Glass-Forming Cholesteric Liquid Crystal Oligomers for New Tunable Solid-State Laser

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Cholesteric liquid crystals (CLCs)—supramolecular helical assemblies of nematic liquid crystal (NLC) layers with a periodic helical pitch—have attracted a great deal of attention owing to their wide range of potential applications in displays, full-color recording media, polarizers, and reflectors.[1] The CLC mesophase appears from intrinsically chiral compounds or mixtures, where at least one of the components has an enantiometric chiral center. At the CLC mesophase, the orientational order of CLC molecules is similar to that of NLC. However, the local director of each NLC layer spatially and periodically rotates clockwise or counterclockwise with respect to the helical axis, resulting in the formation of right-handed or left-handed CLCs, respectively. When the CLC materials are sandwiched between a pair of substrates with homogeneous anchoring surfaces, the helical axis is spontaneously oriented to the orthogonal direction of the substrate surface. Due to the supramolecular helical structures, the planar CLC cell shows a negative birefringence with an extraordinary refractive index (n_e) along the helical axis. Selective light reflection is one of the most unique and important optical properties of the CLC helical structures. The peak wavelength of the selective light reflection (λ_{max}) is numerically expressed as $\lambda_{max} = n_{av}\ p$, where n_{av} is average refractive index and p is the helical pitch length. The reflection bandwidth ($\Delta\lambda$) is determined by $\Delta\lambda = p(n_e - n_o)$, where n_o is ordinary refractive index. Another outstanding feature is the light reflection with a chiroptical property. When a linearly polarized light propagates into the planar CLC cell along the helical axis, the CLC molecules can reflect circularly polarized (CP) light with the same CLC supramolecular helical handedness at λ_{max} with $\Delta\lambda$. In contrast, CP light with the opposite CLC helical handedness transmits through the planar cell without light reflection.

Recently, the CLCs have garnered considerable attention from the intriguing research field of photonic crystals (PCs).[2] The PCs are periodically modulated structures of dielectric materials on a scale comparable to the wavelength of light, leading to the appearance of forbidden regions in the photon dispersion diagram. The specific regions are nowadays known as photonic band-gaps (PBGs). Such periodic helical structures of CLCs can be regarded as 1D PCs. Following the archetypal report one decade ago,[3] much effort has established a new perspective on the CLC for optically excited laser emission from both fundamental and technologic viewpoints. When a light-emitting organic dye is embedded in the CLC, optical excitation gives rise to stimulated laser-emission peak(s) at edge(s) and/or within the CLC PBGs.[4] Among the previous studies, tunable lasers is one of the most leading research topics with the potentials for versatile applications. Hitherto, there have been a variety of examples of the laser wavelength tunabilities by temperature,[5] mechanical stress,[6] photoirradiation,[7] electric field,[8] and chiral-dopant concentration.[9]

Currently, more emphasis in the tunable CLC-laser systems is placed on the position-dependent tuning of the laser-emission wavelengths by continuously gradated PBG (CG-PBG) structures in the planar CLC cells.[10,11] In other words, the CG-PBG structures have the 1D gradation of a CLC helical pitch. Although the CG-PBG structures are obtained by precisely controlling temperature[10] and chiral-dopant concentration[11] of low-molecular-weight CLCs, these strategies might encounter some serious drawbacks as follows. In principle, the low-molecular-weight CLCs are very vulnerable to subtle thermal fluctuations, so that specific temperature-controllers and heating-stages are needed to keep the CG-PBG structures in the lasing experiment.[10] In another strategy, by the gradation of chiral dopant concentration, the CG-PBG structures are not stable due to the fluid diffusion of chiral dopants.[11] Therefore, the CG-PBG structures of low-molecular-weight CLCs are impractical. Very recently, the CG-PBG structures of photopolymerized CLCs have been applied to the position-dependent tuning of laser emission.[12] However, these CG-PBG structures require high threshold excitation energies or peak powers for laser action after the photopolymerization, because the initial CLC helical orientation or light-emitting organic dyes might be deteriorated during radical reactions induced by UV light. In this Communication, we report the synthesis of a glass-forming CLC (G-CLC) and its application in a new type of tunable CLC solid-state laser. As will be seen below, we succeeded in the facile fabrication of robust CG-PBG structures of our light-emitting G-CLC without any covalent bonding through a supercooling process, leading to continuously and reversibly tunable laser emission by optical excitation with relatively low peak powers.

In order to prepare a light-emitting G-CLC, we designed and synthesized three kinds of compounds of **CD8**, **11-BP**, and **DC-OPV** (Scheme 1). The synthesis procedures are described in the Experimental section. First, we used **CD8** as a G-CLC host. Previously, Tamaoki et al.[13] found unique properties of a CLC

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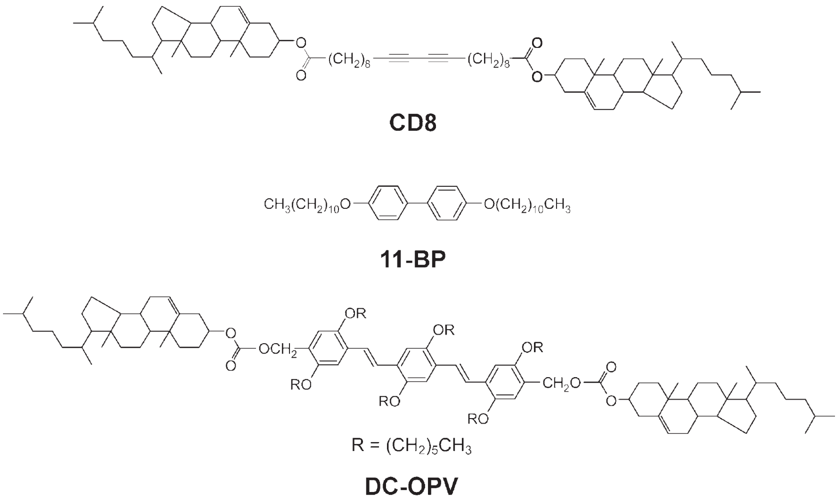

Scheme 1. Chemical structure of a G-CLC for the fabrication of a new type of tunable solid-state CLC laser. The G-CLC was prepared by mixing ternary compounds of **CD8**, **11-BP**, and **DC-OPV** at a weight ratio of 98.4:1.6:1.0, respectively.

oligomer tethering two cholesteryl units at the termini (**CD8**, Scheme 1), which can be practically applied in rewritable full-color recording media. A thin film of **CD8** exhibits a PBG with reflected light, that is, a selective reflection band, in a wide visible wavelength range of 420–610 nm at the CLC mesophase temperature of 87–115 °C. The **CD8** film annealed at CLC temperatures is rapidly cooled to 0 °C, whereupon the selective light reflection can be preserved at room temperature. Such supercooling treatment of **CD8** results in durable formation of a glassy CLC solid state without the aid of any covalent bonding because of its relatively high glass-transition temperature at ~80 °C. This solidified **CD8** film has unique capabilities for not only the desired tuning of PBG by annealing temperature, but also the on-demand preservation of the shifted PBG by the subsequent supercooling treatment. Secondly, **11-BP** was adopted as a dopant in precisely regulating the PBG wavelength and its tuning range. The addition of **11-BP** to **CD8** results in fine control over both PBG wavelength and its thermally induced shift range, which are dependent on the doping amount of **11-BP**.[14] In this study, 1.6 wt% of **11-BP** was doped into **CD8** to obtain a G-CLC host with a PBG shift range from 400 to 600 nm. Thirdly, we used an oligo(*p*-phenylene vinylene) derivative of **DC-OPV** possessing two cholesteryl units at the termini as a light-emitting compound. This **DC-OPV** was designed to be accommodated to the G-CLC host of **CD8** and **11-BP**. In a preliminary experiment, it was confirmed that a typical laser dye, such as Pyrromethene 597, readily crystallizes with domains of micrometer dimension in the G-CLC host, even when the addition amount is only 0.4 wt% (Fig. S1, Supporting Information). In contrast, a homogeneous light-emitting G-CLC can be prepared by mixing ~1.0 wt% **DC-OPV** into **CD8** and **11-BP** (vide infra).

A light-emitting G-CLC was prepared from a homogeneous dichloromethane solution including **CD8**, **11-BP**, and **DC-OPV** at a weight ratio of 98.4:1.6:1.0 through evaporation in vacuo to remove the solvent. This G-CLC was placed between two thin glass substrates (~$0.15 \times 18 \times 9.0\,\text{mm}^3$) with an uniaxially rubbed poly(vinyl alcohol) film surface. The thickness of G-CLC film was adjusted using crosslinked polymer microparticles with a diameter of ~10 μm. The solidified G-CLC film was prepared by supercooling from the CLC mesophase temperature to 0 °C. Polarized optical microscopic observation showed Grandjean texture, indicative of the perpendicular orientation of G-CLC helical axis with respect to the substrate surface. In addition, this film showed a uniform optical domain without any crystallization of **DC-OPV**.

Figure 1A shows CP transmission spectra of a G-CLC film measured with right-handed CP (R-CP) and left-handed CP (L-CP) probe light. First, the G-CLC thin film was solidified by supercooling from a CLC temperature of 78 °C. The CP-transmission spectral shape was drastically altered by the polarization state of the CP probing light. The R-CP transmission spectrum showed a single broad band centered at 413 nm from the electronic absorption of **DC-OPV** (spectrum e). Converting from R-CP to L-CP probing light, we found not only the electronic absorption band of the **DC-OPV** chromophore, but also a characteristic reflection band at 600 nm arising from the CLC PBG (spectrum a). The differential transmittance between R-CP

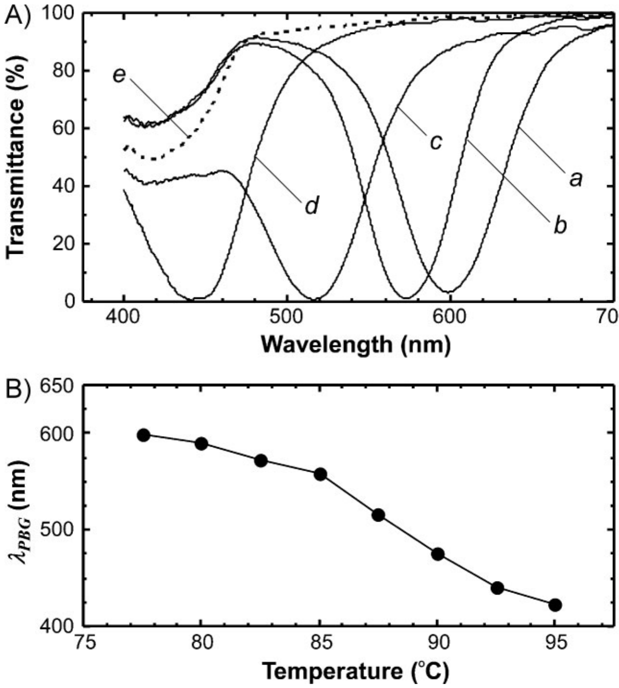

Figure 1. A) L-CP transmission spectra of a G-CLC film that was solidified by supercooling from annealing temperatures at 78 °C (spectrum a), 83 °C (spectrum b), 88 °C (spectrum c), and 93 °C (spectrum d). The representative R-CP transmission spectrum of G-CLC supercooled from 78 °C is shown by the dashed curve (spectrum e). The R-CP transmission spectra had the same appearance even when the annealing temperatures were changed. B) Changes in the λ_{PBG} of the supercooled G-CLC film as a function of the annealing temperature.

and L-CP light around 410 nm originates from the Borrmann effect in absorbing CLC system.[15] The PBG wavelength in the L-CP transmission spectrum shifted to shorter wavelengths at the oblique-incidence angle (θ) of the probe light. This behavior follows the geometric relation of $\lambda_{\max} = np \cos \theta$. The result suggests that this G-CLC film retains a left-handed helical molecular sense even at a glassy CLC solid state.

The PBG of a G-CLC film, observed as a selective reflection of L-CP light, could be precisely tuned by changing the annealing temperatures at which the supercooling was started. When the G-CLC film was supercooled from the CLC temperatures at 83, 88, and 93 °C, the PBG wavelengths appeared at 573, 517, and 440 nm, respectively (spectra b–d). Figure 1B compiles the dependence of annealing temperature on the maximum PBG wavelength (λ_{PBG}). The PBG wavelength gradually decreased as the annealing temperature increased. The PBG tuning range was relatively wide from 400 to 600 nm. Due to the formation of a glassy CLC solid state, the tuned PBG wavelengths of G-CLC film remained extremely intact at room temperature, even after being stored for over 10 months. In this way, the supercooling process of the G-CLC film from CLC temperatures enabled the persistent preservation of the shifted PBG wavelengths in a widely visible range.

Fluorescence spectral measurements provide invaluable information on intermolecular interaction between aromatic chromophores at electronically excited states within the microscopic environment, leading to intrinsic emission species such as monomer and excimer fluorescence. We pursued the excited-state aggregation behavior of the G-CLC film during the course of phase changes by the annealing temperature. Figure 2 shows the changes in the fluorescence spectra of the G-CLC film as a function of the annealing temperature. The fluorescence spectra were measured by exposure to 418-nm light for selective excitation of **DC-OPV**. This is because **DC-OPV** has an absorption band centered at 418 nm, whereas there is no intrinsic absorption band above 320 nm in either **CD8** or **11-BP** (Fig. S2).

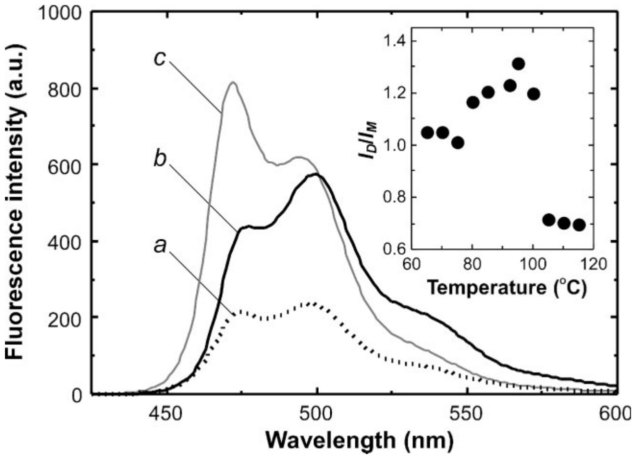

Figure 2. Changes in fluorescence spectra of a G-CLC film prepared by supercooling from annealing temperatures at 65 °C (spectrum a), 90 °C (spectrum b), and 115 °C (spectrum c). The excitation wavelength was set at 418 nm. The inset represents the changes in the I_D/I_M ratio of the G-CLC film as a function of the annealing temperature.

When the G-CLC film was solidified by supercooling from crystal phase at 65 °C, two main fluorescence bands appeared at the maxima of 470 and 500 nm (spectrum a). The fluorescence intensities were relatively weak due to light scattering from the polycrystalline structure. In order to clarify the characteristic fluorescence bands, we measured a fluorescence spectrum of a dilute **DC-OPV** solution ($c = 1.0 \times 10^{-5}$ mol/L). In the solution, a broad fluorescence band with a maximum emission wavelength at 470 nm and a weak shoulder band around 500 nm (Fig. S3) were observed. By comparing the fluorescence spectra between the crystal state and dilute solution, it can be clearly inferred that the emission peak at 470 nm is attributed to monomer fluorescence, while the peak around 500 nm stems from excimer fluorescence. Subsequently, the G-CLC film was supercooled from the CLC mesophase at 90 °C (spectrum b). The fluorescence spectral shape was drastically altered, as compared to that of the crystal state (spectrum a). We observed the predominant excimer emission band in the intensity due to overlapping with the **DC-OPV** chromophore at the glassy CLC state. Successively, when the G-CLC film was prepared from isotropic temperature of 115 °C, the monomer emission was intensified rather than the excimer (spectrum c). This probably happened from the segregation of **DC-OPV** by annealing at the isotropic phase.

In order to quantitatively evaluate the microscopic interaction of electronically excited **DC-OPV**, the ratio of the fluorescence intensity at 500 nm (excimer fluorescence, I_D) to that at 470 nm (monomer fluorescence, I_M) was plotted as a function of the annealing temperature (inset of Fig. 2). Of interest is a prominent enhancement of I_D/I_M in the temperature range from 80 to 100 °C, implying that **DC-OPV** preferentially adopts the excimer formation even at glassy CLC solid state. Such observation is consistent with some precedents of various liquid crystal molecules confirmed by fluorescence measurement.[16]

Our G-CLC film has unique capabilities that not only enable the fine tuning of the PBG wavelength by the CLC annealing temperature, but also allow the on-demand preservation of the shifted PBG through the subsequent supercooling treatment. Taking advantage of these salient features, we can envisage that the continuously gradated PGB (CG-PBG) structure is easily inscribed inside our G-CLC film by the supercooling treatment in order to create a new tunable CLC solid-state laser. Figure 3A shows a photograph of the CG-PBG region in a G-CLC film, which was solidified by the supercooling from the annealing temperatures with continuous changes from 85 °C (right side) to 95 °C (left side). Interestingly, we found that the color reflected by the CLC PBG alters from blue to green along the 1D gradation of the annealing temperature. Furthermore, when the annealing temperature was tuned again, we could obtain various PBG structures in the G-CLC film. This tuning process of the various PBG states was repeatedly reversible (Fig. S4).

Considering the CG-PGB structure inscribed in the G-CLC film (Fig. 3A), we demonstrated the local-position-dependent tuning of laser emission. For this purpose, we constructed a novel optical system to enable spectral measurements of local reflection and emission as well as in situ observations of the optical images at the microscopic level. The detailed setup is described in the Experimental section. Figure 3B shows the microscopic-reflection (upper) and optically-excited laser-emission (lower) spectra of the CG-PGB structure in the G-CLC film. We carried out the stepwise

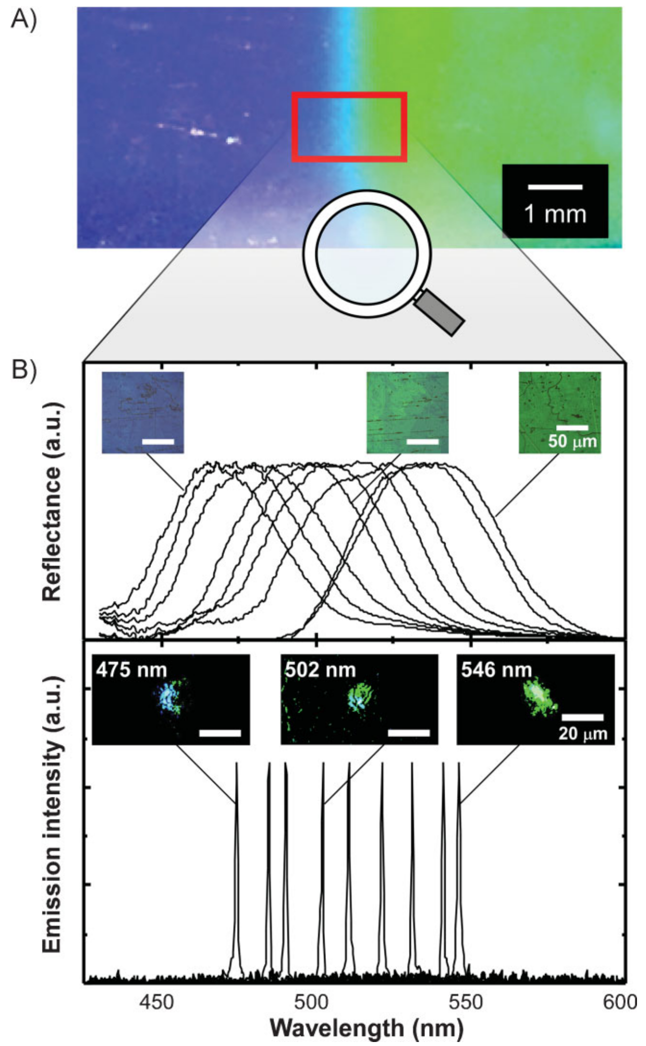

Figure 3. A) Photograph of a G-CLC film with CG-PBG structure. This G-CLC film was prepared by supercooling from annealing temperatures with the continuous changes from 85 °C (right side) to 95 °C (left side). The photograph was taken at room temperature. B) The local position-dependent reflection (upper) and optically excited laser-emission spectra (lower) of a G-CLC film with CG-PBGs. The spectra were taken upon stepwise translation of the measuring spot. The laser-emission spectra were obtained by optical excitation with 418 nm light with an energy of approximately 500 nJ pulse^{-1}. The insets show the microscopic images of reflection (upper) and laser emission (lower), and the left, middle, and right photographs correspond to the images with PBGs centered at 470, 490, and 540 nm, respectively. The scale bars of reflection and laser emission images represent 50 and 20 μm, respectively.

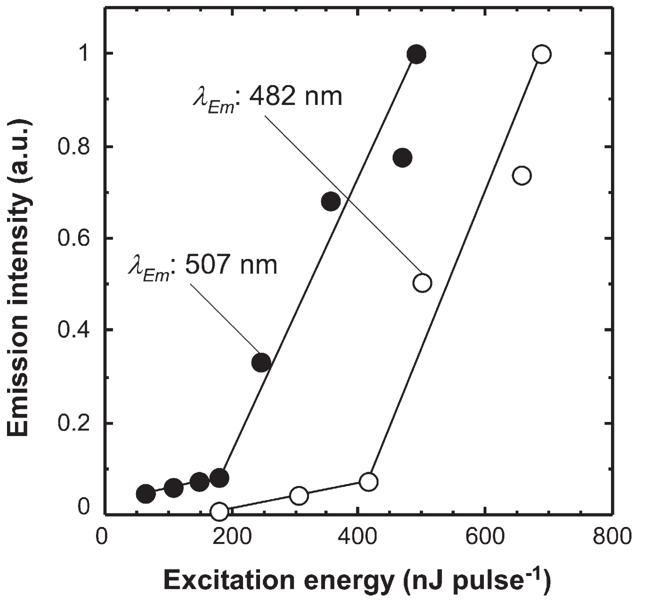

Figure 4. Changes in the emission intensity from the G-CLC film at 482 nm (open circles) and 507 nm (closed circles) as a function of excitation energy of 418 nm light. The observed emission wavelengths at 482 and 507 nm are close to the monomer and excimer fluorescence wavelengths, respectively, as shown in Figure 2.

measurements of local reflection spectra in the CG-PBG region upon translating the G-CLC film with respect to a probing light. We could measure the PBG wavelengths with a continuous shift from 470 to 550 nm and simultaneously observe the gradation of reflected color from blue to green (upper insets in Fig. 3B).

As an extension of our findings, we attempted to measure the local laser-emission spectra in the CG-PBG region. A single laser-emission peak appeared by optical excitation at 418 nm with the pulse energy of approximately 500 nJ pulse^{-1}. When the local excitation area in the CG-PBG region was translated in a stepwise manner, the laser-emission peak gradually shifted in a range from 475 to 550 nm. Except for this wavelength range, the laser action could not be generated. Because the laser emission from CLCs took place at the edge(s) of the PBG wavelengths, which overlap with the fluorescence band of G-CLC film (spectrum b, Fig. 2).[7b,17] Additionally, the color in the microscopy image of the laser emission altered from blue to green (lower insets, Fig. 3B). All such laser-emission peaks always appeared at the longer-wavelength edges of the CLC PBGs for each local position, probably due to the fact that the light-emitting **DC-OPV** chromophores are well aligned in parallel with the local molecular direction of the G-CLC matrix.[5b] At this lasing stage, the spectral linewidths were as narrow as $\sim$0.7 nm. The quality factor (Q) values were estimated to be approximately 7.5×10^2 from the laser emission spectra. The Q values were adequately high among other CLC systems.[3–12] Moreover, the CP spectral analysis indicated that the laser-emission peaks from this G-CLC film have a left-handed circular polarized (L-CP) state (Fig. S5), which was the same handedness as the molecular helical sense of this G-CLC matrix (Fig. 1A). Generally, the polarization degree of CP emission is defined as the g value. The CP degree of emission (g) is expressed as $g = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R stand for the emission intensities of L-CP and R-CP states, respectively. For purely single-handed CP emission, it is apparent that the absolute value of g equals 2. Therefore, the observed laser-emission peaks showed high g values of more than +1.9.

Figure 4 shows the changes in the emission intensity from the CG-PBG structure of the G-CLC film as a function of the excitation energy. We pursued the emission spectra changes at 482 and 507 nm, close to the monomer and excimer fluorescence wavelengths of the G-CLC film, respectively (Fig. 2). When the excitation energy exceeded the threshold at 500 nJ pulse^{-1} or less, the emission spectra changed to a single laser-emission peak. Importantly, it was found that the threshold excitation energy for the laser-emission peak at 507 nm (240 nJ pulse^{-1}) is lower than that at 482 nm (500 nJ pulse^{-1}). This behavior probably follows the empirical fluorescence result that the intensity of excimer fluorescence is higher than that of monomer fluorescence at this glassy CLC solid state (spectrum b, Fig. 2). The excitation peak power to generate the laser action at 507 nm was calculated to be $\sim$13 MW cm^{-2}. This threshold excitation power is an adequately low value as compared to that in previous reports on lasing action from the photopolymerized CLCs.[12a,18] Although the PGB structures of CLCs can be easily preserved by photopolymerization, they remain a serious problem for applications. It is plausible that the photopolymerization brings about the deterioration of the initial CLC helical orientation or decomposition of light-emitting organic dyes by radical species, thereby leading to the requirement of high-threshold excitation energies for laser action.[12b] On the other hand, we succeeded in the efficient generation of laser action with relatively low threshold optical excitation of the CG-PBG structure of our G-CLC film, which was preserved without any covalent bonding through the supercooling process. Taking the overall results in account, such technologically relevant performances might be limited to this kind of chemically designed G-CLCs.

In conclusion, we have developed a new potential utility of G-CLC oligomers for continuously and reversibly tunable laser action by low-threshold optical excitation. The G-CLC film had dual capabilities to tune the PBGs by the annealing temperature as well as to preserve the tuned PBGs by the subsequent supercooling process. The supercooling procedure enabled the facile fabrication of CG-PBG structures inside the G-CLC film. A single laser-emission peak could be continuously tuned in a visible range by stepwise translation of the local optical excitation area in the CG-PBG region. We succeeded in the efficient laser action from the CG-PBGs of our G-CLC film by optical excitation with relatively low threshold peak powers due to the preservation of CLC helical structures through non-covalent bonding. Moreover, a wide variety of PBGs could be reversibly prepared and persistently preserved through a supercooling process of the G-CLC film. Such salient performances cannot be attained by commercially available CLCs. Our findings are of interest in the chemical approach to new light-emitting G-CLCs for technological development of next-generation molecular optoelectronics devices. To develop solid-state lasers that are tunable in the full visible-wavelength range, the elaboration in the molecular design and synthesis of G-CLC materials is in progress.

Experimental

Materials: A light-emitting G-CLC was prepared from a homogeneous solution of trinal compounds of **CD8**, **11-BP**, and **DC-OPV**. **CD8** and **11-BP** were synthesized according to previous procedures through esterification [13] and Williamson synthesis [14], respectively. **DC-OPV** was synthesized according to the following procedure. Briefly, 2,5-bis(hexyloxy)-1,4-bis[(2,5-bis(hexyloxy)-4-formyl-phenylenevinylene)]benzene was converted into the corresponding bis(hydroxymethyl) derivative through reduction in the presence of sodium borohydride and, then, subjected to a reaction with cholesteryl chloroformate to give **DC-OPV** as yellow powder in total yield of 69%. m.p. 140–143 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, 20 °C, Me_4Si, δ [ppm]): 0.68 (s, 6H, CH_3) 0.85–2.00 (m, 142H, CH, CH_2, CH_3), 2.42 (m, 4H, CH_2), 3.96–4.05 (m, 12H, $ArOCH_2$), 4.50–4.55 (m, 2H, $OCOOCH$), 5.21 (s, 4H, CH_2OCOO), 5.42 (m, 2H, CH), 6.92 (s, 2H, Ar-H), 7.11 (s, 2H, Ar-H), 7.14 (s, 2H, Ar-H), 7.45 (4H, s, $CH{=}CH$). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) m/z: calcd. 1767.36; found 1767.97 (Fig. S6).

Optical Measurements: A novel optical system was arranged to measure the microscopic reflection and emission spectra in addition to observing the in situ microscopic images (Fig. S7). Reflection spectra were acquired through a motorized illuminator for a microscope (BX-RLA2, Olympus) equipped with a 100 W halogen lamp. Emission spectra were measured using a pulsed laser beam at 418 nm from a optical parametric oscillator excited by the third-harmonic light from a nanosecond pulsed *Q*-switched Nd:yttrium aluminum garnet (Nd:YAG) laser beam (Surelite I-10 & OPO Plus, Continuum). This excitation wavelength almost coincided with the absorption band of the **DC-OPV**. The pulse duration was $\sim$6 ns and the repetition frequency was 10 Hz. The excitation beam propagating along the surface normal was focused through a microscopic objective lens (SLMPLanN × 20, Olympus) to obtain a circular spot with a diameter of $\sim$20 μm on the G-CLC film. The collinearly transmitted emission from the sample was collected and focused onto the entrance of an optical fiber connected with a spectrometer (USB4000/HR4000CG, Ocean Optics). The microscopic reflection and emission images were taken on a complementary metal semiconductor (CMOS) camera (Moticam2000, Shimadzu).

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