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Photochromic and fluorescent LC gels based on bent-shaped azobenzene-containing gelator

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Photochromic LC-gels based on low-molar-mass azobenzene-containing bent-shaped gelator and nematic liquid crystals were prepared. LC-gels are capable of reversible melting under E-Z isomerization of azobenzene chromophores induced by UV-irradiation. It is shown that light and heat actions allow one to manipulate phase behaviour, fluidity and optical properties of the prepared LC-gels. The observed phenomenon was applied for the creation of nematic and cholesteric mixtures with phototunable degree of linearly or circularly-polarized fluorescence. The elaborated systems could be considered as promising soft-matter materials for optics and photonics applications.

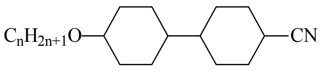
Among the different types of smart materials gels are the one of the most promising stimuli responsive systems which are gained a significant interest due to the large variety of unique properties. In particular, there are the possibilities of the fast and reversible switching of the mechanical properties under different fields and actions, such as light, pH changes, mechanical force, etc. A special interest presents light-responsive gels [1-13] because the light is the one of the most useful and simple tools for the fast, distant and localized modification of the mechanical and optical properties of the materials including gels.

Another promising type of the responsive systems are the liquid crystalline (LC) gels capable of forming of anisotropic films or layers with photo-, thermo- and electro-switchable optical properties allowing a creation of a novel type of materials with controllable supramolecular structure. [11-22] In the paper by Kato et al [13] photoinduced gel-sol transition in photochromic LC-gels with hydrogen-bonded azobenzene-containing gelators was described. Authors have demonstrated possibilities of photooptical patterning and photorecording, but they did not consider in their work effects of photofluidization under UV-irradiation.

Recently we have used photochromic azobenzene-containing LC acrylic polymer for gelation of low-molar-mass nematic mixture. [22] It was shown that dissolution of LC polymer in amount of only 2.5 wt% in nematic mixture **MLC6816** (Merck Ltd) at 120 °C (corresponded to isotropic state) followed by cooling down results in formation of the solid-like photochromic LC gel. Gelation is associated with a phase separation and formation of microsized LC polymer domains which form a physical "network" containing encapsulated nematic host. It was found that UV-irradiation leading to the E-Z isomerization processes are accompanied by disruption of H-aggregates formed by azobenzene moieties and by partial dissolution of polymer. Nevertheless in this work we did not find any evidences of isothermal photoinduced melting of the gel.

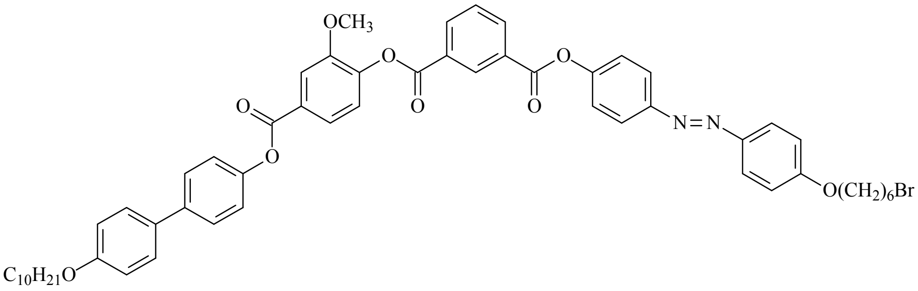
In the current short preliminary communication we are presenting the first results of the investigation of LC gel with photooptically induced gel-sol transition. We have examined a lot of liquid crystal – gelator pairs in order to find substances allowing to form LC gels capable to proceed isothermal photoinduced melting. As a result of this search we have found that new bent-shaped compound **10BVIABr** could be successfully used as gelator for LC mixture **MLC6816** (Scheme 1a). Synthesis and detailed characterization of a novel photochromic azobenzene-containing bent-shaped compound **10BVIABr** are presented in Supporting Information (Figures S1-S5).

Nematic LC mixture MLC 6816

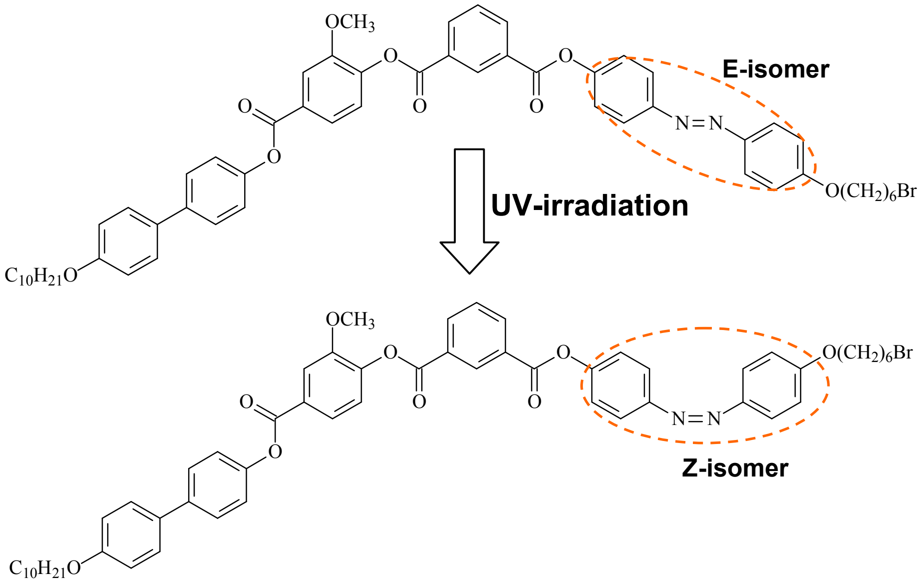


n=2, 3, 4, 7

Gelator 10BVIABr



a



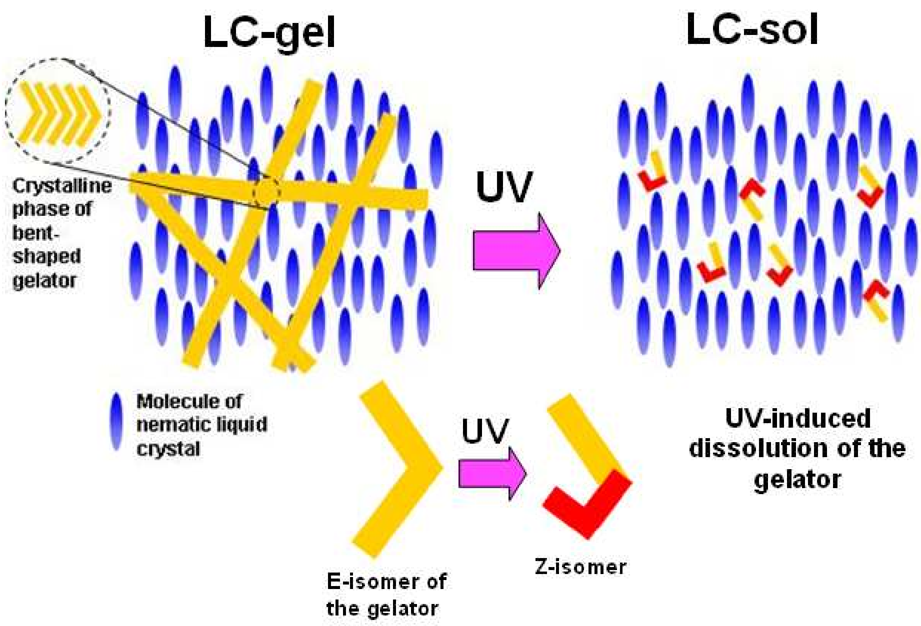
b

Scheme 1. (a) Structure of the nematic LC mixture **MLC6816** components and photochromic bent-shaped gelator **10BVIABr**. (b) E-Z isomerization of bent-shaped molecule of **10BVIABr**.

Heating of the nematic **MLC6816** mixture doped with 1.0-2.6 wt% of bent-shaped compound **10BVIABr** up to 120 ^{o}C results in complete mutual dissolution of the components and formation of transparent isotropic liquid. Subsequent cooling down of the liquid to room temperature induces an appearance of the strong turbidity due to isotropic phase – nematic phase transition. This process is accompanied by the slow formation of the gel which is completed after ca. 10 hours (Figure 1a). Gel formation is most probably associated with formation of the physical "solid network" composed of **10BVIABr** crystallites (Scheme 2). As seen from Figure 1c, DSC curves of nematic gels contain two peaks, one of them corresponds to the melting transition of the gel (at ca. 70 ^{o}C), whereas peak at 81 ^{o}C relates to isotropization of the sample. These transitions are confirmed also by polarized optical microscopy (POM) observations.

It is noteworthy that UV-irradiation of the LC gel during only 10 min with light of the moderate intensity results in melting of the gel or photoinduced gel-sol transition and appearance of intense orange colour instead pale yellow one (Figure 1b).

Both effects are associated with the process of E-Z isomerization of azobenzene photochromic fragment of **10BVIABr** (Scheme 1b) that leads to the photoinduced melting of the **10BVIABr** crystals and dissolving of the formed Z-isomer in the LC mixture (Scheme 2).



Scheme 2. Schematic representation of the LC-gel structure and its melting under UV-irradiation.

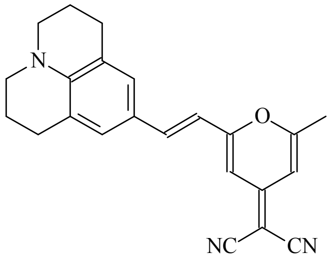
The origin of these effects is related to the fact that the Z-isomer of **10BVIABr** molecules possesses less anisometry as compared to the E-form (Scheme 1b). At room temperature the mixture exposed to UV-irradiation restores the original yellow colour in about 3 days, but the reverse gelation does not occur. Only precipitation of the yellow crystals of **10BVIABr** takes place. However, reheating of the mixture to 120 ° C followed by cooling down and keeping at room temperature for approximately 12 hours again leads to the gelation process.

The polarized optical microscopy (POM) confirmed that the gel formation occurs due to crystallization of the azobenzene gelator (Figures 2a, b), whereas UV-irradiation leads to the complete melting of the crystals and their dissolution (Figure 2c, Scheme 2).

We have studied the spectral properties of photochromic photoswitchable LC-gel. Figure 3 shows absorption spectra of the cell filled with LC gel during UV irradiation (Figure 3a) and subsequent exposure to visible light (Figure 3b). As is seen from Figure 3a, the gel has a low light transmission in the whole spectral range, which is caused by light scattering due to the presence of two phases, - the LC nematic and crystalline. A small "shoulder" on the spectrum at wavelengths around 360 nm is due to π-π * electronic transition of azobenzene chromophores in the E-form. UV-irradiation results in lowering of the absorption in whole spectral range caused by E-Z isomerization, melting of the gel and dopant dissolution (Figure 3a). In photostationary state is clearly seen a peak with a maximum around 450 nm, which corresponds to the n-π * electronic transition of the azobenzene chromophore. Subsequent irradiation by visible light leads to a decrease in the intensity of the n-π* electronic transition and the strong increase of the absorbance corresponded to the π-π* electronic transition of azobenzene chromophores in the E-form. Simultaneously, the increase in the absorbance in the whole region of the spectrum due to the crystallization process of the E-isomer occurring during the back Z-E isomerization and gelation are observed.

UV-light action results not only in changes in fluidity and optical properties, but also leads to a significant improvement of LC-alignment in cells with uniaxially rubbed polymer-coated glass substrates (Figures 2b, c). Just after gelation uniaxial alignment is disrupted by a dense physical network formation consisted of crystallites of **10BVIABr** (Figure 2b). Photoinduced melting of crystals induces good alignment of LC molecules in the cell (Figure 2c).

The observed phenomenon of the photoinduced gel-sol transition was applied for the photomodulation of fluorescent properties of the LC-mixtures doped with fluorescent dyes. The nematic mixture containing gelator was doped with 0.2 wt% of the dye **DCM2** possessing fluorescence in red spectral region.



DCM2

Nematic mixture in gelled state sandwiched in uniaxially aligned cell has relatively low degree of fluorescence polarization (Figure 4a). Values of emission anisotropy R were calculated using eq. 1:

$$R = (I_{\|} - I_{\perp}) / (I_{\|} + I_{\perp}) \qquad (1)$$

where $I_{\|}$ and $I_{\perp}$ are the intensities of light emission polarized parallel and perpendicular to the alignment direction, respectively. R value for LC-gel is 0.16; such low value is explained by the above-mentioned formation of dense network of gelator crystals preventing good alignment of LC and dye molecules. Subsequent UV-irradiation and photoinduced melting of the gel results in strong increase in degree of polarization up to R=0.36 (Figure 4a), due to the strong improvement of the molecular alignment in LC-cell (see also POM images in Figures 2b, c).

The same idea was applied for the preparation of cholesteric mixture with phototunable circularly-polarized fluorescence. For this purpose nematic gel was doped with the mixture containing of chiral dopants - cholesteryl pelargonate (**CholPel**, 25.9%) and cholesteryl valerate (**CholVal**, 23.6%). Combination of two chiral substances was used in order to avoid any phase separation in the mixture and improve miscibility of the components. As for the nematic gel UV-irradiation results in the gel-sol transition and melting of the cholesteric gel (Figure S6). Concentration of the chiral substances was selected to obtain selective light reflection in red spectral region (Figure S7) coinciding with **DCM2** emission. The obtained mixture forms left-handed helical cholesteric structure. Overlapping of selective light reflection peak (or photonic band gap) of cholesteric phase and fluorescence peak allows one to obtain strong circular polarization of the emitted light. [23-25] As seen from the spectra of circularly-polarized fluorescence (Figure S8) the left-handed component of emission has pronounced gap in intensity coincided with selective light reflection peak of the cholesteric mixture.

Using spectral data and eq. 2 dissymmetry factor g_e characterizing degree of circular polarization of the emitted light was calculated. [23]

$$g_e = 2 (I_L - I_R) / (I_L + I_R) \qquad (2)$$

Figure 4b shows dependence of g_e on wavelength of cholesteric LC-gel before and after UV-irradiation. Negative sign of dissymmetry factor in the range of selective light reflection corresponds to a lower intensity of left-handed circularly polarized light that is explained by the "forbidden" penetration of left-handed component through the cholesteric helical structure with the same handedness. [23-25]

Photoinduced melting of the LC-gel improves planar alignment in the LC-cell and simultaneously increases absolute values of g_e (Figure 4b). In other words, UV-irradiation and photoinduced melting of LC-gel are able to realize photomanipulation of degree of circular polarization in such systems.

Conclusions

In conclusion, for the first time we have prepared photochromic LC-gels based on low-molar-mass bent-shaped gelator which are capable of reversible melting under UV light action. So the light irradiation allows one to manipulate phase behaviour, fluidity and optical properties of gels that can be used for the study of the unusual phase phenomena in LC systems. In addition, nematic and cholesteric mixtures with phototunable degree of linearly or circularly-polarized fluorescence were elaborated exploring effect of gel-sol transition studied in this work. Future investigations will focus on the investigations of the peculiarities of thermal and photo-optical behavior of such systems, as well as the search for new photochromic gelators for different LC matrices.

ACKNOWLEDGMENTS

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Experimental part

Synthesis and detailed characterization of new photochromic azobenzene-containing bent-shaped compound **10BVIABr** are presented in Supporting Information (Figures S1-S5).

The polarizing optical microscope investigations were performed using LOMO P-112 polarizing microscope equipped by Mettler TA-400 heating stage. DSC curves were obtained using Perkin Elmer DSC 8500 calorimeter. Photochemical investigations were performed using an optical set up equipped with a DRSh-350 ultra-high pressure mercury lamp and UV LED (380 nm). To prevent heating of the samples due to the IR irradiation of the mercury lamp, a water filter was introduced in the optical set-up. To assure the plane-parallel light beam, a quartz lens was applied. Using the filters a light with the wavelength 436 nm was selected. The intensity of light was measured by LaserMate-Q (Coherent) intensity meter and was equal to ~8.0 mW/cm^2 (380 nm) for LED and ~1.0 mW/cm^2 (436 nm) for lamp. Spectral measurements were performed using Unicam UV-500 UV-Vis spectrophotometer.

Linearly and circularly polarized fluorescence was measured using M266 spectrometer (Solar Laser Systems). As excitation source 532 nm diode laser MGL-FN-532-1W was used.

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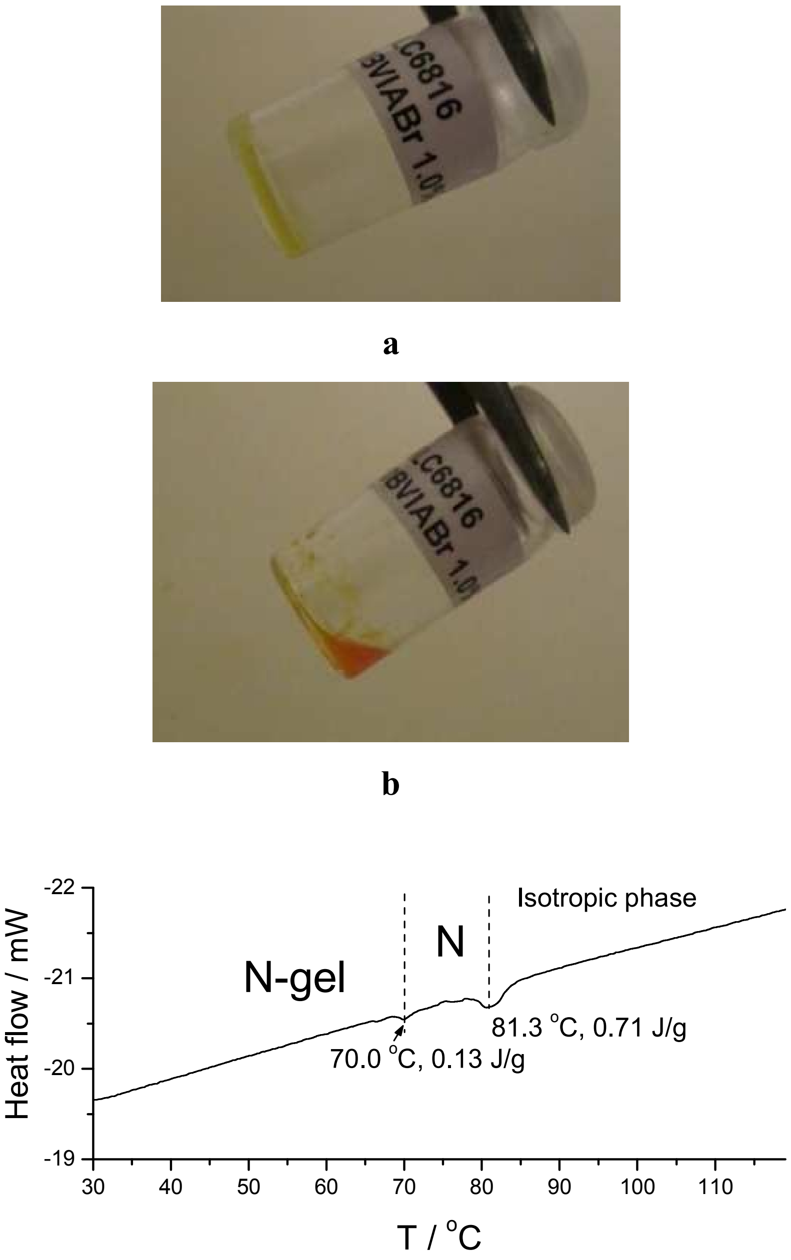


c

Figure 1. Photos of LC mixture containing 1.0 wt% of gelator **10BVIABr** before (a) and after (b) UV-irradiation (380 nm, ~8 mW/cm^2, 10 min). (c) DSC curve of the nematic gel containing 2.6 wt% of the gelator (first heating scan obtained with rate 10 ^{o}/min).

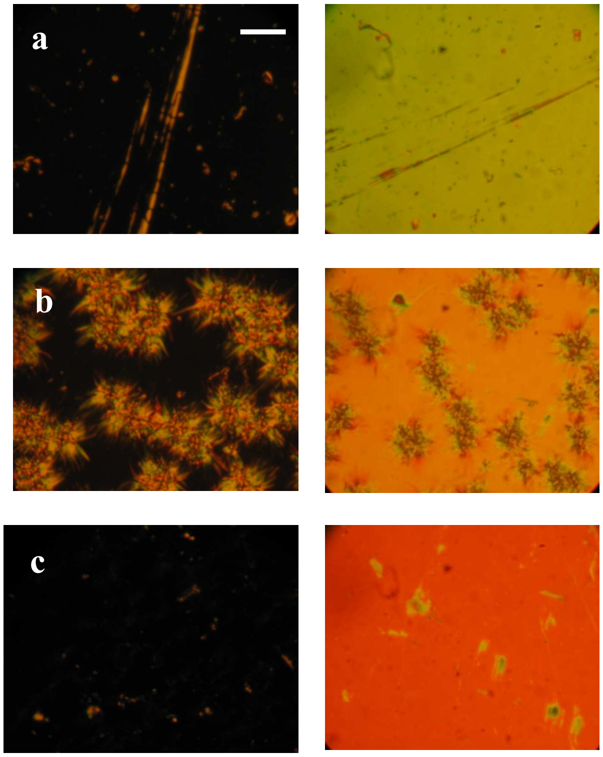
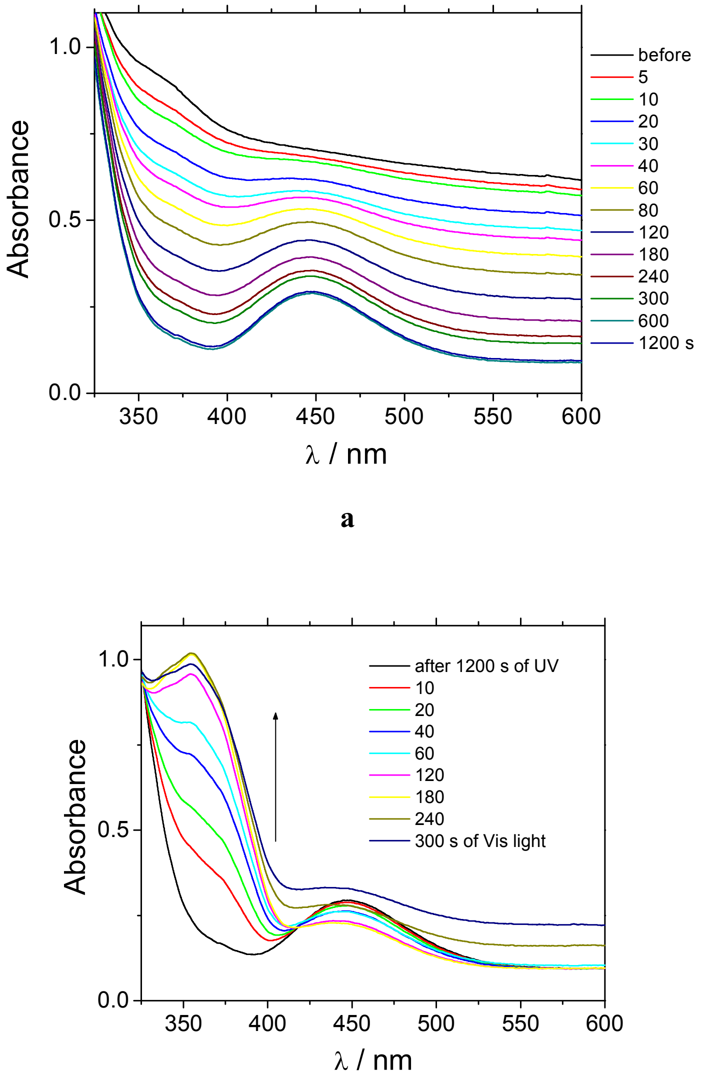


Figure 2. (a) Microphotos of the images taken from polarized microscope in crossed polarizers for mixture containing 1 wt% of gelator just after cooling from 120 ^{o}C to room temperature. (b) The same cell after annealing at room temperature for two days. (c) After UV-irradiation (380 nm, ~8 mW/cm^2, 10 min).Cell thickness is 5 µm; glass substrates are coated with polyvinyl alcohol layer uniaxially rubbed in one direction. At the right of the Figure the same samples rotated at 45 ^{o}C in respect of left ones are shown. Scale bar is 100 µm.



a

b

Figure 3. Changes in absorbance spectra of the gel containing of 2.6 wt% of gelator (a) during UV-irradiation (380 nm, ~8 mW/cm^2) and (b) subsequent visible light irradiation (436 nm, ~1.0 mW/cm^2). Cell thickness is 30 μm.

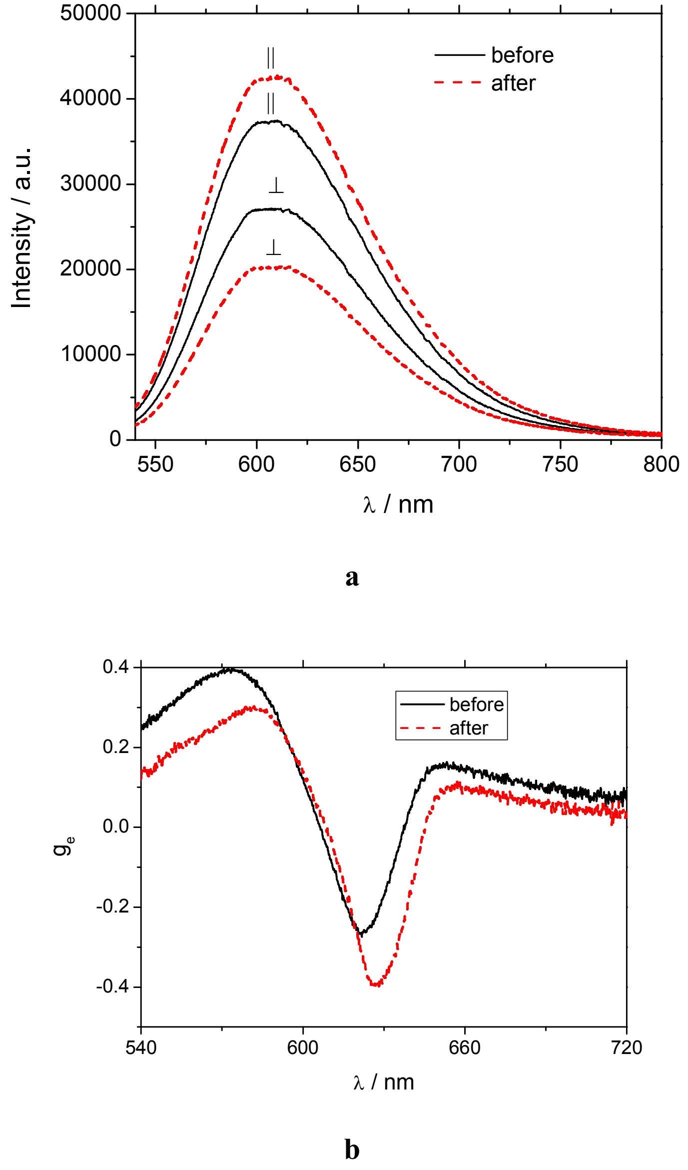


Figure 4. (a) Polarized fluorescence spectra of the aligned cell (5 μm) filled with the mixture **MLC6816+10BVIABr 1.0% + DCM2 0.2%** before and after photoinduced gel-sol transition (10 min of UV-irradiation, 380 nm). Excitation wavelength is 532 nm. Anisotropy of fluorescence polarization at 607 nm before irradiation R=0.16, after irradiation R=0.36.

(b) Changes in dissymmetry factor after photoinduced gel-sol transition during UV-irradiation (380 nm, 20 min) of the cholesteric mixture (**MLC6816 48.8% + CholPel 25.9% + CholVal 23.6% + 10BVIABr 1.5% + DCM2 0.2%**).