Trans-cis photoisomerization-induced tilted anchoring in photoactive guest-host liquid crystalline systems

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Abstract. We report on UV light-induced tilted anchoring in a mixture of the nematic liquid crystal N-(4-methoxybenzylidene)-4-butylaniline (MBBA) with a photoactive liquid crystalline azo dye (4-hexyloxybenzoxy-4'-cyanoazobenzene) at 1 wt.% concentration. The surface anchoring found in this guest-host liquid-crystal system confined in homeotropic thin films is due to trans-cis photoisomerization of the guest azo molecules upon UV light.

1. Introduction
Of great interest for various applications of liquid crystals (LCs) are highly aligned and well ordered LC layers [1-3]. For the nematic LCs (as most exploited LCs) three basic types of LC alignment (known as anchoring) can be achieved depending on the boundary conditions: homeotropic, planar and tilted [4]. In order to control the LC surface anchoring, temperature-driven or light-driven layers acting as command surfaces, are commonly applied [5-10]. In all cases, both anchoring and orientational order are affected. The substantial depression of the order near the LC surface attracts a considerable attention [11-14] since this unwanted effect destroys the surface-induced order, and thereby the homogeneity of the anisotropic properties of the LCs [15].

Here we report on a kind of photo-induced anchoring at the surface of LCs, namely trans-cis photoisomerization-induced tilted anchoring, in a photoactive guest-host LC system. In particular, a homeotropic layer of a LC mixture consisting of a nematic LC as the host, and a photo-responsive LC azo dye as the guest, was considered.

2. Experimental
In the investigated mixture, the nematogen N-(4-methoxybenzylidene)-4-butylaniline (MBBA) was the host compound. The nematic-isotropic transition of this LC (from Reahim) is at 43°C. The azo dye 4-hexyloxybenzoxy-4'-cyanoazobenzene (UI-147, the chemical structure is given in figure 1) was the photoactive guest. In the guest-host system, this liquid-crystalline compound synthesized at the Centre for Soft Matter Research in Bangalore, India, was present at a concentration of 1 wt.% (not eutectic mixture).

For the investigation, a sandwich type cell was prepared in a manner similar to that described in [16]. The cell of dimensions 1.5 cm × 2 cm, was assembled from two parallel 1 mm thick glass plates,
and had a gap of 2 mm, defined using cooper spacers. They also served as electrodes. Initial homeotropic orientation of the LC layer was achieved using self-assembled layers of lipid lecithin [17]. The employed procedure of dipping the glass plates in a lecithin/chloroform solution of 20μM concentration resulted in loosely packed orienting layers [18]. The cell was filled with the LC mixture in its isotropic phase, and subsequently cooled slowly to the nematic phase to achieve good homeotropic orientation of the molecules. An identical cell, filled with MBBA only, was used as a reference. The samples were placed between two crossed polarizers (figure 2).

![Molecular structure of the LC azobenzene dye UI-147. The phase transition temperatures are also given.](image1)

**Figure 1.** Molecular structure of the LC azobenzene dye UI-147. The phase transition temperatures are also given.

![Schematic representation of the experimental set-up used in this work.](image2)

**Figure 2.** Schematic representation of the experimental set-up used in this work.

3. Results and Discussion

Figure 3 presents the changes in the texture of the LC mixture upon light illumination. In the absence of the illumination by the LEDs, the field of view under the polarizing microscope in the crossed polarizer configuration is that of a good homeotropic alignment, proved also by conoscoppy. In the following, the time elapsed after switching the UV source on, is denoted as \( t \). It must be emphasized that once turned on, the UV source remained in the on condition for the rest of the experiment. At the beginning (\( t = 0 \), before the UV is on), a dark image, corresponding to the nematic phase with homeotropic orientation, is seen. Upon illumination by the two LEDs, the field of view changed as presented in figure 3. After \( t = 45 \) s, the texture starts changing from the cell periphery with the appearance of defects (figure 3(a)) spreading to the center. The bright part on the bottom right corner in the micrograph shown in figure 3(a) represents the change in LC anchoring to a tilted orientation.

Since the change is from a homeotropic to a tilted nematic orientation, a new state of anchoring starts to develop at the surface. The observed tilt-angle texture implies that the degree of homeotropic orientation within the sub-surface region of the LC layer decreases. The UV light-induced effect is continuously accumulated thus encompassing the whole cell area (figure 3(b)). The umbilicus-like texture visible in figure 3(b) indicates the presence of a conical degeneration of the LC director [4].
Figure 3. Polarizing microscope images of the textures observed for the LC mixture upon UV illumination after a lapse of:
(a) 45 s;
(b) 1 min 30 s;
(c) 2 min 15 s;
(d) 3 min;
(e) 4 min.

The blue light illumination starts after the instance (b).

The light intensities are:
UV LED - 11 mW/cm²;
blue LED - 15 mW/cm².

At $t = 1 \text{ min } 30 \text{ s}$, the blue LED was turned on, while keeping the UV LED also on. The effect from the blue light is the gradual shrinking of the tilted area, from the periphery to the center (figure 3(c)). The reduction of the tilted anchoring at the surface upon blue LED illumination results in a complete diminishing of the UV-induced effect, as seen in figure 3(d) and (e). Such reversibility suggests that the observed texture changes are not a consequence of the sample heating.

The spontaneous return to the homeotropic state is achieved by switching the UV light off. This indicates that the observed UV light-induced anchoring modification is monostable unlike the bistable reported in the literature [7]. This process is relatively slow, occurring on the timescale of an hour. At higher intensity of the LEDs, the observed texture changes become faster. All these features, as well as the texture changes as given in figure 3, are exactly reproducible upon illumination over repeated cycles. We have to point out that the above changes are not observed in pure MBBA sample under the same experimental conditions, at higher intensities of the UV LED, even up to 23 mW/cm². This rules out pure thermal effects (and heat transport) as the cause for the observed features.

Our results on UV light-driven anchoring can be compared to temperature-driven anchoring transitions reported for nematics [5,6], even in the presence of photoactive agent, in particular, an azo compound [8]. The theory of temperature-driven anchoring transitions explains them as due to: (i) decrease of the surface order parameter and (ii) the competition of aligning effects of both surface and subsurface region (the surface melting region). The first effect occurs at low temperatures while the
second is expected close to the nematic-isotropic (N-I) transition. Specific for our system is the ability of blue light to overcome the UV-driven effect and to quench the anchoring change. The non-thermal nature of the observed tilted anchoring is supported also by direct proof of the magnitude of the eventual temperature change (the heating) of the cell due to the UV light illumination in our experiment. For the purpose, the LC cell was replaced by a cholesteric LC thermographic sheet. The temperature variation estimated by thermal mapping with this sensitive thermoindicator was less than 1 K. Such a temperature change is negligible to bring about the nematic-isotropic phase transition, thereby proving that the UV-driven effect of tilted anchoring at the LC surface is not thermally induced (in any form, either non-local or local, e.g. by UV light absorption-induced thermal effects).

The tilted anchoring observed in our sample can be explained as due to a conformational change of the UI-147 azo compound. The loosely packed lecithin layer contains a lot of cavities. Those vacancies are naturally accommodated by LC molecules resulting in pronounced homeotropic anchoring. In the absence of the UV radiation, the UI-147 molecules are in the trans-conformation. Since the UI-147 molecule is polar, the concentration of trans-conformers in the near(sub)surface region is very high due to preferred adsorbance of polar azo molecules. Moreover, being highly polar in contrast to MBBA molecules, the azo-molecules presumably replace majority of them from the surface cavities. The molecular length of trans- and cis-conformers are respectively: 2.62 nm and 1.81 nm [19]. Now taking into account the average length of lecithin molecules to be ca. 3 nm [20], which scales with those of azo-conformers, we can assume formation of rugged interface upon UV photoizomerization. The latter modifies the LC surface leading to change of the surface anchoring similar to the case of surface-induced disorder [12]. In this sense, the effect observed here resembles the surface-melting transition (an effect due to depression of the order close to the surface) [11-14].

One of the related phenomena is the surface polarization. In particular it plays an important role for the flexoelectricity in LCs [21]. Thus, the near(sub)surface region enriched with highly polar azo-molecules serves as a ‘command surface’ for some pronounced photo-induced effects, e.g. it is responsible for the photoflexoelectricity found in homeotropic layer of a mixture of nematic LC with the same photoactive LC azo dye upon UV light illumination (in particular, at the wavelength of 365 nm) [22]. Upon UV illumination, the trans-conformers absorbing the light are transformed to cis form, and in the process losing their rod-like shape. As a consequence of anisotropy change, the nematic order in the sub-surface region is disturbed, leading to the umbilicus-like texture observed in our experiment (figure 3(b)). The observed photo-induced effect is a trans-cis photoizomerization-induced tilted anchoring at the LC surface. Conversely, the back recovery process takes place due to conformer cis-to-trans photoizomerization when the blue light is introduced.

The trans-cis photoisomerization of azobenzene dye UI-147 in the MBBA/UI-147 mixture under the conditions of the present experiment can be evidenced by monitoring the photo-induced change of the absorption of light passing through the LC layer. Figure 4 shows the absorption spectra in the wavelength range 420 – 500 nm obtained without and with illumination of the sample by the LEDs inserted within the spectrophotometer instrument, thus reproducing the experimental conditions close to those by the inspection of the tilted anchoring effect. The observed photo-induced spectral changes (figure 4) are indicative of the efficient interaction of the light of both UV and blue LEDs with the MBBA/UI-147 guest-host system, in spite of the relatively low light intensities. On the other hand, no change in the MBBA absorption (the reference cell) was present upon illumination with the LEDs under the same experimental conditions.

The change of the near(sub)surface region of the layer of the examined MBBA/UI-147 guest-host system upon UV light can be detected by reflectance measurements. Figure 5 plots reflectance spectra (recorded over the wavelength range from 200 nm to 500 nm) for MBBA/UI-147 without and with UV light illumination, when no cover glass plate was present for the LC sample. Even small, the difference in the optical response of MBBA/UI-147 system in both cases indicates the photo-induced change directly at the surface of the LC sample.
4. Conclusion
We have reported an UV light-induced (not thermally-induced) effect of tilted anchoring in a photoactive guest-host LC system (1 wt.% guest) upon a relatively low intensity UV-light illumination (of the order of 10 mW/cm²). This surface-induced effect is based on trans-cis photoisomerization of the guest azo-dye molecules. The near (sub)surface region of the LC layer rich with azo molecules is responsible for the observed trans-cis photoisomerization-induced surface anchoring. The tilted anchoring close to the surface is closely related to the LCs applications and has to be taken into account, especially at high light intensity, when this effect can limit and even frustrate the LCs laser-driven applications based on trans-cis photoisomerization.

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