

Defect Mode Emission of a Dye Doped Cholesteric Polymer Network

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We have observed enhanced fluorescence and laser emission due to a photonic defect mode in a dye doped cholesteric polymer network. The defect is caused by a phase jump of the cholesteric helix at the interface of two stacked layers of a cholesteric polymer film. Fluorescence spectra show an additional resonant mode inside the photonic stop band. Pulsed excitation gives rise to laser emission of the defect mode, with an exceptionally low lasing threshold. The defect mode emission has a circular polarization whose sense of rotation is opposite to that of the cholesteric helix.

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Recently, much interest has focused on the photonic properties of cholesteric liquid crystals (CLCs). They are one-dimensional self-assembling photonic crystals, formed by rodlike molecules which arrange themselves in a helical structure [1]: In planes perpendicular to the helical axis, the molecules have a preferred average orientation, characterized by the so-called director. Along the helical axis, the director is continuously rotated, which results in a twisted birefringent medium. CLC films show a photonic stop band for circularly polarized light with the same handedness as the cholesteric helix, i.e., propagation is forbidden in a certain frequency range. Light with opposite circular polarization is virtually unaffected by the cholesteric medium [2]. Indeed, photonic band-edge lasing [3] of dye doped low molar mass CLCs [4] and also of CLC polymer networks [5,6] has been repeatedly demonstrated. CLC elastomers allow for a mechanical tuning of the stop band [5,7], due to the coupling of the polymer network and the cholesteric structure. A high density of chemical cross-links in polymeric CLC films stabilizes the cholesteric order, resulting in a reduced lasing threshold, higher quantum yield, and improved emission stability [6]. Introduction of a defect in a photonic crystal can give rise to an additional resonant mode inside the photonic band gap [8,9]. Such defect modes are localized at the position of the defect and may be used for narrow band filters [10,11] and low threshold lasers [12,13]. For CLCs, recently two ways to introduce a defect have been proposed, either by replacing a thin layer of the CLC by an isotropic material [14], or by introduction of a phase jump in the cholesteric helix [15]. We followed the second approach, which cannot be accomplished with a low molar mass CLC. Therefore we used two layers of a highly cross-linked CLC polymer film to create a phase jump of 90° in the cholesteric structure. In this Letter, we show that the defect mode gives rise to an additional circular polarized fluorescence peak and low threshold laser emission of dispersed fluorescent dye molecules.

The polymeric CLC film was generated by UV polymerization of a cholesteric mixture [6] of diacrylate

monomers, doped with the laser dye DCM (0.3 wt %). A uniformly planar oriented CLC film of the monomers was obtained between buffed, polyimide-coated glass substrates. They enforce a well-defined director orientation at the film surfaces and an alignment of the cholesteric helix parallel to the film normal. After UV polymerization, one of the substrates was removed, and the now rigid film (thickness $\approx 17 \mu\text{m}$) could then be peeled off. We stacked two layers of the polymerized film on a glass substrate. At the interface between the two layers, the alignment of the director of the bottom layer was orthogonal to that of the top layer (Fig. 1). Careful rubbing and slight pressure were sufficient to ensure strong cohesion of the two layers. Experiments were performed with the setup shown in Fig. 2, which allows for successive fluorescence, lasing, and transmission and reflection measurements at the same sample spot. The sample was pumped with the frequency-doubled pulses of a Q -switched Nd:YAG laser ($\lambda = 532 \text{ nm}$, pulse duration $\approx 7 \text{ ns}$). Fluorescence spectra undistorted by stimulated emission were obtained by excitation with a cw second harmonic Nd:YAG laser. The strongly attenuated laser beams were focused on the sample film by a collecting lens (resulting for pulsed excitation in a theoretical beam spot diameter of approximately $5.5 \mu\text{m}$). We simultaneously detected the forward and backward emitted light (cf. Fig. 2), using two separate spectrometer channels (resolutions 0.5 and 1.5 nm, respectively).

As a reference, we studied the fluorescence of a single layer of our CLC film; Fig. 3(a) shows the left- and right-handed circular polarized (“l-cp” and “r-cp”) emission

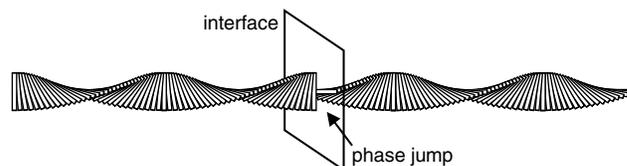


FIG. 1. Sketch of the defect introduced in the cholesteric helix.

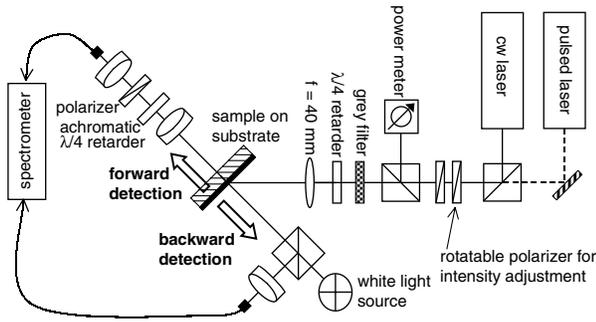


FIG. 2. Sketch of the experimental setup.

contributions. As our material forms a right-handed cholesteric helix, the l-cp emission component is virtually unaffected by the cholesteric medium, and resembles essentially the fluorescence of the dye in an ordinary solvent. The r-cp emission is suppressed inside the stop band, the emission peaks framing the gap corresponding to the resonant modes available for band-edge lasing. Because of Fabry-Perot interference, there is a sequence of peaks at each side of the gap. Their spacing depends on the film thickness. A quantitative analysis [16] of the spectrum yields the optical parameters of the film at the illuminated spot: $\alpha = (n_e^2 - n_o^2)/(2\bar{n}^2) = 0.0807$, $\bar{n}p = 596.0$ nm, and $N = 40$, where n_o , n_e are the refractive indices of the birefringent planes, $\bar{n} = [(n_e^2 + n_o^2)/2]^{1/2}$, p is the cholesteric pitch, α is the relative dielectric anisotropy, and N is the total number of repetition units (i.e., director revolutions) along the film normal.

Fluorescence spectra of the double-layer film containing the phase jump are shown in Fig. 3(b). We simultaneously measured forward and backward emission of the sample (as indicated in Fig. 2), and decomposed the forward emission into the l-cp and r-cp emission contributions. The r-cp spectrum qualitatively resembles the result obtained for the single layer. However, most remarkably, the l-cp spectrum is no longer flat, but exhibits a pronounced peak near the center of the stop band. This additional emission peak can be attributed to the localized defect mode, generated by the phase jump of the cholesteric helix. Its circular polarization can be well understood referring to the simulation results of Kopp *et al.* [15], who studied light propagation through a CLC film containing a 90° phase jump of the cholesteric helix in the center of the film. They have predicted the presence of a defect mode in the center of the stop band, peaked at the location of the defect, with exponentially decaying tails. In the peak region, the defect mode is reported to have a circular polarization with the same handedness as the cholesteric helix. Approaching the film boundaries, there is an increasing relative contribution with opposite circular polarization. Thus, the polarization at the film boundary, which is the polarization of light finally emitted by the defect mode, is in general elliptical. On increasing the film thickness above a certain crossover value (equal l-cp and r-cp emission contributions), for a right-handed CLC the l-cp emission component becomes dominant. We computed the reflection properties of a two-layer system with the parameters $\bar{n}p$ and α derived

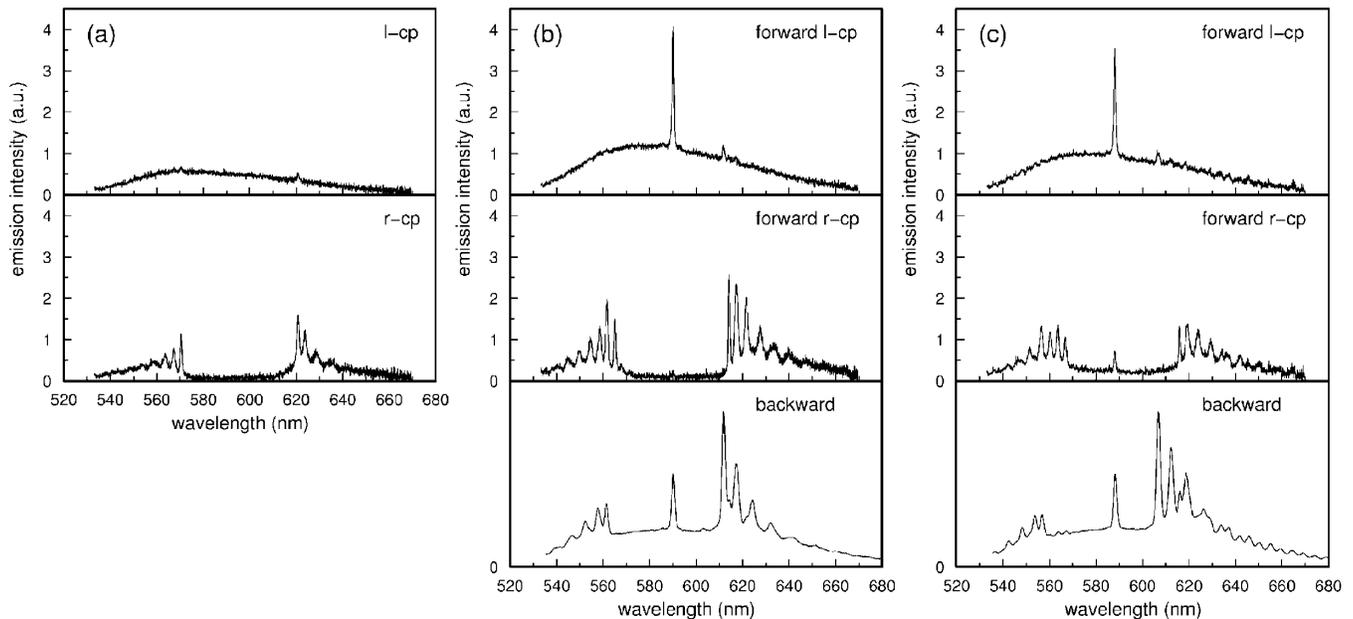


FIG. 3. Fluorescence of cholesteric films. (a) Single layer: l-cp (top) and r-cp (bottom) emission contributions. (b), (c) Fluorescence at two spots of the double layer with small (b) and large (c) mismatch of the cholesteric pitch: l-cp (top) and r-cp (middle) forward emission contributions, and total backward emission (bottom, not corrected for the polarization dependent detection sensitivity).

from our experimental single-layer fluorescence spectrum, using the fast version [17] of the numerical Berreman method [18]. We found the crossover for $N \approx 15$ director revolutions along one layer. Thus, our sample (with $N \approx 40$) is well in the saturation regime [15], where l-cp defect mode emission is to be expected—in accordance with our experimental result.

Thin CLC films usually show a slight spatial variation of the optical properties. Because of small tilts of the

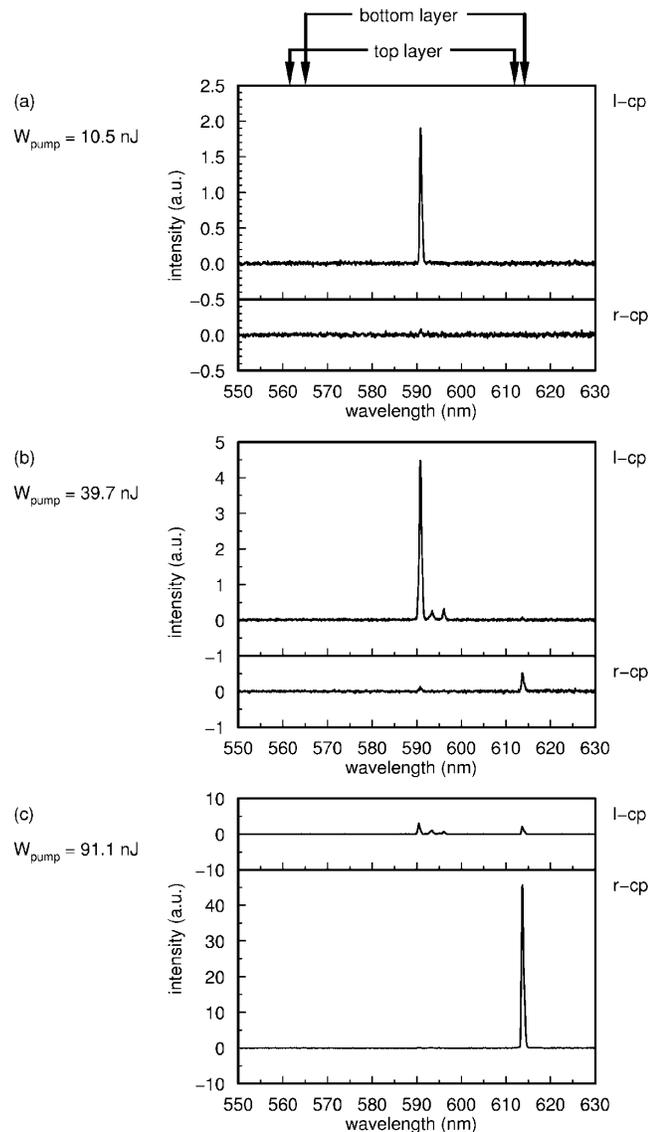


FIG. 4. Laser lines observed for various pump energies W (as indicated on the left). At low pump energies, l-cp defect mode lasing is observed (a). At higher pump energies, additional small l-cp lines show up in the defect mode region, and r-cp laser emission at the long-wavelength band edge sets in (b). Further increasing the pump energy results in a dominant band edge laser line (c). The arbitrary intensity units are the same in all plots. The arrows at the top of the figure indicate the position of the resonant modes framing the band gap of the bottom and top layer, respectively.

substrates, the film thickness is not perfectly uniform, resulting in a spatial variation of the helical pitch and of the total number of director revolutions along the film normal: Locally, the cholesteric helix adjusts its pitch as close as possible to the bulk value while still matching the boundary conditions imposed by the surface alignment [1]. The fluorescence spectra for forward and backward emission presented in Fig. 3(b) show a small mismatch of the stop bands ($\bar{n}\Delta p \approx 3.0$ nm). We assign the backward and forward detected emission to be mainly originating from the top and bottom layer, respectively (the spectra shown in Fig. 3 were obtained with the top layer facing the backward-detection unit, the glass substrate facing the forward-detection unit). Obviously, at the excited spot of the film, the two layers have slightly different cholesteric pitches. The fluorescence spectra suggest that, due to the mismatch Δp of the cholesteric pitch, the two layers to some degree retain their identity as independent emitting films. However, the mismatch does not suppress the formation of the defect mode. We even observed defect mode emission for a mismatch $\bar{n}\Delta p \approx 17$ nm [Fig. 3(c)], where we find a substantial r-cp contribution to the emission peak. For all investigated sample spots, the location of the defect mode peak roughly coincides with the average of the stop band centers of the two layers.

Using pulsed excitation, we observe l-cp laser emission of the defect mode [Fig. 4(a); excitation at the same sample spot as used for the fluorescence measurement of Fig. 3(b)]. The emission as a function of pump energy is shown in Fig. 5(a). The lasing threshold ($W \approx 2.5$ nJ, corresponding to a pump energy per excited sample area of roughly 10 mJ/cm²) is much lower than thus far reported for band-edge lasing of CLCs. Saturation is

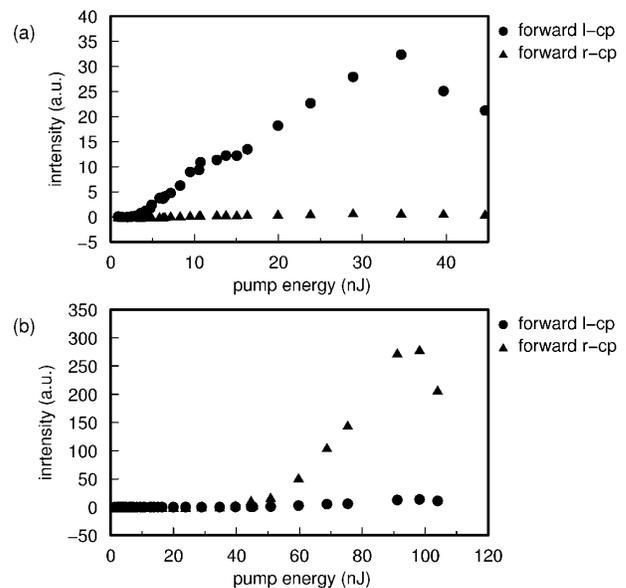


FIG. 5. Laser emission of the defect mode (a) and the band edge mode (b) as a function of pump energy.

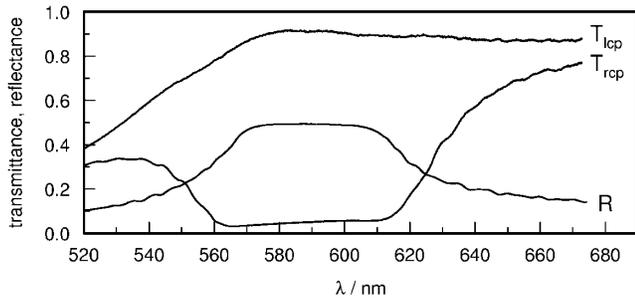


FIG. 6. Reflectance (R) and circularly polarized transmittances (T_{lcp} , T_{rcp}) of the double layer system.

reached for $W \approx 35$ nJ. Further increasing the pump energy, emission becomes very unstable, and additional small l-cp laser lines show up in the defect mode region [Fig. 4(b)]. The high energy density of the lasing defect mode obviously causes some irreversible damage of the cholesteric structure: After having exceeded the saturation value once, the quantum yield of the defect mode lasing is significantly reduced.

At high pump energies, an additional r-cp laser line at the long-wavelength band edge of the bottom layer [Figs. 4(b) and 4(c)] shows up. The laser emission of the band-edge resonance is shown in Fig. 5(b) as a function of pump energy. The lasing threshold ($W \approx 50$ nJ) is well beyond the saturation value for the defect mode. For $W \approx 100$ nJ, laser emission reaches a maximum which is much higher than that observed for the defect mode: As the resonant mode at the band edge has a larger spatial extension along the film normal, a larger amount of the homogeneously distributed dye molecules can contribute to the laser emission.

One should mention that the defect mode did not show up at all examined sample spots: Obviously, our simple lamination procedure does not provide close contact of the two layers (as sketched in Fig. 1) at all places. The simulation results of Yang *et al.* [14] suggest that a small gap between the cholesteric layers leads to a shift of the defect mode resonance towards one of the band edges. However, for all examined sample spots showing a defect mode, the resonance is quite near the band gap center. Finally, one should note that the defect mode did not show up in transmission and reflection measurements (Fig. 6). Reasons are the very small linewidth (numerical reflectivity calculations yield $\Delta\lambda \approx 0.039$ nm), and the large illuminated area ($\varnothing = 1.5$ mm), which results in an averaging over spots with varying resonance frequencies and sample areas exhibiting no defect mode at all.

In conclusion, we have given experimental proof that in a cholesteric medium a resonant defect mode can be created by introduction of a phase jump of the cholesteric helix. The observed polarization of the fluorescence peak and laser line due to the defect mode is consistent with the

simulation results of Kopp *et al.* [15]. We have found that the polarization is affected by a mismatch of the helical pitch of the two CLC layers. This will be investigated in detail in further studies; included will also be systems with an inhomogeneous dye distribution matching the spatial extension of the defect mode, which might result in a reduced lasing threshold.

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