Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Widely tunable photonic bandgap and lasing emission in enantiomorphic cholesteric liquid crystal templates

Jia-De Lin,‡[a] Hong-Lin Lin,‡[a] Hsin-Yu Lin,‡[a] Guan-Jhong Wei,‡[a] Yu-Chou Chuang,[a] Lin-Jer Chen,[a] Shuan-Yu Huang,[b,c] Chia-Yi Huang,[d] Ting-Shan Mo,[e] and Chia-Rong Lee[a]*

[a] *Department of Photonics and Advanced Optoelectronics Technology Center, National Cheng Kung University, Tainan 701, Taiwan*

[b] *Department of Optometry, Chung Shan Medical University, Taichung 402, Taiwan*

[c] *Department of Ophthalmology, Chung Shan Medical University Hospital, Taichung 402, Taiwan*

[d] *Department of Physics, Tunghai University, Taichung, 407, Taiwan*

[e] *Department of Electro-Optical Engineering, Kun Shan University of Technology, Tainan 710, Taiwan*

*‡These authors contributed equally in this work*

## Electronic Supplementary information

### 1. Sample Preparation

The cholesteric liquid crystal (CLC)-monomer materials used for fabricating the CLC polymer templates mainly include nematic liquid crystal (NLC), E7 (from Fusol-Material), left-handed chiral dopant, S811 and S1011 (both from Fusol-Material), right-handed chiral dopant, R811 and R1011 (from Merck and Fusol-Material, respectively), chiral monomer, RM691 (from Merck), achiral diacrylate monomer, RM257 (from Merck) and photoinitiator, Irg184 (from Pufeng). In the E7 host, the HTP values of R811, R1011, S811, S1011, and RM691 are around 11.24 $\mu m^{-1}$, 37.7 $\mu m^{-1}$, –11.24 $\mu m^{-1}$, –37.7 $\mu m^{-1}$, and 3.73 $\mu m^{-1}$, respectively. The photoinitiators can absorb UV light to generate free radicals which may trigger the chain polymerization process of RM691 and RM257, where the function of RM257 is to strengthen the crosslinking polymerization. The recipes for left- and right-handed CLC-monomer mixtures reflecting in red (blue) region, labeled by L-CLC$_{red}$ and R-CLC$_{red}$ (L-CLC$_{blue}$, and R-CLC$_{blue}$), respectively, are listed in Table S1. The extra addition of 4.0 *wt*% S1011 and 4.0 *wt*% R1011 in mixtures L-CLC$_{blue}$ and R-CLC$_{blue}$ can largely increase the resultant HTP value such that the photonic bandgap (PBG) can blue-shift from red to blue region. In these mixtures, L-CLC$_{red}$ and L-CLC$_{blue}$ (R-CLC$_{red}$ and R-CLC$_{blue}$) are used for fabricating the gradient-pitched R-CLC (L-CLC) polymer template. The two templates with opposite handednesses are designed to be merged to develop an enantiomorphic CLC polymer template with a large pitch gradient.

| Materials | NLC | Chiral dopant | | | | Chiral monomer | Achiral monomer | Photo-initiator |
|---|---|---|---|---|---|---|---|---|
| | E7 | R811 | S811 | R1011 | S1011 | RM691 | RM257 | Irg184 |
| R-CLC$_{blue}$ | 59.3 | 19 | 0 | 4 | 0 | 15 | 2.5 | 0.2 |
| R-CLC$_{red}$ | 66 | 16.3 | 0 | 0 | 0 | 15 | 2.5 | 0.2 |
| L-CLC$_{blue}$ | 56.8 | 0 | 21.5 | 0 | 4 | 15 | 2.5 | 0.2 |
| L-CLC$_{red}$ | 60.3 | 0 | 22 | 0 | 0 | 15 | 2.5 | 0.2 |

**Table S1.** Recipes of the right-handed and the left-handed CLC-monomer mixtures reflecting in red/blue regions, labeled by R-CLC$_{red}$/R-CLC$_{blue}$ and L-CLC$_{red}$/L-CLC$_{blue}$, respectively. The unit of each concentration shown above is *wt*%.

In addition, the refilled material is dye-doped NLC (DDNLC), including NLC of 99.36 *wt*% 5CB (from Sigma-Aldrich) and laser dyes of 0.1 *wt*% DCM and 0.54 *wt*% C153 (both from Exciton). Four primary steps for fabricating the refilled enantiomorphic template sample are listed as follows:

(i) Before UV-curing stage. The empty cell is made by assembling two clean glass sides with anti-parallel rubbing, with two long and narrow plastic spacers with thickness of 23 μm placed in parallel on the left and right short edges of the overlapped slides in between. The long edges of the empty cell are sealed. Mixtures L-CLC$_{red}$ and L-CLC$_{blue}$ (R-CLC$_{red}$ and R-CLC$_{blue}$) are simultaneously injected into the empty cell from the right and left opens of the cell and then diffuse in opposite directions. The reverse diffusion of the CLC-monomer mixtures is a key step in fabricating a cell with a large pitch gradient. The cell is placed inside a hot stage with a temperature of 60 °C in a dark room for 2 days to complete the reverse diffusion process. The clear temperatures ($T_c$) of R-CLC$_{blue}$ and R-CLC$_{red}$ or L-CLC$_{blue}$ and L-CLC$_{red}$ are both approximately 50 °C; thus, the CLC mixtures are both in the isotropic state during the diffusion process. The isotropic CLC mixtures have high fluidities (low viscosities) and low-order parameters. The high fluidities of the isotropic CLC mixtures can speed up the mixture diffusion and decrease the fabrication time of the gradient-pitched cell. By contrast, the low-order parameters of the isotropic CLC mixtures can increase the chance of forming a focal conic texture or the likelihood of defects, which may result in significant scattering if the cell undergoes thermal diffusion and then cooling. To avoid scattering, a rapid annealing process (RAP) is adopted to immediately eliminate the formation of focal conic domains or defects in the cell during thermal diffusion. During the RAP, the cell is initially placed in a hot stage at 48 °C for 15 s and then removed from the hot stage to tightly touch a metal plate at room temperature (approximately 22 °C) for 165 s. This process is repeated for 30 to 40 cycles until most of the focal conic domains change to a planar state. The RAP leads to a temperature difference between the surface and the inside of the CLC mixture via the rapid heating and cooling treatments, consequently, inducing thermal stress. The thermal stress can produce molecular vibration and rotation as well as further molecular reorientation.

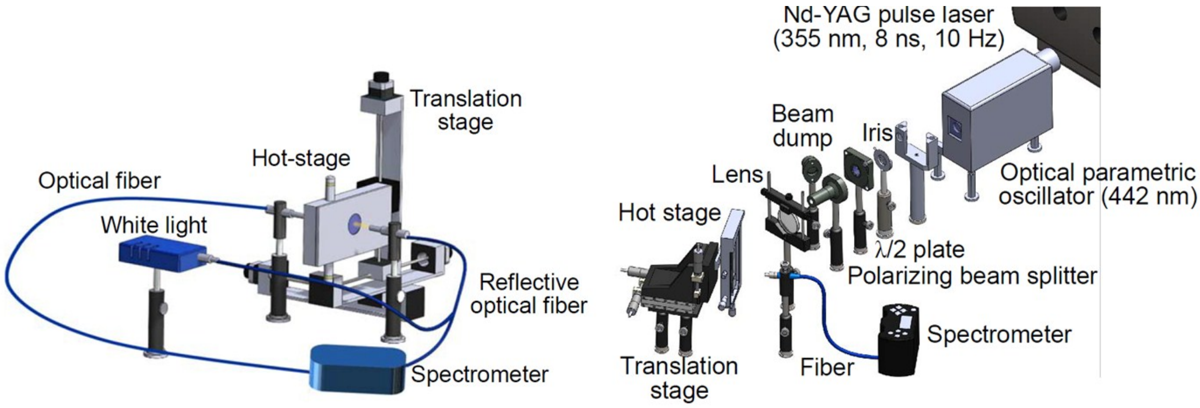
(ii) After UV-curing stage. One UV light with an intensity of 1.1 mW/cm$^2$ is employed to irradiate and cure the two gradient-pitched left- and right-handed CLC-monomer blended cells for 40 mins until the completion of the photopolymerization procedure.

(iii) After washing-out stage. Each cured cell is then immersed in acetone for 24 hours to completely wash out the residues of nonreactive CLC and monomers, and then dried out in an oven for vaporizing the remnant acetone. The two pre-sealed substrates of each washed-out cell are carefully separated. Two transparent polymer template films, with L-CLC and R-CLC pitch gradients, could be observed to adhere on the inner surface of the front substrate which is first imposed under the UV irradiation at the curing step. The two gradient-pitched L- and R-CLC polymer templates are merged to form a gradient-pitched enantiomorphic template, where the locations in the two oppositely-handed templates reflecting light at identical color regions are well overlapped. The cell gap is 23 μm.

(iv) After refilling stage. The NLC or DDNLC is then refilled into the gradient-pitched enantiomorphic template to form a highly reflective photonic bandgap and laser device with a spatial-tunability over the entire visible region.

**2. Experimental setups**

Two experimental setups for measuring the reflection and lasing emission spectra of the samples are schematically illustrated in Fig. S1. In the first setup, a reflective optical fiber is employed to propagate a white light, which originates from a tungsten halogen lamp (LS-1, Ocean), to irradiate the sample. The reflected light from the sample is received by the fiber optic probe of the same fiber that is connected to the spectrometer (USB2000, Ocean Optics). The sample is placed in a hot stage (LTS 120, Linkam) to control its temperature. The hot stage is fixed on a translation stage to measure the reflection spectra of the changeable position in the sample. A schematic illustration of the setup is provided in Fig. S1(a). Figure S1(b) displays the setup for measuring the lasing emission spectra of the sample. The cell is installed on the hot stage, which is pre-fixed on a translation stage to control the temperature and pumped region of the cell. An optical parametric oscillator (basiScan/HE, GWU Lasertechnik) that is pumped by a third-harmonic light from a Nd:YAG pulse laser (Quanta-Ray Lab-130, Spectra Physics) is used as an optically pumped source to excite the lasing emission. The pulse duration and the repetition rate are 8 ns and 10 Hz, respectively. The wavelength of the pumped beam used in this work is 442 nm, corresponding to the maximum absorption of the laser dye C153. The energy of the pump source can be adjusted by the combination of a half-wave plate and a polarizing beam splitter. The pulse beam is focused on the cell by a lens [focal length ($f$) = 5 cm] with an incident angle ($\theta$) = 15° for exciting the lasing emission of the cell. The diameter of the focused pulse beam is around 250 μm. The lasing emission can be detected along the cell normal with a fiber-based spectrometer (Jaz-Combo-L, Ocean, optical resolution: ~1.0 nm).




(a) (b)

**Figure S1.** Experimental setups for measuring (a) the reflection and (b) the lasing emission spectra of the samples.

### 3. Reflection spectra of CLC templates

Figures S2(a) and S2(b) show the reflection spectra measured at positions from $x$ = 0 mm to $x$ = 18 mm at a 1 mm/step and the corresponding reflective images for the gradient-pitched R-CLC and L-CLC mixture cells measured at before-curing stage, respectively. The corresponding results of the gradient-pitched R-CLC and L-CLC mixture cells at after-curing stage are shown in Figs. S2(c) and S2(d), respectively. The multiple shoulder-peaks on reflectance curves are resulted from the resonant modes in CLC. The experimental results imply that the superposition of the spatially tunable left- and right-handed PBGs can be realized by merging the gradient-pitched R-CLC and L-CLC mixture cells since their spectral widths are highly overlapped.

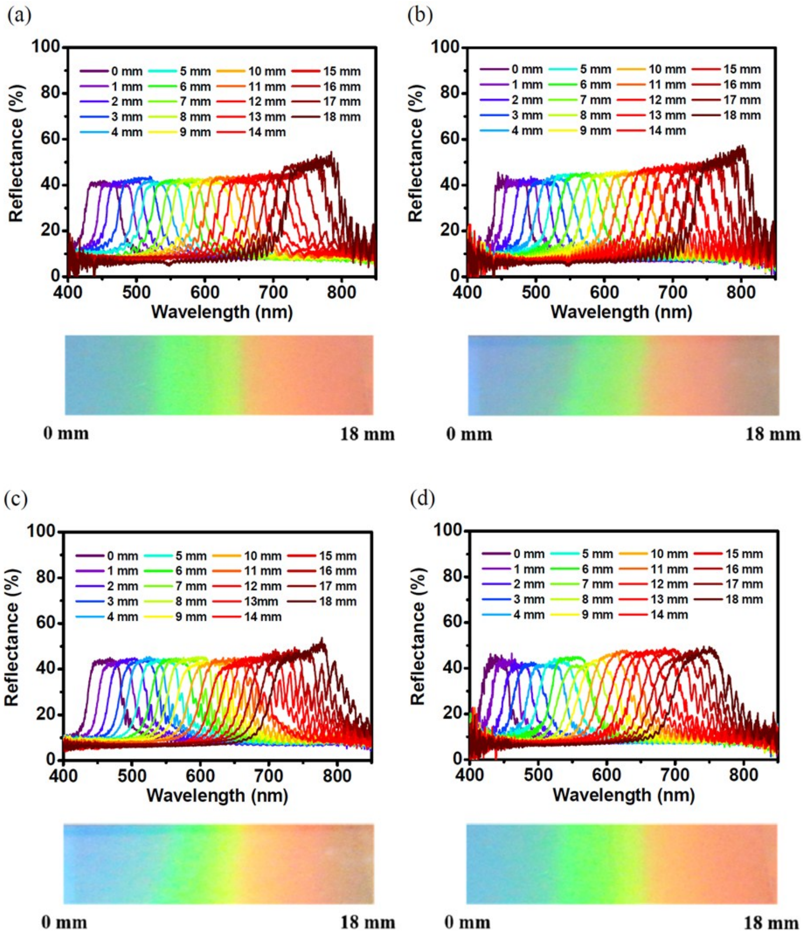



**Figure S2.** Reflection spectra and the corresponding reflective images for the gradient-pitched (a), (c) R-CLC mixture and (b), (d) L-CLC cells measured at various positions from $x$ = 0 mm to $x$ = 18 mm at (a), (b) before-curing and (b), (d) after-curing stage. The step of the measured position is 1 mm.

## 4. Characteristics of the NLC-refilled gradient-pitched enantiomorphic template sample

Figures S3(a) and S3(b) present the comparison between the reflection and transmission spectra of the NLC-refilled enantiomorphic template sample measured at some selected positions $x$ = 0, 4, 8, 12, and 16 mm at $T$ = 35 °C and $T$ = 48 °C, respectively. Their corresponding calculated scattering ratio spectra are presented in Figs. S3(c) and S3(d), respectively. The calculated scattering ratio herein is defined as "100% − (transmittance + reflectivity)." The results in Figs. S3(c) and S3(d) show that the scattering tends to increase with the decrease in wavelength. The higher loss of light in the short wavelength region results from the significant scattering caused by the Rayleigh scattering effect of the template with LC nanopores.

The reasons for the oscillations of the calculated scattering ratio spectra measured at $T$ = 35 °C and $T$ = 48 °C displayed in Figs. S3(c) and S3(d), respectively, are different. The former results mainly from the oscillations of the transmission spectra due to the waveplate effect [Fig. S3(a)]. The latter is attributable to the slight inconsistency in the spectral location between the peak of the narrow reflection bands and the corresponding valley of the narrow transmission band at each position [Fig. S3(b)].

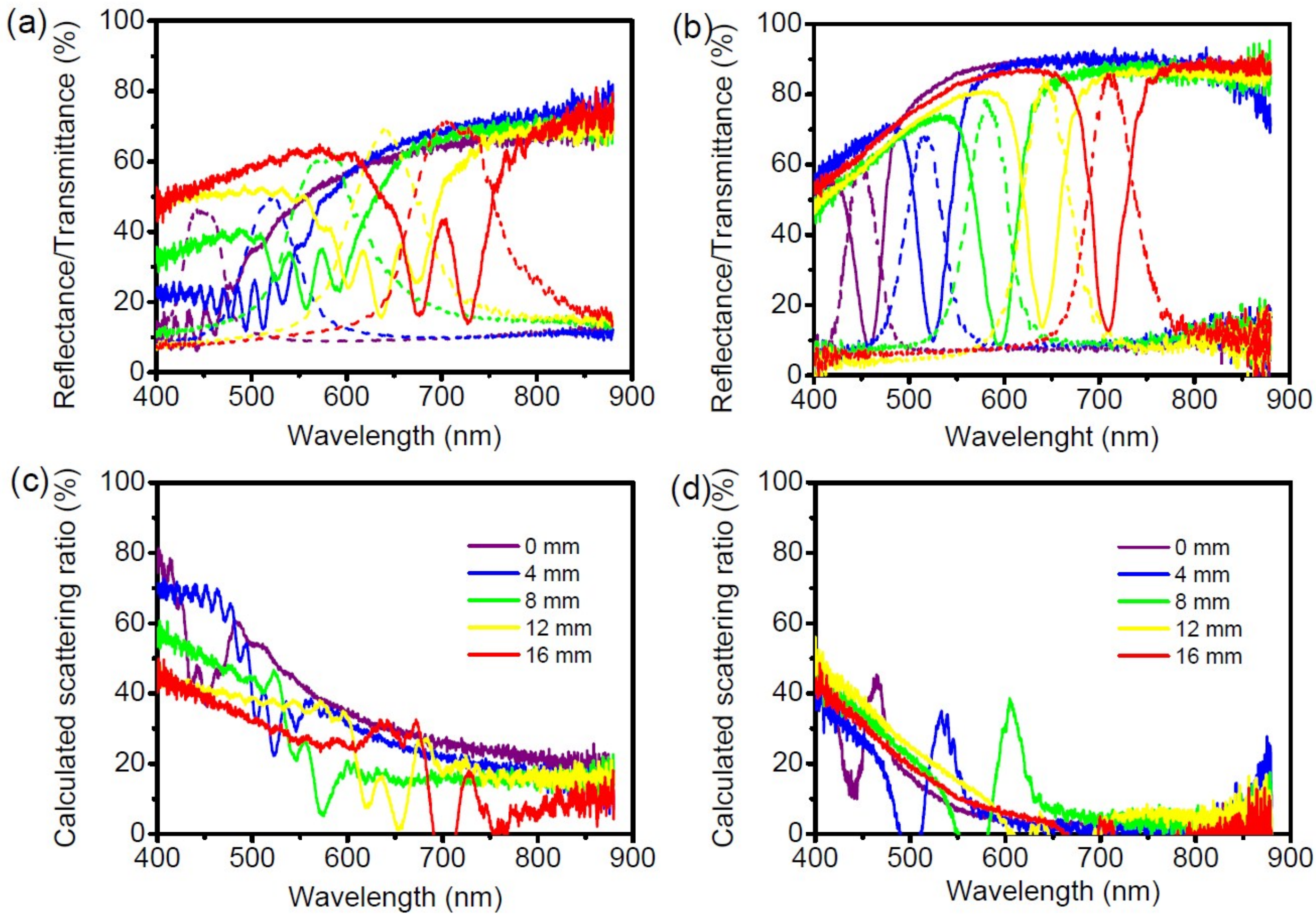



**Figure S3.** Reflection and transmission spectra (solid and dash curves, respectively) of the NLC-refilled enantiomorphic template sample measured at $x = 0$, 4, 8, 12, and 16 mm at (a) $T = 35$ °C and (b) $T = 48$ °C. The calculated scattering ratio spectra at $x = 0$, 4, 8, 12, and 16 mm at (c) $T = 35$ °C and (d) $T = 48$ °C.

Figures S4(a) and S4(b) show the angular variations of the transmission spectra of the NLC-refilled enantiomorphic template sample measured at $x = 18$ mm at $T = 35$ °C and $T = 48$ °C, respectively. Given that this PBG device is on the basis of the CLC structure, its angle dependencies are similar to those of a planar CLC. For examples, the PBG blue-shifts and the bandwidth and reflectivity of the PBG device become wider and lower with the increasing incident angle ($\theta_{inc}$) of the white light relative to the normal of the sample.

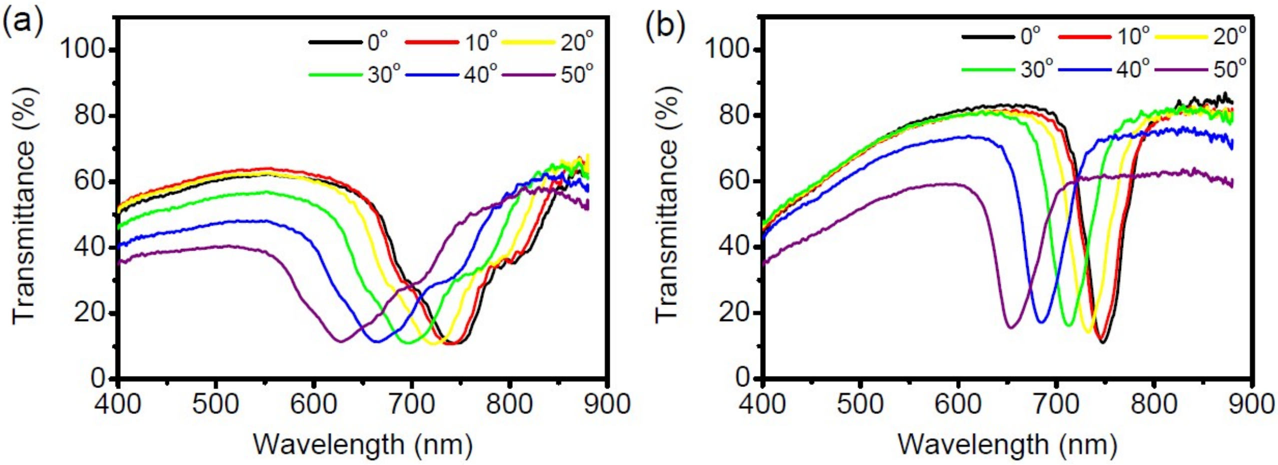



**Figure S4.** Angular variation of the transmission spectrum of the NLC-refilled enantiomorphic template sample measured at $x$ = 18 mm from $\theta_{inc}$ = 0° to $\theta_{inc}$ = 50° at (a) $T$=35 °C and (b) $T$=48 °C, where $\theta_{inc}$ indicates the incident angle between the incident white light and the sample normal.

## 5. Characteristics of the DDNLC-refilled gradient-pitched enantiomorphic template sample

The energy thresholds for the lasing emissions at various positions of the DDNLC-refilled gradient-pitched enantiomorphic template can be determined by the variations of the peak intensity and the corresponding full-width at half-maximum (FWHM) with pumped energy, as presented in Fig. S5. When the pumped energy of the incident pulse is above the energy threshold, the peak intensity rises abruptly and the FWHM decreases dramatically, which is a typical fingerprint for lasing action.

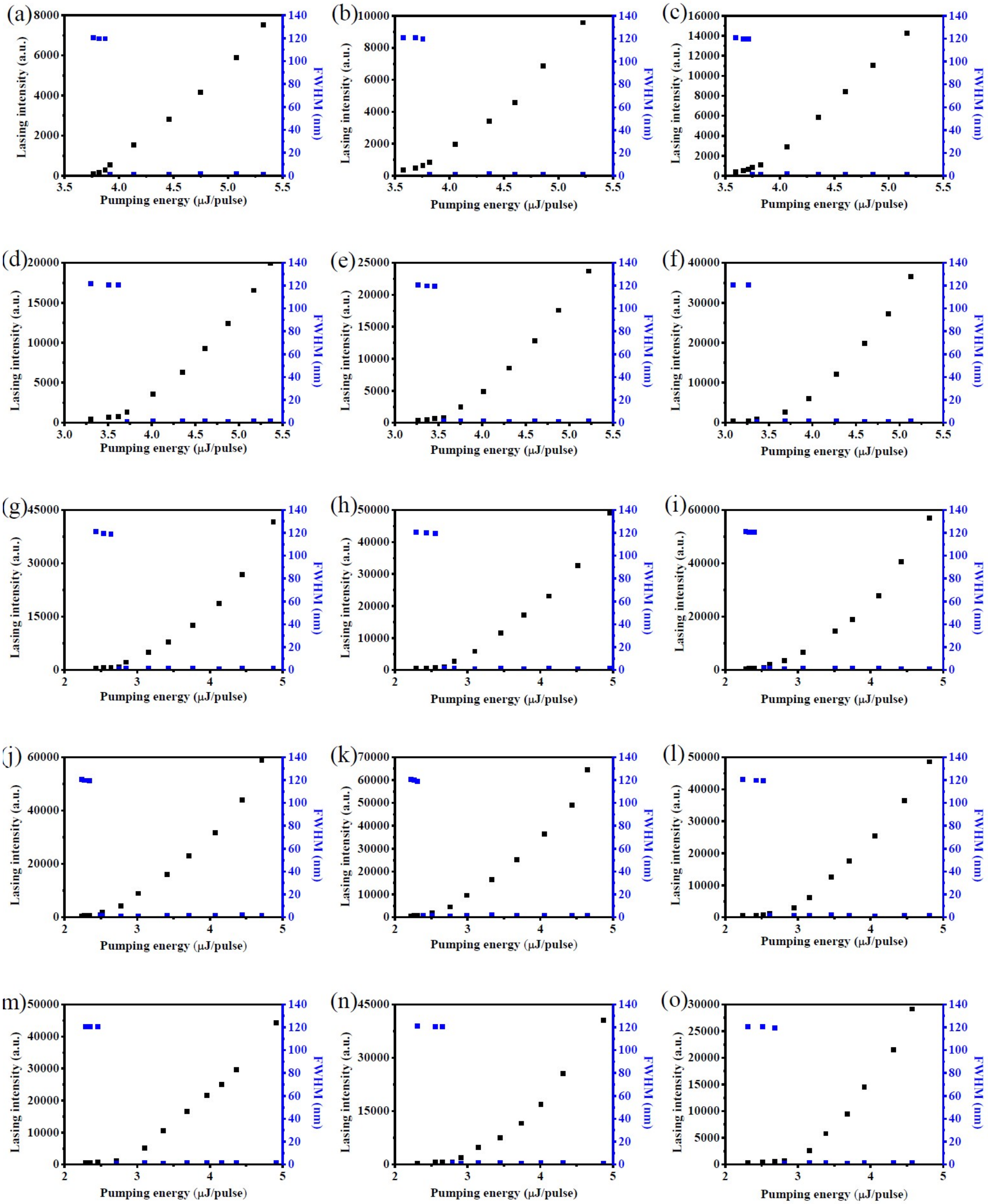



**Figure S5.** Variations of the intensity of the lasing peak and the corresponding FWHM of the lasing emission of the DDNLC-refilled gradient-pitched *enantiomorphic* template laser with pumped energy measured at positions of $x$ = (a) 4, (b) 4.5, (c) 5, (d) 5.5, (e) 6, (f) 6.5, (g) 7, (h) 7.5, (i) 8, (j) 8.5, (k) 8.9, (l) 9.5, (m) 10, (n) 10.4, (o) 11 mm, respectively, at 48 °C.