Robust organic lasers comprising glassy-cholesteric pentafluorene doped with a red-emitting oligofluorene

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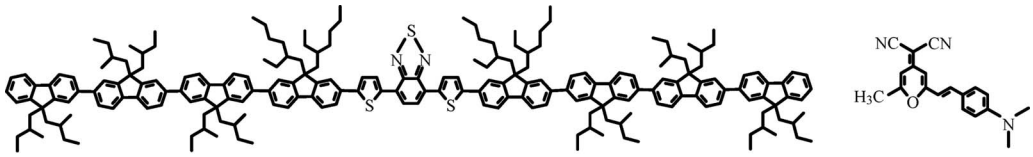
Doped with a red-emitting oligofluorene, fluid and glassy cholesteric liquid crystal (CLC) films are characterized by similar lasing thresholds and efficiencies. With picosecond excitations the output from a glassy CLC laser is temporally stable, but that from a fluid CLC laser decays with time. The difference in stability is attributable to external perturbations on supramolecular structure in the fluid but not the solid state, such as heating through optical pumping, light-induced pitch dilation, and laser-induced flow. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3073713]

Consisting of a helical stack of quasinematic layers, a cholesteric liquid crystal (CLC) film constitutes a one-dimensional photonic bandgap serving as a resonator for the embedded light-emitting molecules to undergo lasing.[1] To exploit their potential for practical application, CLC lasers have been actively pursued for both fixed[1–5] and tunable[6–11] lasing wavelengths using fluid CLCs in most cases. The helical stacking in fluid CLC films, however, is susceptible to external perturbations such as heating via optical pumping, light-induced pitch dilation, and laser-induced flow,[12–15] all posing potentially adverse effects on the laser performance. To impart device robustness, solid films comprising of photopolymerized[4] and glassy cyclosiloxane[5] CLCs have also been explored. Using glassy liquid crystalline pentafluorenes, we report herein the feasibility of robust glassy CLC lasers with a sharply defined stop band, producing temporally stable energy output with otherwise comparable performance to conventional fluid CLC lasers.

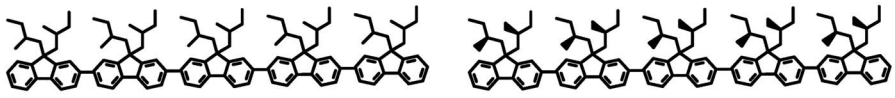
Of all the light emitters that have been attempted, 4-(dicyanomethylene)-2-methyl-6- (*p*-dimethylaminostyryl)-4*H*-pyran (DCM), as depicted in Fig. 1, is the most widely used for CLC lasers presumably for its solubility and alignment with the local director. A high orientational order parameter is expected to reduce threshold, to increase efficiency, and to deliver spectral purity.[16–18] In a recent report,[19] a red-emitting oligofluorene (OF-r) (Ref. 20), 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-benzothia-diazole, as depicted in Fig. 1, was compared to DCM in 22-μm-thick fluid CLC films prepared with a mixture of a CLC, CB-15, and a nematic liquid crystal, ZLI-2244–000. Compared to DCM, 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 multimode regime, OF-r was more than twice as efficient as DCM.

For the preparation of robust CLC lasers, nonemissive glassy CLCs with absorption edges deep in the ultraviolet (UV) region are highly desirable to avoid photoexcitation of the host. A unique feature of glassy CLCs is their ability to preserve helical stacking of molecules in the solid state through glass transition without encountering crystallization. In addition, the ability to form monodomain films exhibiting a square-top stop band is especially beneficial. At the same time, light emitters must be soluble in glassy CLCs to host up to a few weight percent. Of all the prospective glassy CLCs that we have developed in our laboratory,[21–24]



OF-r: *G* 104°C *N* 304°C *I*

DCM: *K* 227°C *I*



F(MB)5-N: *G* 92°C *N* 171°C *I*

F(MB)5-Ch: *G* 91°C *Ch* 173°C *I*

FIG. 1. Molecular structures of light emitters, OF-r and DCM, as well as F(MB)5-Ch and F(MB)5-N used for the preparation of glassy CLC host films. The phase-transition temperatures of F(MB)5-Ch, F(MB)5-N, and OF-r were reported in Refs. 20–22, and those of DCM by Swanson *et al.* (Ref. 26).

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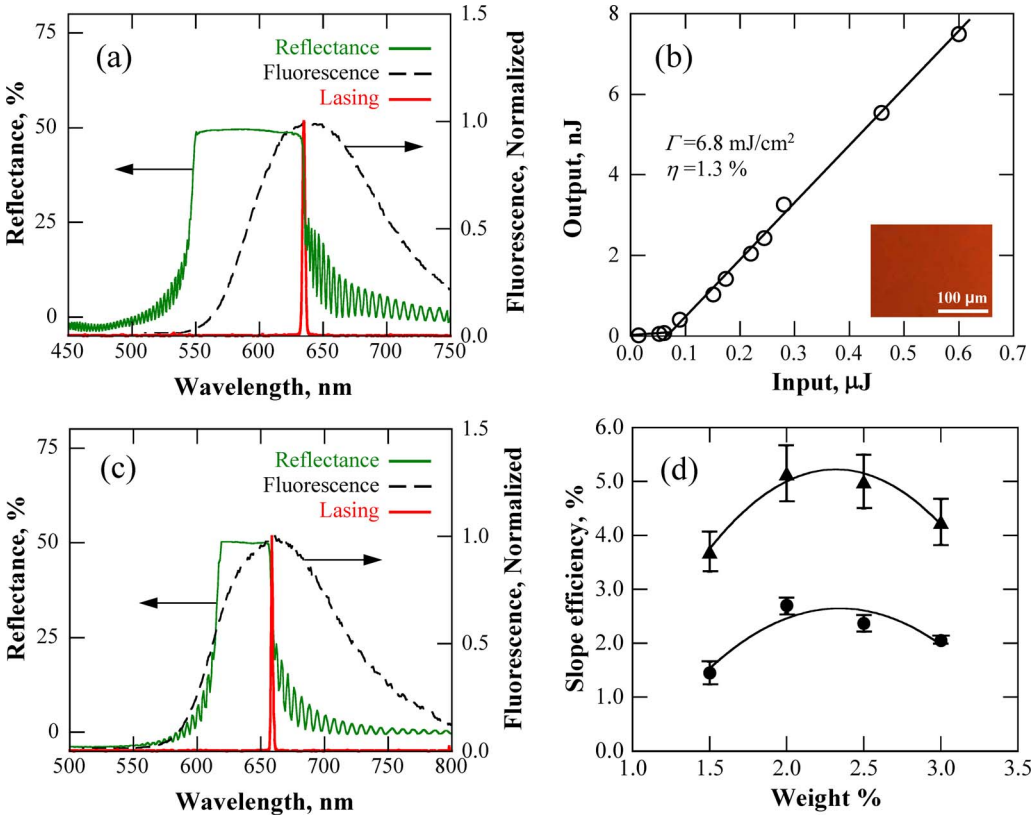

FIG. 2. (Color online) (a) Fluorescence spectrum (dashed curve) of OF-r at 1.5 wt % in a glassy nematic F(MB)5-N film, reflection spectrum (solid green curve), and lasing peak at 635 nm (red solid curve) with a pump fluence of 121 mJ/cm^2 at 10 Hz of a glassy CLC film consisting of 1.5 wt % OF-r in F(MB)5-Ch:F(MB)5-N at a 24.0:76.0 mass ratio. (b) Lasing output as a function of pump energy for the same glassy CLC film doped with OF-r as in (a); monodomain character of the glassy CLC film verified with a polarizing optical micrograph included as the inset. (c) Fluorescence spectrum (dashed curve) of OF-r at 2.0 wt % in a nematic ZLI-2244–000 film, reflection spectrum (solid green curve), and lasing peak at 658 nm (red solid curve) with a pump fluence of 30 mJ/cm^2 at 10 Hz of a 22-μm-thick fluid CLC film consisting of 2.0 wt % OF-r in CB-15:ZLI-2244–000 at a 35.6:64.4 mass ratio. (d) Slope efficiency as a function of wt % OF-r for glassy (●) and fluid (▲) CLC lasers determined with initial slopes of output-input relationships beyond thresholds, as illustrated in (b) for a glassy CLC film containing 2 wt % OF-r.

penta[9,9-bis(2*S*-methylbutyl)fluorene] [F(MB)5-Ch], and penta[9,9-bis(2-methylbutyl)-fluorene] [F(MB)5-N], were identified to meet the demands for accommodating OF-r. The molecular structures of F(MB)5-Ch and F(MB)5-N depicted in Fig. 1 are accompanied by identical glass transition temperature, T_g, and clearing temperature, T_c, within an experimental error of ± 2 °C.

The F(MB)5-Ch:F(MB)5-N mass ratio was adjusted in the presence of OF-r so that the stop band's low-energy edge was aligned with the fluorescence maximum of OF-r. Monodomain glassy-cholesteric films containing OF-r at 1.5–3.0 wt % were prepared between fused-silica substrates coated with rubbed polyimide films following previously reported procedures.[21,24] Measured with UV-vis-near infrared spectrophotometry (Lambda 900, PerkinElmer),[21,24] the right-handed stop band of a 22-μm-thick glassy CLC film comprising 1.5 wt % OF-r in F(MB)5-Ch:F(MB)5-N at a mass ratio of 24.0:76.0 is represented by the solid curve in Fig. 2(a). To avoid interaction with the stop band[16,25] and to simulate linearly polarized photoluminescence from quasinematic layers within a cholesteric film, a nematic liquid crystal film should be used to gather the fluorescence spectrum of OF-r. The fluorescence spectrum, shown as the dashed curve in Fig. 2(a), was measured for OF-r at 1.5 wt % in a 22-μm-thick glassy-nematic liquid crystal film of F(MB)5-N, which was further characterized by linearly polarized fluorescence spectroscopy[22] to arrive at $S_{em}=0.54$, the orientational order of the OF-r molecules' emission dipoles in the quasinematic layers in the glassy-cholesteric film. As an illustration of laser output characterized by an apparatus described elsewhere[19] with 532 nm irradiation at 35 ps pulse duration, a sharp peak at 635 nm is recorded in Fig. 2(a) at the pump fluence of 121 mJ/cm^2. Plotted in Fig. 2(b) is the output-input relationship for the determination of threshold, $\Gamma=6.8$ mJ/cm^2, and slope efficiency, $\eta=1.3\%$. The absence of disclinations in the glassy CLC film was revealed by the polarizing optical micrograph reproduced as the inset in Fig. 2(b).

As reported previously,[19] ZLI-2244-000 and CB-15 (EM Industries) were used to prepare a nematic fluid film to quantify S_{em} at 0.60 and a fluid CLC film for the investigation of lasing behavior. At a cholesteric-to-nematic mass ratio of 35.6:64.4 in the presence of OF-r at 2.0 wt %, the fluid CLC film exhibited a stop band with its low-energy edge aligned with the fluorescence maximum. With a pump fluence of 30 mJ/cm^2, lasing occurred at 658 nm, as also shown in Fig. 2(c). As shown in Fig. 2(d), 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 films. Although the slope efficiency of the fluid CLC film is about twice that of the glassy CLC film, with OF-r at 2.0 wt % the laser output from the glassy CLC film was approximately 30% higher than that from the fluid CLC film before leveling off at a pump fluence up to 550 mJ/cm^2.

A glassy CLC film comprising of 2.0 wt % OF-r in F(MB)5-Ch:F(MB)5-N at a mass ratio of 24.1:75.9 (with η

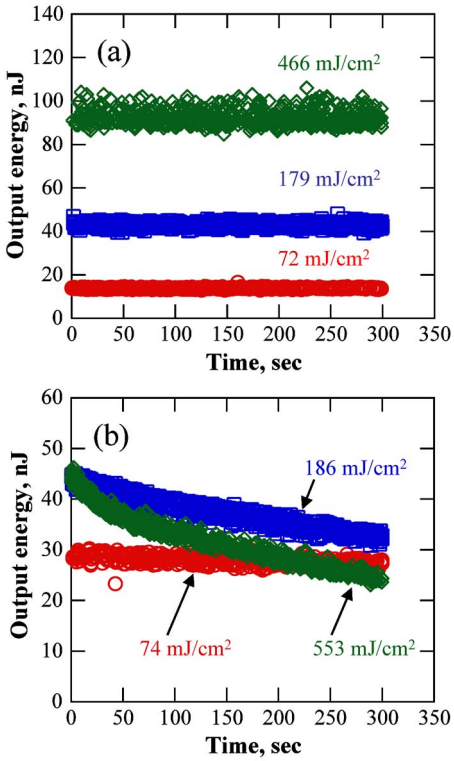

FIG. 3. (Color online) Time dependence of lasing output from (a) a glassy CLC film, (b) a fluid CLC film, both containing OF-r at 2.0 wt %, at specified pump fluences and 10 Hz each on a pristine spot on the films.

=2.7%) was used to test the temporal stability of lasing output with increasing pump fluences all at 10 Hz. The expectation that solid CLC films would produce temporally stable lasing output was realized according to Fig. 3(a). The observed stability of laser output also served to validate photostability of all material components in the glassy CLC film. A fluid CLC film containing 2.0 wt % OF-r in CB-15:ZLI-2244–000 at a mass ratio of 35.6:64.4 (with η=5.2%) was also subjected to stability test. As shown in Fig. 3(b), the lasing output decays with time due to heating via optical pumping that might have caused a spectral shift of the stop band, light-induced pitch dilation, and laser-induced fluid flow, any or all of which would disrupt the CLC structure and the orientational order of OF-r molecules. Left at room temperature for a few hours after the first series of lasing experiments, the fluid CLC film recovered its lasing output profile to that of the pristine film.

In summary, monodomain fluid and glassy CLC films containing a red-emitting oligofluorene up to 3.0 wt % were prepared for an evaluation of laser threshold, slope efficiency, and the temporal stability of laser output. The thresholds to lasing are 7.0 versus 6.8 mJ/cm^2 for the fluid and glassy CLC films, respectively, and the maximum slope efficiency of the fluid film is about twice that of the glassy film, 5.2 over 2.7%. Nevertheless, the glassy CLC film produced output energy approximately 30% higher than the fluid CLC film because of the more sustainable lasing at increasing pump fluence with the solid film. Furthermore, the glassy CLC film produced temporally stable laser output up to a pump fluence of 466 mJ/cm^2 at a repetition rate of 10 Hz. In contrast, the laser output from the fluid CLC film consistently diminished with time.

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