SPECIAL TOPIC — Physical research in liquid crystal

Bichromatic coherent random lasing from dye-doped polymer stabilized blue phase liquid crystals controlled by pump light polarization*

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In this paper, we investigate the bichromatic coherent random lasing actions from the dye-doped polymer stabilized blue phase liquid crystals. Two groups of lasing peaks, of which the full widith at half maximum is about 0.3 nm, are clearly observed. The shorter- and longer-wavelength modes are associated with the excitation of the single laser dye (DCM) monomers and dimers respectively. The experimental results show that the competition between the two groups of the lasing peaks can be controlled by varying the polarization of the pump light. When the polarization of the pump light is rotated from 0° to 90°, the intensity of the shorter-wavelength lasing peak group reduces while the intensity of the longer-wavelength lasing peak group increases. In addition, a red shift of the longer-wavelength modes is also observed and the physical mechanisms behind the red-shift phenomenon are discussed.

Keywords: bichromatic emission, random lasing, blue phase, liquid crystals

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1. Introduction

Random lasers, in which the multiple light scattering provides the optical feedback, have drawn considerable attention over the past decades because of their distinctive features, including omni-directional emission, flexible shape, and low fabrication cost.[1] The random lasing (RL) was first predicated by Letokhov in 1968,[2] and after 26 years, the laser-like emission from a solution containing rhodamine 640 and TiO_2 particles was observed by Lawandy *et al.*[3] In 1999, the extremely narrow lasing peaks from the ZnO powers were found by Cao *et al.*[4] Afterwards, RL was reported in many materials, such as elastic particles, polymer films, and even human tissue.[5–7] The single dye doped systems studied by Lawandy *et al.* presented a peculiar feature: the appearance of bichromatic emission with well-defined wavelength peaks.[3] Later on, the bichromatic emission phenomena in the systems consisting rhodamine 640 in methanol and TiO_2 particles were studied by Sha *et al.*[8,9] Recently, the bichromantic RL was also observed from the alumna porous ceramic infiltrated with rhodamine B and the powder of rhodamine-doped submicrometer silica particles.[10,11] However, in the previous research, the full width at half maximum (FWHM) of the bichromatic lasing peaks was several nanometers; in other words, only the bichromatic incoherent RL was observed. To date, the bichromatic coherent RL emission, the FWHM of which is less than 0.4 nm, has not been demonstrated experimentally.

Liquid crystals (LCs), as a kind of soft matter which combines crystalline-like solid ordering with fluid-like behavior, are one kind of ideal host mediums for random lasers owing to the anisotropic refractive indices and the high optical sensitivity to the external stimuli.[12–14] The tunable RL in nemetic, cholesteric, smectic A and polymer dispersed LCs has been intensively studied.[12,14–17] Nevertheless, the study of RL from the blue phase liquid crystals (BPLCs) is very scarce. So far, only Chen *et al.* and Zhu *et al.* have reported on the investigation of RL in BPLC and polymer-stabilized blue phase liquid crystals (PSBP-LCs).[18,19] Blue phases (BPs) usually exist in a narrow temperature range between the chiral nematic phase (N^*) and isotropic phase (Iso),[20] and have caused great interest in the fields of photonics and display devices due to their structures and unique optical properties.[21,22] The temperature range of the BPs can be extended to more than 60° by the polymer networks.[23] BPs possess self-organized three-dimensional (3D) photonic bandgap (PBG) structures formed by stacking double twist cylinders,[24] and thus have been widely used as media for band-edge lasers.[21,25,26] However,

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multiple scattering and interference effects, both of which are crucial for the optical feedbacks to the RL, can arise from the disordered platelet texture in BP systems caused by random distribution of platelet size, orientation, and the discontinuous platelet boundaries. Moreover, the index mismatch between polymer and mesogen also contributes to multiple scattering in PSBP-LCs.

In this paper, we present our recent investigation of the bichromatic coherent random lasing actions from the dye-doped polymer stabilized blue phase liquid crystals. We first prepared the single laser dye (DCM)-doped PSBP-LC samples and then studied the random emission spectra of these samples by means of the optical pumping method. We observed that some samples we tested exhibited a peculiar bichromatic coherent RL emission phenomenon under the 532-nm YAG nanosecond pulse laser pumping. The shorter- and longer-wavelength lasing peak groups were centered at 612 nm and 652 nm, respectively, and the FWHM of the peaks in the groups was about 0.3 nm. We guess that such a bichromatic RL emission was caused by the simultaneous excitation of the dye monomer and dimer species. We also find that the relative intensity between the bichromatic coherent emission peak groups could be controlled by the polarization of the linearly polarized pump light. When the polarization of the pump light rotated from 0° to 90°, the intensity of the shorter-wavelength lasing peak group reduced while that of the longer-wavelength peak group increased. This indicates that the mode competition in the bichromatic RL lasing peak groups is sensitive to the polarization of pump light. To the best of our knowledge, this exotic pump light polarization controlled bichromatic coherent RL from dye-doped PSBP-LC samples has not been reported so far. Our findings show that it is possible to tune the properties of the bichromatic coherent RL from the doped PSBP-LCs by the polarization of the pump light.

2. Sample preparation and experimental setup

The PSBP materials used in this study were prepared by mixing a nematic LC with positive dielectric anisotropy (LC-1, Yongsheng Huatsing Liquid Crystal Co., Ltd), two chiral dopants (R5011 and R811, Merck), two photo-polymerizable monomers (C12A, Aldrich, and RM257, Merck), a photo-initiator (Irgacure184, Aldrich), and a laser dye (DCM, Exciton).

During the sample preparation, we selected the weight ratios of the chiral dopants carefully to make sure that the band edge of the PSBP-LCs was far away from the emission spectrum of the DCM. The compositions and the weight ratios of the four samples used were listed in Table 1. The mixtures were first heated to isotropic state and infiltrated into cells assembled from two indium–tin-oxide (ITO) coated glass substrates and spaced approximately 20 μm apart. The phase sequence of samples was evaluated using a polarized optical microscope (POM) equipped with a hot stage, with an accuracy of 0.1 K while cooling the cells at a rate of 0.2 K/min. Each sample was irradiated with UV light of 2.0 mW/cm^2 (measured at 365 nm) at the temperature where the blue phase would form. Figure 1(a) shows the platelet texture of the four samples at room temperature under the transmission-type POM. The temperature ranges of BPs before and after polymerization are summarized in Table 1. In order to measure the reflective wavelength of PSBPs, the samples with the same components and weight ratio without dye were prepared and the reflective wavelengths of four samples were centered at 520 nm, 526 nm, 529 nm and 502 nm respectively [see Fig. 1(b)]. In the RL experiment, the samples were pumped by a 532-nm laser pulse derived from a Q-switched Nd: YAG laser with pulse duration of 8 ns and a repetition rate of 10 Hz. A half-wave plate was placed in front of a cylindrical lens (10-cm focal length on z axis) to change the polarization of the pump beam. The sample was placed in x–y plane, and θ is the angle between the polarization of the incident light and x axis [see Fig. 1(c)]. The output lasing emission was measured using a fiber optic spectrometer with a spectral resolution of 0.11 nm and was monitored in real time by a computer.

The mechanism of the RL action from the dye-doped PSBP-LCs is illustrated in Fig. 1(c). In the dye-doped PSBP materials, the platelet size and the crystal orientation are randomly distributed, as indicated in Fig. 1(a). On the microscale, the discontinuous platelet boundaries and the index mismatch between the polymer and the LC molecules can cause strong light scattering. The light waves emitted from the laser dye undergo multiple scattering among the platelets, and some of them may return to their initial position from which they were scattered before, forming closed-loop paths. The light waves along these paths have a longer lifetime. When the gain becomes larger than the loss, the RL will be engendered.

Table 1. Composition and transition temperatures of samples 1–4.

Sample No.	Liquid crystal			Monomer		Initiator	Dye	Transition temperature/°C			
	LC-1/ wt%	R811/ wt%	R5011/ wt%	RM257/ wt%	EHA/ wt%	184/ wt%	DCM/ wt%	before curing		after curing	
								N*-BP	BP-I	N*-BP	BP-I
1	80.5	4.6	2.6	6.5	5.0	0.3	0.5	51.0	54.5	< 25.0	65.0
2	79.9	5.7	2.4	6.3	4.9	0.3	0.5	50.0	54.3	< 25.0	65.2
3	63.7	26.5		5.0	4.0	0.3	0.5	33.6	37.9	< 25.0	46.0
4	84.2		3.0	6.7	5.3	0.3	0.5	55.0	57.2	< 25.0	66.5

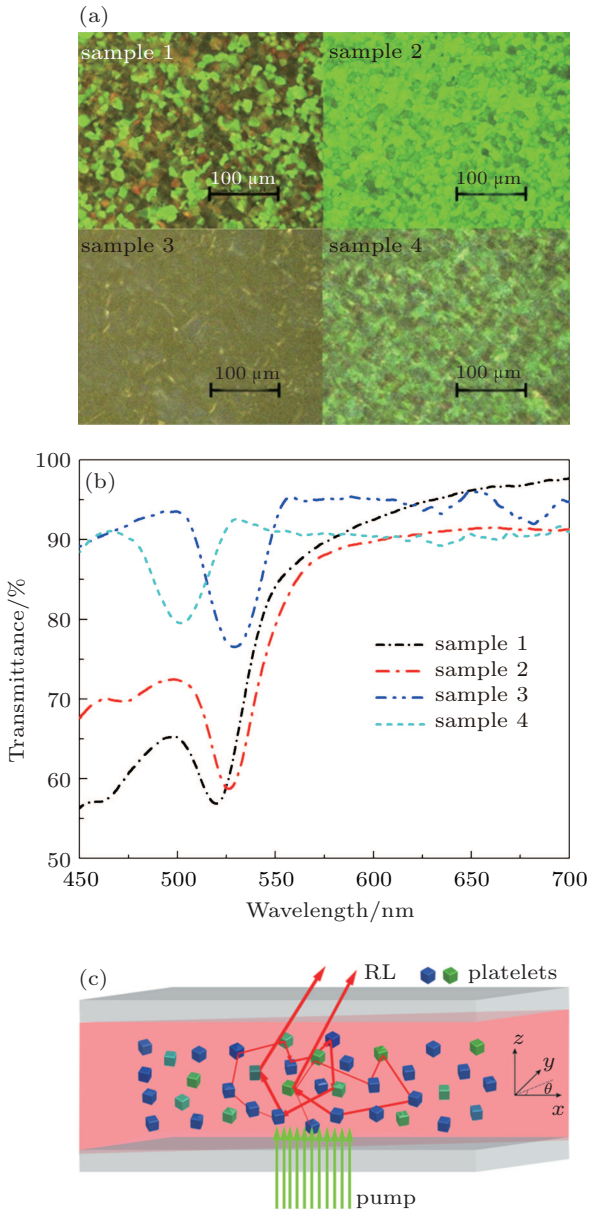


Fig. 1. (color online) (a) Transmission polarized optical microscopy images. (b) Transmittance spectra of samples 1–4 without dye at room temperature. (c) Schematic illustration of the multiple light scattering in the dye-doped PSBP-LCs, θ is the angle between the polarization of the incident light and x axis.

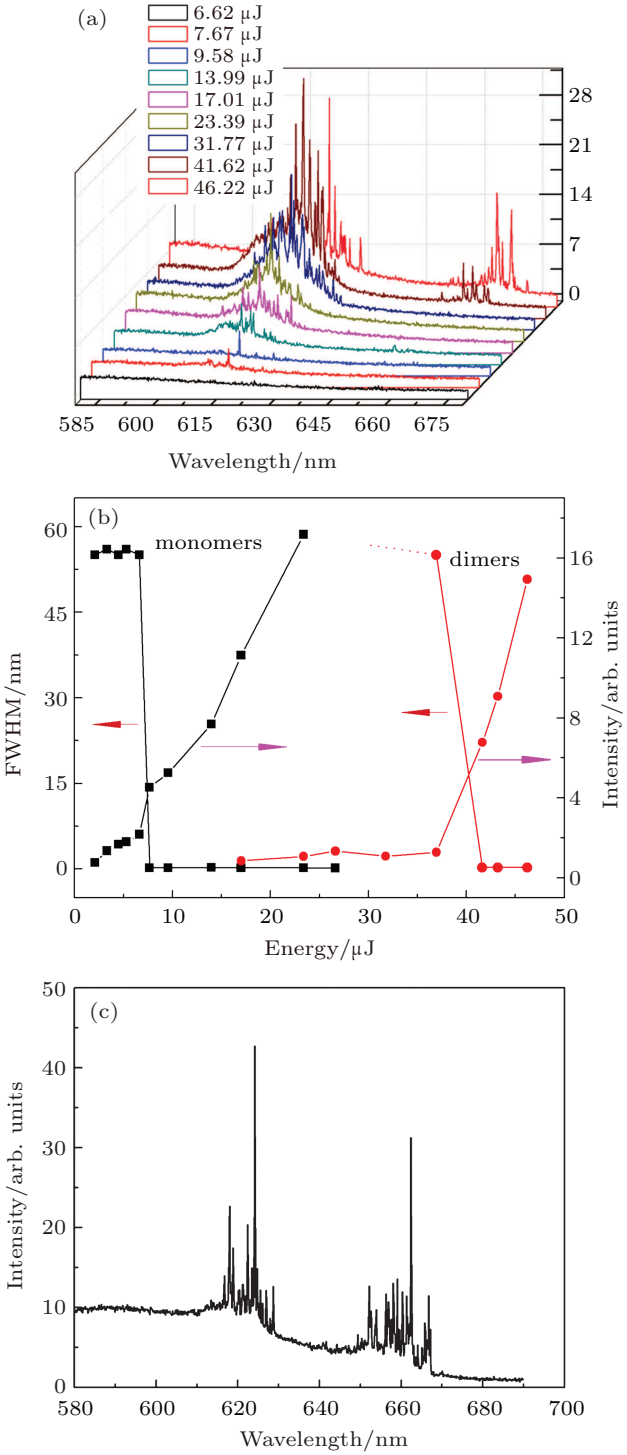


Fig. 2. (color online) (a) Evolution of the emission spectra as a function of pump energy and (b) the corresponding peak intensity and FWHM of the monomer and dimer emission peaks for sample 1. (c) The typical laser emission spectra obtained from sample 2.

3. Results and discussion

Figure 2(a) depicts the evolution of the emission spectra as a function of pump energy for sample 1. At low pump energy, the spectrum consists of a single broad spontaneous emission peak with a bandwidth of approximately 57 nm. Upon increasing the pump energy to approximately 7.24 μJ/pulse, the discrete sharp peaks in the wavelength range of 616–628 nm emerge above the spontaneous emission spectrum. The FWHM of these peaks reduces to about 0.3 nm and the corresponding Q factor, determined by $\lambda/\Delta\lambda$, is over 2000. The intensity of the peaks enhances rapidly when the pump energy further increases. As the pump energy is larger than 46 μJ/pulse, another group of lasing spikes in the wavelength range of 653–665 nm appears. According to the theory proposed by Varelink *et al.*,[27] the bichromatic lasing emission is due to the presence of the two fluorescent aggregates: monomers and dimers. The dye monomers are directly excited by the pump light at 532 nm while the dye dimers are excited by radiative and non-radiative energy transfer processes from the excited monomers to the dimers in the ground state. The group of the shorter-wavelength lasing

peaks is attributed to the monomer emission and the group of the longer-wavelength peaks is attributed to the dimer emission. Figure 2(b) shows the FWHM and intensity variation of the bichromatic peaks at the ranges of 616–628 nm and 653–665 nm as a function of pump energy. The black squares correspond to the monomer emission and the red circles correspond to the dimer emission. Figure 2(b) clearly illustrates the existence of two RL thresholds. When the pump energy increases to 7.24 μJ/pulse, the emission centered at 620 nm presents a strong line width reduction, from 57 nm to 0.3 nm. The monomer starts to lase first because the emission cross section of monomer is larger than that of dimer, making the monomer gain greater than the dimer one.[27] As the pump energy further increases, the dimer emission occurs and the RL is generated for both species. The two thresholds for the monomer and dimer emission are 7.24 μJ/pulse and 40.29 μJ/pulse, respectively. The bichromatic RL is also observed from sample 2, just as shown in Fig. 2(c). The shorter-wavelength peak group locates in the range of 618–624 nm and the longer-wavelength peak group locates in 652–665 nm region. The peak group positions in Fig. 2(c) are similar to the peak group positions in Fig. 2(a).

The typical laser emission spectra of samples 3 and 4, and the corresponding peak intensities and FWHM as a function of pump energy are depicted in Figs. 3(a) and 3(b). The bichromatic RL emission is not observed. When the excitation spot is moved across the entire surface of the two samples, only one group of lasing modes is detected. The peak group from sample 3 locates in the range of 605–617 nm and the peak group from sample 4 locates in the range of 601–611 nm. The explicit difference between samples 1, 2 and samples 3, 4 is the weight ratios of the chiral dopants. In order to clarify the effects of the chiral dopants on the bichomatic emission, we prepared and tested a series of dye-doped PSBP samples containing different weight ratios of chiral dopants and studied their lasing emission. The results show that the bichromatic emission has nothing to do with the weight ratios of chiral dopants. We believe that there are two factors that can explain the absence of the longer-wavelength lasing peaks on samples 3 and 4. The first is that the amount of dye dimers in samples 3 and 4 is lower than that in samples 1 and 2. The second is that the closed-loop paths in samples 3 and 4 are not suited for the formation of the longer-wavelength lasing modes.

Although the band-edge lasing is a very common lasing form for the cholesteric LC and the BPLC samples, we believe that the detected lasing emission from samples 1–4 is RL rather than multi-wavelength band-edge lasing. The reasons can be explained as follows. Firstly, for the band-edge lasing, the emission peaks usually appear at the short- or long-wavelength side of the band edge because the group velocity of photons is suppressed inside the PBG and the photonic density of states at the band edge is significantly enhanced. The wavelengths of the lasing emission observed from our samples are far away from the photonic band edge [Fig. 1(b)], indicating that the lasing does not result from the bandgap edge of the PSBP-LCs. Besides, when the direct current electric field applied to the sample changes from 0 V/μm to 6 V/μm, a blue shift of the PBG is observed, whereas the wavelength range of the emission peaks is completely unchanged. This also indicates that the lasing emission is uncorrelated to the PBG. Thirdly, the frequencies of each lasing modes and the relative strength change randomly from one excitation pulse to another, which is the feature of RL action.

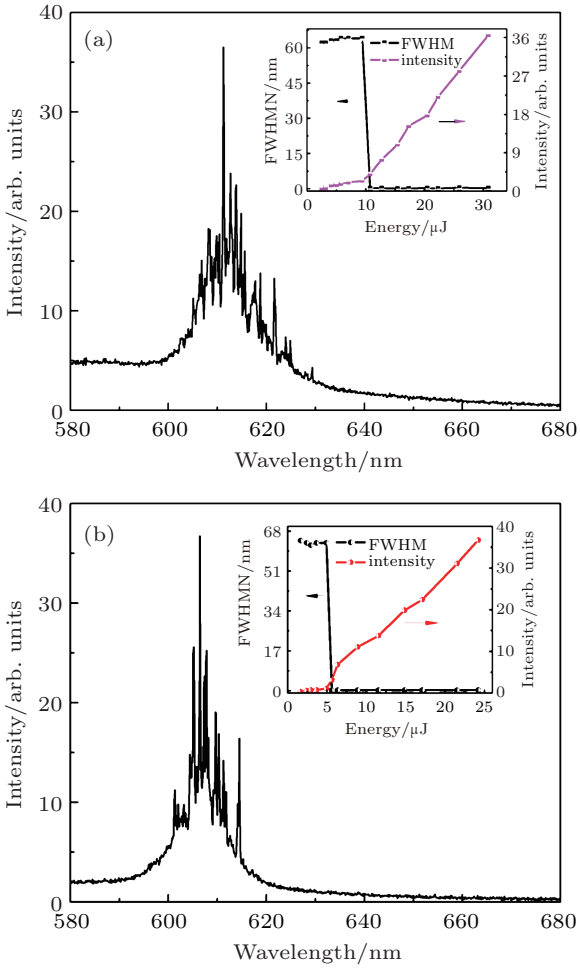


Fig. 3. (color online) The typical laser emission spectra obtained from (a) sample 3 and (b) sample 4. The inset shows the dependence of the peak intensity and FWHM on the pump energy.

Previous research has shown that the bichromatic incoherent RL emission could be tuned by changing the dye concentration, the density of scatterers, the pump energy, and the pump rate.[9,28,29] In this work, we confirmed that the bichromatic coherent lasing modes can be controlled by the polarization of the pump light. Figures 4(a) and 4(b) show the intensity variation in the lasing peak groups from sample 1 and sample 2 versus angle θ, respectively. The pump energy of sample 1 is set at 46.22 μJ/pulse and that of sample 2 is set

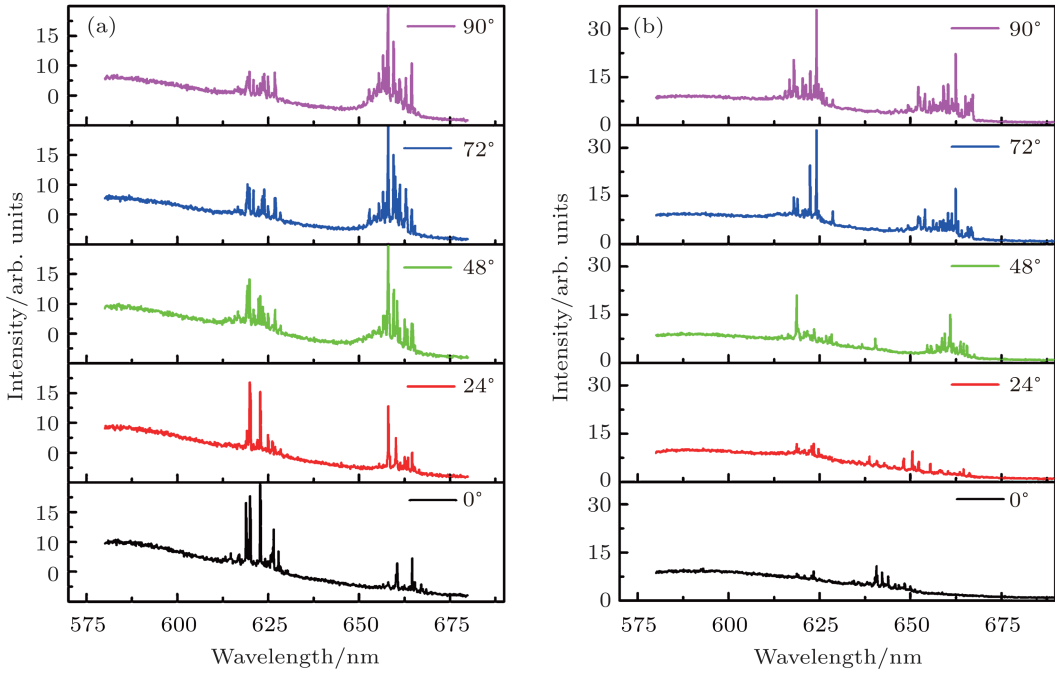


Fig. 4. (color online) The bichromatic RL spectra as a function of angel θ from (a) sample 1 and (b) sample 2 The pump energies are fixed at 46.22 μJ/pulse and 56.07 μJ/pulse respectively.

at 56.07 μJ/pulse. For the RL from sample 1, when $\theta = 0°$, the intensity of the shorter-wavelength peaks in the range of 616–628 nm is about three times larger than that of the longer-wavelength peaks in the range of 653–665 nm. However, when θ increases from 0° to 90°, the intensity of the shorter-wavelength peaks gradually reduces while the intensity of longer-wavelength peaks increases and more sharp peaks appear. The intensity conversion between the two groups of peaks occurs again when θ changes from 90° to 180°. For the bichromatic RL emission from sample 2, there are two interesting features in the lasing intensity versus angle: one is the synchronous increase of the intensity of the two group of peaks and the other is the red shift of the wavelength position of the longer-wavelength peak group. When the polarization of the pump light is parallel to the x axis ($\theta = 0°$), the shorter- and longer-wavelength lasing peak groups locate in the range of 618–624 nm and 640–647 nm, respectively, and the intensity of these lasing modes is quite low. When θ increases from 0° to 48°, the intensity of the two lasing peak groups increases synchronously, and at the same time the range of the longer-wavelength peaks is red-shifted by about 15 nm, from 640–647 nm to 652–665 nm. As the angle θ increases from 48° to 90°, the intensity increases further and more sharp peaks appear.

The underling mechanism of this pump polarization controlled bichromatic RL is considered below. For the RL from disordered materials, the lasing modes are very sensitive to the initial and boundary conditions.[1] Because the light scattering is generally polarization sensitive,[30] the pump light with different polarizations will trigger a distinctive initial pumping and scattering profile, and then will make the emitted photons propagate and amplify in different multiple scattering paths. The distinctive initial scattering profile and the mode competition give rise to the intensity fluctuations of the two groups of modes. For the lasing from sample 1, when the θ is less than 24°, the multiple scattering effect on the shorter-wavelength modes is stronger than that of the longer-wavelength modes. However, with the increase of θ, the multiple scattering effects on the longer-wavelength modes become stronger than that on the shorter-wavelength modes. The intensity of the two groups of peaks from sample 2 increases simultaneously with θ. It implies that the competitiveness between the shorter- and longer-wavelength modes is roughly equal, and there is no one group of modes that can be able to surpass the other when θ increases from 0° to 90°. There are two possible reasons responsible for the red shift of the longer-wavelength peak group in Fig. 4(b). The first one is the reabsorption effects. The reabsorption process is common in organic laser dyes because of the possible overlap of the absorption and emission cross sections of monomers and dimers. The dimer–dimer reabsorption can induce the red shift of the longer-wavelength peaks.[28] The second possible reason is the frequency-pulling (FP) analog effect. According to Barbosa–Silva's work, the analog of the FP effect appears because of the interaction between the excited monomer and dimer dipoles and it will lead to the change of the resonance wavelength separation of monomers and dimers.[10] Just as shown in Fig. 4(b), the length of the central wavelength of monomer and dimer modes changes from 32 nm to 47 nm when θ increases from 0° to 48°.

4. Conclusion

In this paper, we presented our recent investigation on the bichromatic coherent RL from the dye-doped PSBP-LCs. We observed two groups of lasing peaks with linewidth of about 0.3 nm (FWHM) in the range of 616–665 nm. We pointed out that, the shorter-wavelength lasing peak group was associated with the excitation of the DCM monomers, while the longer-wavelength lasing peak group was associated with the excitation of the DCM dimers. Our experimental results showed that the relative intensity between the two groups of bichromatic RL peaks could be controlled by the polarization of the pump light. When the polarization of the pump light was rotated by 90°, the intensity of the shorter-wavelength group of emission peaks reduced while the intensity of the longer-wavelength group of emission peaks increased. In addition, we have also found that the wavelength of the longer-wavelength group of lasing peaks from sample 2 was red-shifted by about 15 nm when the angle θ increased from 0° to 48°. To our best knowledge, these bichromatic coherent RL phenomena are reported for the first time. In the future, we will do further research so as to understand the difference on the bichromatic coherent RL actions from different samples.

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