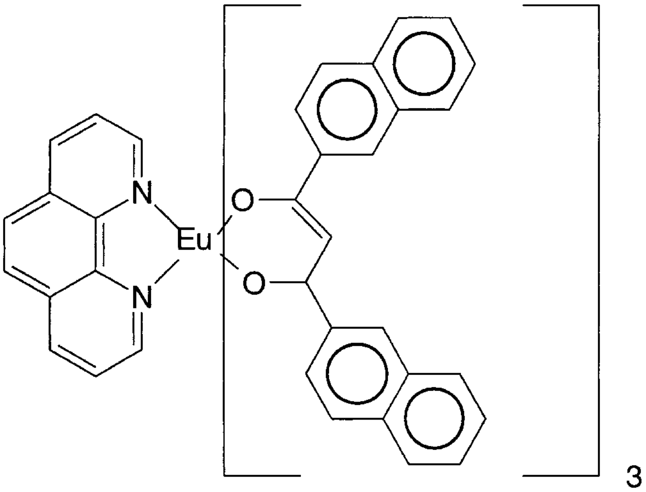

Figure 1. The chemical structure of the red-emitting organolanthanide 'ADS053RE', supplied by American Dye Source Inc. The organic ligand absorbs light in the deep blue and near UV, with an absorption maximum at 370 nm. The excitation is transferred to the central europium atom that emits a sharp red line centred at 612 nm, FWHM 8 nm.

We dissolved ADS053RE into a CNLC matrix with the CNLC reflection band tuned so that the ADS053RE emission band is fully contained in the stopband. This ensures that $g \approx g_{MAX}$ under normal viewing angle. We located the very narrow emission band close to the short wavelength ('blue') reflection band edge. This leaves >50 nm 'leeway' for the reflection band to shift to shorter wavelengths under non-normal viewing without the dye emission drifting out of the reflection band, thus also addressing the second of the described problems. An additional advantage of using such a narrow bandwidth dye is that subsequent conversion of circularly polarized into linearly polarized light can be facilitated efficiently with a quarter wave plate.

2. Experimental

For the CNLC, we used the commercially available two-bottle kit BL130/BL131 from E. Merck, Darmstadt, which allows for tuning of the reflection band by diluting a CNLC (BL131) with an achiral nematic (BL130). As dye, we used the organolanthanide 'ADS053RE', see figure 1. Dyes were dissolved in methanol and the dye solution was added to the CNLC mixture with a microlitre syringe to allow for precise control of concentration. Dye-doped CNLCs were then gently heated and stirred for several hours to evaporate methanol. By capillary action, the dye-doped CNLC was filled into commercially available LC test cells with aligning surfaces, supplied by E.H.C. of Tokyo. The cell thickness was 180 µm. Absorption and transmission measurements were carried out with a UNICAM 4 UV/Vis spectrometer. Dye luminescence was excited by irradiation with a fluorescent lamp at 365 nm, close to the ADS053RE absorption maximum. At this wavelength, cell absorbance was approximately 2.5, ensuring that almost all (>99%) of the incoming light was absorbed. For the characterization of CP, cells were mounted so that they could be rotated around the vertical axis for studies of non-normal emission. A Fresnel rhomb was used to convert the emitted light of CP with opposite senses into light with mutually perpendicular linear polarizations independent of wavelength. Light leaving the rhomb was collected and focused by a lens. A linear polarizer that could be rotated around the axis of light propagation was introduced to discriminate between the different polarizations. One end of a liquid light guide was placed into the focus of the collection lens. The other end of the light guide was fed into a diffraction grating/ANDOR CCD camera spectrograph.

3. Results and discussion

Figure 2 shows the selective reflection band of our CNLC mixture under normal viewing, and when the cell was rotated around the vertical axis for different angles. Within the reflection band, approximately half of unpolarized incoming light is reflected, corresponding to one (in our case, the right-handed) CP. We see that off-normal viewing is accompanied by a 'blueshift' of the reflection band, in accordance with equation (2). Also shown in figure 2 is the photoluminescence emission band of ADS053RE, centred at 612 nm. This narrow emission band is fully contained within the reflection band. However, the short wavelength edge of the CNLC reflection band has deliberately been placed close to the dye emission to allow some leeway for blueshift resulting from non-normal viewing. It can be clearly seen from figure 2 that the dye emission band remains contained within the CNLC reflection band even when viewed under 30° to the normal.

Figure 3 shows the right-handed and the left-handed circularly polarized emission spectra of ADS053RE dissolved in CNLC under normal observation. We find a polarization ratio of $r = 4.1:1$ in favour of left-handed emission at maximum emission, corresponding to g (612 nm) = 1.27; cf. equation (1). In previous studies of the emission from dye-doped CNLCs, similar or slightly higher values for g were found within the selective reflection band [4, 8]. However, in these previous studies, dye emission bands were broader than the CNLC reflection band. The spectrally averaged values of $g(\lambda)$, $\bar{g}$, were severely reduced from g_{MAX} due to the spectral overlap of the emission bands with regions at the edges, and outside, the reflection bands. In our case, due to the complete containment of the emission band within the stopband, the degree of circular polarization $g(\lambda)$ is high and of equal sign throughout the emission band, hence $\bar{g} \approx g_{\mathrm{MAX}}$.

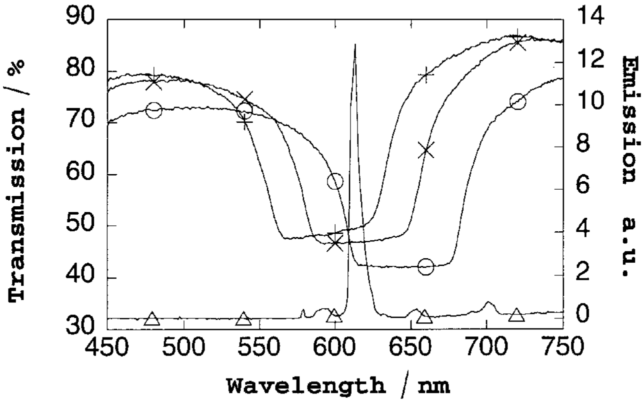

Figure 2. Transmission spectra (left hand vertical axis) of the CNLC cell used when viewed normally (0°, ○), under 20° to the normal (×), and under 30° (+). The selective reflection band can be clearly seen, and it shifts to shorter wavelengths ('blueshift') with increasing viewing angle. Also shown is the ADS053RE emission band (Δ, right hand vertical axis).

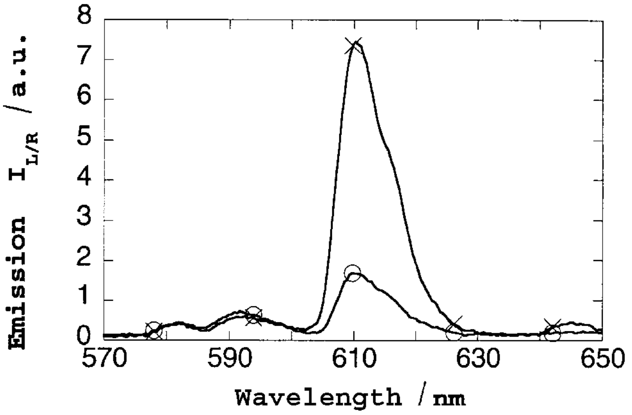

Figure 3. Left-handed CP (LHCP, ×) and right-handed CP (RHCP, ○) emission spectra $I_{\mathrm{L/R}}(\lambda)$ from the cell when viewed under normal angle. From the polarization ratio $I_{\mathrm{L}}/I_{\mathrm{R}}$, $g(\lambda)$ can be calculated according to equation (1).

In figure 4, we show g (612 nm) for off-axis viewing of our cells under angles ranging from −40° to +40° with respect to the cell normal. As we had seen in figure 2,

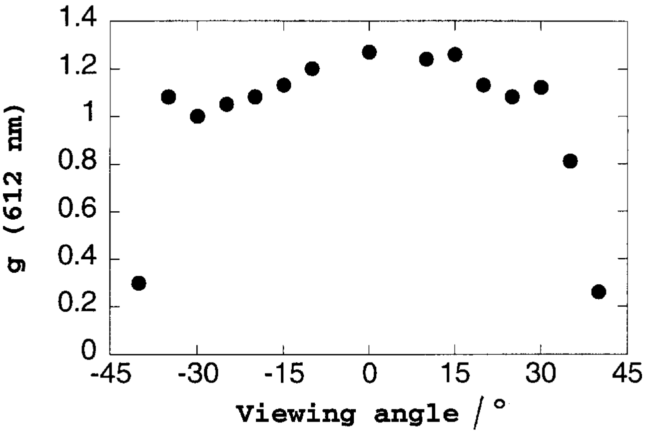

Figure 4. Values of g (612 nm) found for luminescence from the cell when viewed under angles with respect to the normal ranging from −40° to +40°.

the short wavelength edge of the CNLC reflection band under normal viewing is placed close to the dye emission band. Therefore, the emission band remains within the CNLC reflection band even when the reflection band blueshifts under off-axis viewing. Consequently, g (612 nm) remains rather high even under off-axis viewing angles up to $\approx 30°$.

4. Summary and conclusions

In the present study, we have explored a novel approach to the manufacture of a light source with a high overall degree of CP from a dye-doped CNLC. The key idea is to avoid emission band overlap with spectral regions at the edge of, or outside, the CNLC reflection band by using organolanthanide dyes with extremely narrow emission bandwidths. Figure 3 confirms the success of this approach, showing highly circularly polarized emission across the entire dye emission band with $g \approx g_{\mathrm{MAX}} = 1.27$. For conventional dyes, problems resulting from emission band overlap with reflection band edges and regions outside the reflection band will be aggravated by off-axis viewing; this leads to a blueshift of the reflection band so that it cannot remain centred with respect to the dye emission band. Due to the placement of the short wavelength reflection band edge close to the narrow dye emission band, our system has proven remarkably robust against off-axis viewing. A high degree of CP is retained even when observed under $+/-30°$.

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