New Photoactive Guest-Host Nematics Showing Photoflexoelectricity

Alexander G. Petrov [a] , Y. G. Marinov [a] , G. B. Hadjichristov [a] , S. Sridevi [b] , Uma S. Hiremath [b] , C. V. Yelamaggad [b] & S. Krishna Prasad [b]

[a] Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria

[b] Centre for Soft Matter Research, Jalahalli, Bangalore, India

Version of record first published: 14 Jun 2011

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

New Photoactive Guest-Host Nematics Showing Photoflexoelectricity

ALEXANDER G. PETROV,[1] Y. G. MARINOV,[1]
G. B. HADJICHRISTOV,[1] S. SRIDEVI,[2]
UMA S. HIREMATH,[2] C. V. YELAMAGGAD,[2] AND
S. KRISHNA PRASAD[2]

[1]Institute of Solid State Physics, Bulgarian Academy of Sciences,
Sofia, Bulgaria
[2]Centre for Soft Matter Research, Jalahalli, Bangalore, India

Here we present new results on guest-host nematic systems featuring an optical degree of freedom based on the trans-cis photoizomerization of a single azo-bond or two azo-bonds in guest mesogens, with or without a longitudinal dipole moment. Homeotropic nematic layers in horizontal electric fields, subjected to illumination by UV or white light, were investigated. A marked, reversible UV increase of the flexoelectrooptic effect was found in case of guest molecules with a longitudinal dipole moment.

Keywords Azo-bond isomerization; electrooptic effect; photoflexoelectricity; surface vs. bulk contribution

1. Introduction

Flexoelectricity is a mechano-electric property of liquid crystals (LC) that relates their mechanical and electrical degrees of freedom. In photoactive LC materials there exist a third, optical degree of freedom. The combined effect of these three degrees of freedom was first registered in lyotropic LC bilayer lipid membranes (BLM) containing retinal acetate [1]: a reversible photoinduced enhancement of the direct flexoelectric response of such a membrane in the regime of curvature oscillations was found and related to the change of the dipole density by photoisomerization of retinal. This effect was then called photoflexoelectricity. Subsequently, photoflexoelectric effect was observed in photoactive BLMs containing *in-situ* generated CdS nanoparticles, under bandgap illumination [2]. More recently, UV-light-dependent changes of the flexoelectric deformation in guest-host dye-nematic mixtures were found in the regimes of flexoelectric twisting of a hybrid aligned nematic layer [3] and flexoelectric bending of a homeotropic layer [4]. In this way, the influence of light on the converse flexoelectric effect in bulk thermotropic LC materials was also demonstrated. In such

materials, the difference between the flexoresponse (i.e., the electric field-induced curvature deformation) without and with UV light permits to consider this effect as another manifestation of photoflexoelectric phenomenon, i.e., as a converse photoflexoelectric effect in a LC system with 3 generalized degrees of freedom [cf. 5].

2. Theoretical Remarks

Flexoelectric bending of a homeotropic layer is obtained by applying a d.c. electric field E normal to the director (Fig. 1). Optical path difference Δl of a nematic layer with a thickness d and birefrigence Δn vs. electric field [6–9] is proportional to the 2nd power of E and to the 2nd power of the sum $(e_{3x} + m_p)/K_{33}$, where e_{3x} is the bend flexocoefficient, m_p, the surface polarization, and K_{33} the bend elastic constant:

$$\Delta l = \Delta n \left(\frac{e_{3x}^*}{K_{33}} \right)^2 E_{\text{eff}}^2 \frac{d^3}{12}, \tag{1}$$

where

$$E_{\text{eff}}^2 = \frac{E^2}{\left(1 + \frac{d}{2b} - \frac{\Delta \varepsilon \varepsilon_o E^2 d^2}{12 K_{33}} \right)^2}. \tag{2}$$
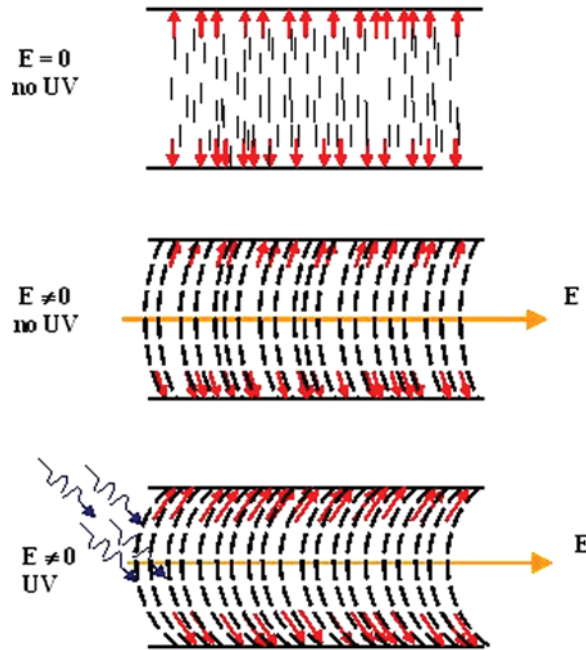

Figure 1. Flexoelectric deformations of homeotropic nematic layer (E = 0, no UV) under the action of an in-plane electric field and UV illumination. The change of surface polarization under UV is indicated. (Figure appears in color online.)

Eeff is an effective electric field depending on the dielectric anisotropy $\Delta\varepsilon$ and anchoring energy W with $b = K_{33}/W$ as the extrapolation length and ε_o, the free-space permittivity.

For larger electric fields [9]:

$$\Delta l = \Delta n \left(\frac{e_{3x}^*}{K_{33}}\right)^2 E_{\text{eff}}^2 \frac{d^3}{12}\left[1 - (\Delta_1 + \Delta_2)E_{\text{eff}}^2\right]^2 \tag{3}$$

where

$$\Delta_1 = \frac{1}{4}\frac{e_+ e_{3x}^*}{K_{33}^2}d^2, \quad \text{and} \quad \Delta_2 = \frac{1}{3}\frac{\Delta K}{K_{33}}\left(\frac{e_{3x}^*}{K_{33}}\right)^2\frac{d^2}{1 + d/2b}, \tag{4}$$

$e_+ = e_{1z} + e_{3x} \neq 0$ is the anisotropy of splay and bend flexoelectric coefficients and $\Delta K = K_{11} - K_{33} \neq 0$ is the anisotropy of the splay and bend elastic constants.

3. Experimental

The nematic phase of 4-butyl-cyclohexane carboxylic acid 4-pentyloxy-phenyl ester (CM80 for short) was used as host matrix since the compound is not UV sensitive, and, as a matter of fact, the cyclohexane ring provides an enhanced UV stability. Also to be pointed out is the fact that CM80 is a negative dielectric anisotropy compound, a feature essential for the technique employed here to detect the flexoelectric effects, because homeotropic layers under horizontal electric fields are
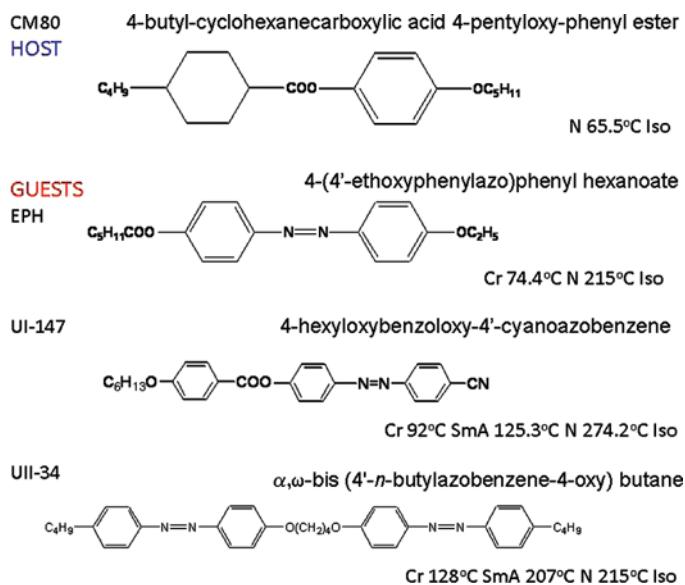

Figure 2. Molecular structures and phase transition temperatures of the host nematogen and the three guest photoactive mesogens. To be noted is the molecule, UII-34, a double azo-bond, fully symmetric compound with no longitudinal component of the dipole moment. (Figure appears in color online.)

A. G. Petrov et al.

dielectrically stable. Three different azobenzene-based compounds, labelled EPH, UI-147 and UII-34, and exhibiting a nematic mesophase, were used as photochromic guest systems; they were all synthesized at the Centre for Soft Matter Research in Bangalore. The concentration of the guest compounds was kept at a low level of 1 wt%, so as to avoid radiation depletion, while still permitting us to light-modulate both bulk and surface flexoelectric properties of the nematic layer. The molecular structures of the host and guest compounds are given in Figure 2.

The sandwich cells used in the present study were prepared in a slightly modified fashion than described in [9]. The cells were assembled from two parallel glass plates of 0.7 mm thickness, separated by 100 μm thick stainless steel spacers, also serving as electrodes. The distance between the electrodes was 2 mm. To promote homeotropic nematic orientation of the molecules, the inner side of the glass plates was silanized by an aqueous solution having 0.08 ml ODS-E silane (Aldrich) in 250 ml distilled water. The cleaned glass plates were dipped in the silane solution and quickly withdrawn. The number of dip-withdraw cycles was also varied in the range of 1 to 6, and in the course of the experiments we found that the required level of weak anchoring
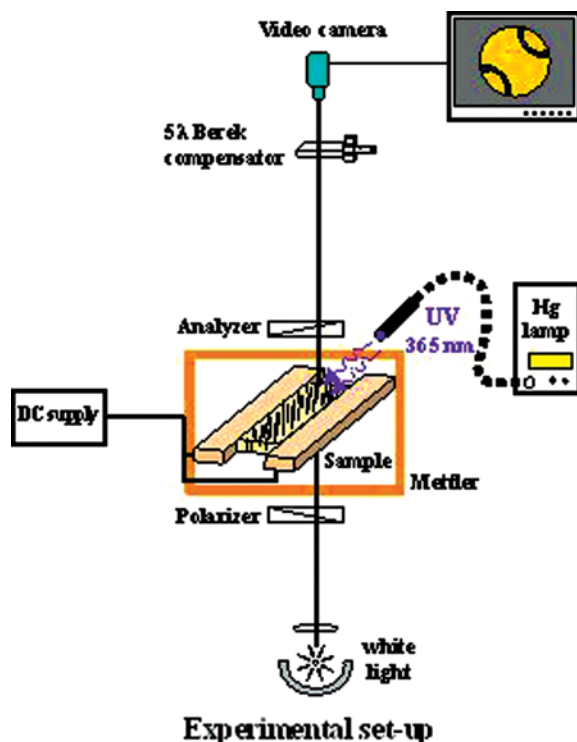

Figure 3. Experimental set-up: Intensity-stabilized UV source with a fiber-optic guide (Hamamatsu LC5, Japan, maximum UV power 3.5 W/cm^2). UG-1 Schott glass filter (Newport, peak wavelength 365 nm). UV power meter (Hamamatsu C6080-03). Polarizing optical microscope (Leica DMRXP) a digital camera (Optronics). 5λ Berek compensator (Leica) attached to the polarization microscope. Homeotropic nematic samples between crossed polarizers, subjected to a horizontal electric field directed at 45° to the polarizers. DC voltage from a Keithley Electrometer (Model 6517A). (Figure appears in color online.)

is achieved for 6 cycles. The silane layer thus deposited was stabilized by baking the glass plates for 3 hours at 150°C. The cells were then filled with the guest-host mixtures in their isotropic phase, subsequent to which the samples were cooled to the nematic phase to achieve good quality homeotropic orientation.

The UV apparatus used for inducing photoisomerization consisted of an intensity-stabilized UV source with a fiber-optic guide (Hamamatsu LC5, Japan, maximum UV power $3.5 \, W/cm^2$). To avoid the degradation of the samples by deep-UV, also present in the source, a UG-1 Schott glass filter (Newport, peak wavelength 365 nm) was inserted before the sample. For the experiments, the output from the lamp source was varied in the range 20%–35% of the maximum UV power. The actual power of the radiation passing through the filter, and falling on the sample, positioned about 2.5 cm from the filter, was measured with a UV power meter (Hamamatsu C6080-03) kept in the sample position. Thus the 20-35% range variation translates to an UV intensity of 2.2–3.8 mW/cm^2 on the sample. Optical absorption data were obtained over the wavelength range 250-800 nm, using UV-3101PC Shimadzu spectrophotometer. The solution spectra were taken with a 10^{-5}–10^{-6} Molar solution, having 1,4 dioxane/dichloromethane/chloroform as the solvent for EPH/UI-147/UII-34 respectively. Absorption spectra have also been recorded in the mesophase of the mixtures, for which the sample was contained between two quartz plates. The spectrum for pure CM80 does not show any significant absorption in the wavelength range of the *trans* and *cis* absorption bands of the azo group, while mixtures with 1%UI-147 or 1%EPH feature a strong absorption peak at about 360 nm and a shoulder at about 420 nm before UV illumination, reduced 360 nm peak intensity and appearance of an absorption peak at 420 nm after
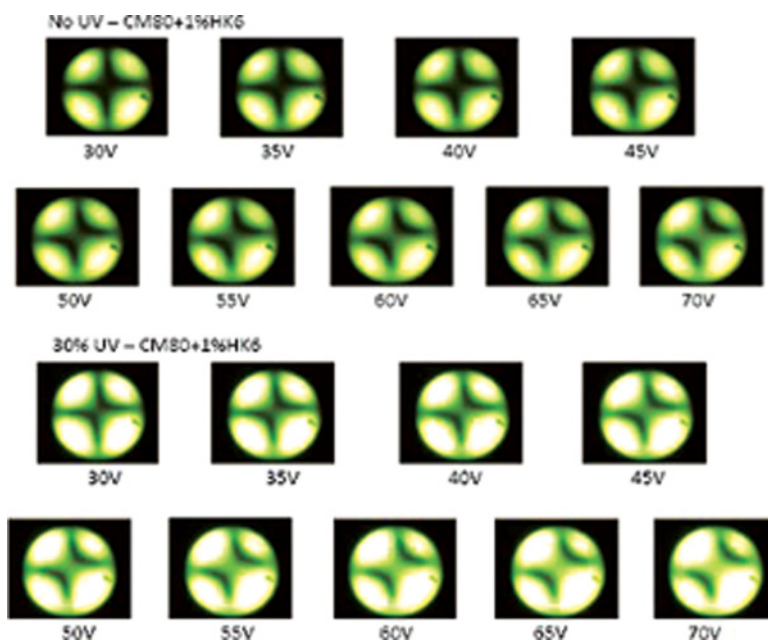

Figure 4. Conoscopic pictures of the mixture CM80 + 1%UI-147 under increasing electric fields, without and with 30% of the maximum (3.5 mW/cm^2) UV power. (Figure appears in color online.)
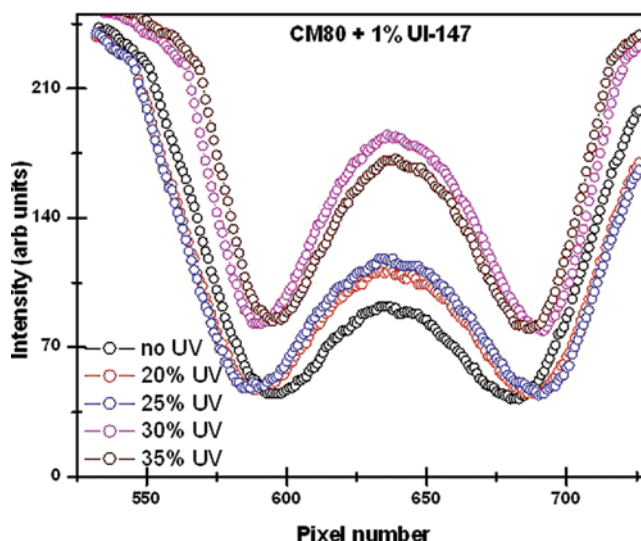
A. G. Petrov et al.

Figure 5. Intensity profiles across conoscopic pictures of the mixture CM80 + 1%UI-147 at a fixed electric field (30 V/mm) and with increasing UV power.

UV illumination, and restoration of the original profile of the absorption spectrum after white light illumination (not shown).

Photoflexoelectric studies of the samples were carried out by measuring the optical path difference with the help of a polarizing optical microscope (Leica DMRXP). Homeotropic nematic samples placed between crossed polarizers, were subjected to a horizontal electric field directed at 45° to the polarizers (Fig. 3). The field-induced biaxiality of the sample was measured by a 5λ Berek compensator (Leica) attached to the polarization microscope. For static flexoelectric measurements the applied DC voltage from a Keithley Electrometer (Model 6517A), created a static bend deformation that is further influenced by UV. The conoscopic images of the LC azo-dye mixtures (see Fig. 4) were acquired by an Optronics digital camera and intensity profiles across images were taken when appropriate (see Fig. 5). The experiments were carried out at room temperature (25°C).

4. Results and Discussion

The flexoelectric bending of the samples was studied in transmitted light. All the three mixtures exhibited good homeotropic orientation, as evidenced by polarization microscopy, especially in the form of conoscopic images (Fig. 4). The clearing temperature of the host compound, CM80 (65.5°C), is hardly altered by the addition of the dyes, owing to the small concentration of the guest compounds. Further, the negative dielectric anisotropy feature of the host compound remains intact in the mixtures also. As seen from Table 1, UV illumination at 365 nm for 2 min lowers the clearing temperature by some 2°C. More importantly, this effect is reversible, as noted for the condition when the sample is illuminated with white light to facilitate the reverse isomerization to the *trans* form.

On Figure 6 the flexoelectric optical path difference vs. the square of electric field for the pure CM80 is represented. The shape of the curve deviates from a

Table 1. Clearing temperatures of the guest-host mixtures before and after UV illumination. Data obtained with 3.8 mW/cm^2 UV light power

LC mixture	CM80 + 1%UI-147	CM80 + 1%EPH
Before UV	65.1°C–64.6°C	64.8°C–63.8°C
After UV for 2 min	63.9°C–63.6°C	62.8°C–62.2°C
After white light for 10 min	65.3°C–64.9°C	64.6°C–63.9°C

straight line, in accordance to the theory for a negative dielectric anisotropy (Eq. (2)). No influence of UV illumination could be noted whatsoever: the host does not have any optical degree of freedom.

Figure 4 compares the conoscopic figures of CM80 + 1%UI-147 mixture with and without UV, clearly showing the enhancement of flexoelectric deformation by UV illumination. This is especially clear from the intensity profiles of the pictures in a direction, normal to the electric field (Fig. 5), showing an increased splitting Maltese cross in the range up to 25%UV power, followed by a saturation around 30% UV and furthermore some decrease of the splitting at 35%UV.

Note that this non-monotonicity appears for 35% data only. We have taken maximum precaution to avoid local heating of the sample arising from the irradiation. However, we cannot completely rule that out. In such a scenario, when the UV power is very high (∼35%), it is possible that a small amount of local heating also exists. This heating would reduce the orientational order in the medium, and like any other order parameter dependent phenomenon, would reduce the photo-flexo value.
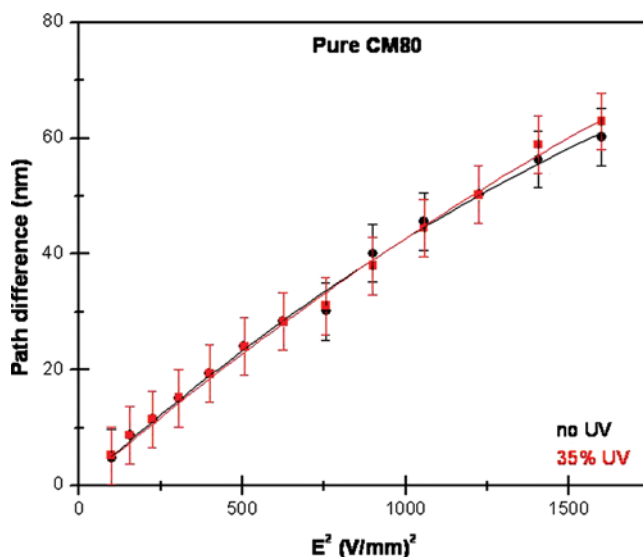
Figure 6. Flexoelectrically induced birefringence vs. square of the electric field, showing no difference between no-UV and UV, for the host compound CM80.
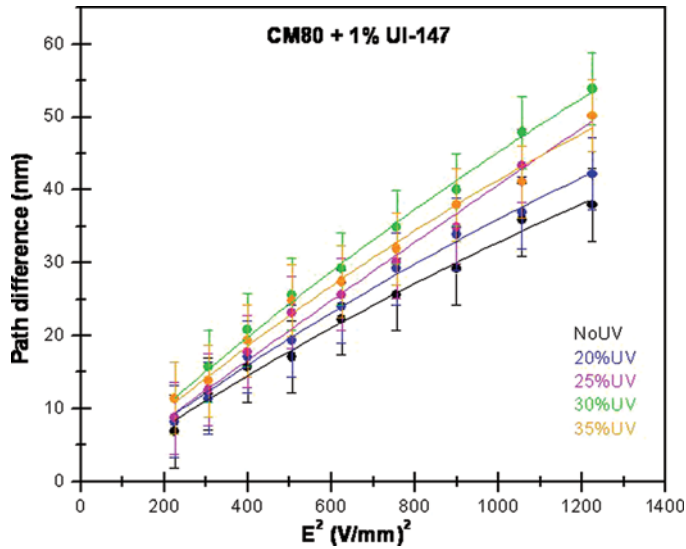
Figure 7. Flexoelectrically induced birefringence for the CM80 + 1%UI-147 mixture vs. square of the electric field, under increasing power of UV illumination.

Figures 7 and 8 demonstrate the influence of UV illumination with increasing power upon the photoflexoeffect in UI-147 and EPH. For both mixtures saturation of the increment around 30% UV can be noted, followed by a small reduction at larger UV power. Photoelexoeffects in both UI-147 and EPH mixtures are compared
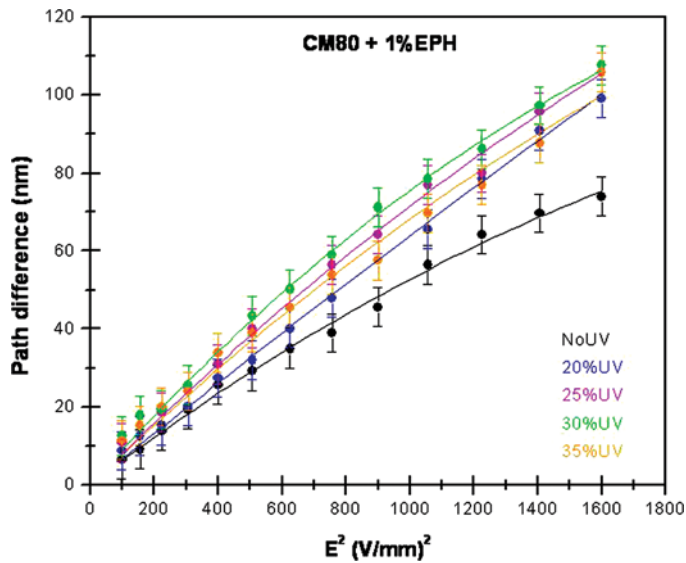

Figure 8. Flexoelectrically induced birefringence for the CM80 + 1%EPH mixture vs. square of the electric field, under increasing power of UV illumination.
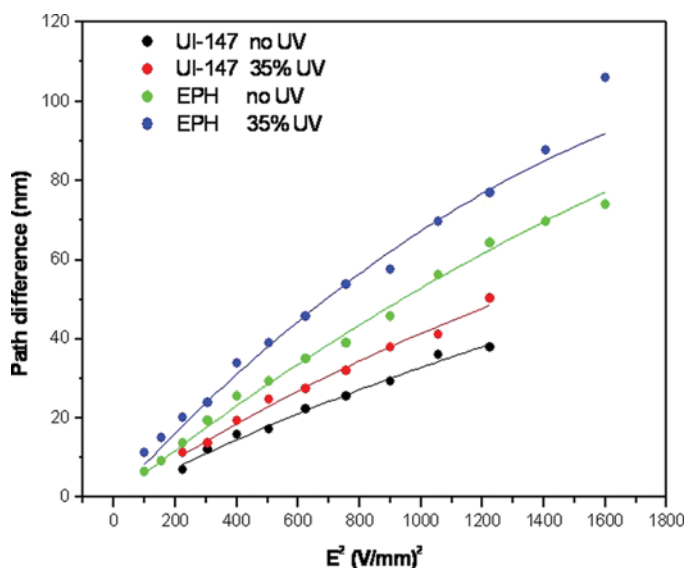
Figure 9. Comparison of the flexoelectrically induced birefringence for two mixtures under same UV power.

in Figure 9, and exhibit some 40% photo-enhancement of the dark response at 34 V/mm by 30%UV.

Figures 10 and 11 demonstrate a very small positive UV effect in the symmetric, double azo-bond compound UII-34, almost within the error limits.

Under UV illumination guest molecules isomerize from *trans* to *cis* form, the latter having a pronounced banana shape. This shape change could alter the bend
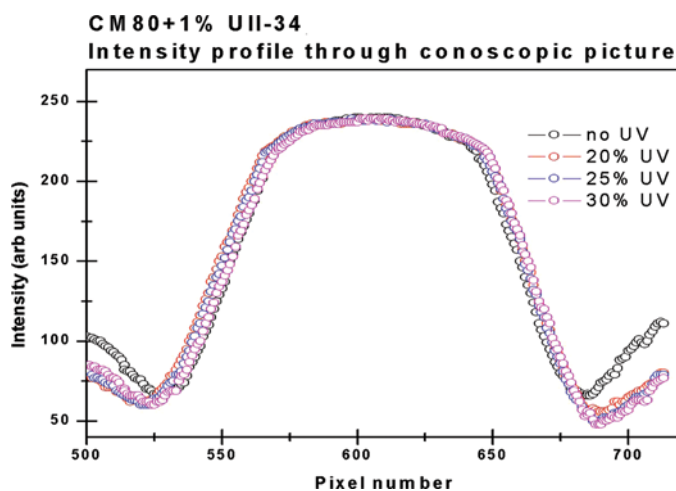

Figure 10. Intensity profiles across conoscopic pictures of the mixture CM80 + 1%UII-34 at the same electric field (22.5 V/mm) and with increasing UV power.
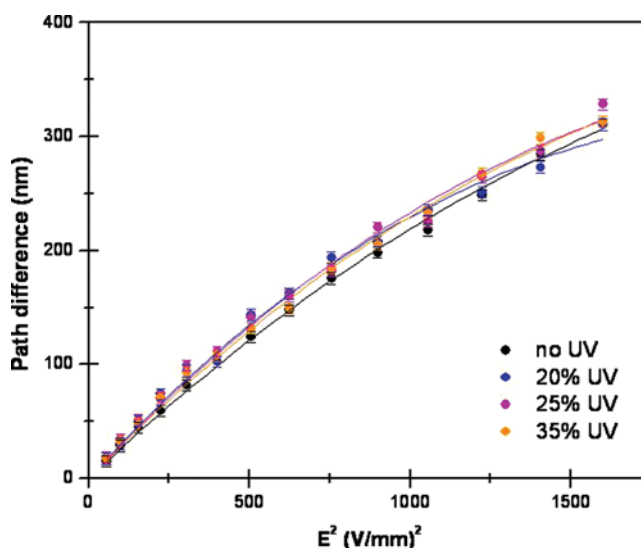
Figure 11. Flexoelectrically induced birefringence for the CM80 + 1%UII-34 mixture vs. square of the electric field, under increasing power of UV illumination.

flexocoefficient e_{3x} of the mixture, and also the longitudinal dipole moment of the surface-adsorbed guest molecules (Fig. 2), and in turn the value of surface polarization m_p. According to the theory above, the algebraic sum of these two coefficients governs the amount of the flexoelectric bending. Moreover, the anchoring strength could also be, in principle, influenced by UV [4].

In the symmetrical molecule case of UII-34 the surface polarization contribution is clearly absent. Therefore, the very weak effect observed in Figure 11 may be due to the variation of bulk part only. Note that even if all the double azo-bonds molecules are isomerized from *trans* to *cis* form, the relative banana shape effect could still not surpass 1%, the bulk concentration of the bananas. The effect that we observe is macroscopic one and therefore expected to have, at least at low UV intensities both types of conformers, where either one or both azo-bonds were izomerized. Since the absorption spectrum dispays bands for either trans or cis, it is not possible to conclude from absorption whether only one or both azo bonds have isomerized. Perhaps orientational order parameter measurements looking for the order of the azo molecules may provide an answer.

On the contrary, a polar-non polar asymmetry in the end substituents like in EPH and UI-147 could easily provoke more than 1000 times enhancement of the *surface* concentration of unipolar oriented guest molecules (as compared to their small *bulk* concentration) making m_p term comparable to e_{3x} term; therefore even a small reduction between the longitudinal dipole from trans to cis conformer [4] will be amplified and produce an observable enhancement of flexoelectric bending, providing both terms are of opposite signs. Further microscopic considerations, e.g., discussion of the difference between UI-147 and EPH (Fig. 9), require a detailed experimental clarification of not only the amplitudes, but also of the signs of the two terms (surface polarization and bend flexocoefficient) [cf. 4], which is a topic for future work.

5. Conclusions and Perspectives

Our findings confirm experimentally the hypothesis of the molecular nature of the photoflexoeffect in homeotropic nematics, advanced earlier [4].

New types of opto-optic and electro-optic switches and displays could be constructed based on the photoflexoelectricity employing the newly reported guest-host nematics.

Acknowledgment

References

[1] Petrov, A. G., Shonova, N., Komitov, L., Naydenova, S., Stoylova, S., Petkova, J., & Spassova, M. (1993). *20 Years Jubilee Proceedings of Institute of Solid State Physics*, ISSP: Sofia, Bulgaria.

[2] Spassova, M., Petrov, A. G., & Fendler, J. H. (1995). *J. Phys. Chem.*, *99*, 9485.

[3] Hermann, D. S., Rudquist, P., Ichimura, K., Kudo, K., Komitov, L., & Lagerwall, S. T. (1997). *Phys. Rev. E*, *55*, 2857.

[4] Marinov, Y., Shonova, N., Blinov, L. M., & Petrov, A. G. (1998). *Europhys. Lett.*, *41*, 513.

[5] Petrov, A. G. (1999). *The Lyotropic State of Matter*, Gordon and Breach: NY-L.

[6] Helfrich, W. (1971). *Phys. Lett.*, *35A*, 393.

[7] Schmidt, D., Schadt, M., & Helfrich, W. (1972). *Z. Naturforsch.*, *27a*, 277.

[8] Derzhanski, A., & Petrov, A. G. (1979). *Acta Physica Polonica*, *A55*, 747.

[9] Kumar, Pramoda, Marinov, Y. G., Hinov, H. P., Uma Hiremath, S., Yelamaggad, C. V., Krishnamurthy, K. S., & Petrov, A. G. (2009). *J. Phys. Chem. B*, *113*, 9168.