

An Unusual Effect of Liquid Crystal Host on the Absorption Properties of “Guest–Host” Mixture

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We have observed for the first time the effects of considerable changes in the order parameter and the wavelength shift of the maximum absorption in the “guest–host” mixture of liquid crystal (“host”) with dichroic dye (“guest”) under UV-light illumination, dependent on the liquid crystal host. [DOI: 10.1143/JJAP.43.1100]

KEYWORDS: liquid crystal, dichroic dye, “guest–host” effect, absorption spectra, order parameter

The quality of “guest–host” liquid crystal display (GH-LCD) strongly depends on the molecular interaction between the “host” liquid crystal (LC) and the “guest” dye.¹⁾ A significant change in the guest–host polar interaction occurs in UV-light-excited dye molecules.²⁾ We have observed for the first time the effects of considerable changes in the order parameter and the wavelength shift of the maximum absorption in the GH mixture under UV-illumination, dependent on the LC host. The guest molecule was a molecule of the anthraquinone dye AD-1 with a negative dichroism, which contains four large alkylcyclohexylbenzoyl substituents in its structure (Fig. 1). The negative dichroism was due to the summing long-wave electron transition oscillator (LETO) of the anthraquinone molecule oriented almost parallel to the *X*-axis¹⁾ (Fig. 1). Thus the direction of the LETO is perpendicular to the long molecular axis of the AD-1 molecule (*Y*-axis, Fig. 1). In the GH mixture the latter indicates, that the absorption oscillator is perpendicular to the LC alignment direction, which coincides with the long axis of the AD-1 molecule.^{1,2)}

We investigated the behavior of the anthraquinone guest dye in different GH-LC mixtures: ZLI-5800-000 (Merck) and RDP84633 (DIC). The concentration of the anthraquinone dye was $c = 3 \text{ wt}\%$ in both mixtures. Before UV illumination the dichroic spectra of the GH-LC mixtures were absolutely the same ($S = -0.36$, $\lambda_{\text{max}} = 463 \text{ nm}$) (Fig. 2, left). After the UV illumination (23.97 mW/cm^2 at 365 nm), the dichroic spectra of the Merck GH-LC mixture remained unchanged, while those of the DIC GH-LC mixture altered considerably. A surprisingly large decrease in the order parameter (from $S = -0.36$ to $S = -0.03$) together with a marked wavelength shift of the maximum absorption λ_{max} (from 463 nm to 400 nm) was observed in DIC GH-LC mixture after UV illumination (Fig. 2, right).

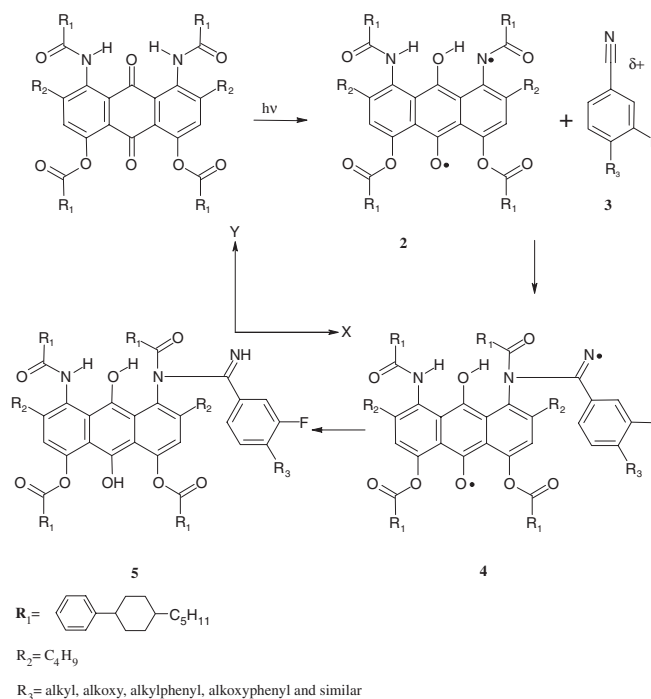


Fig. 1. Photochemical reduction of the anthraquinone dye AD-1 in the DIC GH-LC mixture RDP84633 with the participation of fluorobenzonitrile molecules.

Such a peculiar behavior of the anthraquinone dye AD-1 absorption spectra in the strongly polar LC mixtures, containing fluorobenzonitriles under UV irradiation, could be due to the photochemical reduction of the anthraquinone dye with the participation of fluorobenzonitrile molecules. After UV irradiation, the anthraquinone dye transformed into an electronically excited state (Fig. 1), where one of the

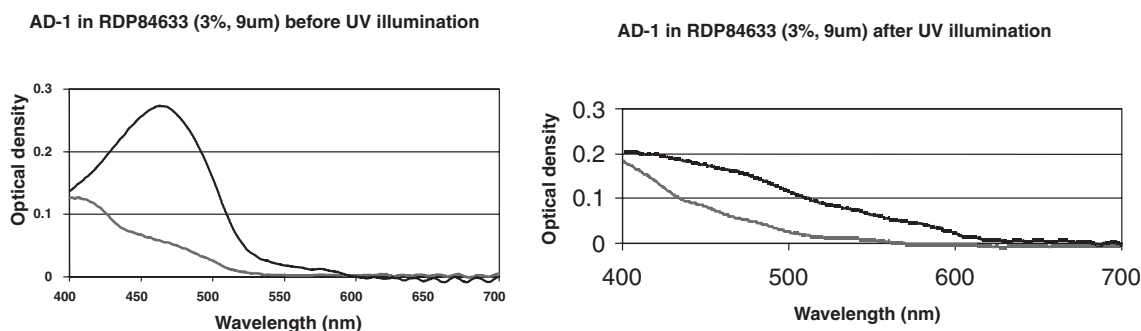


Fig. 2. Polarized dichroic spectra of AD-1 (3 wt%) in the DIC GH-LC mixture RDP84633 before (left) and after (right) UV illumination. The spectra of the Merck GH-LC mixture MLC 5800-000 remain the same (left).

resonance structures of the excited state of the dye was a biradical molecule (2). The fluorine atom in the fluorobenzonitrile molecule (3) increased the positive charge ($\delta+$) on the carbon atom of the nitrile group. Thus the attack of a nitrogen radical of the amide group of the dye on the carbon atom of the nitrile group became possible and resulted in an intermediate molecule (4). This intermediate molecule was transferred into a more stable hydroquinone compound (5). The evidence of the formation of the hydroquinone compound³⁾ after the UV irradiation of the DIC GH-LC mixture is the appearance of a sharp absorption band at 3500 cm^{-1} in the IR spectrum of the UV-irradiated DIC

GH-LC mixture with AD-1, which we observed in our experiment. Probably during this reaction, the angle of AD-1 absorption oscillator LETO goes closer to the magic angle $\alpha = \cos^{-1}(1/\sqrt{3})$ and the order parameter of the dye becomes almost zero.¹⁾

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