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Mechanistic insight into circularly polarized photoluminescence from a chiral-nematic film

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Circularly polarized photoluminescence (CPPL) was characterized for rod-like molecules of Exalite 428 helically arranged in a chiral-nematic liquid crystalline film. With an unpolarized excitation at 370 nm, CPPL intensities measured at 428 nm, and a selective reflection wavelength ranging from 7.2 to 72.6 μm, the observed dissymmetry factor, g_e, was found to be in excellent agreement with theoretical prediction, without resorting to adjustable parameters. As a result, new insight into liquid crystal-induced CPPL has emerged. Specifically, it was found that circular dichroism and circular polarization of the excitation beam prior to inducing linearly polarized photoluminescence (LPPL) at quasi-nematic layers play an insignificant role. The relatively large g_e value in the spectral region far removed from the selective reflection band was attributed to the circular polarization of LPPL emanating from all quasi-nematic layers comprising the chiral-nematic film. In the absence of a fluorescent dye, the propagation of unpolarized light through the chiral-nematic film under otherwise identical conditions results in no circular polarization. The present study has provided a foundation for generating circularly polarized light by way of photo-excitation with unpolarized light of a chiral-nematic film containing a fluorescent dye.

1. Introduction

The generation and propagation of polarized light is essential to optical information processing, display, and storage. Because of the availability of appropriate materials, linear polarization has reached a more advanced stage of research and development than circular polarization. Nevertheless, circularly polarized light is an attractive alternative remaining to be explored for practical applications. A helical arrangement of fluorescent guest molecules enforced by a chiral-nematic liquid crystalline host has been shown to be capable of circularly polarized photoluminescence (CPPL) [1]. The degree of CPPL is measured by the dissymmetry factor, $g_e \equiv 2(I_L - I_R)/(I_L + I_R)$, in which I_R and I_L denote the right- and left-handed emission intensity, respectively. Note that g_e equals 2 for pure, one-handed CPPL. A CPPL theory for the guest with a photoluminescence wavelength much shorter than the selective reflection wavelength (λ_R) of the host has also been formulated for the description of g_e as a function of $\lambda^* \equiv \lambda_{PL}/\lambda_R$, where λ_{PL} is the photoluminescence wavelength. With circularly polarized excitations, the observed g_e for 1,6-diphenylhexatriene (DPH) in a chiral-nematic fluid host consisting of nematic BDH 18523 and cholesteryl oleate was found to be in good agreement with the theoretical prediction without recourse to adjustable parameters [2]. One of the findings is that with a left-handed circularly polarized excitation, a maximum g_e of 0.76 occurs at $\lambda^* = 0.018$, i.e. at $\lambda_R = 25.2\,\mu m$ which is much longer than the emission at $\lambda_{PL} = 458$ nm. With an $n = 1.500$, the film thickness of 11 μm corresponds to 65% of a helical pitch length, p.

This work was motivated by two objectives: (i) to appraise the relative importance of various factors contributing to the significant CPPL in a loosely pitched, chiral-nematic film; (ii) to assess the extent of CPPL under an unpolarized excitation, as opposed to CP excitation implemented previously [2]. Moreover, rod-like Exalite 428 [3] as depicted in figure 1(*a*) was employed as the fluorescent dye instead of DPH. It is generally accepted that DPH molecules possess a predominantly all-*trans* configuration in anhydrous organic

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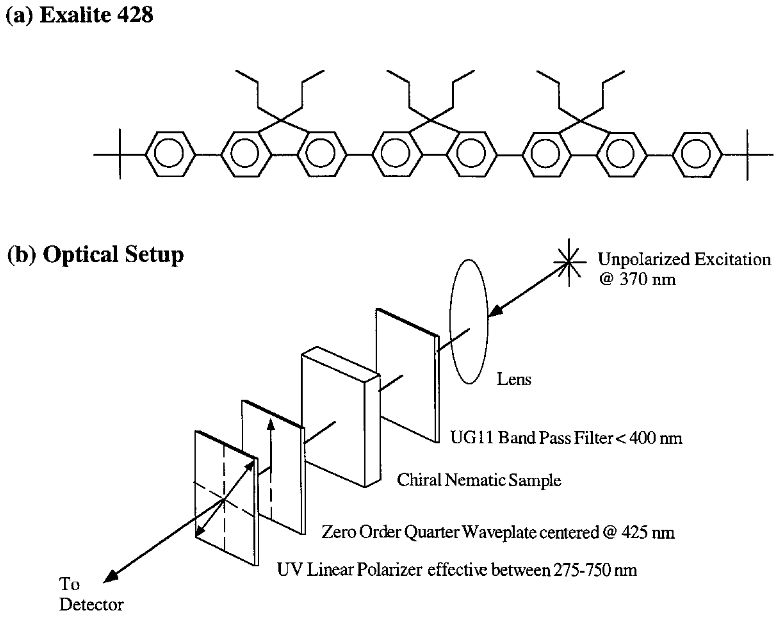

Figure 1. (*a*) Chemical structure of Exalite 428 as a fluorescent dye; (*b*) optical set-up incorporated in a spectrofluorimeter (MFP-66, Perkin-Elmer) for the characterization of CPPL induced by unpolarized light.

media [4]. Nevertheless, experimental evidence exists which indicates about 10% contribution to PL in methylcyclohexane by a *cis*-isomer at room temperature with an excitation wavelength, λ_{ex}, of 370 nm [5]. The possibility of *trans*↔*cis* isomerization is expected to complicate the measurement of g_e because of the difference between the two isomers in terms of their absorption and emission spectra and the associated characteristics, such as extinction coefficient, absorption and emission transition moments, and PL quantum yield.

2. Experimental

The room-temperature chiral-nematic liquid crystal consisting of nematic BDH 18523 (Merck) and cholesteryl oleate (Janssen Chimica), fused silica substrate (Optovac) and its surface treatment, and the measurement of native pitch length by the Cano-wedge method are as described previously [2]. The fluorescent dye used in this study, Exalite 428 (>98%, Exciton, Inc.), was used as received without further purification. Its absorption and fluorescence spectra in cyclohexane are as presented in figure 1 of [3], indicating the absence of reabsorption of the emission intensity measured at 428 nm. The chiral-nematic fluid film lightly doped with Exalite 428 was contained between a pair of fused silica substrates and its thickness defined by glass fibre spacers. For the present study, we selected a film thickness of 11.5 ± 0.2 μm, as measured from the interference fringes of the air gap on a UV-Vis spectrophotometer (Lambda 9, Perkin-Elmer). The same instrument was used to measure the absorbance of excitation and linear dichroism involving Exalite 428. Photoluminescence was characterized using a spectrofluorimeter (MPF-66, Perkin-Elmer).

The optical set-up as depicted in figure 2 of [6] was used without a condensing lens to allow for the measurement of the second- and fourth-rank order parameters, i.e. $\langle P_2 \rangle$ (or S_{em}) and $\langle P_4 \rangle$, governing linearly polarized photoluminescence (LPPL). A low-power unpolarized light source at 370 nm with a full width at half-maximum of 15 nm was employed for the characterization of CPPL with the optical set-up shown in figure 1 (*b*). The transmittance and polarization efficiency of the analyser (i.e. quarter wave plate plus linear polarizer) were characterized for correcting the LPPL and CPPL spectra. [7]. Optical birefringence as a function of wavelength was

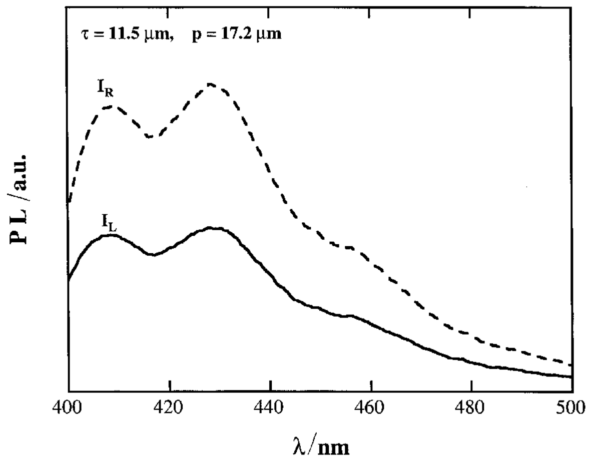

Figure 2. CPPL spectra resulting from an unpolarized excitation at 370 nm of a chiral-nematic film with $\tau = 11.5\,\mu m$, $p = 17.2\,\mu m$ and containing Exalite 428 at 0.52 wt %.

determined based on the phase difference experienced by monochromatic polarized light propagating through a nematic liquid crystalline film [8].

3. Results and discussion

Mixtures of nematic BDH 18523 and cholesteryl oleate, known to give a LH chiral-nematic fluid film [2], were prepared as a transparent host for Exatile 428 at a doping level of 0.52 wt %. In the present study, up to 4 wt % of cholesteryl oleate was employed to produce a wide range of pitch length: $4.8\,\mu\mathrm{m} \leqslant p \leqslant 48.4\,\mu\mathrm{m}$, corresponding to $7.2\,\mu\mathrm{m} \leqslant \lambda_R = pn \leqslant 72.6\,\mu\mathrm{m}$. With an unpolarized excitation at 370 nm, CPPL was characterized for 11.5 μm films. Typical CPPL spectra are shown in figure 2 for a film with $p = 17.2\,\mu\mathrm{m}$, indicating a stronger I_R than I_L because of the left-handed helical structure of the host. The two circularly polarized intensities at $\lambda_{PL} = 428$ nm were used to calculate g_e. Experimentally determined g_e, with an uncertainty of ±5%, is presented in figure 3 for a total of seven films covering a ten-fold variation in p.

The essence of the CPPL theory is illustrated in figure 4, in which an arbitrary quasi-nematic layer at $z = -b$ containing uniaxially aligned dye molecules is shown. The dye molecules are helically twisted counterclockwise between adjacent layers along the $+z$-direction because of the left-handed structure of the host. An unpolarized excitation beam entering the chiral-nematic film at $z = -\tau$ undergoes circular dichroism and circular polarization before arriving at $z = -b$. In the CPPL theory [2] the circular dichroism and circular polarization of the excitation beam were treated within Good and Karali's formalism [9] through a complex index of refraction. Photoexcitation of the dye molecules located at $z = -\mathrm{b}$ produces LPPL, which is then circularly polarized on propagation to $z = 0$. Input parameters include film thickness (τ), absorbance of excitation ($\bar{A}$ as evaluated below), Δn and n of the host at the excitation and emission wavelengths; also order parameters characterizing linear dichroism, S_{ab}, and LPPL, S_{em} and $\langle P_4 \rangle$, of quasi-nematic layers comprising the chiral-nematic film.

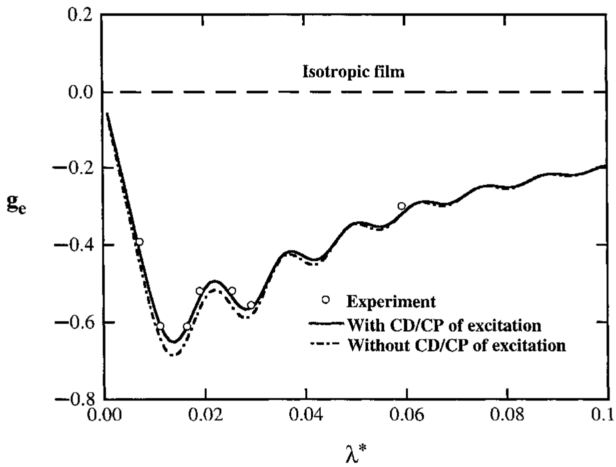

Figure 3. Experimentally measured g_e represented as open circles with an uncertainty of ±5% in comparison with the theoretical predictions with the following parameters determined *a priori*: $\tau = 11.5\,\mu\mathrm{m}$, $4.8\,\mu\mathrm{m} \leqslant p \leqslant 48.4\,\mu\mathrm{m}$, $\lambda_{ex} = 370$ nm, $\lambda_{PL} = 428$ nm, $n = 1.500$, $\Delta n = 0.052$ (at 370 nm) and 0.051 (at 428 nm), $\bar{A}/\tau = 532\,\mathrm{cm}^{-1}$, $S_{ab} = 0.51$, $S_{em} = 0.51$ and $\langle P_4 \rangle = -0.034$.

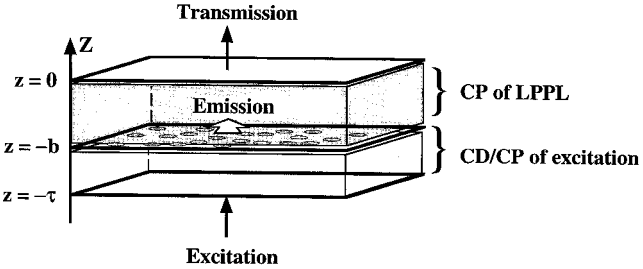

Figure 4. A mechanistic description of CPPL consisting of circular dichroism and circular polarization of excitation followed by circular polarization of linearly polarized photoluminescence initiated at an arbitrary quasi-nematic layer at $z = -b$.

At $\lambda_{ex} = 370$ nm and $\lambda_{PL} = 428$ nm, Δn was experimentally determined to be 0.052 and 0.051, respectively. Furthermore, the cholesteryl oleate-BDH 18523 mixture was found to have a constant index of refraction at concentrations up to 10 wt % of cholesteryl oleate [2]. Therefore, n can be treated as constant at 1.500 for the interpretation of g_e. A nematic fluid film $10.4 \pm 0.1\,\mu\mathrm{m}$ thick doped with Exalite at 0.52 wt % was prepared for the characterization of linear dichroism. The absorbances of the dopant at 370 nm were evaluated at $A_\parallel = 1.116$ and $A_\perp = 0.273$, i.e. the absorbance measured parallel and perpendicular to the nematic director, which yield $S_{ab} = 0.51$ and an average absorbance $\bar{A} = 0.554$ [10]. With linearly polarized excitations at 370 nm, the LPPL spectra were also collected for the determination of order parameters at the emission maximum of 428 nm: $S_{em} = 0.51$ and $\langle P_4 \rangle = -0.034$ using equations (39) and (40) in [2]. Note that for $S_{em} \leqslant 0.60$, $\langle P_4 \rangle$ can be negative due to repulsive forces or other dipole–dipole interactions [11]. In the present treatment, it was assumed that both the absorption and emission transition moments lie parallel to the long axis of the dopant molecule.

An unpolarized beam can be represented by the sum of equal amounts of left- and right-handed circularly polarized beams with a random phase relationship between the two [12]. With an unpolarized excitation and with all the system parameters independently evaluated as described above, the CPPL theory was found to predict g_e to within experimental uncertainty, as shown in figure 3, which also indicates an insignificant contribution from circular dichroism or circular polarization of the excitation beam to the observed g_e prior to inducing photoluminescence. All computations were performed by discretizing the 11.5 μm film into 2 nm increments to ensure numerical convergence. Therefore, circular polarization of LPPL originating in quasi-nematic layers helically placed relative to each other in the chiral-nematic film is the predominant contributing factor to the observed g_e for emission outside the selective reflection band. This conclusion can be further illuminated with a composite film of a thin nematic layer doped with Exalite 428 followed by a blank chiral-nematic film, both having the same S_{ab}, S_{em}, and $\langle P_4 \rangle$ as determined above. Photoexcitation by unpolarized light of the fluorescent dye in the nematic layer will produce LPPL, which then undergoes circular polarization while propagating through the blank chiral-nematic film. A combination of the LPPL theory [13] governing emission from the doped nematic layer and the theory of circular polarization [9] governing propagation through the blank, chiral-nematic film was used to predict g_e with the same values for all the parameters except τ. The numerical results are displayed in figure 5 for three cases: a 2 nm thick doped nematic layer followed by a blank chiral-nematic film with a thickness of 11.5, 2 and 1 μm. As a matter of fact, the solid curve in figure 3 represents an integration of the contributions from photoexciting all the 2 nm thick, quasi-nematic increments comprising the doped chiral-nematic film. Therefore, circularly polarized light can be generated by unpolarized photoexcitation of a doped chiral-nematic film or a composite of a doped, nematic layer and a blank, chiral-nematic film. In contrast, unpolarized light propagating through a chiral-nematic film outside the selective reflection band will not be circularly polarized to an appreciable extent [9].

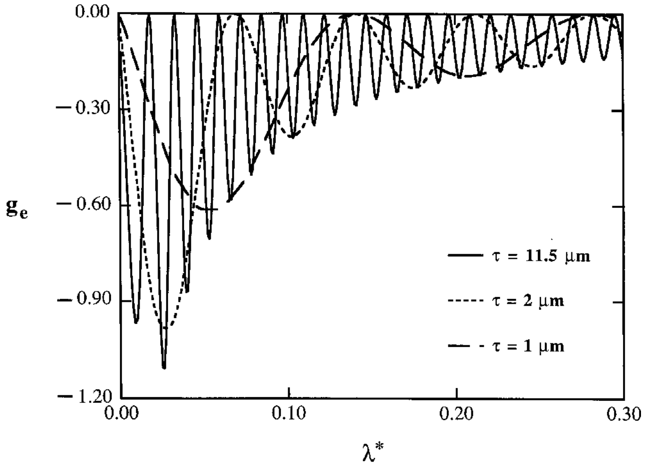

Figure 5. The predicted g_e for three composite films, each consisting of a 2 nm thick, nematic layer followed by a blank, chiral-nematic film with $\tau = 11.5$, 2, or 1 μm and all other parameters assuming the same values as specified for figure 3.

4. Summary

A rod-like fluorescent dye, Exalite 428, without a potential complication arising from *cis–trans* isomerism was lightly doped into a series of chiral-nematic fluid films, non-absorbing at both the excitation and emission wavelengths. These optical elements were used to gather definitive information on CPPL and to unravel the seemingly complex optical process. Specifically, the experimentally measured g_e was interpreted in terms of a CPPL theory incorporating anisotropic absorption (i.e. circular dichroism), anisotropic emission (i.e. linearly polarized photoluminescence) within, and propagation (i.e. circular polarization) through, the periodically structured film. With the assumption that both the absorption and emission transition moments are parallel to the long molecular axis of the fluorescent dye molecule, anisotropic absorption and photoluminescence were characterized for a lightly doped nematic film to yield order parameters governing quasi-nematic layers comprising the chiral-nematic film. With all the system parameters determined *a priori*, the theory was found to predict the experimental observation to within experimental uncertainty. From a fundamental standpoint, the large degree of CPPL originating from unpolarized excitation in loosely pitched chiral-nematic films was found to be contributed primarily by the circular polarization of linearly polarized photoluminescence originating in quasi-nematic layers; on the other hand, circular dichroism and circular polarization of the excitation beam prior to photoexcitation play a rather insignificant role. In contrast, no circular polarization resulted from the propagation of unpolarized light outside the selective reflection band. From a practical standpoint, CPPL outside the selective reflection band constitutes a viable approach to the generation of polarized light from an unpolarized source.

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