

Novel cholesteric materials doped with CdSe/ZnS quantum dots with photo- and electro-tunable circularly polarized emission

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ABSTRACT

Optical materials based on cholesteric liquid crystals (LCs) doped with fluorescent CdSe/ZnS quantum dots (QDs) have been developed and demonstrated to have a wide photonic band gap. It has been shown that the fluorescence emission of QDs embedded in LCs is circularly polarized and that the dissymmetry factor of this polarization may be optically or electrically controlled via conformational changes in the helical structure of the LC matrix. The possibility of photochemical patterning or image recording using these materials has been demonstrated; the recorded information can be read through changes in the dissymmetry factor of circular polarization of QDs emission. The developed photo- and electro-active materials with a controlled degree of fluorescence circular polarization may be used as on-demand single photon sources in photonics, optoelectronics, and quantum cryptography, as well as for development of nanophotonic systems capable of low-threshold lasing.

Keywords: Cholesteric liquid crystals; circularly polarized fluorescence; photonic band gap; quantum dots; electro-optical control.

1. INTRODUCTION

Low-molecular-weight polymer-based cholesteric liquid crystals (LCs) are smart stimulus-responsive materials with promising applications in optoelectronics and photonics¹. In our study, new optical materials based on cholesteric liquid crystals (LCs) doped with fluorescent CdSe/ZnS quantum dots (QDs) have been developed and demonstrated to have a wide photonic band gap. It has been shown that the fluorescence emission of QDs embedded in LCs is circularly polarized and that the dissymmetry factor of this polarization may be optically or electrically controlled via conformational changes in the helical structure of the LC matrix. The possibility of photochemical patterning or image recording using these materials has been demonstrated; the recorded information can be read on the basis of changes in the dissymmetry factor of circular polarization of QD emission. The developed photo- and electro-active materials with a controlled degree of fluorescence circular polarization may be used as on-demand single photon sources in photonics, optoelectronics, and quantum cryptography, as well as for development of nanophotonic systems capable of low-threshold lasing.

The cholesteric helical structure can be considered as a one-dimensional photonic crystal whose band gap has a spectral position (λ_{\max}) determined by the helix pitch (P) and proportional to the average refractive index (n_{av}):

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$$\lambda_{\max} = n_{\text{av}} P \quad (1)$$

The pitch of the helix can be controlled by the chemical structure of the LC, concentration of chiral additives (dopants), or external electric field or light, which may induce conformational changes in LCs¹⁻⁵. Earlier, different approaches to the development of low-molecular-weight cholesteric materials with optically controlled helix pitch and band gap positions were described²⁻⁴. Most of these approaches were based on the introduction of chiral photochromic molecules capable of photoisomerization and drastic changes in their helical twisting power (the capacity of a chiral dopant or chiral molecular fragment for inducing cholesteric helix) into cholesteric materials. Optical excitation modifies the helix twisting, which results in a change in the photonic band gap position. In cholesteric materials doped with fluorescent species, propagation of circularly polarized light with the handedness coinciding with the direction of the cholesteric helix is prohibited, which leads to strong circular polarization of fluorescence in the spectral region of selective light reflection^{6,7}.

Earlier, we developed a novel optical cholesteric material with optically controlled circularly polarized emission⁸. Chiral dopants made from cyclic siloxanes or sorbide were used as a cholesteric matrix into which fluorescent organic dyes or semiconductor nanoparticles (i.e., QDs) were embedded. UV irradiation caused a shift of the reflection peak position and, hence, changes in the emission intensity and degree of circular polarization, characterized by the fluorescence polarization dissymmetry factor g_c :

$$g_c = 2 (I_L - I_R) / (I_L + I_R) \quad (1)$$

where I_L and I_R are the intensities of the left- and the right-handed circularly polarized light, respectively. Later, we also demonstrated that cholesteric materials containing fluorescent dyes may possess phototunable lasing properties⁹. A serious disadvantage of organic fluorescent dyes is their photobleaching under intense optical excitation. In contrast, QDs are characterized by a high photostability, a broad absorption band and a narrow, size-tunable fluorescence band^{10,11}. For the best of our knowledge, there are only a few studies on circularly polarized light emission from QDs dispersed in cholesteric materials^{8,12}.

Here, we report on the development of glass-forming cholesteric LC materials (CLCMs) with optically controlled circularly polarized fluorescence emitted by embedded QDs and describe their optical properties. For preparing CLCM1, a glass-forming cholesteric cyclosiloxane cholesteric matrix material exhibiting selective light reflection of left-handed circularly polarized light with $\lambda_{\max} \sim 450$ nm was used. Two types of CdSe/ZnS QDs of different sizes (and, respectively, fluorescence emission wavelengths) and a chiral photochromic dopant capable of photoisomerization were introduced into a cholesteric glass-forming matrix. This approach allowed us to increase the possible spectral shift of the maximum of the fluorescence polarization dissymmetry factor (g_c , Eq. 2) and to demonstrate the possibility of photochemical patterning using this material.

We have also developed polymer-stabilized cholesteric materials with electrically controlled circularly polarized fluorescence (CLCM2 and CLCM3). If external electric field is applied to them, the planar texture of the cholesteric systems is usually broken into domains where the helix axes are randomly orientated, which leads to degeneration of selective light reflection and light scattering (Figure 1). Further increase in the intensity of the field applied results in realignment of the LC molecules into a uniform homeotropic transparent texture. The rate of field-induced domain reorientation is on the microsecond scale. After removal of the electric field, the LC molecules do not return rapidly to the initial planar orientation, because the highly scattering focal conic texture with a random orientation of the helix axes has a long lifetime^{1,13}. In order to exclude this undesirable effect, a small concentration of a bifunctional monomer was introduced and polymerized to form a three-dimensional network (Figure 1)^{14,15}.

This network acts as a “memory” due to its helical topology allowing for rapid reorientation into the initial planar-oriented, aligned cholesteric state. This so-called polymer-stabilized cholesteric LCs (PSCLCs) are promising materials for electrooptics and display technologies.

2. MATERIALS AND METHODS

2.1 Materials

A commercial mixture of cyanobiphenyl derivatives (E48, $\Delta n = 0.231$ at 589 nm) was purchased from Merck (Darmstadt, Germany) and used as a nematic LC host. The chiral dopant 4-(2-methylbutyl)-4'-cyanobiphenyl (CB15, Table 1) and the bifunctional monomer RM257 containing three aromatic rings and two acrylic bonds were also purchased from Merck (Darmstadt, Germany). The photoinitiator 2,2-dimethoxy-1,2-diphenylethan-1-one (Irgacure 651) was purchased from Ciba AG (Basel, Switzerland). Cyclosiloxane (SilBlue) was purchased from Wacker Chemie (Munich, Germany). Poly[1-[4-(3-carboxy-4-hydroxy-phenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt was purchased from Sigma-Aldrich (St. Louis, MO, USA). The chiral photochromic dopant 2,5-bis(4-methoxycinnamoyl)-1,4;3,6-dianhydro- D-sorbitol (Sorb) was synthesized as described in Ref. [16].

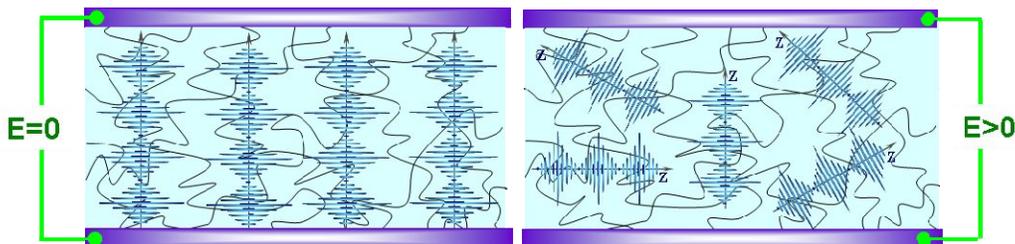


Figure 1. The electro-optical effect caused by application of electric field to a planar-oriented film of a polymer-stabilized cholesteric liquid crystal.

2.2 Synthesis of quantum dots

CdSe/ZnS core/shell QDs were synthesized as described earlier^{17, 18}. Here, we used homogeneous QDs (size deviation, 10%) with CdSe cores approximately 2.5 or 4.5 nm in diameter with approximately two monolayers of the ZnS shell¹⁹ and a quantum yield exceeding 60%. The synthesized QDs contained TOPO/TOP surfactants on their surface²⁰. Photoluminescence of QDs was found to be stable during photopolymerization and fluorescence excitation with the variation of photoluminescence emission during photopolymerization not exceeding 10%.

2.3 Material and cell preparations

Liquid crystal materials were prepared by dissolving the components in chlorophorm and slowly evaporating the solvent, and drying the material in vacuum (at 120°C for CLCM1 and at room temperature for CLCM2 and CLCM3). The preparation was not accompanied by aggregation or phase separation, and the mixtures prepared were homogeneous. The absence of nanoparticle aggregates of any significant size was confirmed by fluorescent and polarized optical microscopy. Note that dissolving of QDs did not lead to any noticeable changes in the optical quality of planar-oriented films, which remained transparent.

For optical and photo-optical studies, 20 μm thick films sandwiched between two flat glass plates were prepared. The thickness of the test samples was controlled with Teflon spacers. In order to obtain a good planar texture, we used the LC photo-alignment technique²¹. Glass plates were spin-coated with 2 mg/mL poly[1-[4-(3-carboxy-4-hydroxy-phenylazo) benzenesulfonamido]-1,2-ethanediyl sodium salt. After drying at room temperature, glass plates coated with this polymer were irradiated with polarized polychromatic light by means of a mercury lamp ($\sim 15 \text{ mW/cm}^2$, 30 min). A Glan-Taylor prism was used as a polarizer.

The planar texture of CLCM1 was obtained by annealing the samples, which were heated to temperatures well above the glass transition temperature (140°C) and slowly cooled (1°C/min). Prior to absorbance and fluorescence measurements in irradiated CLCM1 samples, they were heated for about 20 min and slowly cooled to room temperature at a rate of 1°C/min. For CLCM2 and CLCM3, ITO-coated glass plates were used as substrates. After filling with the material, the

prepared cells were UV irradiated (10 min, 365 nm, $\sim 1 \text{ mW/cm}^2$) in order to induce photopolymerization of the diacrylate RM257.

2.4 Study of phase behavior and optical and electro-optical analyses

The phase transition temperatures of the mixtures were determined by means of a LOMO P-112 polarizing optical microscope (St. Petersburg, Russia) equipped with a Mettler TA-400 heating stage (Mettler-Toledo, Greifensee, Switzerland). The transmittance spectra of planar-oriented films were recorded using a Unicam UV-500 UV-Vis spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA).

Photochemical investigations were performed using an optical setup equipped with a DRSh-350 ultra-high pressure mercury lamp (Zenith Trading Ltd., St. Petersburg, Russia). To prevent the heating of the samples due to the IR irradiation of the mercury lamp, the illumination was performed through a water filter. To obtain a plane-parallel light beam, a quartz lens and a 365-nm optical filter were used. The intensity of light was measured by a LaserMate-Q (Coherent Inc., Santa Clara, CA, USA) intensity meter ($\sim 2 \text{ mW/cm}^2$).

Electric field was applied to the cells containing photopolymerized CLCM2 or CLCM3 with the use of a Philips 2422 530 AC power supply (Royal Philips Electronics, Amsterdam, Netherlands) with a voltage adjustment range of 0–260 V.

The fluorescence spectra were recorded using an M266 Automated Monochromator/Spectrograph (SOLAR Laser Systems, Minsk, Belarus) with CCD U2C-16H7317 (Ormins, Minsk, Belarus) and a home-made light-collecting system with two Semrock 488-nm RazorEdge[®] ultrasteep long-pass edge filters (Rochester, NY, USA). An LGN-519M Ar⁺ laser (Plasma Ltd, Ryazan, Russia) operating at 488 nm was used for fluorescence excitation. The direction of detection was normal to the film plane, whereas the excitation beam from the opposite side of the film was oriented at a certain angle to the normal. The circularly polarized absorbance and fluorescence spectra were obtained using a combination of a linear polarizer with a broad-band quarter-wave plate.

2.5 High resolution analysis of quantum dot distribution in the liquid crystal matrix

The spatial distribution of QDs in the liquid crystal matrix was analyzed using a unique combined AFM–ultramicrotome setup based on an NTEGRA Tomo machine (NT-MDT, Russia)²². This approach permits the reconstruction of the 3D-structure of the specimens through their microtoming along the Z axis followed by sequential recording of the AFM images of the block face of each section in the XY plane.

3. RESULTS AND DISCUSSIONS

3.1 Analysis of quantum dot spatial distribution in the liquid crystal matrix

Figure 2 shows a typical reconstructed 3D image of CLCM1 samples doped with the fluorescent QDs-530 and QDs-604. It should be mentioned that the obtained 3D image was also typical of similar cholesteric liquid crystals analyzed earlier²³. Figure 2a shows that there were no QD aggregates in the sample and that the introduction of QDs did not cause any detectable distortions of the planar texture of the cholesteric matrix. High-resolution images of the sections of the CLCM1 sample were further recorded for the sections made in the direction coinciding with the cholesteric helix axis (Figure 2b) and in the direction perpendicular to this axis (Figure 2c). Figures 2b and 2c show that the QDs in the matrix (dashed white circles) were not aggregated; the images show the QD characteristic sizes corresponding to individual nanoparticles. Figure 2b also shows that individual QDs did not perturb the planar texture of the liquid crystal matrix.

3.2 Effect of UV irradiation on circularly polarized fluorescence of quantum dots incorporated in CLCM1

The basic component of the CLCM1 matrix, SilBlue, is characterized by a clearing temperature of 180–182°C and a glass transition temperature of about 50°C. A derivative of isosorbide and cinnamic acid (Sorb) was used as a chiral photochromic dopant responsible for helix phototuning properties¹⁶. The chiral photochromic dopant Sorb is itself characterized by a high helical twisting power ($\sim 40 \mu\text{m}^{-1}$) and induces the formation of a right-handed cholesteric helical structure. UV irradiation induces thermally irreversible E–Z isomerization of Sorb at C=C bonds¹⁶.

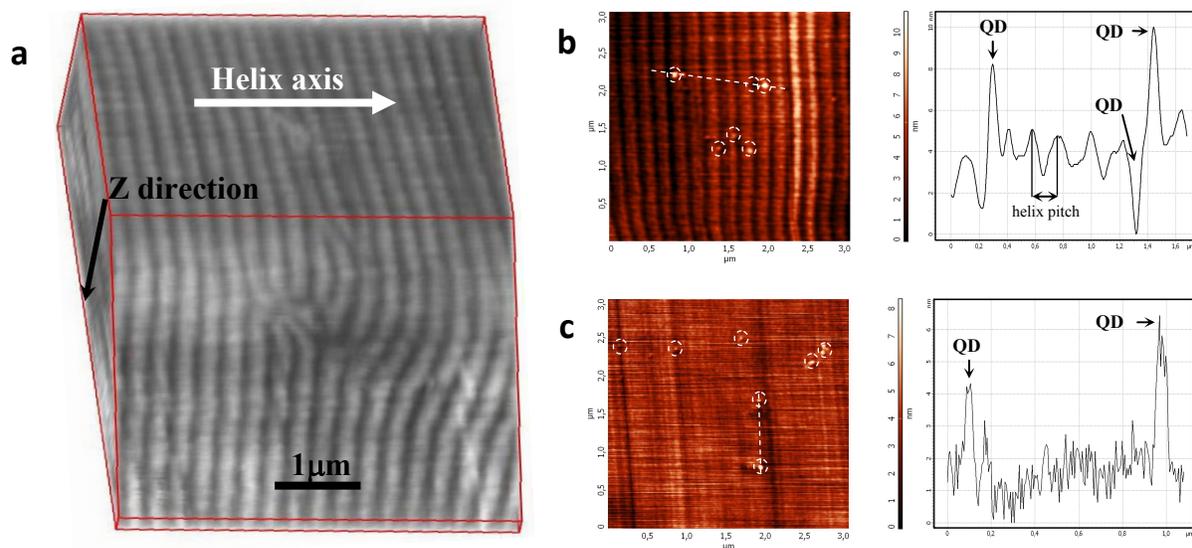


Figure 2. AFM images of CLCM1 doped with fluorescent quantum dots (QDs) at a concentration of 0.55 wt%. (a) A reconstructed 3D image of CLCM1 obtained by sequential microtoming of the material and AFM scanning of the block face of each section. Fourteen 100-nm sections have been analyzed. (b) An AFM image of a CLCM1 section along the helix axis. (c) An AFM image of a CLCM1 section perpendicular to the helix axis. In Panels b and c, the QDs are indicated with dashed white circles; dashed white straight lines show the projections of cross-sections.

This process is accompanied by a decrease in the helical twisting power and molecule anisotropy. Introduction of Sorb into the SilBlue matrix leads to partial helix untwisting and a shift of selective light reflection towards the red region of the optical spectrum. Two types of QDs, with green ($\lambda_{\max} \approx 530$, 0.5 wt%) and red ($\lambda_{\max} \approx 604$, 0.05 wt%) emissions were used in CLCM1. The larger amount of green QDs was necessary to obtain comparable emission intensities in the green and red spectral regions. UV irradiation through a mask for different periods of time and annealing at temperatures above that of glass transition of planar-oriented CLCM1 films induced a shift of the selective light reflection peak to shorter wavelengths. These spectral changes were caused by E-Z isomerization of the chiral photochromic dopant Sorb and a decrease in its helical twisting power.

Figures 3a and 3b show left- and right-handed circularly polarized fluorescence excited with an Ar⁺ laser (488 nm) before and after UV irradiation. Here, the right-handed component of circularly polarized emission consists of the main peak corresponding to the emission of red QDs (604 nm) and a short-wavelength shoulder at ~550 nm accounted for by green QDs. The shape of the left-handed circularly polarized emission spectrum is more complex. Comparison of this shape with those of transmittance spectra shows coincidence of the peak gap in the left-handed component of fluorescence with the photonic band gap. The shift of the selective light reflection peak to shorter wavelengths is accompanied by a shift of the gap in the left-handed component of emission (Figure 3b). The right-handed component of emission remains unchanged upon UV irradiation due to left-handed twisting of the cholesteric helix^{6, 7}. In other words, UV irradiation allows one to manipulate the polarization components of the fluorescence emission.

We used the right- and left-handed circularly polarized fluorescence spectra and Eq. (2) to calculate the fluorescence dissymmetry factor (g_c) for films before and after UV irradiation (Figure 4a). The dissymmetry factor was negative in the spectral regions corresponding to the photonic band gap and completely coincided with the peaks of the selective light reflection. A negative sign of the dissymmetry factor was correlated with left-handedness of the helical supramolecular structure of CLCM1 determined by cholesterol chiral groups. It is noteworthy that the peak of the dissymmetry factor gradually shifted to shorter wavelengths during UV irradiation (Figure 4b).

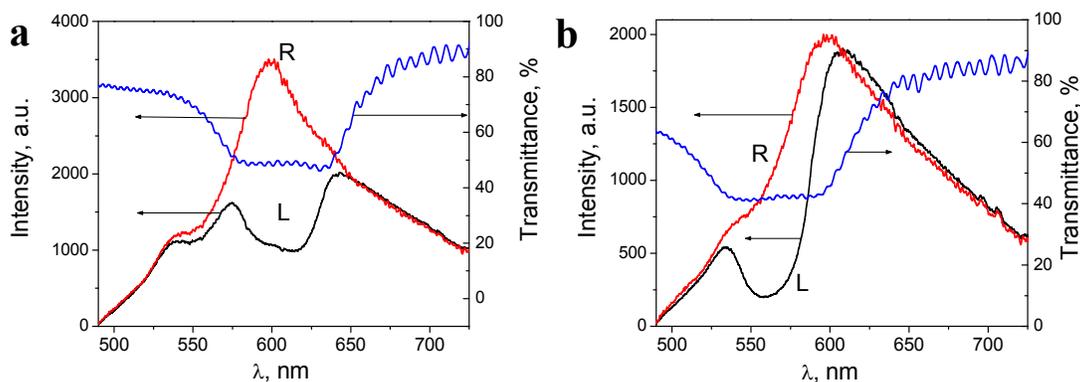


Figure 3. Effect of UV-irradiation on left- and right-handed circularly polarized fluorescence of quantum dots incorporated in CLCM1. (a) Left-handed (L) and right-handed (R) circularly polarized fluorescence of QDs embedded into CLCM1 and nonpolarized transmittance spectra of CLCM1 before UV irradiation. (b) The same as in (a), after 1 min of UV irradiation.

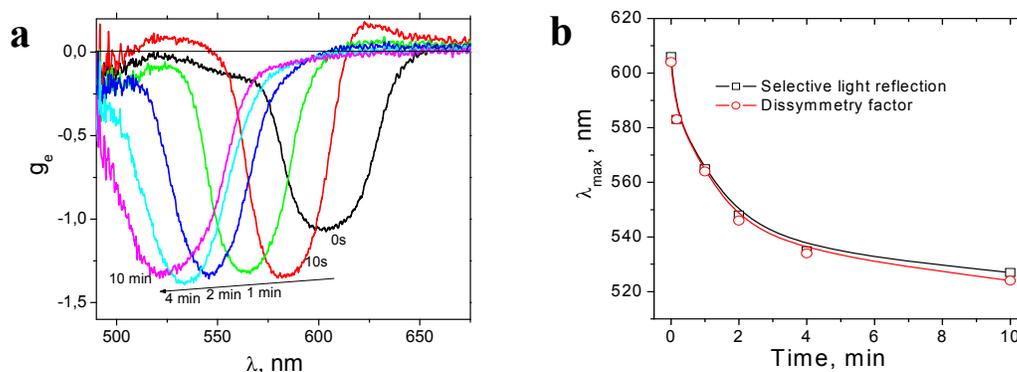


Figure 4. Effect of UV irradiation on the fluorescence dissymmetry factor of quantum dots (QDs) embedded in CLCM1. (a) Changes in the fluorescence dissymmetry factor of QDs embedded in CLCM1 upon UV irradiation of the sample for different periods of time. (b) Dependence of the selective light reflection maximum wavelength of the CLCM1 matrix and the maximum wavelength position of the fluorescence dissymmetry factor on the duration of UV irradiation.

3.3 Effect of external electric field on circularly polarized fluorescence of quantum dots incorporated in CLCM12 and CLCM3

The optical properties of cholesteric systems can be also controlled by applying an external electric field. We have demonstrated a pronounced electric field-induced modulation of the degree of circular polarization of fluorescence in the cholesteric mesophase. For this purpose, two mixtures of polymerizable cholesteric formulations containing green (CLCM2) and red (CLCM3) QDs with clearing temperatures in the ranges of 39.3–41.4°C and 44.0–49.2°C, respectively, were prepared. Mixing of the cyanobiphenyl derivatives E48 and CB15 yields a cholesteric mesophase with a high positive dielectric anisotropy, which determines its high sensitivity to the electric field. We used the ratio between the nematic mixture E48 and the chiral compound CB15 at which the selective light reflection (the photonic band gap) covered the emission of either green or red QDs. The wavelengths of selective light reflection (the centers of photonic bands after photopolymerization) were 544 and 620 nm for CLCM2 and CLCM3, respectively. Small amounts of the

mesogenic diacrylate RM257 in the presence of the UV-sensitive photoinitiator Irgacure 651 gave rise to a 3D polymer network stabilizing the planar texture.

For investigation of the electro-optical response of polymer-stabilized cholesteric systems containing QDs, CLCM2 and CLCM3 were introduced into ITO-coated cells (see Methods for more detail). In order to photopolymerize the diacrylate RM257 in the presence of the photoinitiator Irgacure 651 after simultaneous formation of the planar orientation provided by LC photoaligning, the cells were UV irradiated. Application of an electric field to the cell resulted in strong light scattering (a decrease in transmittance, Figure 5a). Indeed, it is known that cyanobiphenyl-containing mesogens tend to be oriented along the electric field due to the positive dielectric constant anisotropy. This tendency leads to disruption of the LC planar texture by the electric field and its rapid reversible transition¹.

The changes in the QDs fluorescence dissymmetry factor with increasing electric field intensity are shown in Figure 4b. In contrast to CLCM1, the signs of the dissymmetry factors for CLCM2 and CLCM3 are positive, because the chiral substance CB15 induces a right-handed cholesteric helix. Transition from the planar-oriented state to the focal conic texture is accompanied by a noticeable decrease in the circular polarization of emission, with a dissymmetry factor decreasing 2.5-fold (Figure 5b). The observed effect is explained by considerable disturbance of the planar orientation of the helical structure; all spectral changes are completely reversible and can be repeated many times.

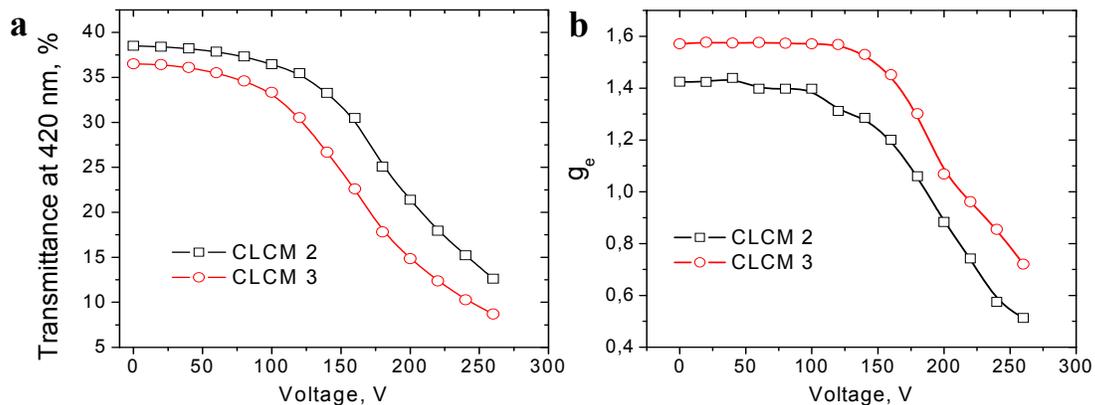


Figure 5. Effect of external electric field on the light transmittances and fluorescence dissymmetry factors of CLCM2 and CLCM3. (a) Dependences of the transmittances of photopolymerized CLCM2 and CLCM3 at 420 nm on the voltage applied. (b) Dependences of the fluorescence dissymmetry factor on the voltage applied to cells filled with CLCM2 or CLCM3.

4. CONCLUSIONS

Thus, we have developed polymer-stabilized QD-doped LC materials with a wide photonic band gap and optically and electrically controlled intensity and degree of circular polarization of QD emission. UV irradiation of photosensitive cholesteric materials containing a chiral photochromic dopant resulted in a shift of the dissymmetry factor of QD emission. These results demonstrate the possibility of photochemical patterning or image recording, where the recorded information can be read from the changes in the circular polarization of QD emission. Application of an electric field to the electro-optical cell containing polymer-stabilized cholesteric materials with a positive dielectric anisotropy led to a drastic decrease in the degree of circular polarization of QD emission due to field-induced disturbance of the planar orientation of the helical structure.

Materials with optically and electrically controlled fluorescence polarization may be used as on-demand single photon sources for photonics, optoelectronics, and quantum cryptography^{12, 24}, as well as for development of nanophotonic systems capable of low-threshold lasing²⁵. Future experiments are planned with other types of fluorescent nanocrystals, such as CdSe nanorods, where the combination of linearly polarized emission of nanorods and LCs should result in strongly enhanced electro-optical properties.

5. ACKNOWLEDGMENTS

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