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Fluorescent Liquid-Crystal Gels with Electrically Switchable Photoluminescence**

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Fluorescent self-assembled liquid gels have been prepared for the first time through the use of a gelator showing aggregation-induced enhanced emission. The photoluminescence, arising from the fibrous aggregates of the gelator, can be repeatedly switched by an electric field. Modulating the excitation light through electric-field-induced liquid-crystal orientation offers new ways to achieve and explore electrically controllable photoluminescence.

1. Introduction

Self-assembled liquid-crystal (LC) gels generally refer to small-molecule LCs gelled by a noncovalent network built up by fibrous aggregates of a gelator, which is initially dissolved in the LC host but aggregates (crystallizes) on cooling. The presence of fibrous aggregates (diameters usually on the order of hundreds of nanometers) can impart interesting properties to the LC materials, such as fast electro-optical switching in twist nematic cells,[1] bistable nematic LC states,[2] scattering-based electro-optical switching of nematic[3] and cholesteric LCs,[4] and pitch compensation facilitating bulk alignment of ferroelectric LCs.[5] Using gelators containing photoisomerizable azobenzene chromophores in their structures, patterning,[6] or diffraction gratings[7] can also be obtained from self-assembled LC gels. In this paper, we report the first LC gels whose fibrous aggregates are strongly fluorescent, and demonstrate the possibility of using an electric field to switch the photoluminescence of this new material. The revealed mechanism, which is based on modulation of the excitation light through electric-field-induced LC orientation, opens new ways to achieve electrical control in photoluminescence and may offer new possibilities to explore the use of photoluminescence in display applications.[8]

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2. Results and Discussion

The gelator molecule used in this study (chemical structure shown in Fig. 1) is 1-cyano *trans*-1,2-bis(3′,5′-bis-trifluoromethyl biphenyl)ethylene (CN-TFMBE). CN-TFMBE is known to display aggregation-induced enhanced emission (AIEE);[9,10] that is, contrary to conventional fluorophores, it is highly fluorescent in the solid (aggregated) state while being virtually nonfluorescent in the solubilized state. Park and co-workers have reported that CN-TFMBE can gel a number of organic solvents such as tetrahydrofuran (THF) and chloroform, and that the fibrous aggregates formed in the organogels are strongly fluorescent.[10] As gelator, CN-TFMBE is special in that the strong specific, highly unidirectional intermolecular interactions, which are responsible for the formation of fibrous aggregates, are attributed to π–π stacking interactions of the aromatic cores as well as interactions induced by CF_3 units, instead of H-bonding in most gelators. We found that CN-TFMBE can also gel LCs. To prepare LC gels, a small amount of the gelator (0.5–2 wt %) was dissolved in a nematic LC with a high clearing (nematic-to-isotropic phase transition) temperature T_{ni}, the used nematic LC being BL006 whose characteristics are also given in Figure 1. When heated to the isotropic phase of BL006, at $T > T_{ni} = 115\,^{\circ}C$, CN-TFMBE was dissolved in the LC host, and showed no photoluminescence upon excitation. On cooling the mixture to $T < T_{ni}$, over a wide range of temperatures, gelator molecules remained solubilized in the nematic phase of BL006; only on further cooling to room temperature, the aggregation of CN-TFMBE took place in BL006 and an LC gel was formed. At a cooling rate of $1\,^{\circ}C\,min^{-1}$, judging from the temperature at which fibrous aggregates were discernible using optical microscopy, the aggregation temperature was found to be about 40 and 75 °C for 1 and 2 % of CN-TFMBE, respectively. The LC gel state was revealed by the loss of gravitational flow of the LC mixture and the appearance of strong photoluminescence. The transition between a homogeneous nonfluorescent mixture and a fluorescent LC gel is thermally reversible, that is, the fibrous aggregates melted on heating, resulting in the disappearance of photoluminescence, but reformed on cooling, leading to the recovery of photoluminescence.

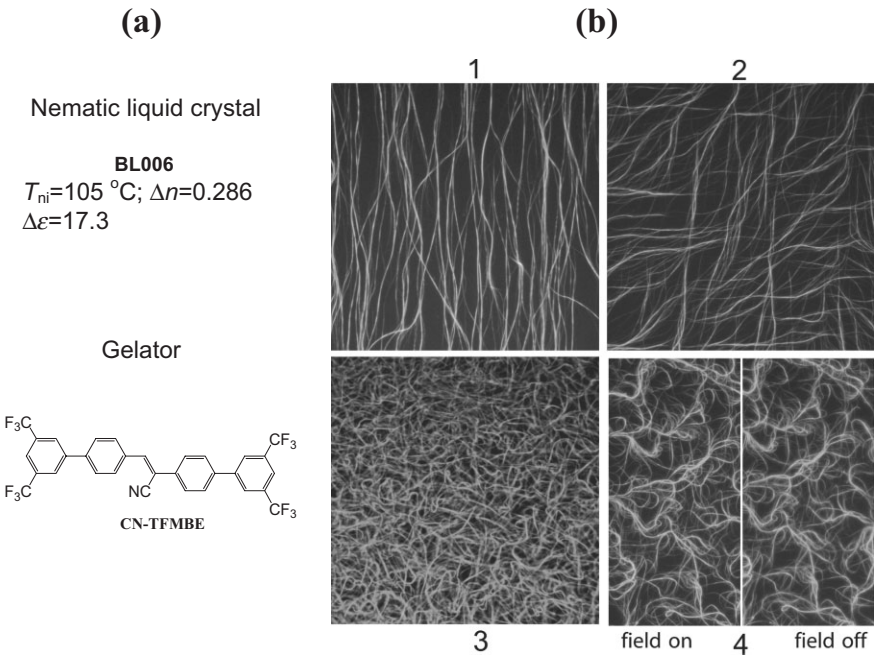

Figure 1. a) Characteristics of the nematic liquid crystal BL006 (birefringence (Δn) and dielectric anisotropy ($\Delta\varepsilon$) measured at 20 °C, from Merck; T_{ni}: nematric-to-isotropic phase transition temperature) and chemical structure of the gelator CN-TFMBE. b) Fluorescence microscopy images of self-assembled nematic (images 1 and 2) and cholesteric gels (images 3 and 4), showing the fluorescent fibrous aggregates formed in various predetermined LC orientational states: homogeneous LC orientation in a parallely rubbed cell (image 1); twist LC orientation in a perpendicularly rubbed cell (image 2); planar texture (image 3) and homeotropic LC orientation induced by an electric field (image 4). Image area: 300 μm × 300 μm.

Since the gelation process occurs after BL006 enters into its nematic phase, it is possible to induce a specific LC orientational state (or texture) by surface effects or by using an electric field, before the aggregation of the gelator is allowed to take place on cooling the mixture to room temperature. In this way, the effects of various LC orientational environments (or templates) on the organization of the fluorescent fibrous aggregates of CN-TFMBE can readily be investigated by means of fluorescence microscopy. The sample images in Figure 1 were obtained with the mixture of BL006–CN-TFMBE (1 %), using an excitation filter of 450–490 nm and detection of photoluminescence at >510 nm. The results clearly show that the alignment and morphology of the fibrous aggregates are dictated by the predetermined orientational state of the LC host. Image 1 shows the fluorescent fibrous aggregates formed in an ITO-coated (ITO: indium tin oxide), 5 μm cell with parallely rubbed surfaces, in which LC molecules are oriented along the rubbing direction, that is, homogeneous LC orientation. Image 2 shows the fibers formed in a 5 μm cell with perpendicularly rubbed surfaces, in which LC orientation is twisted. The resultant twisting of the fibers is obvious. Images 3 and 4 show the fibrous aggregates formed in a cholesteric LC obtained by doping BL006 with 5 wt % of a chiral dopant, R811, in a 10 μm cell. In one case (image 3), the aggregation of the gelator was allowed to proceed in the planar texture of the chiral nematic LC, for which helical axes are aligned perpendicularly to the substrate surfaces. The chiral rotation of LC molecules in planes parallel to the substrate surfaces led to the formation of in-plane, dense, and twisted fibers of the gelator. In the other case (image 4), prior to the aggregation of the gelator, the homeotropic texture of the LC host was set by applying an electric field (60 V) to align LC molecules perpendicular to the substrate surfaces, the electric field being held during the aggregation process. Part of the image shows the fibrous aggregates formed at room temperature under the electric field, while the other part shows the fibers after turning off the field; no noticeable difference could be observed between the field-on and field-off states. In contrast to images 1–3, the fibers formed under the homeotropic LC texture apparently are not aligned in the LC orientation direction. This may be explained by the following analysis. At the beginning of the aggregation of the gelator, even if the first fibers are preferentially aligned normal to the substrate surface under the influence of the LC orientation, as the aggregation process develops, the fibers grow to lengths much longer than the 10 μm gap of the cell (300 μm × 300 μm image area in Fig. 1). They must fold and reorganize to lie in the plane of the substrate. For all samples, after the aggregation process was fully completed, the integrated network of the fibrous aggregates appeared to remain the same in the field-off and field-on states.

For the fibrous aggregates formed under the homogeneous LC orientation (image 1 in Fig. 1), their preferential alignment along one direction, that is, the rubbing direction, results in polarized fluorescence emission. Figure 2 shows the emission

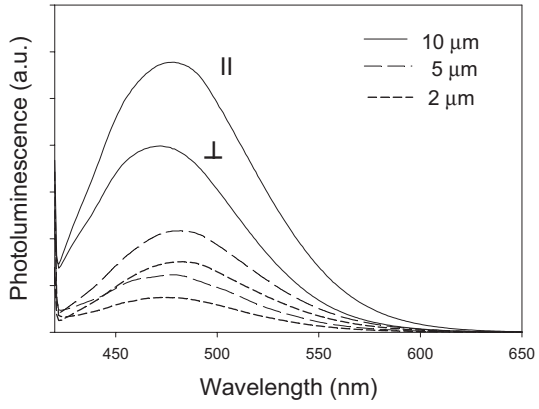

Figure 2. Polarized fluorescence emission spectra of a nematic LC gel (BL006 with 1 % CN-TFMBE) formed in parallely rubbed cells with 2, 5, and 10 μm gaps, respectively. The spectra were recorded under unpolarized excitation and with the emission polarization set to be parallel and perpendicular to the rubbing direction. For each thickness, the spectrum with the greater absorbance is the one recorded with parallel polarization.

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spectra ($\lambda_{ex} = 410$ nm) of the BL006–CN-TFMBE (1 %) gel prepared in cells of various gaps. For each sample, the spectra were recorded under unpolarized excitation, but with an emission polarizer set to be parallel and perpendicular to the rubbing direction. At the used excitation wavelength, no photoluminescence from the LC host was observed. In addition to different emission intensities, which are normal due to the different amounts of fibers in the cells, all samples displayed polarized emission. The 2 μm cell, however, showed the highest dichroism with $A_{\parallel}/A_{\perp} \approx 2$ ($A_{\parallel}/A_{\perp}$): absorption parallel (perpendicular) to rubbing direction) measured at 480 nm, followed by the 5 μm cell with $A_{\parallel}/A_{\perp} \approx 1.8$ and the 10 μm cell with $A_{\parallel}/A_{\perp} \approx 1.5$. The effect of the cell thickness on the degree of polarized emission may reflect its effect on the quality of alignment of the fibrous aggregates. Indeed, better alignment of fibers was observed in cells with a smaller gap.

In addition to the polarized emission from aligned fibrous aggregates, the most interesting feature of these fluorescent LC gels is that not only their optical transmittance can be switched by an electric field as a result of field-induced orientation of LC molecules but their photoluminescence from the fibrous aggregates of the gelator can also be switched. The two types of switching are shown in Figure 3 using, as an example, the results obtained with the fluorescent cholesteric LC gel (94 % BL006, 1 % CN-TFMBE, and 5 % R811) prepared under homeotropic LC orientation in a 10 μm cell. The fluorescence emission spectra of the LC gel with and without the application of a voltage (42 V) through the cell are compared in Figure 3a, with the inset showing the UV-vis spectrum of the mixture in the cell. It is seen that the photoluminescence intensity is reduced by a factor of more than five in the field-on state. Plotted in Figure 3b are the changes in fluorescence intensity emitted from the cell as a function of applied voltage, as well as the changes in transmittance of a probe light (633 nm, from a He–Ne laser) through the cell. In the field-off state (0 V), the optical transmittance is low because of the strong light scattering caused by small LC domains cut by the fibrous aggregates of the gelator. By increasing the voltage to

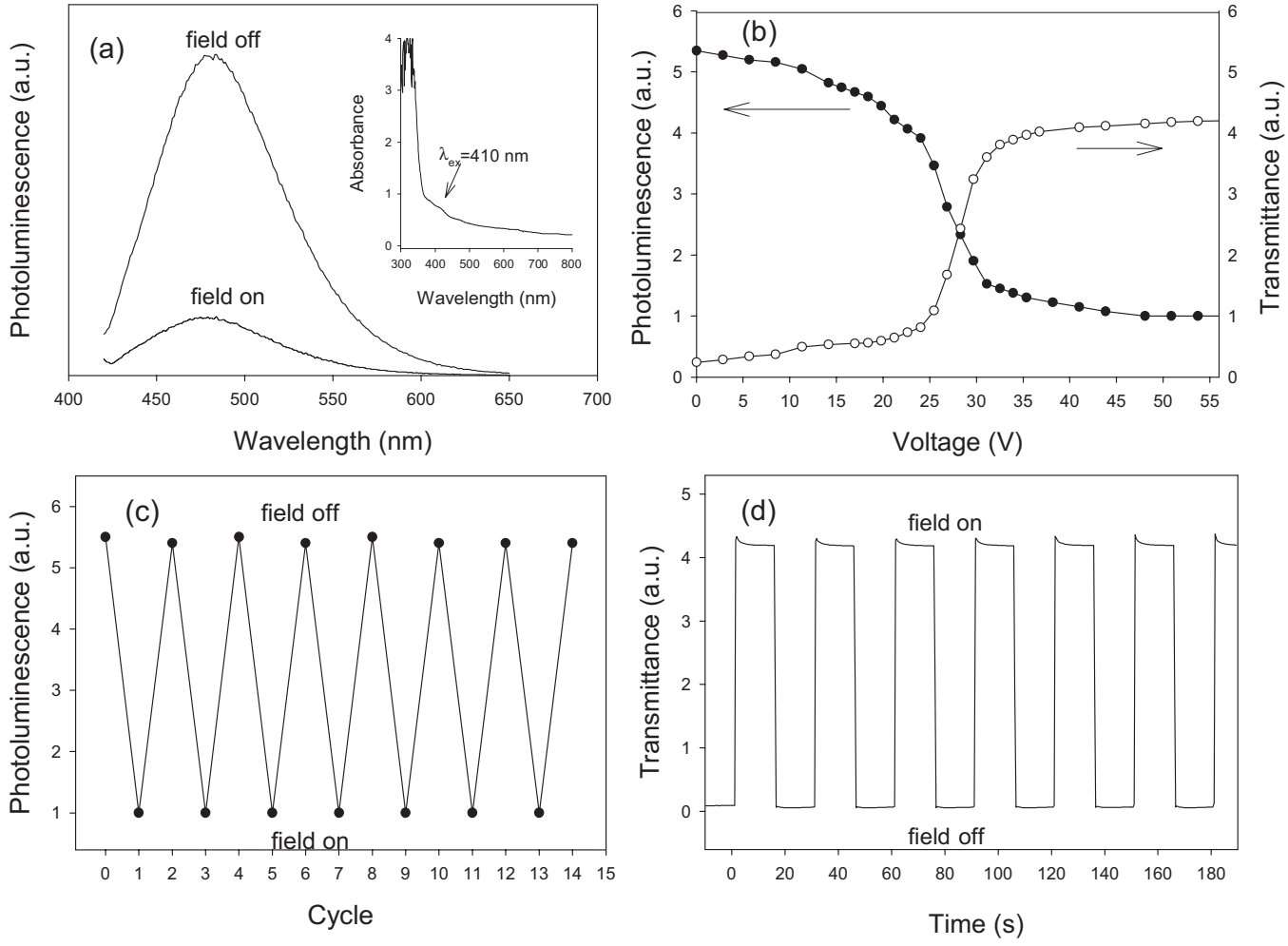

Figure 3. Electrical switching of photoluminescence and optical transmittance of a cholesteric LC gel (BL006 with 1 % CN-TFMBE and 5 % R811) in a 10 μm cell. a) Fluorescence emission spectra at field-off (0 V) and filed-on (42 V), with the inset showing the UV-vis spectrum of the mixture in the cell. b) Plots of photoluminescence (measured at 482 nm) and optical transmittance (measured using a probe light at 633 nm) versus applied voltage (ac 800 Hz root mean square). c) Repeated switching of photoluminescence between the field-off (0 V) and field-on state (42 V). d) Switching of optical transmittance in response to a square-wave electric field between 0 and 40 V (15 s duration).

above a threshold (ca. 25 V), LC molecules align along the field direction, which homogenizes the sample and optical transmittance increases. The opposite behavior can be noticed for the change in photoluminescence intensity (emission measured at 482 nm). The gel displays the strongest photoluminescence in the field-off state; with the electric field applied, the photoluminescence starts to decrease and it drops at the same threshold voltage as for the switching of the optical transmittance. It is thus clear that the electric-field-induced orientation of LC molecules is also the origin of changes in the photoluminescence. Both types of electrical switching are totally repeatable and appear to be stable. Figure 3c shows the reversible change in photoluminescence intensity for several cycles of switching between a field-off (0 V) and field-on state (42 V), while Figure 3d shows the response of optical transmittance to a square-wave electric field between 0 and 40 V, with a duration of 15 s for field-off and field-on states. It should be mentioned that after LC molecules are aligned by the electric field, further increase in voltage showed little direct effect on the photoluminescence of the fluorophore. As can be seen in Figure 3b, after the optical transmittance reaches a plateau at high voltages (45–55 V), the fluorescence intensity becomes almost constant. We performed measurements using a voltage as high as 150 V; no meaningful decrease in fluorescence was observed above 50 V (less than 4 % of the initial fluorescence intensity).

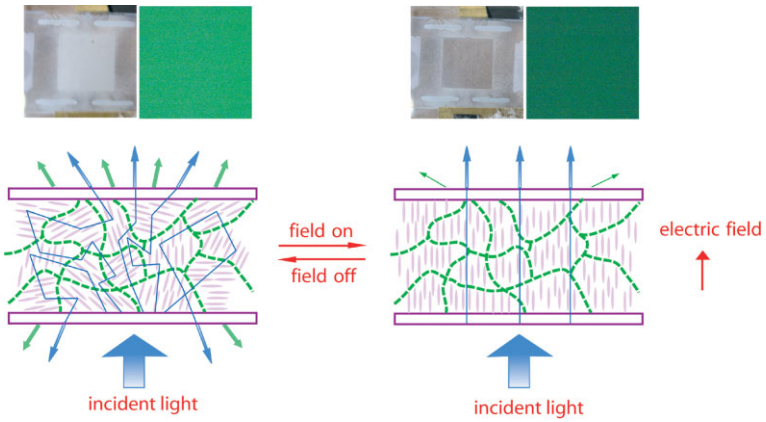

Figure 4. Schematic illustration of the mechanism for electrically switchable photoluminescence of fluorescent LC gels: different photoluminescence intensities at the field-off and field-on state are attributed to different numbers of gelator molecules excited by the incident light modulated by electric-field-induced orientation of LC molecules (see text for details). Changes in transparency and in brightness of photoluminescence are shown by photos of the cell and by fluorescence microscopy images.

Changes in photoluminescence under the effect of an electric field were measured for LC gels whose fibrous aggregates were formed in different LC orientational states (Fig. 1). With other conditions, such as the concentrations of the gelator and chiral dopant remaining the same, the highest contrast of photoluminescence, defined as the ratio of the emission intensity in the field-off state to that in the field-on state, was observed for LC gels prepared under the homeotropic LC orientation. Combined with the results of optical transmittance measurements, we found that the contrast of photoluminescence is directly related to the contrast of optical transmittance. Lower optical transmittance of the LC gel at the field-off state generally gives rise to stronger fluorescence emission from the fibrous aggregates, while higher transmittance at the field-on state results in lower fluorescence emission. Actually, this relation is also noticeable from Figure 3b. Moreover, from using fluorescence microscopy, we found no evidence of significant changes in alignment and organization of the fibrous aggregates in response to field orientation of LC molecules. This is understandable because the fibrous aggregates, which have an average diameter around 400–500 nm (from scanning electron microscopy (SEM) images), are unlikely to be able to follow the orientation of surrounding LC molecules. On the basis of all these results, we propose a mechanism for the observed electrical switching of photoluminescence of LC gels, which is schematized in Figure 4. In this study, the incident light used to excite the fluorescent fibrous aggregates (410 nm for fluorescence emission spectra and 450–490 nm for fluorescence microscopy) was different from the probe light used for the optical transmittance measurement (633 nm). However, for the sake of simplicity, the same incident light is drawn in the illustration for both optical transmission of the LC gel and for excitation of the fibrous aggregates.

In the field-off state, the fibrous aggregates in the LC gel create a highly inhomogeneous state with a large number of randomly oriented LC domains; the incident light is strongly scattered (low optical transmittance). In this case, photons of the incident light going through the LC gel may experience multiple refractions inside the sample mainly due to the changing refractive index at the interfaces of LC domains, before they can get out of the LC gel. Such randomly traced paths of photons should maximize their chance to encounter, and, if the wavelength is appropriate, be harvested by fluorescent gelator molecules on the fibrous aggregates. The result is a strong fluorescence emission. By contrast, in the field-on state, LC molecules are oriented along the electric-field direction to form a homogeneous LC monodomain, which reduces considerably the scattering of incident light (high optical transmittance). In the transparent state, photons of the incident light traverse the sample straight and encounter a minimum number of gelator molecules on their way out of the sample, giving rise to low fluorescence emission. Also shown in Figure 4 are photographs of a cholesteric LC gel in the cell in the field-off and field-on states, showing the electrical switching of both optical transmittance (transparency) and photoluminescence. This mechanism of electrical switching of photoluminescence is different from a known approach reported in the literature,[11] which consists of using a fluorophore (oligothiophenes) that, by being miscible in the LC host and able to follow the LC orientation, can change its photoluminescence as a result of field-induced LC orientation.

According to the above mechanism, high contrast of electrically switchable photoluminescence can be achieved if the incident light (or backlight) can excite a maximum of gelator mole-

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cules in the field-off state but as few gelator molecules as possible in the field-on state. Obviously, many factors can affect the contrast. One of them is the network of fibrous aggregates of the gelator, which, by greatly affecting the morphology of LC domains and the achievable LC orientation, determines the contrast of optical transmittance of cholesteric LC gels.[4] For instance, for the same cholesteric LC gel (94 % BL006, 1 % CN-TFMBE, and 5 % R811), with the fibrous aggregates formed under the planar texture (image 3 in Fig. 1), the sample displayed much stronger photoluminescence in both field-off and field-on states. However, the contrast of photoluminescence was lower (ca. 2.5) than that of the LC gel prepared under the homeotropic texture (ca. 5.5). In the case of planar texture, the dense, twisted, in-plane network of the fibrous aggregates can enhance the photoluminescence at the field-off state, due to the highly scattering state of the LC gel and the improved exposure of gelator molecules to photons of the incident light. But, at the same time, such a network of fibers prevents the LC gel from forming a highly homogeneous (transparent) state in the field-on state, due to the restricted field orientation of the LC molecules and significant light scattering by the fibrous aggregates, which results in a strong remaining fluorescence at the field-on state and a lower contrast of photoluminescence. In the case of homeotropic texture, the network of fibers is formed with surrounding LC molecules oriented by an electric field. Fibrous aggregates formed inside this LC orientational template should adopt a morphology exerting less resistance to LC orientation at the field-on state. This explains the high contrast of optical transmittance and, as a result, high contrast of photoluminescence of the LC gels.

Using cholesteric LC gels prepared under the homeotropic texture, we also investigated the effects of other parameters on the contrast of photoluminescence. The results in Figure 5 show the effects of changing the concentration of gelator and chiral dopant. On one hand, at a given concentration of the chiral dopant R811 (5 %), the highest contrast of photoluminescence was obtained with about 1 % of CN-TFMBE. Either reducing or increasing the concentration of gelator, which mainly changes the density of the fluorescent fibers, resulted in a decrease in the contrast of photoluminescence. On the other hand, with the same concentration of gelator (1 %), by increasing the content of the chiral dopant, which decreases the helical pitch in the chiral nematic phase, higher contrast of photoluminescence was observed at ca. 5–7 % of R811. Together with the possibility of using LC orientational states to change the morphology of the fibrous aggregates, these results suggest that it would be possible to optimize the contrast of electrically switchable photoluminescence of the LC gels by varying the combination of many parameters.

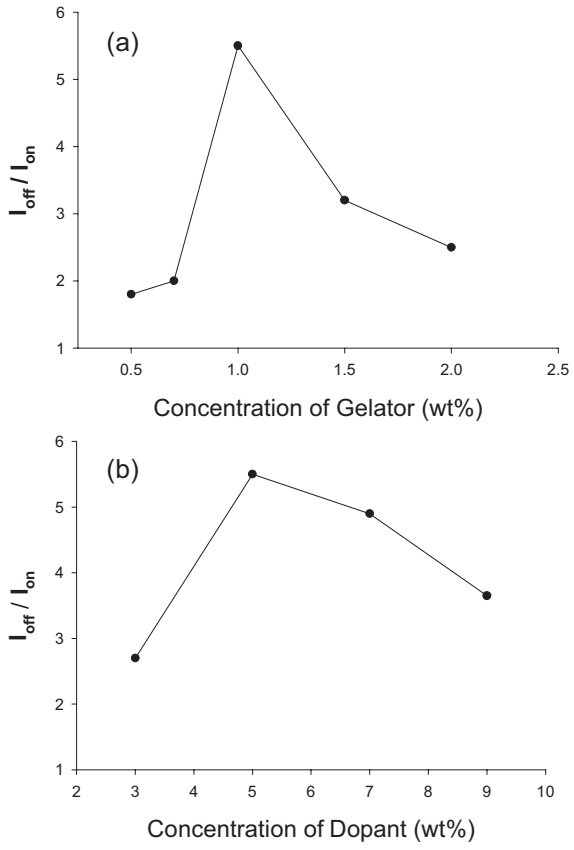

Figure 5. a) Contrast of photoluminescence switchable between the field-off (0 V) and field-on states (42 V) versus the concentration of the gelator CN-TFMBE for a cholesteric LC gel (1 % R811). b) Contrast of photoluminescence versus concentration of the chiral dopant R811 for cholesteric LC gels containing 1 % of CN-TFMBE.

3. Conclusion

To summarize, we report the first study on self-assembled LC gels whose fibrous aggregates are strongly fluorescent due to the AIEE displayed by the gelator CN-TFMBE. We demonstrate a very interesting property of such fluorescent LC gels: in addition to the switching of optical transmittance, their photoluminescence intensity can also be switched using an electric field. The switching mechanism for this new material is based on different numbers of gelator molecules on the fibrous aggregates that can be excited by the incident light modulated through electric-field-induced orientation of LC molecules. We show that a high contrast of photoluminescence can be achieved with LC gels that are strongly scattering at the field-off state and highly transparent at the field-on state. The combination of various parameters, including the morphology of fibrous aggregates governed by the LC orientational state, and concentrations of gelator and chiral dopant, determines the contrast of photoluminescence. The discovery of using electric-field-induced orientation of LCs to control and switch the photoluminescence emitted from fluorescent LC gels may open new ways to explore the use of photoluminescence for display applications.

4. Experimental

The synthesis of the gelator CN-TFMBE has been previously reported [10]. Both the nematic LC, BL006, and the chiral dopant, R811, were purchased from Merck. To prepare an LC gel, weighed BL006,

CN-TFMBE, and R811 (in the case of chiral LC gels) were first dissolved in THF, a common solvent for all compounds; then, the mixture was dried in a vacuum oven to remove the solvent. To enter the mixture in a chosen ITO-coated, rubbed cell (E.H.C. Japan), it was heated to 140 °C and flow-filled into the cell through a capillary effect. To obtain LC gels whose fibrous aggregates were formed under different LC orientational states or textures, the cell, placed inside a microscope hot stage (Instec), was heated to 130–140 °C for 5 min, and then cooled to 85 °C, at which BL006 was in its nematic or chiral nematic phase while the gelator CN-TFMBE remained dissolved in the LC host (no aggregation). The sample was held at this temperature for 5 min to allow the surface-induced orientational state or texture to develop; in the case of the homeotropic texture, an electric field (a.c., 800 Hz) was applied to align LC molecules. Afterwards, the cell was taken out of the hot stage for fast cooling to room temperature to allow the aggregation of the gelator inside the predetermined LC orientational template. To observe the fluorescent aggregates, a fluorescence microscope (Leica DMRX) equipped with an excitation filter (450–490 nm) was utilized; the green color of the fibrous aggregates was due to the detected emission of photons of longer wavelengths (> 510 nm).

Steady-state fluorescence emission spectra (excitation at 410 nm) were recorded on a SPEX 1680 double-monochromator spectrophotometer, slit widths being set to 10 nm band pass for both excitation and emission. For these measurements, the cell containing the LC gel was positioned with its normal making an angle of 45° to the excitation beam and 135° to the emission path to the detector [12]. For polarized emission measurements, a polarizer was placed in front of the photodetector, while no polarization of the excitation beam was utilized. Optical transmittance of the LC gels was measured using a probe light from a low-power He–Ne laser (633 nm, 4 mW), with a high-speed photodetector (Displaytech) connected to a digital oscilloscope (Tektronix, TDS 420 A). For the measurements of electrical switching of both photoluminescence and optical transmittance, a high-voltage waveform generator (WFG500, FLC Electronics) was used to apply either ac (800 Hz, sinusoidal) or square-wave (15 s duration) electric fields through the cell.

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