Circularly Polarized Lasers from Solid Films Comprising Chiral Conjugated Oligomers Doped with Functionalized Oligofluorenes

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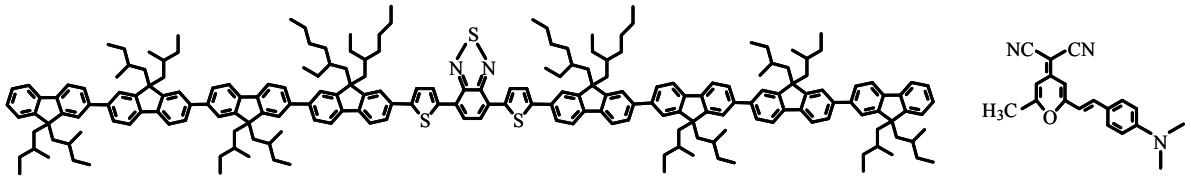
Since the first successful demonstration of circularly polarized lasers using cholesteric liquid crystal films three decades ago, intensive efforts have been made to overcome hurdles to potential applications as medical diagnostics, quantum cryptography, optical interconnects, optical switches and modulators. The orientational order parameter governing the laser dye's emission dipole is critical to spectral purity. The most commonly used laser dye, **DCM** (4-(dicyanomethylene)-2-methyl-6-(4-dimethyl-aminostryl)-4H-pyran), is capable of a very modest orientational order parameter less than 0.40. In addition to ensuring spectral purity, a high orientation order parameter is expected to increase lasing efficiency and to decrease threshold.

A series of fluorene-based conjugated oligomers have been developed in our laboratory for full-color and white organic light-emitting diodes. These materials are promising for lasing in cholesteric liquid crystal hosts because of their high photoluminescence quantum yields, high orientional order as a dopant or in neat film, and relatively broad emission across the visible spectrum. Here we report the comparison results of **DCM** and one of the oligofluorenes, **OF-r**, or 4,7-bis[5-(9,9-bis(2-ethylhexyl)-9',9',9'',9'', 9''',9'''-hexakis(2-methylbutyl)-7,2';7',2'';7'',2'''-tetrafluoren-2-yl)-thien-2-yl]-2,1,3-benzothiadiazole in fluid choleteric film (the mixture of nematic liquid crystal, ZLI-2244-000 from Merck, with the cholesteric liquid crystal, CB15 from Merck). The

molecular structures of light emitters, **OF-r** and **DCM** are depicted in Figure 1. In order to evaluate the emission order parameters of **DCM** and **OF-r** dyes, we measured the emission intensities polarized parallel and perpendicular to the director in the nematic liquid crystals doped with the dyes and then found the emission order parameters to be 0.60 for **OF-r** and 0.36 for **DCM**. As shown in Figure 2, **OF-r**-doped CLCs displayed a much higher temporal and spatial stability in the output radiation, due to the higher value of **OF-r**'s order parameter that prevents strong competition between the high- and low-energy edge frequency modes. In **DCM**-doped CLCs, strong competition between the modes could take place in case of a dye with a low order parameter, which can create temporal and spatial instabilities.



OF-r: *G* 104 °C *N* 304 °C *I*

DCM: *K* 227 °C *I*

Figure 1: Molecular structures of light emitters, **OF-r** and **DCM**

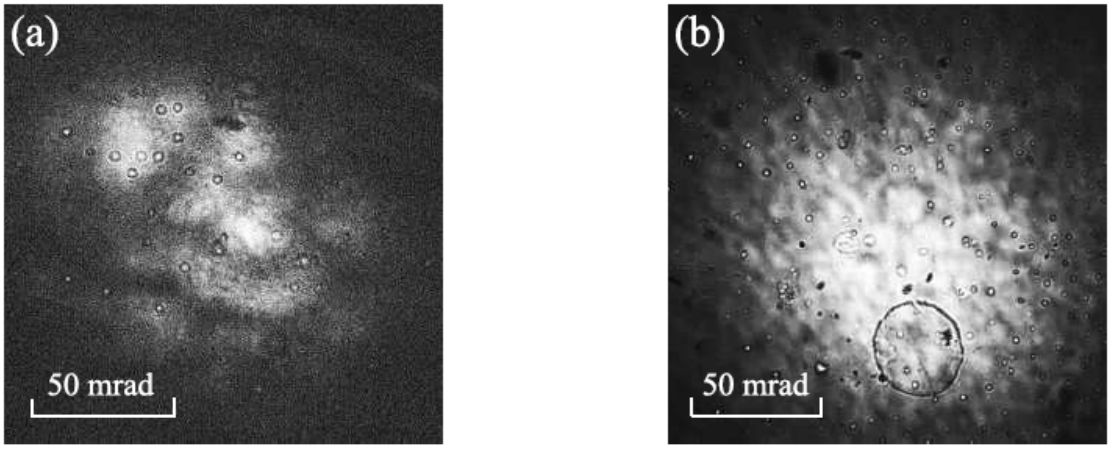


Figure 2: Intensity distribution of the laser output measured using a CCD camera in (a) 1.00 wt. % **DCM**-doped CLC and (b) 2.00 wt. % **OF-r**-doped CLC. The dark ring at the bottom of the picture is a camera artifact.

We also measured the laser output characteristics of **DCM**- and **OF-r**-doped CLCs in two different regimes corresponding to generating a transverse single fundamental spatial mode and a multi-mode ring pattern. As shown in Figure 3, in transverse single-mode regime, the same threshold and slope efficiency were obtained for the two light emitters. However, **OF-r** exhibited superior spatial and temporal stability and a sustained increase in laser output at increasing pump energy, generating output energy five times that of **DCM**. In transverse multi-mode regime, **OF-r** was more than twice as efficient as **DCM**.

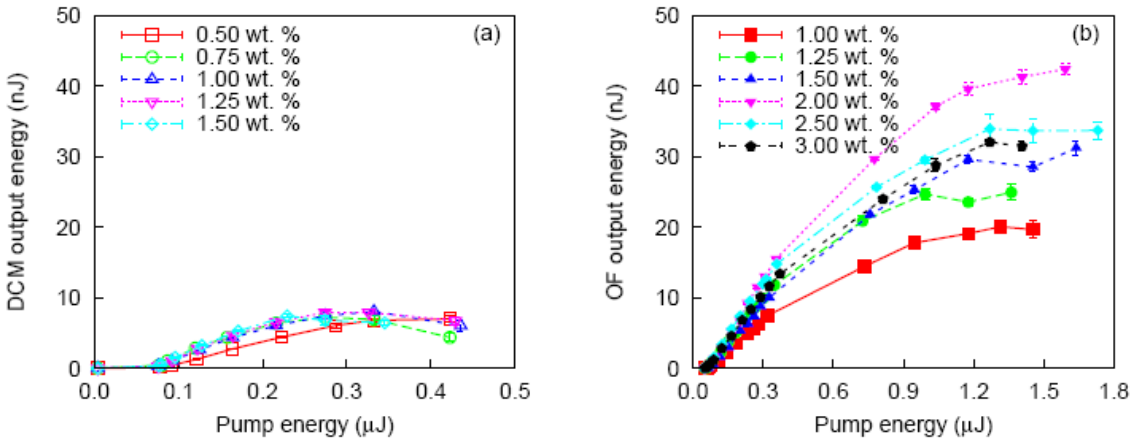
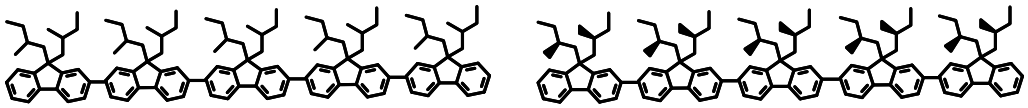


Figure 3: Laser output energy plotted as a function of the incident pump energy of (a) **DCM** and (b) **OF-r**-doped CLC samples in transverse single-mode regime.

Extrinsic factors that may disturb the host film's helical stack or laser dye's orientational order would cause adverse effects on lasing. Optical pumping and lasing could result in heating, causing the stop-band to undergo a red or blue shift depending on the type of cholesteric liquid crystal used as the host. A rise in temperature would also reduce dye molecules' orientational order parameter. Optical torque on the cholesteric liquid crystal structure could lead to a deterioration of laser performance. Yet another potential problem is laser induced fluid flow disturbing the stop-band. In short, cholesteric liquid crystal fluids as the hosts are vulnerable to any or all of these adverse effects, which can be avoided by using solid cholesteric liquid crystals in principle. Prior attempts to use solid cholesteric liquid crystal films, however, suffered from spectral impurity of lasing apparently because of the difficulty preparing highly ordered, disclination-free films.

Our research was motivated to identify potential laser dyes characterized by a high fluorescence quantum yield and a high orientational order parameter governing emission dipoles, and to impart device stability and robustness by using solid cholesteric liquid crystals as the hosts. To ensure device stability and robustness, our promising laser dyes are doped in low-molar-mass cholesteric glassy liquid crystals (GLCs) comprising chiral conjugated oligomers also developed in our laboratory. Here we report the comparison results of **OF-r** doped in fluid CLCs (ZLI-2244-000 and CB15) and glassy CLCs, which is the mixtures of **F(MB)5-Ch,** penta[9,9-bis(2*S*-methylbutyl)fluorene] and **F(MB)5-N**, penta[9,9-bis(2-methylbutyl)-fluorene], as depicted in Figure 4.



F(MB)5-N: *G* 92 °C *N* 171°C *I* **F(MB)5-Ch:** *G* 91 °C *Ch* 173 °C *I*

Figure 4: Molecular structures of **F(MB)5-Ch** and **F(MB)5-N** used for preparation of glassy CLC host films.

Representative reflection spectrum, fluorescence spectrum, and the lasing peak of **OF-r**-doped glassy CLC and its lasing output energy as a function of pump energy are plotted as Figure 5. At an increasing concentration of **OF-r**, the improvement in laser gain appears to have been overcome by concentration quenching. As shown in Figure 6, the maximum slope efficiency is expected at an optimum concentration between 2.0 and 2.5 wt% of **OF-r** in both glassy and fluid CLC film.

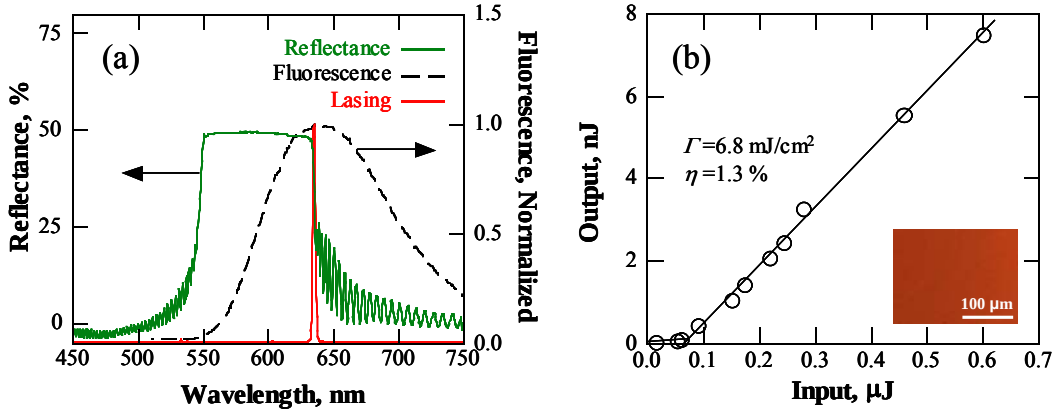


Figure 5: Glassy CLC film consisting of 1.5 wt% **OF-r** in **F(MB)5-Ch:F(MB)5-N** at a 24.0:76.0 mass ratio: (a) Reflection spectrum (solid curve), **OF-r** fluorescence spectrum from a nematic **F(MB)5-N** film (dashed curve), and the lasing peak at 635 nm with a pump fluence of 121 mJ/cm^2 at 10 Hz, and (b) Lasing output energy as a function of pump energy.

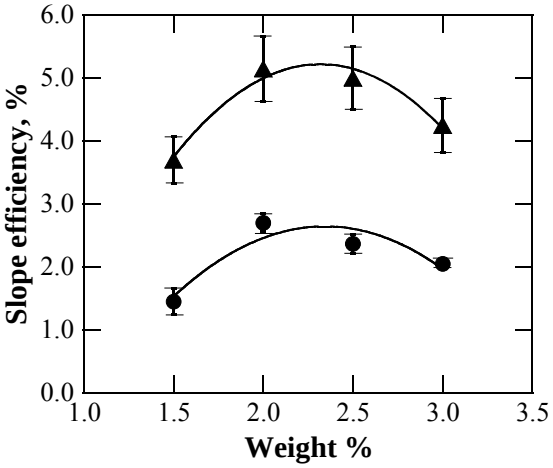


Figure 6: Slope efficiency as a function of wt% **OF-r** in glassy (●) and fluid (▲) CLC lasers. For glassy CLC films with **OF-r** at 1.5, 2.0, 2.5, and 3.0 wt%, the **F(MB)5-Ch:F(MB)5-N** mass ratios are 24.0:76.0, 24.1:75.9, 24.2:75.8, and 24.3:75.7, respectively. For fluid CLC films with **OF-r** at 1.5, 2.0, 2.5, and 3.0 wt%, the **CB-15:ZLI2244-000** mass ratios are 35.5:64.5, 35.6:64.4, 35.7:64.3, and 35.9:64.1, respectively. All the efficiency data were gathered from the initial slopes of output-input relationships.

The expectation that solid CLC films would produce temporally stable lasing output was realized by the data compiled in Figure 7a. A fluid CLC film containing 2.0 wt% **OF-r** in **CB-15:ZLI2244-000** at a mass ratio of 35.6:64.4 (with η=5.2%) was also subjected to stability test. As shown in Figure 7b, the lasing output decays with time, and the decay rate increases with pump fluence most likely due to heating, optical torque, and laser-induced flow that tend to disrupt the CLC structure and the orientational order of **OF-r** molecules.

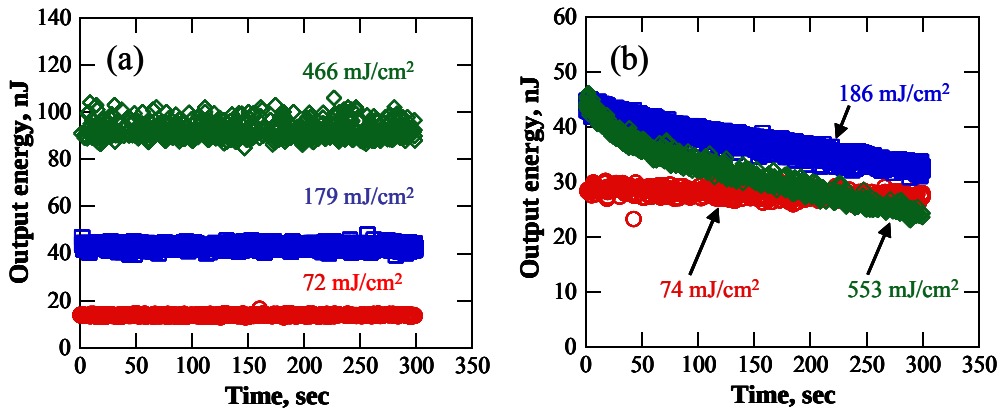


Figure 7: Time dependence of lasing output from (a) a glassy CLC film and (b) a fluid CLC film, both containing **OF-r** at 2.0 wt%, at specified pump fluences and 10 Hz

The fluid CLC film of the same composition as used in Figure 7b was further pumped with a fluence of 550 mJ/cm^2 at 10 Hz. The output energy from the first series of lasing experiments diminished with time, as shown in Figure 8, which is consistent with the observations presented in Figure 7b at a pump fluence of 186 or 553 mJ/cm^2. The second series of experiments was conducted after the CLC film had been left at room temperature for 0.5 h. As presented in Figure 8, the lasing output decreased by 35 to 40 % because fluid CLC film did not have sufficient time to recover from external perturbations incurred during the first series of experiments. The film was then left at room temperature for 20 h before the third series of experiments was performed. The pristine film's output energy as a function of time was restored, indicating a full recovery of order in the fluid CLC film and the absence of photodegradation of materials. The chemical integrity of all material components used in this study is ascertained by the temporal stability of laser output shown in Figures 7a and the full recovery of output energy demonstrated in Figure 8 up to a pump fluence of 466 mJ/cm^2 for the glassy CLC film and 563 mJ/cm^2 for the fluid CLC film, respectively.

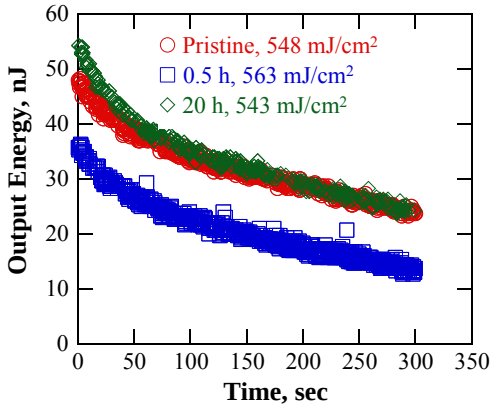


Figure 8: Lasing output from a fluid CLC film containing **OF-r** at 2.0 wt% pumped with 550±12 mJ/cm^2 at 10 Hz rested for 0.5 and 20 h time intervals between three runs.