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A novel photoelectrooptical effect based on Freedericksz-type transition in nematic mixtures of azoxy compounds and cyanobiphenyls

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In mixtures of nematic liquid crystals with opposite signs of dielectric anisotropy (alkylcyanobiphenyls and azoxybenzenes), a possibility of photoinduced Freedericks-type transition was realized, which could be observed both by optical transmission in a standard geometry and by changes in electric conductivity. UV irradiation leads to lowering of the planar-to-homeotropic transition threshold, and at a certain bias voltage a photoinduced transition could be realized. *Trans-cis* isomerization of azoxy component decreases the anisometry of its molecules, resulting in higher positive dielectric anisotropy of the material. Prospects of application of the reported effect in optoelectronic devices are discussed.
Keywords: nematic liquid crystals, alkylcyanobiphenyls and azoxybenzenes.

В смесях нематических жидких кристаллов с противоположными знаками диэлектрической анизотропии (алкилцианобифенилы и азоксибензолы) реализована возможность фотоиндуцированного перехода типа Фредерикса, который можно наблюдать как по оптическому пропусканию в стандартной геометрии, так и по изменениям электропроводности. УФ-облучение приводит к снижению порога перехода из планарной в гомеотропную текстуру, и при некотором напряжении смещения возможна реализация фотоиндуцированного перехода. *Транс-цис*-изомеризация азокси-компонента снижает анизометрию его молекул, что приводит к увеличению положительной диэлектрической анизотропии материала. Обсуждаются перспективы использования этого эффекта в оптоэлектронных устройствах.

Новий фотоелектрооптичний ефект на основі переходу типу Фредерікса у нематичних сумішах азоксисполук та ціанобіфенілів. *Л.М.Лисецький, О.М.Самойлов, С.С.Міненко, О.П.Федоряко, Т.В.Бідна.*

У сумішах нематичних рідких кристалів з протилежними знаками діелектричної анізотропії (алкілціанобіфеніли та азоксибензоли) реалізовано можливість фотоіндукованого переходу типу Фредерикса, який можна спостерігати як за оптичним пропусканням у стандартній геометрії, так і за змінами в електропровідності. УФ-опроміню-

вання призводить до зниження порогу переходу з планарної у гомеотропну текстуру, і при певній напрузі зміщення можлива реалізація фотоіндукованого переходу. *Транс-цис*-ізомеризація азоксикомпонента знижує анізометрію його молекул, що призводить до збільшення додатної діелектричної анізотропії матеріалу. Обговорюються перспективи застосування цього ефекту в оптоелектронних пристроях.

In our recent papers [1, 2], we described certain anomalous properties of nematic liquid crystal (LC) mixtures composed of alkylcyanobiphenyls and azoxy compounds. Since these components have opposite signs of dielectric anisotropy ($\Delta\varepsilon > 0$ and $\Delta\varepsilon < 0$, respectively), compensation occurs at a certain concentration, with a sharp fall in optical transmission due to enhanced director fluctuations. Characteristics of such mixtures could be controlled by UV irradiation, which causes partially reversible *trans-cis* isomerization of azoxy compounds and the changes in molecular anisometry resulting in variation of mesomorphic, dielectric and other properties.

In a parallel set of considerations, nematic LCs with negative $\Delta\varepsilon$ are promising for various applications, but there are problems with ensuring their vertical (homeotropic) alignment [3]. This particularly refers to azoxy nematics, with their dipole moments roughly normal to the long molecular axis. Addition of cyanobiphenyls to nematics with large negative $\Delta\varepsilon$ allowed partial solution of this problem [3, 4]. Such an approach seemed very promising, accounting for various photoinduced effects that could be observed in nematic and other LC systems containing azoxy nematics [5–7]. One can also note other reported possibilities to efficiently control the dielectric anisotropy by addition of small amounts of appropriate compounds (e.g., certain dye molecules added to cyanobiphenyl LC matrix [8]).

The general idea of realizing a Freedericksz-type transition in an azoxy nematic-based LC system with addition of 4-pentyl-4′-cyanobiphenyl (5CB) was proposed in our earlier paper [2]. It was assumed that in such system the electric field-driven planar-to-homeotropic transition could be accompanied by other effects that could be observed under UV irradiation of such mixture. UV-induced *trans-cis* transformations of azoxy molecules could be superimposed on the electric field-induced reorientations, giving rise to various "photoelectrooptic" effects.

In this paper, we report our realization of some of such effects.

We used the same nematic liquid crystals 5CB and ZhK440 (a mixture of 4-*n*-butyl-4′-methoxyazoxybenzene and 4-*n*-butyl-4′-heptanoylazoxybenzene in 2:1 ratio) as in our previous work [2]. For electrooptical measurements, we used a standard geometry of the twist cell (thickness 20 μm) with ITO conductive coating. After application of polyimide layer, the cell was annealed at 180°C for 2 hs with subsequent unidirectional rubbing. Electrooptical voltage-transmission curves were measured in crossed polarizers in the 0–10 V range at 1000 Hz. UV irradiation was carried out using an emitter based on DRT-240 Hg lamp in geometry with known spectral distribution of illuminance [9]. Irradiation for 15 min ensured effective illuminance of ~2 J/cm^2, which, according to [10], should result in a photostationary state with about 50 % of azoxy molecules in the *cis*-form. The measurements were repeated after dark storage of the sample for 24 h, when most of the excited molecules were expected to return to their more stable *trans*-conformation. The obtained results are summarized in Fig. 1.

One can see that the Freederiksz threthold is considerably lowered after irradiation, which can be explained by smaller molecular anisometry of the *cis*-form with the small negative dielectric anisotropy changed to more positive values, with subsequent increase in the positive $\Delta\varepsilon$ of the mixture. This change is partially reversible — after dark storage (or irradiation with wavelengths above 400 nm), the characteristics are moving towards their initial form.

In another set of experiments, we tried to realize the photoinduced planar to homeotropic transition in a similar system. UV irradiation conditions were the same as above, and electric conductivity was measured in a 50 mm thick cell using a LCR meter as described in [1]. One of the components of ZhK440 (4-*n*-butyl-4′-methoxyazoxybenzene) was used as photosensitive azoxy compound (ZhK1). The results are shown in Fig. 2. The reorientation of the liquid crystal system resulted in a sharp increase in electric conductivity, with partial reversibility obtained under irradiation through ZhS-10 filter.

Thus, we have shown a possibility of a novel photoelectrooptic effect in nematic mixtures of cyanobiphenyl and azoxy compounds, with conversion of light into elec-

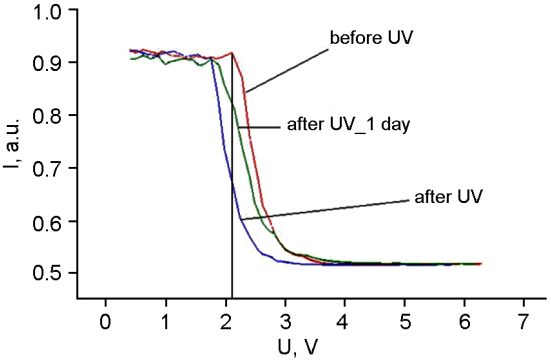

Fig. 1. Voltage-transmission curves for 20 μm thick twist cells with LC mixture 80 % ZhK440 + 20 % 5CB before UV irradiation, after irradiation and after subsequent dark storage for 24 h. The vertical line indicates the bias voltage at which the photoinduced transition could be realized.

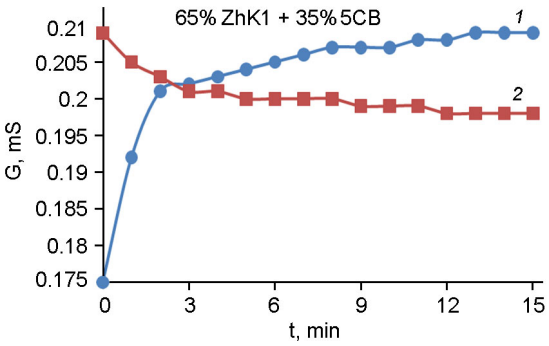

Fig. 2. Electric conductivity of LC mixture azoxy nematic ZhK1 + 5CB (planar cell) as function of UV irradiation time (2 J/cm^2, cell thickness 50 μm) at 2 V bias voltage (*1*) and under reverse irradiation (*2*).

tric signals. Further studies are under way, with improved characteristics expected upon addition of carbon nanotubes.

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