

Photo-stimulated electro-optic response of liquid-crystalline system with *trans-cis* photo-isomerizable agent

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Abstract. A rather strong photo-stimulated enhancement of photo-induced bend flexoelectric effect based on *trans-cis* photoisomerization of azo bond was found in a guest-host system formed from the nematic liquid crystal (LC) *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA) as a host, and the azobenzene LC 4-hexyloxybenzoxo-4'-cyanoazobenzene, as a guest photoactive agent at 1 wt.% concentration. Upon application of electric field, thin homeotropic layers of thickness 100 μm containing this photo-sensitized LC mixture were investigated as subjected to a relatively weak illumination with UV light ($\lambda = 375$ nm, from narrow-band light-emitting diode, LED). The stimulation of the photoactive electro-optic response of azobenzene-doped MBBA (owing to enhanced photo-induced bend flexoelectric effect driven by the photo-isomerizable dopants) was achieved by pre-resonant excitation of the photoactive agent. The degree of the effect measured is of potential interest for thin-film photoactive electro-optic applications. The UV light-induced effect in azobenzene-doped MBBA was reversible; the back (relaxation) process was stimulated by light in the blue from a LED with broadband spectrum centered at 455 nm.

1. Introduction

In the field of liquid crystal (LC) physics, flexoelectricity is well known [1, 2]. Under external electric field applied on the LC cells, the LCs exhibit flexoelectric polarization with magnitude depending on the LC material. The flexo-electric effect can be stimulated by light [3]. In the past, photo-induced dipolar flexoelectricity in homeotropic guest-host nematics upon UV illumination has been reported for a guest-host system formed by the photo-responsive azobenzene compound *p*-nitro-*p'*-diethylamino-azobenzene (D1), as a guest in a small concentration, and the nematic LC *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA) as a host [4]. This UV light-induced effect related to the photo-dependent flexopolarization, labelled thereafter photoflexoelectric effect (PFE), results from *trans-cis* photoisomerization of the azo bonds of the guest compound.

The photoactive properties of azobenzene molecules are well known [5, 6]. In particular, azobenzene-doped nematics exhibit a wide variety of photo-physical and photoswitching effects [3, 7, 8], and the useful functions of this important class of synthetic photochromic LC materials have attracted much attention due to the large potential for specialty and high-technology applications [9-13]. Recently, we have investigated photosensitive guest-host systems composed of a nematic LC (as a host) mixed with the novel photoactive azobenzene compound LC 4-hexyloxybenzoxo-4'-

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cyanoazobenzene (UI-147) as a guest [14–16]. For thin (100 μm or less) homeotropic layer of such LC mixtures, the decisive role of the subsurface layer for the observed PFE was concluded. Here, we present an experimental study on PFE in thin (100 μm) homeotropic layers of nematic MBBA doped with UI-147 molecules. The enhanced photo-stimulated electro-optic response of this photosensitized nematic LC material is characterised in terms of the PFE concept [3,4,17,18], but our research is focused mainly on the photo-stimulation of the photo-physical mechanism involved that is closely related to the practical applicability of the effect and corresponding photoactive LC materials.

2. Experimental

The host compound in the investigated LC mixture was the commercial nematogen *N*-(4-methoxybenzylidene)-4-butaniline (abbreviated as MBBA), known for a long time. The nematic-isotropic transition of this LC (from Reahim) is at 43°C. The photoactive agent in the mixture was the LC 4-hexyloxybenzoyloxy-4'-cyanoazobenzene (abbreviated as UI-147, the chemical structure is given in figure 1 a). This stable (chemical- and photo-stable) azo-containing LC compound was synthesized at the Centre for Nano and Soft Matter Sciences in Jalahalli (Bangalore, India) and exhibited photophysical properties very suitable for photoactive device applications [15]. In present study, the concentration of the 'guest' UI-147 in the guest-host UI-147/MBBA molecular system was 1 wt.%. The nematic phase of UI-147 is at a relatively high temperature. However, a photoactive room-temperature LC material can be composed from UI-147 by mixing with proper room-temperature nematic LC [15], as MBBA.

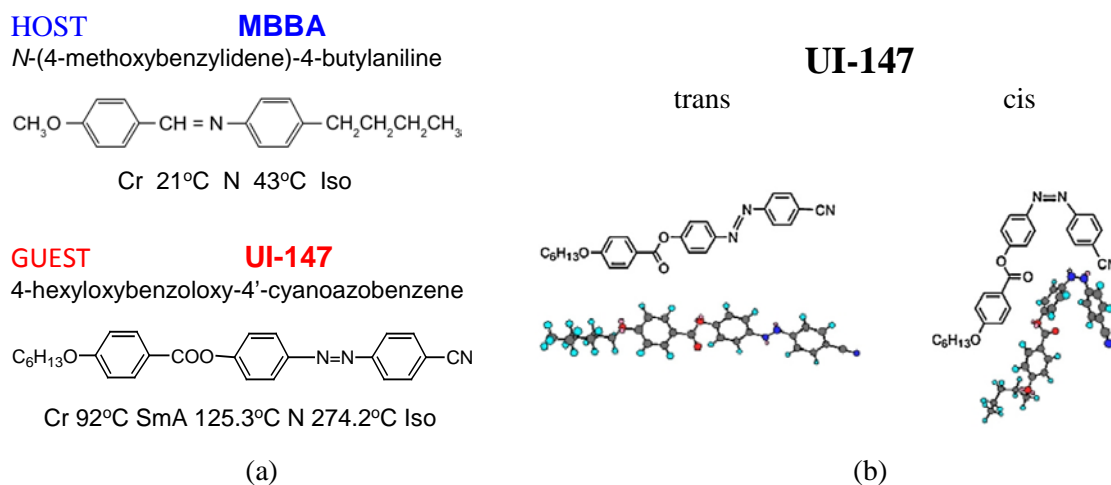


Figure 1. (a) Molecular structure of the host MBBA and azobenzene dopant UI-147. The phase transition temperatures are given. (b) *Trans* (in the left) and *cis* (in the right) conformers of UI-147.

For the investigation, homeotropic layers of UI-147/MBBA with a thickness of 100 μm were prepared. The LC mixture was sandwiched in glass cells as described in [16, 19]. Cells of dimensions 1.5 cm \times 2 cm were assembled from two parallel 1 mm-thick glass plates. The copper spacers between the plates served as electrodes, with their separation being 2 mm. Initial homeotropic orientation of the LC layer was achieved using self-assembled layers of lipid lecithin [20, 21]. Identical cells, but filled with pure MBBA, were also prepared in order to be measured as reference cells in our study.

The photo-stimulated electro-optic response of the prepared UI-147/MBBA layers was studied by measurement of probe beam transmittance through the LC cells placed between crossed polarizers and subjected to a transversal DC electric field. The measurements were performed using the experimental setup schematically shown in figure 2. Linearly-polarized output of He-Ne laser (wavelength $\lambda = 633$ nm) with a power of ~ 1 mW was used as a probe beam at normal incidence on the sample. The power stability of this laser source was better than $\pm 1\%$.

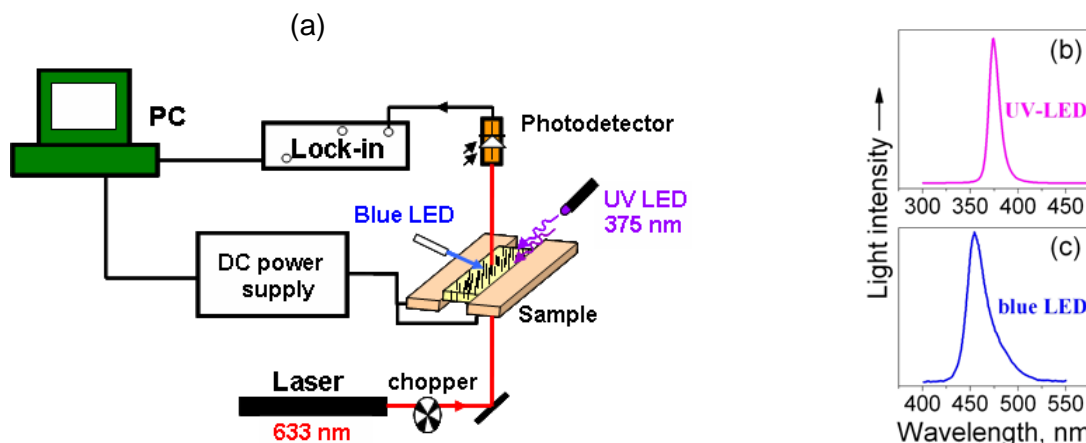


Figure 2. (a) Schematic drawing of the experimental set-up used in this work. In the right: spectral characteristics of the LEDs employed: (b) UV-LED; (c) blue LED.

The azobenzene conformers in the samples were photo-driven with two continuous light sources (light-emitting diodes, LEDs), ‘UV-LED’ and ‘blue LED’, of a relatively low optical power but highly directed unpolarized outputs. The emission from the UV-LED (type NSHU550A, Nichia Corporation, Japan) with a flux 2 mW (can type, lens window, directivity 10°) was at $\lambda = 374.6$ nm. (Since this wavelength is close to the spectral range of the visible, the light is actually UV-visible, and can be observed with naked eye). The UV-LED was narrow-band ($\Delta\lambda = 12$ nm fwhm). The second LED (LED ENERGY curing unit, model 405-8B, Optica Laser, Bulgaria) emitted a broader spectrum ($\Delta\lambda = 23$ nm fwhm) with a peak at 454.5 nm.

The LED illuminators were mounted on holders with micrometer motion. Thus, the UV-visible and the blue light spots of non-focused light were carefully coincided at the central zone of the LC cell, probed with He-Ne laser beam. Through a circular diaphragm, the diameter of both spots on the sample was kept fixed to extent slightly smaller than the gap between the cell electrodes. The light intensities on the sample surface was adjusted by varying the distance between the LEDs and the sample. In order to avoid the unwanted effect of so called ‘surface melting’ (light-induced tilted anchoring) well established for the photoactive UI-147/MBBA mixture under study [22], the light intensity from the UV-LED on the sample was kept below 3 mW/cm^2 . The blue LED light (attenuated) intensity on the sample was $\sim 50 \text{ mW/cm}^2$. Special care was taken to minimize, if not completely eliminate the effects from the unwanted stray and reflected light from various sources on the measured signal modulated by PFE.

DC voltage up to 40 V (applied between the copper electrodes of the cells) was supplied by Instek GPD-4303S Programmable Linear DC Power Supply. The same 4-channel device was employed to supply the two LEDs (DC voltage stability $\pm 0.01\%$) and to command their output on/off functions. The DC electric field-dependent light transmittance of the LC cells was measured with a silicon photodiode as a detector, and computer-controlled lock-in amplifier (SR830 DSP, Stanford Research Systems). The PFE was also measured as depending on alternating current (AC) electric field applied on the LC cell. In this case, a sinusoidal voltage was applied and the field frequency was swept in the range from 1 Hz to 1 kHz. A computer handled the data acquisition from the lock-in instrument and also controlled the frequency sweeps.

The morphology of the samples was characterized by a transmission optical microscope (Zeiss NU-2 Universal Research Microscope). The optical absorption of the samples in the wavelength region of 300 – 800 nm, and at room temperature (ca. $22 - 24^\circ\text{C}$), was measured by means of Perkin Elmer Lambda 1050 spectrophotometer. The spectral resolution was 1 nm. During the PFE experiment the sample temperature was maintained (to within $\pm 0.1^\circ\text{C}$) by a Mettler FP82 hot stage.

3. Results and Discussion

The homeotropic alignment of the prepared layers was inspected by a polarizing microscope set for crossed polarizer configuration. The high quality and extent of uniformity of the homeotropic orientation in the absence of electric field and light illumination by the LEDs was confirmed by conoscopy. Also, the lack of a ‘surface melting’ of the samples upon the UV-light illumination with a relatively low intensity we have employed ($< 3 \text{ mW/cm}^2$) was verified by optical microscopy.

As known, the azobenzenes exhibit *trans* and *cis* isomers. Figure 3 (a) reports the UV-visible absorption spectrum of UI-147 where the specific spectral shapes due to the *trans* and *cis* isomers of this azobenzene are seen (the bands at 335 nm and 450 nm, respectively). Figure 3 (b) compares the optical absorption measured for the LC cell with UI-147/MBBA mixture to that with pure MBBA (both not illuminated). The effect from the UI-147 dopants can be clearly seen.

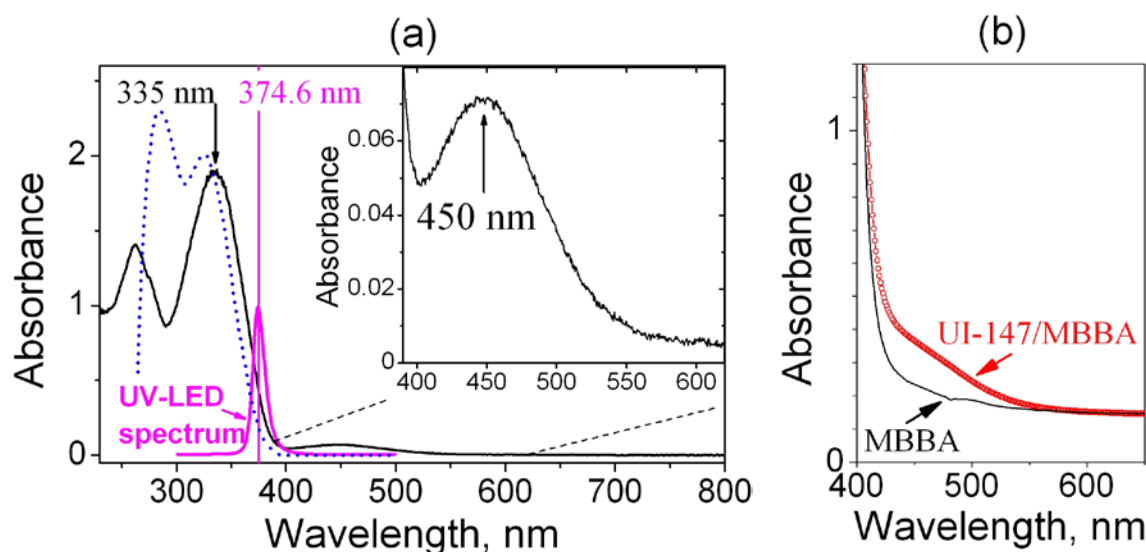


Figure 3. (a) UV-VIS absorption spectra of chloroform solutions of 0.01 % UI-147 (solid line) and 0.13mM MBBA (dotted, blue). The insert shows an expanded part of UI-147 spectrum in the blue-green region; (b) The optical absorption measured for UI-147/MBBA mixture (1 wt.% UI-147) and pure MBBA, both in 100 μm -thick cells with homeotropic alignment, not illuminated by the LEDs used here. The spectra were recorded under identical conditions.

By illumination at a wavelength lying in the absorption region, azobenzene molecules can undergo *trans-cis-trans* conformation (isomerization). This is the operation mechanism of the azobenzene-containing and azobenzene-doped LC materials for photo-control in electro-optics and photonics [3, 7–13, 23–31]. Upon illumination by UV light with appropriate wavelength and intensity, the UI-147 molecules isomerize from *trans* to *cis* form. Thus, by absorbing the UV light energy, the molecule shape of this organic compound is changed from rod-like to a bent-shaped one (see figure 1b). The corresponding change in the optical absorption after this photo-induced effect in the studied UI-147/MBBA mixture under the actual conditions of our experiment on PFE (reported below), is evident in figure 4. The resulting difference spectrum for UI-147/MBBA (see the insert in figure 4) represents the spectral absorption band of the *cis*-conformers of UI-147. Its presence indicates an efficient *trans*-to-*cis* photoisomerization of this azobenzene, even when a small part of the UV-light energy is absorbed by UI-147.

Actually, by UV-visible light ‘pumping’ of the UI-147 photo-agent one should consider in our case a combination of three factors: (i) the relatively low intensity of the UV-visible light incident on the sample; (ii) UI-147 excitation in the wing of its absorption band (pre-resonance condition, see figure 3

a); and (iii) the UV-light intensity loss due to the strong absorption from the host MBBA itself (figure 3b). Overlapped with the UI-147 absorption, the host MBBA absorption is crucial for the light pumping in the *trans*-form absorption band of UI-147, because this azobenzene is only 1 wt.% in the UI-147/MBBA mixture. Since the main absorption band of UI-147 is somewhat shifted to the longer wavelengths with respect to the MBBA absorption (figure 3a), the pre-resonant excitation of UI-147 becomes a favourable way for *trans*-to-*cis* photoisomerization. Upon pre-resonance conditions, the excitation wavelength is longer than the resonance wavelength but still corresponds to some small portion of the absorption spectrum. Usually, such an excitation is applied to avoid the non-desirable resonant molecular fluorescence. This approach is commonly used in resonance Raman spectroscopy (especially in various techniques of the coherent Raman spectroscopy). The pre-resonant excitation allows the loss and the other effects due to absorption to be minimized, generates much less molecular fluorescence and background noise.

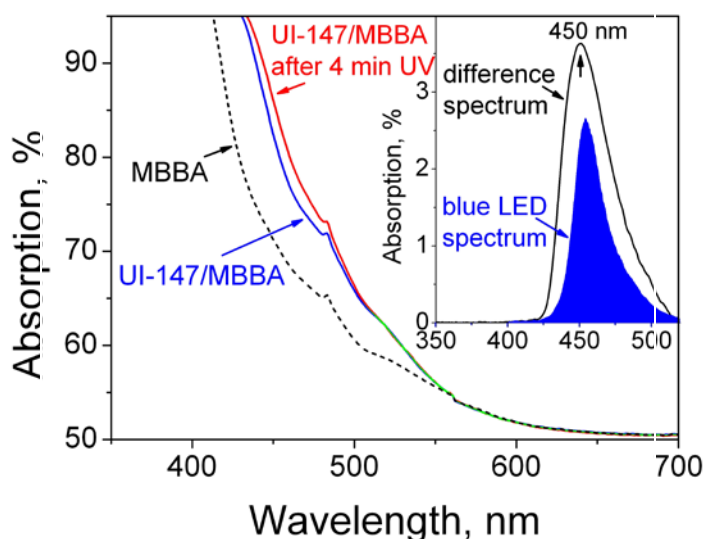


Figure 4. Absorption spectra of UI-147/MBBA recorded without (blue curve) and with (red curve) 4 min illumination with the UV-LED putted within the spectrophotometer. For the sake of comparison, the absorption spectrum of reference MBBA cell is also given (dotted). The spectra were taken under identical conditions and were corrected by the absorption recorded for an empty glass cell identical to the cells containing the LCs. The shoulders at ~ 480 nm are due to apparatus artifacts (from the lighting lamps of the spectrophotometer). In the insert is shown the difference of the UI-147/MBBA spectra (illuminated – non-illuminated UI-147/MBBA).

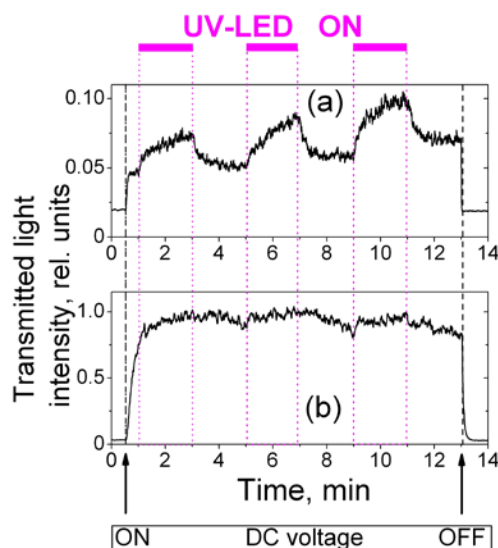


Figure 5. The time dependence of the variation of the intensity of probe He-Ne laser beam transmitted through homeotropic cell with UI-147/MBBA (a) and pure MBBA (b), both 100 μm -thick, in response to the light from UV-LED and the DC voltage ON-OFF switching. The illumination time intervals were fixed at 2 minutes alternated with equal dark periods (the periodical ON-switching of the UV-LED illuminator is indicated at the top). The UV-LED light intensity on the sample was 1.2 mW/cm^2 , the DC voltage applied on the cell was 40 V, the temperature of the cell was 28°C .

Being considerably weaker in the blue spectral region (the absorption region of the UI-147 *cis*-form), the MBBA absorption (extended up to 520 – 550 nm, figure 3 b) should not strongly affect the photo-induced *cis*-to-*trans* back-isomerization. By comparison of the difference spectrum in figure 4

with the spectral band of our blue LED (see the insert in figure 4), one can expect (due to their optimal overlap) an efficient *cis*-to-*trans* back-photoisomerization of UI-147 azobenzene in the UI-147/MBBA cell under study. In fact, this was confirmed in our experiment and the observed chromism was fully reversible indeed. On the other hand, no change in the MBBA absorption was present upon illumination with the LEDs under the same experimental conditions.

Based on the above absorption spectral behaviors and the observed efficient interaction of the irradiation of both UV-LED and blue LED with the UI-147/MBBA under study, we probed the PFE in this photoactive guest-host system. The photoflexo-electrooptical response of homeotropic layers of UI-147/MBBA placed between crossed polarizers and subjected to in-plane electric field directed at 45° with respect to the polarizer axes orientation (figure 2) was studied by measurement of the changes in the transmitted 'probe'-light intensity by switching the 'pump'-light and electric field applied, as well as by varying the latter.

A time scan for examined UI-147/MBBA thin homeotropic layer being illuminated with the UV-LED, is shown in figure 5(a). As seen, a significant increase in the transmitted light intensity takes place. The mechanism of the registered PFE is similar to the one observed for other guest-host LC systems containing nematic LC as a host and the same photoactive azobenzene compound UI-147 as a guest [14, 15] - the near(sub)surface region rich of azo molecules is responsible for the observed PFE. The azo molecules adsorbed at the top surface and those located within the subsurface region, contribute to the photoflexo-response of the examined guest-host system. It should be noted that under the same experimental conditions, we have found no such effect in the reference MBBA cells (figure 5(b)). We have to point also out that the influence of any scattered light, light reflections, as well as possible luminescence/fluorescence from the UI-147/MBBA cells (excited by the UV-LED) on the measured transmitted light intensity, that could disturb the registered signal resulting from PFE (the transmitted probe light intensity), were negligible, as we have accurately proved in the course of the experiment.

The low intensity of the light illumination minimizes the possible thermo-induced effects. Further, owing to the low level of the incident UV-light intensity, the PFE was properly distinguished from the accompanying phenomenon 'surface-melting' of the photo-driven LC command surface. Such unwanted effect was found in identical cells with homeotropic layers of the same UI-147/MBBA mixture [22]. Upon UV light, the near(sub)surface region enriched with azo-molecules that is responsible for the PFE can be affected by the 'surface-melting' anchoring transition that disturbs the homeotropic alignment. That is why, to avoid this effect in the present experiments, the UV light intensity on the sample was reduced below the levels at which the effect of tilted anchoring occurs ($\sim 10 \text{ mW/cm}^2$ at $\lambda = 375 \text{ nm}$ [22]).

The characteristics of the PFE were consistent with those previously discussed in details in [4]. The magnitude of the flexoelectricity that was photo-induced in the mixture was much higher than that in the nematic host alone. Figure 6 (a) shows the DC voltage-dependent behavior (static electro-optical characteristic measured by chopped at 90 Hz probe beam), and figure 6 (b) - the photo-dependent component of the flexopolarization (the first harmonic of the modulated optical signal from transmittance of the cell) as a function of the frequency of AC electric field applied on the cell (dynamic electro-optical characteristic). The DC voltage dependences of both dark and light flexoresponses followed the theoretical predictions [4,32]. Also, a clear photo-stimulated enhancement of the amplitude of the AC electric field-excited flexo-oscillations was registered.

Figure 7 presents time courses for examined thin homeotropic layer of UI-147/MBBA with exposure to light of both UV-LED and blue LED, showing the quenching and recovery of photo-induced flexoelectric deformations of azobenzene doped MBBA by repeating cycles of alternating switching of the blue LED (the UV-LED is turned-on and remains in the ON state for the rest of the experiment). As seen, the relaxation process is accelerated by the *cis-trans* back-isomerization of the UI-147 azo chromophores after illumination with the blue LED. The lack of noise in the time behaviors is because of the higher level of the signal due to higher intensity of the illumination with the UV-LED

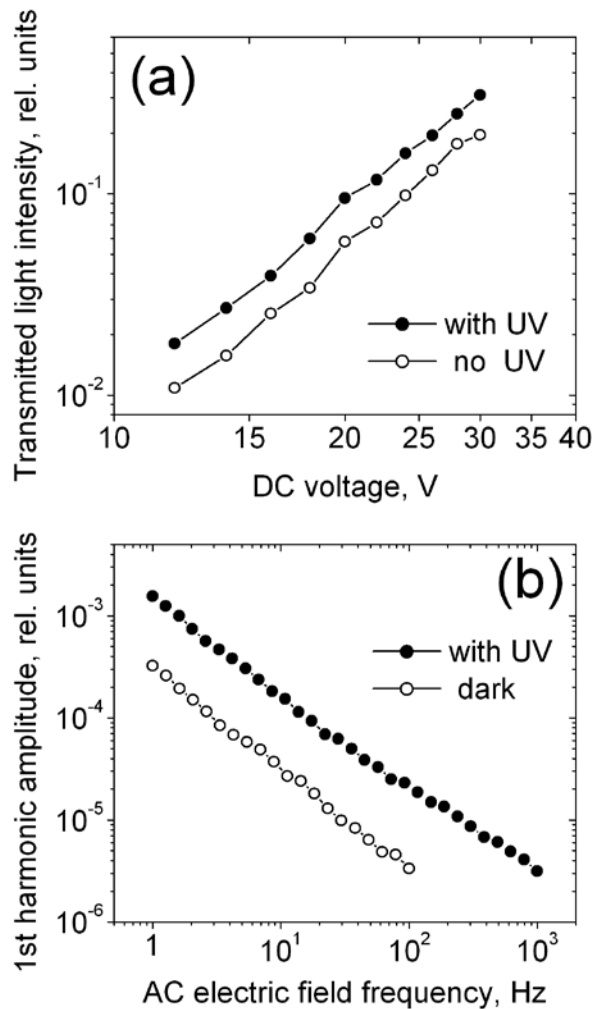


Figure 6. Log-log plot of transmitted light intensity vs DC voltage (saturated flexoresponse) (a) and the frequency dependence of the amplitude of the flexo-oscillations (the first harmonic of the modulated light signal) (b) of the layered UI-147/MBBA. The UV-LED light intensity on the sample was 1.2 mW/cm^2 , the temperature of the cell was 27°C .

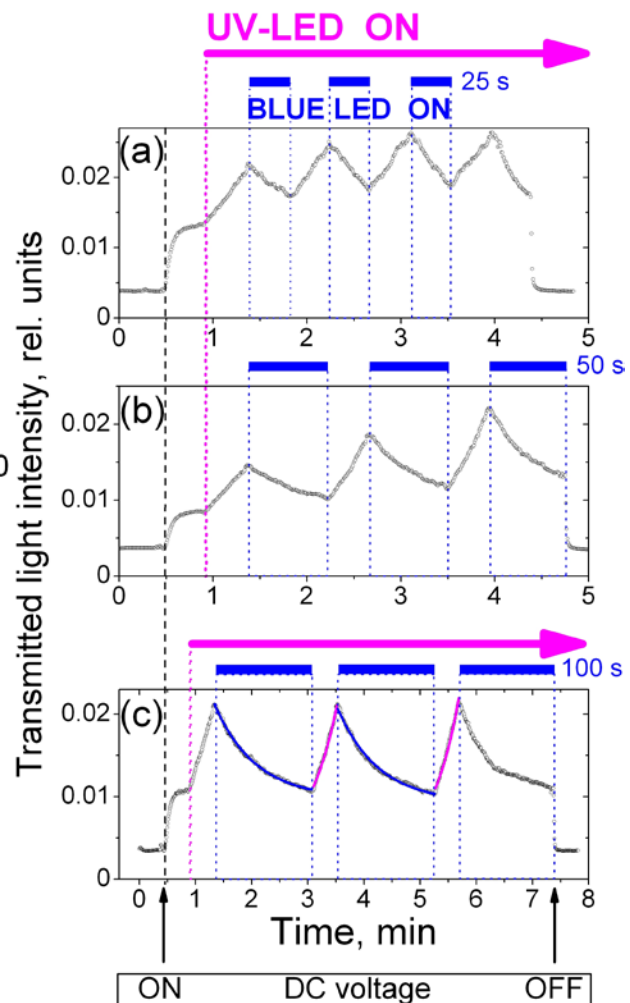


Figure 7. As in figure 5 (a), but the UV-LED lighting was steady, and the illumination with the blue LED was switched-on with periods of: 25 s (a); 50 s (b); 100 s (c), alternated with a switch-off periods of 25 s (the light switching regime is shown at the top). The lines in (c) represent the fits to the experimental data. The UV-LED light intensity on the sample was 3 mW/cm^2 , the DC voltage applied on the cell was 40 V, the temperature of the cell was 28°C .

One can compare the PFE in the measured UI-147/MBBA mixture by varying the blue LED illumination interval. When the duration of the later is long enough (or the blue LED intensity is higher), the signal relaxes to the initial background level (figure 7 c), i.e. a steady dynamic balance at alternating cycles of the UV-visible irradiation occurs. The experimentally obtained temporal variation of both rise and decay parts of the PFE behavior can be exactly fitted by a simple mono-exponential

function. The values of the corresponding rise and decay time constants determined in this case to be ≈ 31 s and ≈ 42 s, respectively, indicate a slow response to the illumination switching, as expected. Compared to relaxation times reported in [4] (≈ 15 s), the photo-stimulated process for the photo-responsive UI-147/MBBA material studied here, is about two times slower. It may be noted that the photoisomerization of azobenzene derivatives is a fast process, e.g. it is completed within 10 ns [33].

At the present level of UV-light intensity, the observed PFE is considerably stronger as compared to the result (12 % – 18 %) reported previously [4] for a guest-host system formed by MBBA as a host and the azobenzene dye D1 as a guest, under comparable experimental conditions (including the azobenzene concentration, the cell thickness, the applied DC voltage and temperature). The reasons could be: (i) a higher photo-induced bend flexopolarization in UI-147/MBBA than that in D1/MBBA (indeed, photoisomerization of the strongly polar UI-147 azobenzene molecules possessing a large longitudinal dipole moment and asymmetric molecular structure (polar-non polar asymmetry in the end substituents) [16], was found to be able to induce a strong PFE in nematic LCs [14, 15]); and/or (ii) stronger or more optimal UV illumination as compared with that used in [4]. Note that the UV illumination at 334 nm (Hg spectral line from a spectral lamp) employed in [4] is close to the absorption peak of the host MBBA (recall figure 3a). In our present experiment, the pre-resonance UV illumination is more favorable because in this way is avoided the strong absorption from the host MBBA (which is a loss, actually, and can bring negative effects), and in the same time provides for a sufficient photoisomerization of the guest.).

Obviously, as compared with high-performance organic photochromic molecular systems that possess very efficient electronic transition and energy transfer processes [34,35], the efficiency and speed of the photochromic function (based on photo-flexo-electro-optic response) of the azobenzene-doped photo-sensitized nematic LC studied here, are lower. Nevertheless, such azo-doped nematics (being sensitive photoactive LC materials with a wide temperature range for the nematic phase) can be still useful for practical applications (e.g., light-commanded electro-optic modulators and switches), in the case when the speed is not of crucial importance.

4. Conclusion

Here we report on enhanced photoflexoelectric effect in azobenzene-doped nematic MBBA. Through an efficient photochromic *trans-cis* photoisomerism, the azobenzene chromophores in MBBA allow the electro-optic response of thin homeotropic layers with the doped MBBA to be efficiently controlled by UV-visible light irradiation of the layers. Based on photo-induced flexoelectric polarization, a reversible and steady photomodulation is achieved by the doped MBBA layers at alternating cycles of the UV-visible irradiation. Even at the relatively low (1 wt.%) concentration of the azo photoresponsive agent and the low-intensity illumination with UV-visible light, the *trans-cis* photoisomerization is sufficient to drive the electro-optics of the doped MBBA layers and to efficiently modulate the intensity of the light transmitted through them.

Our study shows that upon optimal illumination the photo-stimulated electro-optic response of azobenzene-doped nematics can be enhanced to a degree that can be suitable for electro-optic applications utilizing the photoactivity of the azo-dopants. To achieve an efficient *trans-cis* photoisomerization, the preresonant excitation with UV-visible light can be a reasonable alternative against the illumination by UV light at the azobenzene absorption peak. In this way, the amount of the produced *cis*-form of the photoactive dopants can be sufficient to enhance the light-induced flexoelectrooptic effect activated in the doped nematic layers. The results reported here will be useful for the practical applications of LC-based photoresponsive materials for the photo-controlled electro-optics and photonics.

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