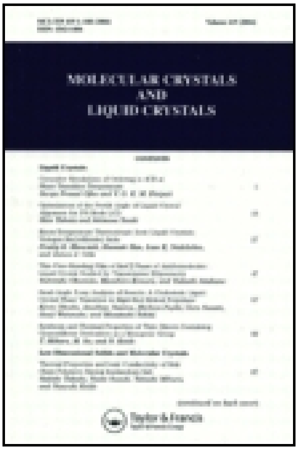

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Mirrorless Lasing and Energy Transfer in Cholesteric Liquid Crystals Doped with Laser Dyes

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Lasing in cholesteric liquid crystal (CLC) films doped with a mixture of laser dyes has been observed under UV excitation with 35ps pulses at 355nm. To probe optical interactions between molecules of different species, the emission and excitation spectra of the constituents have been studied in the 300–700nm range. Two dyes, a Benzofuran and an Oxazine dye were used in the system under study. Energy transfer between the host CLC and the dissolved dyes occurs, in agreement with previous observations. In addition, spectroscopic data indicates that active energy transfer from the host CLC to the Benzofuran dye, and from the Benzofuran dye to the Oxazine dye plays an important role in lasing in these systems. The Benzofuran dye acts as an impedance transformer, facilitating energy transfer from the host CLC to the lasing Oxazine dye.

INTRODUCTION

There has been considerable interest recently in lasing in dye-doped cholesteric liquid crystals. The possibility of lasing in CLC was first proposed by Goldberg et al [1] and subsequently investigated by Il'chishin et al [2]. Lasing in dye doped systems was unambiguously demonstrated by Kopp et. al. [3] and by Taheri and Palffy-Muhoray et al. [4] in the visible range under picosecond pulse excitation at 532nm. More recently Munoz et.al. [5] reported the observation, for the first time, of mirrorless UV-blue lasing in a pure dye-free CLC, under ps pulse excitation at 355nm. In the pure system, the cholesterics LC acts both as the cavity and the active medium and can be viewed on the basis of two equivalent descriptions: photonic band gap [6] or distributed feedback [7]. Lasing in these systems are of

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* Corresponding Author.

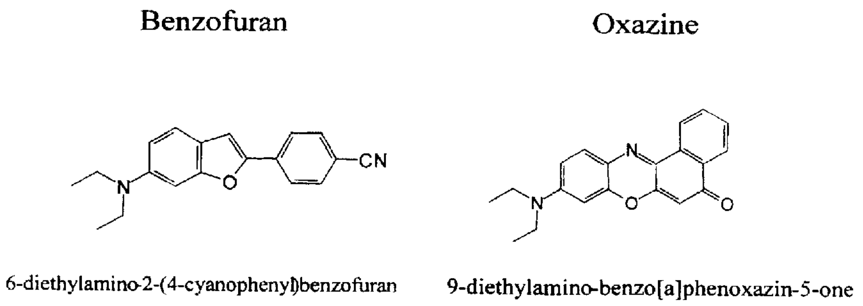
special importance due to a growing interest in compact laser light sources at shorter wavelengths.

Laser emission in dye doped samples, under ps excitation at 355nm, was found to occur, in part due to excitation energy transfer from the host CLC to the lasing dye. The efficiency of this energy transfer mechanism affects the performance of the system; it is also of fundamental interest. The presence of significant energy transfer in dye-doped systems suggests the use of multi-component dye mixtures with a view towards enhancing the lasing characteristics of dye doped CLC lasers.

In this paper we present the results of an investigation of the optical properties and lasing in cholesteric liquid crystals doped with a two-component mixture of laser dyes. It is found that, along with the optical interactions between the CLC and the dye molecules, active energy transfer mechanisms are present between the two dyes, and play an important role in lasing.

EXPERIMENT

Several dye-doped CLC mixtures were prepared using the commercial cholesteric liquid crystal mixture BL061 (EMI industries) and nematic liquid crystal 5CB (4-cyano-4′-n-pentylbiphenyl). Typical mixtures consisted of 72wt% BL061 and 28wt% 5CB. Two fluorescent dyes, Benzofuran (6-diethylamino-2-(4-cyanophenyl)benzofuran) and Oxazine (9-diethylamino-benzo[a]phenoxazin-5-one) were used as dopants in the CLC mixture. The chemical structures of the dyes are shown in Fig. 1.



Benzofuran **Oxazine**

6-diethylamino-2-(4-cyanophenyl)benzofuran 9-diethylamino-benzo[a]phenoxazin-5-one

FIGURE 1 Chemical structures of Benzofuran and Oxazine

The dyes were added to our CLC mixtures with typical concentrations of 0.5 wt% Benzofuran and 1.5 wt.%. Oxazine. In addition to furnishing a high quantum yield, the Benzofuran and Oxazine dyes showed good solubility in our CLC mixture. Cells consisting of glass windows coated with buffed polyimide separated by 25 μm thick spacers were filled with the mixture. The alignment layer gave rise to a uniform planar texture at the cell walls.

Continuous emission and excitation spectra were obtained with a Jovin Yvon-Spex model Flurolog-3 spectrofluorometer, equipped with a 450 W xenon lamp. Samples studied included undoped CLC, as well as mixtures of CLC-Benzofuran, CLC-Oxazine, and CLC-Benzofuran-Oxazine.

For the lasing experiments, pulses of 35ps in duration from a Q-switched and mode-locked Nd:YAG laser (Continuum PY61) were frequency tripled and passed through a waveplate-polarizer attenuator, and focused on the cell using an f = 20cm lens. A schematic of the experimental setup is shown in Fig 2. The emitted light was sent via a focussing lens to a TRIAX 550 (Jovin Yvon-Spex) spectrometer using an i-Spectrum-One intensified CCD (Jovin Yvon-Spex) detector with a 72nm bandwidth. The spectral resolution of system was 0.03nm.

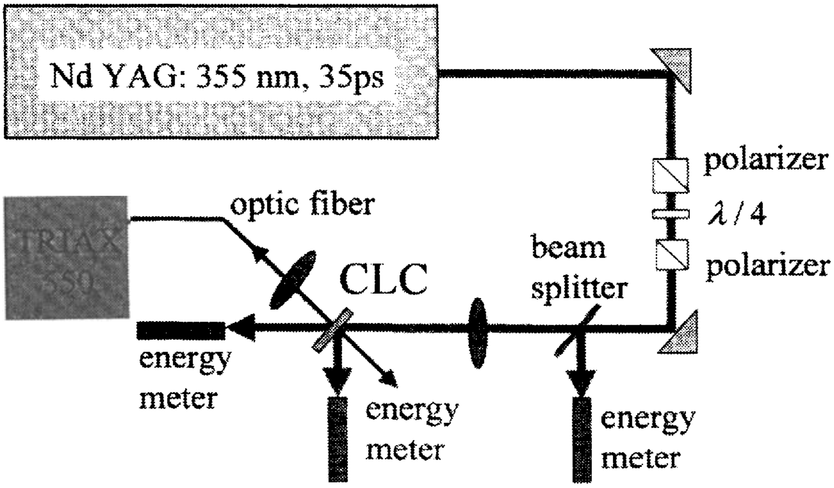


FIGURE 2 Experimental setup

RESULTS

In order to get a better understanding of the basic mechanism for the laser emission, the emission and excitation spectra were studied in the 300–700nm range. Fig. 3 shows the unpolarized emission spectrum of the CLC-Benzofuran-Oxazine system below the lasing threshold with pulsed excitation at

355nm. The small peak in the emission at 385nm is believed to be due to the de-excitation of the host CLC molecules from the lowest excited state to the ground state, while the blue-green and orange-red bands peaking at 475 and 630nm are due, respectively, to the $S_1 \rightarrow S_0$ transitions of the dissolved Benzofuran and Oxazine dye molecules. The reflectance spectrum is shown in this figure for the sake of comparison. The samples were prepared so that the unperturbed peak emission of the dye coincided with the low energy reflection band edge of the CLC, following the method described elsewhere [4,5].

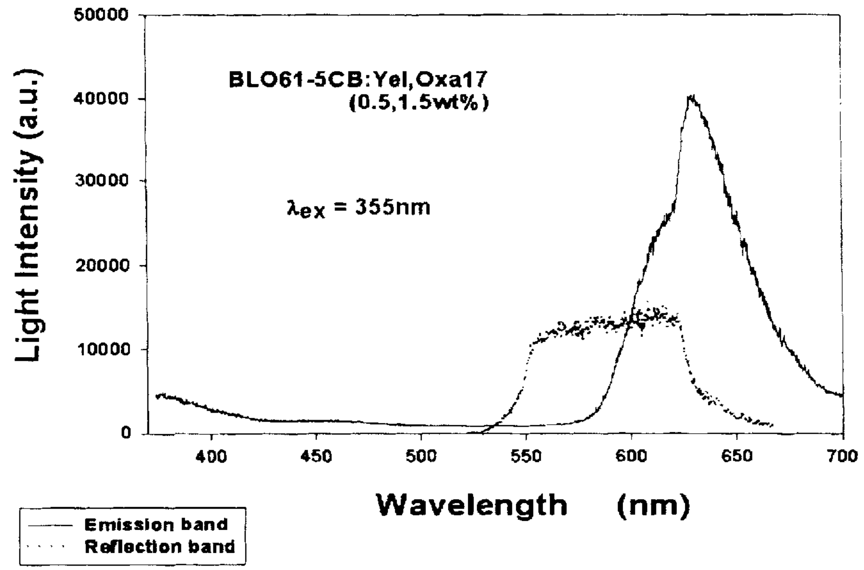


FIGURE 3 Emission and reflection spectra of the CLC mixture doped with Benzofuran and Oxazine dyes

In good agreement with previous results [4,5], the effects of the reflection band on the emission characteristics of the dyes are twofold; suppression of the emission in the band gap and the enhancement of emission at the band edges.

To study the mechanism for light generation and to probe the energy band structure of the dyes, it is useful to measure the excitation spectra for emission at different wavelengths. Fig 4 shows the excitation spectra for emissions at 385, 480 and 630nm, respectively. The location of the reflection band is indicated in the figure. The shoulder observed at ~580nm is due to the reflection band of the cholesteric [2,3,4]. The excitation spectrum of the emission at 630nm can be decomposed into several sub-bands. These sub-bands, as shown in Fig. 4, are absorption bands associated with ground to excited state transition of the Oxazine, peaking at ~490nm, of the Benzofuran, peaking at ~420nm, and of the CLC host, peaking at ~340nm. As the excitation spectra indicate, excitation of either the CLC or the Benzofuran absorption bands can lead to Oxazine emission. Specifically, the structures of the Oxazine and Benzofuran excitation spectra are evidence of energy transfer from the CLC to Oxazine, from the CLC to the Benzofuran, and most importantly, from the Benzofuran to Oxazine.

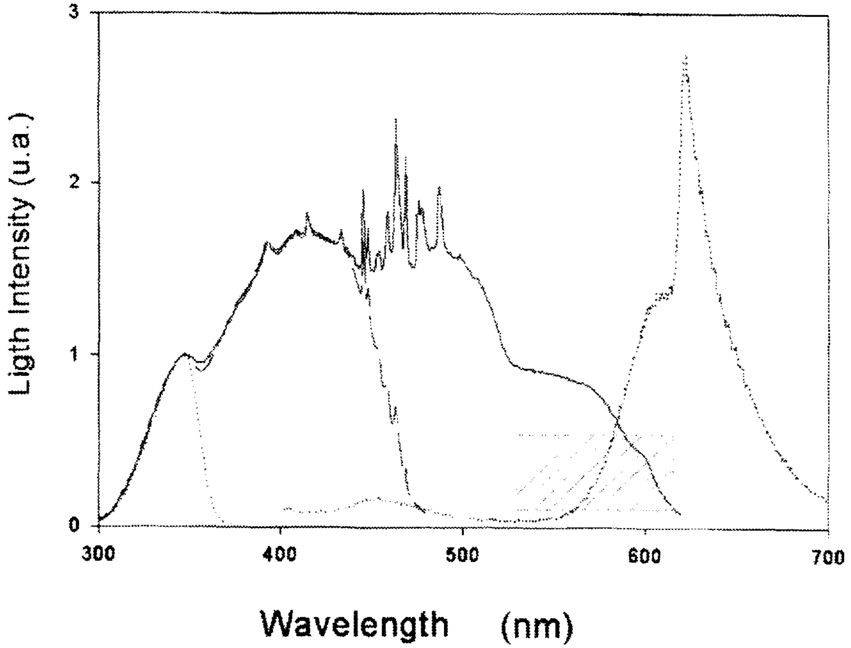


FIGURE 4 Excitation spectra. Solid line: 490nm (Oxazine); dashed line: 420nm (Benzofuran); dotted line: 340nm (CLC host). The location of the reflection band is indicated by shading; the emission spectrum is the dotted curve on the right

The rate of energy transfer from a donor (or sensitizer) to an acceptor (or activator) usually depends on the overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor, as well as on donor-acceptor distance [8,9]. Our results indicate that in the CLC system doped with two dyes under study, sequential radiative energy transfer from the CLC cascading through the Benzofuran to the Oxazine is operational. Studies to further confirm this conclusion are currently under way.

The polarization characteristics of the emission were used to study the effect of the reflection band on the energy transfer mechanism. Figure 5 shows the experi-

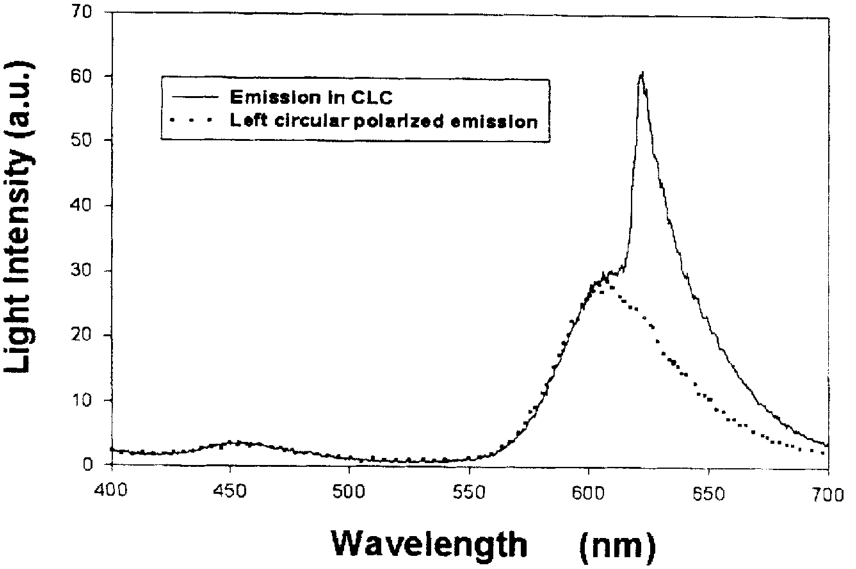


FIGURE 5 Unpolarized and left circularly polarized emission as function of wavelength. The excitation is at 355nm

mental results corresponding to the unpolarized and left circular emission from the right handed CLC host. In addition, the excitation spectra for both emissions were unaltered by the reflection band. This suggests that the band-gap of the host has little effect on the energy transfer process in this system.

As the pump intensity is increased, lasing occurs. Above the laser threshold of 0.692 μJ, strong directional emission as well as nonlinear gain and line narrowing can be observed. Fig. 6 shows the laser line, with FWHM as narrow as 3.5A. Lasing occurs at the edge of the reflection band, in agreement with previous observations in these systems. We note that in CLC-Oxazine samples without Benzofuran, lasing occurs only at significantly higher pump intensities; the laser threshold in these samples is 1.26 μJ, nearly twice that of samples with Benzofuran.

SUMMARY

We have observed mirrorless lasing in CLC samples doped with both Benzofuran and Oxazine dyes under UV pulsed excitation at 355nm. Lasing occurred

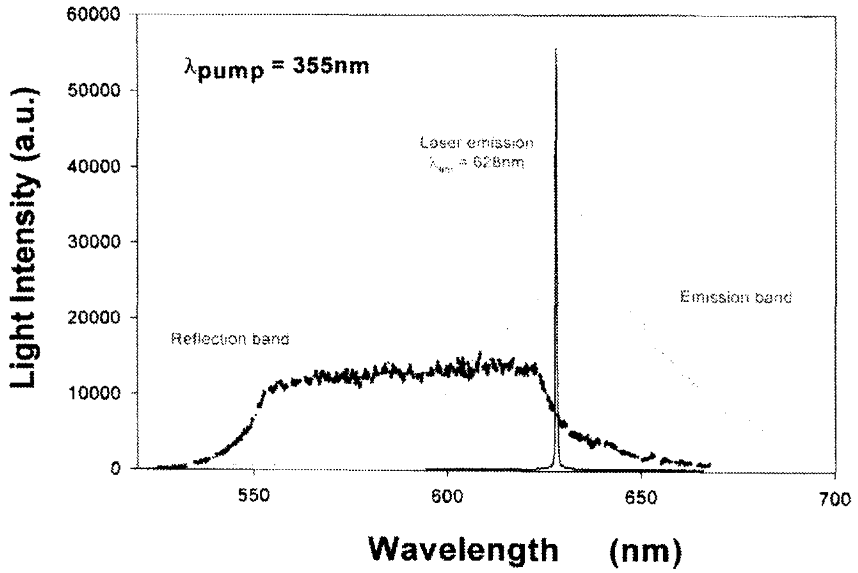


FIGURE 6 Laser emission the CLC-Benzofuran-Oxazine system. Lasing occurs near the peak of the Oxazine emission band

at wavelengths determined by the edges of the reflection band, with linewidths of ~3.5A. In addition of energy transfer from the host CLC to the dissolved dyes in the system, the excitation spectra give evidence of energy transfer from the Benzofuran dye to the Oxazine. The Oxazine is responsible for lasing, which occurs near the peak of the Oxazine emission spectrum. However, with pump pulse energies in the range 0.7–1.2 μJ, lasing occurs only if the Benzofuran dye is present. We interpret therefore the role of the Benzofuran dye, with emission peak at 420nm (nearly the geometric mean of the emission peak of the CLC at 340nm and of Oxazine at 490nm) as that of an impedance matching device, which facilitates energy transfer between the host CLC and the lasing Oxazine dye. Using chromophores in this way to facilitate energy transfer in laser materials may be useful for improving the efficiency of optical materials for device applications.

Acknowledgements

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versidad Autonoma Metropolitana-Iztapalapa and Universidad de Sonora, Mexico, respectively; S.V. Serak was on leave from the Institute of Electronics, Minsk, Belarus.

References

1. L.S. Goldberg and J.M. Schnur, *U.S. patent 3771065* (1973).
2. P. Il'chishin and A.Y. Vakhnin. *Mol. Cryst. Liq. Cryst.* **265**, 687 (1995).
3. V.I. Kopp, B. Fan, H.K.M. Vithana and A.Z. Genack, *Opt. Lett.* **21**, 1707 (1998).
4. B. Taheri, P. Palffy-Muhoray and H. Kabir, *ALCOM Symposium. Chiral Materials and Applications*, Cuyahoga Falls, Feb 18–19 (1999); P. Palffy-Muhoray and B. Taheri, XIII Conference on Liquid Crystals (September 13–17, 1999, Krynica Zdroj, Poland) *Book of Abstracts*, 20 (1999).
5. A.F. Muñoz, B. Taheri, P. Palffy-Muhoray and R. Twieg, *Mol. Cryst. Liq. Cryst.* (in press).
6. M. Soukoulis, ed., *Photonic Band Gaps and Localization*, Vol. 308, NATO ASI Series B: Physics (Plenum Press, New York, 1993).
7. G.H.B. Thompson, *Physics of Semiconductor Laser Devices* (John Wiley and Sons, New York, 1980).
8. G. Blasse and B.C. Grabmaier, *Luminescent Materials* (Springer-Verlag, Berlin, 1994).
9. B. DiBartolo ed. *Energy Transfer in Condensed Matter*, Vol. 114, NATO ASI Series B: Physics (Plenum Press, New York, 1984).