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

Simon K. H. Wei,1 Shaw H. Chen,1,a Ksenia Dolgaleva,2 Svetlana G. Lukishova,2 and Robert W. Boyd2
1Department of Chemical Engineering and Laboratory for Laser Energetics, University of Rochester, Rochester, New York 14623-1212, USA
2The Institute of Optics, University of Rochester, Rochester, New York 14627-0186, USA

(Received 14 September 2008; accepted 31 December 2008; published online 28 January 2009)

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 fixed1–5 and tunable6–11 lasers with a sharply defined stop band, producing temporally stable output. Among these, we report herein the feasibility of robust glassy CLC films with absorption edges deep in the ultraviolet (UV) region.

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‴‴-tetrafluorophenylene)-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

In 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).

0003-6951/2009/94(4)/041111/1/$25.00 94, 041111-1 © 2009 American Institute of Physics

Downloaded 09 Apr 2009 to 128.100.138.3. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp
penta[9,9-bis(2S-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 \(\pm 2^\circ\text{C}\).

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. Measured with UV-vis-near infrared spectrophotometry (Lambda 900, PerkinElmer), the right-handed stop band of a 22-\(\mu\)m-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 and to simulate linearly polarized photoluminescence from quasineumatic layers in the glassy-cholesteric film. As an illustration of laser output characterized by an apparatus described elsewhere, with 352 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\ \text{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, 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 laser 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 \(\eta\))...
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.

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/cm² 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/cm² at a repetition rate of 10 Hz. In contrast, the laser output from the fluid CLC film consistently diminished with time.

The authors thank Stephen D. Jacobs and Kenneth L. Marshall of the Laboratory for Laser Energetics, LLE, at University of Rochester for helpful discussions and technical advice. Simon K. H. Wei acknowledges the support of a Horton Graduate Fellowship administered by the LLE. This work was supported in part by the Department of Energy Office of Inertial Confinement Fusion under Cooperative Agreement No. DE-FC52-08NA28302 with LLE and the New York State Energy Research and Development Authority. The support of DOE does not constitute an endorsement by DOE of the views expressed in this article.