

Circularly Polarized Photoluminescence from Gradient-Pitch Chiral-Nematic Films

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A mixture consisting of a nematic acrylate and a chiral diacrylate lightly doped with Exalite 428, a laser dye, was prepared into thin films for in situ photopolymerization. The laser dye served to regulate the photocuring intensity profile into the film and as a light emitter. With optimized chemical composition, photocuring intensity, and temperature, a gradient-pitch film with a broad resonance band was produced to cover the emission peak of the laser dye. The SEM image provided new insight into the distribution of pitch length across the film thickness, consistent with the selective reflection spectra. Upon UV excitation, the observed sense and degree of circularly polarized photoluminescence were qualitatively interpreted on the basis of the photoexcitation intensity received by the dopant molecules and by the wavelength-dependent interaction of emitted light with an asymmetric structure.

Introduction

Polarized light is essential to optical information processing and display. Passive (i.e. nonemitting) devices are capable of polarization of incident light on the basis of anisotropic absorption,¹ anisotropic scattering,² or selective reflection.³ Active devices emitting polarized light have been the subject of intense investigation as surveyed in a recent review article.⁴ Combining light source, color generation, and polarization in a single optical element, these devices represent a technological advance over passive devices. Feasibility of linearly polarized photo- and electroluminescence has been demonstrated with conjugated polymers or oligomers uniaxially aligned through mechanical stretching,⁵ the Langmuir–Blodgett deposition,⁶ nematic or smectic liquid crystalline mesomorphism,⁷ and epitaxial growth on a rubbed substrate.⁸ Circularly polarized photo- and

electroluminescence have been reported for polythiophene and poly(*p*-phenylenevinylene) functionalized with chiral pendants, showing an insignificant degree of polarization.^{9–11} A much improved degree of circularly polarized electroluminescence was reported using polyfluorenes functionalized with chiral pendants.¹² Moreover, Exalite 428 (a rodlike luminophore) embedded in a glassy chiral-nematic film with a constant pitch produced nearly pure circularly polarized photoluminescence.¹³ In general, organic light emitters show emission spectra broader than the selective reflection (i.e. resonance) bandwidth of constant-pitch chiral-nematic films. The present work aims to explore the ability of a chiral-nematic film with a resonance bandwidth sufficiently broad to cover the emission peak of Exalite 428. In particular, the bandwidth is significantly increased over constant-pitch films by introducing a pitch gradient across the film thickness.¹⁴ The observed circularly polarized photoluminescence is interpreted in terms of the interaction of emitted light with the asymmetric structure.

Experimental Section

Materials. For the preparation of a broadband chiral-nematic film, three main components are identified in Figure 1. Enantiomeric diacrylates **I-R** and **I-S**, derived respectively

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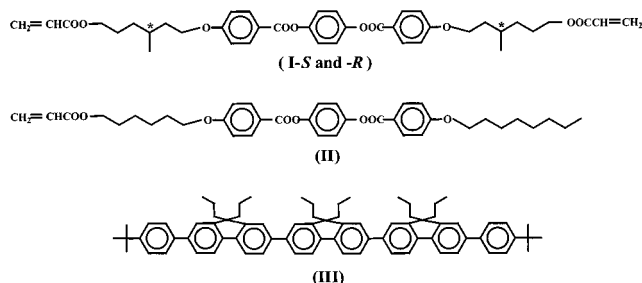


Figure 1. Molecular structures of enantiomeric chiral (I) and nematic (II) monomers and Exalite 428 (III). Note that I-S and I-R were derived from (S)-(-)- and (R)-(+)-citronellol, respectively.

from (R)-(+)- and (S)-(-)-citronellol, and nematic monoacrylate II were synthesized and purified by following literature procedures.^{15,16} The molecular structures were elucidated with ¹H NMR spectroscopy and elemental analysis. Anal. Calcd for I-S: C, 69.95; H, 6.75; N, 0.00. Found for I-S: C, 69.72; H, 7.66; N, 0.02. Found for I-R: C, 69.72; H, 7.66; N, 0.02. Calcd for II: C, 71.69; H, 7.66; N, 0.00. Found for II: C, 71.80; H, 7.08; N, 0.02.

Hot-stage polarizing optical microscopy (DMLM, Leica; FP82HT and FP 90, Mettler) revealed that I-R and -S had a melting point of 67 °C and a cholesteric-to-isotropic transition temperature of 99 °C and II had a melting point of 100 °C and a nematic-to-isotropic transition temperature of 178 °C. Exalite 428, III, was used as received (>98%, Exciton, Inc.) with a reported quantum efficiency of 0.90.¹⁷

Preparation and Characterization of a Photocured Chiral-Nematic Film. A mixture containing I-S/II at 50/50 (w/w), 0.3 wt % of III, 0.3 wt % of a photoinitiator (Irgacure 651, Ciba-Geigy), and 0.04 wt % of an inhibitor (4-methoxyphenol, 99%, Aldrich Chemical Co.) was prepared by codissolution in methylene chloride followed by drying under vacuum. A melting point of 82 °C and a cholesteric-to-isotropic transition temperature of 143 °C were identified for the mixture by hot-stage polarizing optical microscopy. Solid powders were melted at 120 °C between a pair of fused silica substrates (25 mm diameter × 3 mm thickness, Esco Products) coated with Nylon and then buffed. The film thickness was controlled using glass fiber spacers (EM Industries) with a nominal thickness of 14 μm. Upon thermal annealing for 15 min, the fluid film was cured for 25 min with the 365 nm peak of a mercury lamp at a power intensity of 0.62 mW/cm². Film thickness was evaluated at 13.2 ± 0.2 μm on the basis of fringes due to an air gap between the substrates using a UV-vis-NIR spectrophotometer (Lambda 900, Perkin-Elmer). The same instrument was used to gather selective reflection spectra in transmission (at normal incidence) and reflection (at 6° off-normal incidence) modes with unpolarized light source. Fresnel reflections from the air-glass interfaces were accounted for using a reference cell containing an index-matching fluid. Cross sections of films isolated from the substrates were sputtered with approximately 100 Å of gold to improve the contrast of the image acquired with a scanning electron microscope (LEO982 FESEM).

With unpolarized excitation at 360 nm, photoluminescence spectra were gathered on a spectrofluorimeter (Quanta Master C-60SE, Photon Technology International). A liquid light guide (2 mm in diameter × 1 m long, Photon Technology Interna-

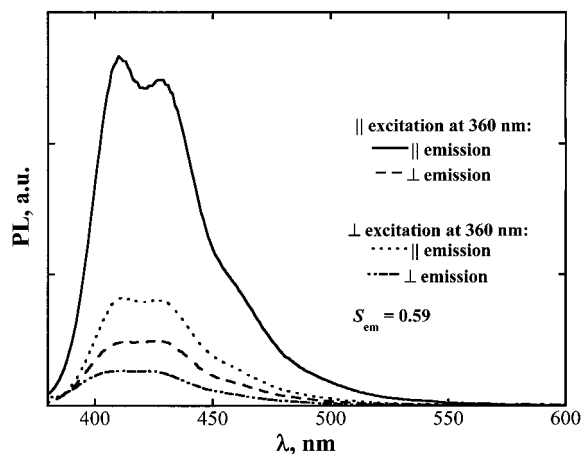


Figure 2. Linearly polarized photoluminescence spectra with excitation at 360 nm of a 14 μm thick photocured, compensated nematic film comprising I-S/I-R/II at 25/25/50 (w/w/w).

tional) was used to focus light from the excitation source at the center of the films along the surface normal through a glass filter (UG11, Corning). The light guide also served as a polarization randomizer for the excitation source. Circularly polarized photoluminescence (CPPL) spectra were obtained using a combination of a zero-order quarter waveplate, centered at 425 nm (AO1521/4-425, Tower Optical), and a dichroic linear polarizer (HNP'B, Polaroid).

Preparation and Characterization of a Photocured, Compensated Nematic Film. A chiral-nematic film can be represented as a stack of helically stacked mesogenic layers, each of which contains uniaxially oriented molecules of Exalite 428. To characterize the orientational order of the rodlike dopant molecules, a photocured compensated nematic film of the same overall composition, I/II at 50/50 (w/w), is the most appropriate. Thus, a mixture containing I-S/I-R/II at 25/25/50 (w/w/w), 0.3 wt % of III, 0.3 wt % of the photoinitiator, and 0.04 wt % of the inhibitor was prepared by following the same procedure as above. A melting point of 78 °C and a nematic-to-isotropic transition temperature of 140 °C were identified for the mixture by hot-stage polarizing optical microscopy. Linearly polarized photoluminescence from the nematic film, photocured at 4.00 mW/cm², was characterized with linearly polarized excitation at 360 nm using a pair of identical linear polarizers (HNP'B, Polaroid Corp.). The emission spectra are presented in Figure 2, from which the order parameter was determined, $S_{em} = 0.59$, using eq 39 of ref 18.

Results and Discussion

The SEM (scanning electron microscopy) image of a cross section of the photocured chiral-nematic film with I-S/II at 50/50 (w/w), as shown in Figure 3, provides a quantitative evaluation of helical pitch length, p , as twice the spacing between neighboring bright or dark lines.¹⁹ The measurement of p was facilitated by contrast enhancement (using SigmaScan Pro 5), resulting in a linear pitch profile: p (μm) = 0.272 + 8.08 × 10⁻³ x (μm), in which x denotes the distance measured from dark side of the film, viz. the surface not exposed to the UV source. The emerging pitch profile suggests that pitch gradient arises from photoinduced migration driven by the tendency of the monomers to swell the emerging polymer network on a competitive basis. Moreover, it appears that the competitive swelling

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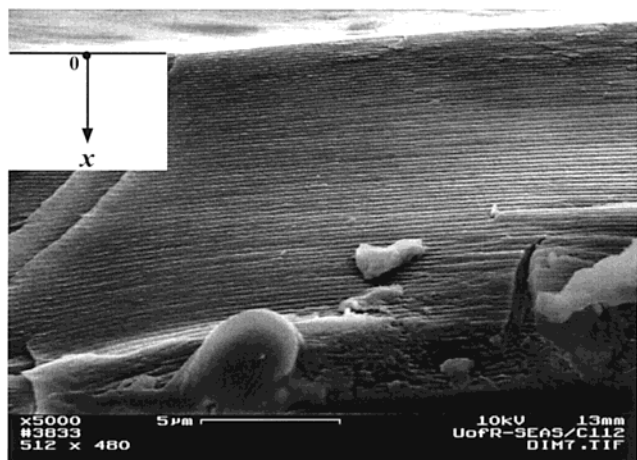


Figure 3. SEM image of the cross section of a photocured chiral-nematic film comprising **I-S/II** at 50/50 (w/w).

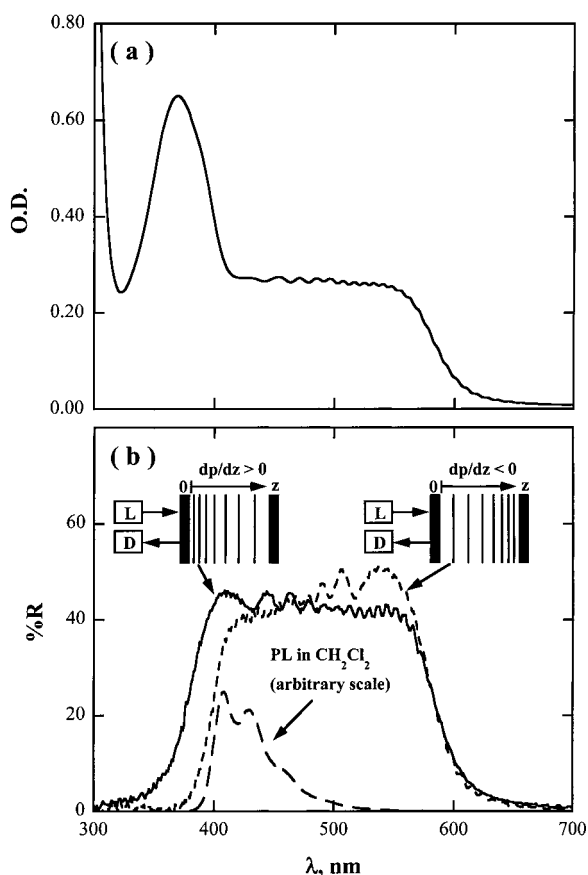


Figure 4. Selective reflection spectra, through transmittance and reflectance measurements with unpolarized incident light, of a photocured chiral-nematic film comprising **I-S/II** at 50/50 (w/w): (a) absorbance at normal incidence; (b) reflectance at 6° off-normal to the film. L and D representing light source and detector, respectively. Emission spectrum of Exalite 428 at 10^{-5} M in methylene chloride with unpolarized excitation at 360 nm shown as dashed curve.

between the two monomers results in the nematic monoacrylate migrating into the curing source while the chiral diacrylate in the opposite direction. The fact that the side of the film exposed to the curing source possesses a long pitch is consistent with the reflection spectra. As shown in Figure 4a, the optical density measured with unpolarized light at normal incidence to the film reveals the absorption peak of Exalite 428

centered at 370 nm, which overlaps with a broad plateau extending to 550 nm. Since neither monomer absorbs light above 320 nm, the observed broad bandwidth is attributed to selective reflection by the chiral-nematic film. The optical density of 0.26 is, in fact, fairly close to the theoretical limit of 0.30 for a perfectly aligned, constant-pitch film capable of selectively reflecting 50% of incident unpolarized light. It is noted that the same spectrum was obtained regardless of how the pitch gradient was oriented with respect to incident light.

To assess the full extent of selective reflection toward the blue region, reflectance was also measured with unpolarized light at an incident angle of 6° for both $dp/dz > 0$ and $dp/dz < 0$, where the z -axis is defined as pointing from the light source to the film. The results are presented in Figure 4b, where L and D represent the light source and the detector in the spectrophotometer. In the case of $dp/dz > 0$, the reflection band extends down to nearly 300 nm. In this orientation, incident light in the neighborhood of 370 nm experiences the short-pitch end of the film before penetrating deep into the film, thereby limiting its loss to absorption by Exalite 428, and hence is effectively reflected. In the case of $dp/dz < 0$, the short-pitch region lies at the far end of the film. According to Figure 4a, about 25% of incident light is transmitted in the neighborhood of 370 nm with a significant loss to absorption by uniformly distributed Exalite 428 and to selective reflection by the film. However, the dotted curve shown in Figure 4b indicates that most of the reflected component is absorbed by Exalite 428 in the long-pitch portion, leading to a vanishing reflectance around 370 nm. These observations are consistent with the pitch gradient revealed by the SEM image, namely, p decreasing monotonically from the side of the film exposed to the curing source. It is also noted that two orientations of the film yield overlapping reflection band at the long wavelength edge of the resonance band. Nonetheless, the observed reflectance is higher with light incident on the long-pitch end ($dp/dz < 0$) than the short-pitch ($dp/dz > 0$) end of the film. In the $dp/dz > 0$ orientation, the long wavelength portion of the spectrum penetrates deeper into the film before encountering reflection thus suffering more optical loss than in the $dp/dz < 0$ orientation.

As is also displayed in Figure 4b, the reflection bands are characterized by oscillations with periods that are nearly mirror images of each other. This oscillatory behavior is unique to a gradient-pitch film, as also revealed by simulations based on the Good-Karali theory.²⁰ The implications of the observed oscillations on circularly polarized photoluminescence within the resonance band will be further assessed in what follows. The chiral-nematic film consists of a stack of quasine-matic layers, each of which is characterized by $S_{em} = 0.59$, as determined by linearly polarized photoluminescence due to Exalite 428 using a photocured, compensated nematic film (see Figure 2). From one quasine-matic layer to the next, the director undergoes an incremental rotation clockwise in the film comprising **I-S/II** at 50/50 (w/w), which was determined to possess a right-handed structure on the basis of the selective

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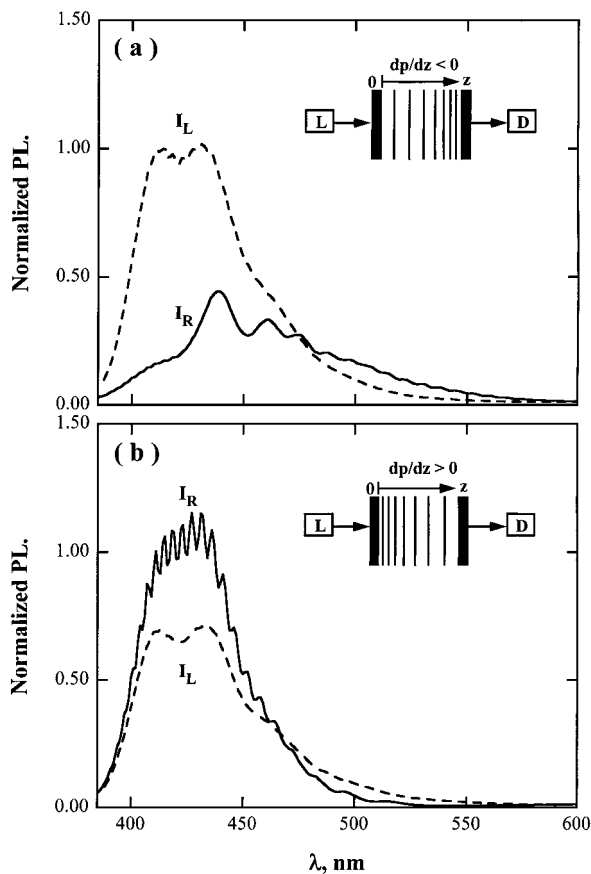


Figure 5. Circularly polarized photoluminescence of a photoexcited chiral-nematic film comprising I-S/II at 50/50 (w/w): (a) $dp/dz < 0$; (b) $dp/dz > 0$. L and D represent the light source and detector, respectively.

reflection of right-handed circularly polarized light as incident.²¹ Light emission from a constant-pitch chiral-nematic film has been investigated, although complete understanding has not been forthcoming. Outside the resonance region, the degree of circular polarization was found to originate in linearly polarized photoluminescence from quasinematic layers with subsequent circular polarization by the rest of the film.²² Inside the resonance region, a high degree of circular polarization accompanied by handedness reversal at the edge of the resonance band has been reported.^{13,23} In the case of a gradient-pitch film, the situation is further complicated by the fact that the film represents an asymmetric cavity.

Polarized photoluminescence resulting from unpolarized excitation at 360 nm is presented in Figure 5, where the emission spectra have been normalized with respect to the left-handed circularly polarized component (I_L) at 414 nm in the $dp/dz < 0$ orientation. That the chiral-nematic film used presents a right-handed helical stack of Exalite 428 is consistent with the observation that I_L appears to be identical in shape to that in methylene chloride; see Figure 4b. In contrast, the right-handed counterpart (I_R) exhibits oscillations closely resembling

those on the reflection bands in both film orientations; see Figure 4b. The interaction of the I_R component with the structure is intrinsically complicated in a gradient-pitch film. A uniform distribution of dopant molecules throughout the film combined with the asymmetry of the structure would indicate that each layer in the film has its emission redistributed anisotropically in a way depending on its location. Furthermore, the extent of interaction is determined by the emission wavelength relative to the local pitch length within the film. A rigorous view of the molecular interaction with the cavity structure accounts for the fact that the emitters "feel" the boundary conditions placed on the electromagnetic field at a given frequency (wavelength) and wavevector (emission direction).²⁴ For one-dimensional cavities such as ours, this is insufficient to modify the total emission quantum yield but can have dramatic effects on the spatial distribution of the emission.²⁵ When the cavity's effective length is long compared to the wavelength, simple propagation physics seems reasonable without resorting to enhancement of the vacuum density of states.²⁶

While it appears that the I_L component does not interact with a right-handed film solely on the basis of the spectral shape, the substantially different intensities from the two film orientations warrant a closer examination. It is shown in Figure 5 that the I_L component for the $dp/dz > 0$ orientation of the film is about 40% lower than that for the $dp/dz < 0$ orientation. This can be explained by the amount of Exalite 428 receiving photoexcitation at 360 nm. It is hypothesized that emission from uniformly distributed luminophores throughout the film is characterized by equal intensities of I_R and I_L , each of which propagates toward the detector and the light source with equal intensities prior to interacting with the structure. In the $dp/dz < 0$ orientation, the photoexcitation beam at 360 nm penetrates deeper into the film before encountering reflection, from which a higher total emission intensity results than the $dp/dz > 0$ orientation. That $I_R < I_L$ at wavelengths up to 475 nm in the $dp/dz < 0$ orientation, as shown in Figure 5a, can be rationalized by the same argument. Most of the Exalite 428 molecules in the film receive photoexcitation except toward the short-pitch edge. The emitted blue I_R is reflected while traveling toward the detector, whereas the I_L component is transmitted without much attenuation. In addition, that $I_R > I_L$ at wavelengths longer than 475 nm can be understood by considering two contributions to I_R arriving at the detector: emission traveling toward the detector without being reflected and that traveling toward the light source while being reflected. The sum of these two contributions to I_R turns out to be greater than I_L beyond 475 nm. In the case of $dp/dz > 0$, the emitted blue I_R occurs mostly after the short-pitch edge close to the excitation source. The portion of I_R traveling toward the detector encounters little reflection, whereas the portion traveling toward the light source is sub-

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stantially reflected. Thus, the sum of these two contributions to I_R arriving at the detector is greater than the emitted I_L component traveling toward the detector without interacting with the structure. Note that I_R in the $dp/dz > 0$ orientation is stronger than that in the $dp/dz < 0$ orientation, indicating that favorable interaction with the structure outweighs the lesser amount of photoexcitation intensity received by Exalite 428. The crossover between I_R and I_L , as shown in Figure 5b, indicates that part of emitted I_R of wavelengths longer than 465 nm traveling toward the detector is reflected and most of emitted I_R of the same wavelengths traveling toward the light source is transmitted, whereas emitted I_L remains unaffected by the structure, resulting in $I_R < I_L$ beyond 465 nm.

Summary

Chiral-nematic films with a broad selective reflection band were prepared via photopolymerization for hosting Exalite 428 as a luminescent guest. The SEM image indicates that the pitch length decreases linearly from the side of the film exposed to the photocuring source, which is consistent with the selective reflection spectra. Linearly polarized photoluminescence spectroscopy of a photocured, compensated nematic film revealed that $S_{em} = 0.59$ for the uniaxial orientation of dopant molecules. The same degree of orientational order was believed to govern the helically oriented Exalite 428 in all quasinematic layers comprising the chiral-nematic film. With unpolarized excitation at 360 nm, the following observations emerged: (i) relatively high degrees

of circularly polarized photoluminescence in the blue region; (ii) the sense of circular polarization affected by the orientation of the pitch gradient with respect to light propagation; (iii) a crossover in the sense of circular polarization at wavelengths longer than 470 nm. Seemingly complex experimental observations were qualitatively accounted for by considering a uniform distribution of luminescent dopant molecules within an asymmetric structure, the intensity of photoexcitation received by the dopant molecules, and the total intensities of polarized emission arriving at the detector as a result of wavelength-dependent interaction with the structure.

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