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Anchoring of 4-Dimethyl-amino Substituted Azobenzene Dyes Doped Liquid Crystals on Substrates

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We study the anchoring of 4-dimethyl-amino substituted azobenzene dyes doped liquid crystals and the formation of permanent gratings in the nematic liquid crystal 5CB. The increase on the dipolar interaction due to trans-cis isomerization, and the resulting anchoring to the substrate, is not enough to explain the formation of permanent gratings as it is commonly believed. We demonstrate that a strong interaction of the acid group in the 4-dimethylamino-2'-carboxylic acid substituted azo (Methyl Red, MR) dye can occur with the solid substrate through hydrogen bonding intermolecular interaction leading to permanent gratings in methyl red doped liquid crystal cells.

Keywords: anchoring of azobenzenes; azo-dye-doped liquid crystal; *cis-trans* photoisomerization; hydrogen bonding interaction

INTRODUCTION

Dye-doped nematic liquid crystals have emerged as an attractive material for nonlinear optics due to their colossal nonlinearity which makes them attractive for low power applications such as image processing, energy transfer, and phase conjugation among others. The reason for the colossal nonlinearity in dye-doped liquid crystals is the enhanced molecular reorientation induced by the dye's torque [1]. The torque originates as a result of the reversible photo-transformation between different dyes isomers [2]. In particular, the *trans-cis* photoisomerization of azo dyes results in drastic changes in the molecular shape, as well

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as in the distribution of permanent dipole moments in the molecular structure [3]. Thus, in azobenzene-dye doped liquid crystals the photo-induced adsorption of the *cis*-isomers on the solid surface leads to anchoring and alignment of the liquid crystal through dipole–dipole interactions [4]. Photo-induced adsorption of the dye at the substrate produces permanent gratings which may be an undesirable side effect in dynamic holography. On the other hand, permanent gratings may be useful on devices such as Bragg reflectors, optical routers and others. So, a clear understanding of the mechanism of dye adsorption will help us to control the phenomena or even eliminate it. Recently, it has been shown that colossal nonlinearities ($n_2 \approx 10^3 \text{ cm}^2/\text{W}$) can be obtained in liquid crystal doped with azo-dyes [5]. It was also shown that the substrate plays a critical role on the magnitude of the nonlinearity but a clear understanding of its origin is still an open matter.

In this work, we report our findings on the formation of photo-induced gratings by azo-dyes doped liquid crystals, and the key role of photo-adsorption of azo-dyes onto the surface and its influence on the liquid crystal molecular reorientation process. A new molecular mechanism of anchoring onto the substrate surface is proposed in order to elucidate the origin of the dye adsorption. We used two chemically similar azo-dyes: 4-dimethylaminoazobenzene-2'-carboxylic acid (Methyl Red or MR) and 4-dimethylaminoazobenzene (Methyl Yellow or MY) to dope the nematic liquid crystal 4-pentyl-4'-cyanobiphenyl (5CB) (see Fig. 1). The main difference between these dyes is the acid group position in the phenyl ring (*i.e.* 2'-COOH on MR) that leads to very different optical absorption spectra of both organic compounds, as shown in Figure 2 for a doping of 1% wt in 5CB liquid crystal. In order to gain a better understanding of the dye adsorption, some theoretical calculations and experimental studies were performed. A general *ab initio* quantum chemistry package (GAMESS) [6], was used to simulate the most stable conformation (*trans-cis*) of MR and MY dyes and to simulate the interaction between the substrate and the photosensitive host-guest. Experimentally, we performed grating formation in dye-doped nematic liquid crystals (NLC) with both dyes.

1. EXPERIMENT DESCRIPTION

First, the glass substrates were cleaned thoroughly using different solvents. A piranha solution was used as a common promoter to increase the -OH group population on the glass surface substrates [7], and thus, enhance their hydrophilic properties. Although permanent gratings can be recorded under different surface treatments: surfactants, rubbing films (PVA), and ITO alone, however, it is well known that piranha

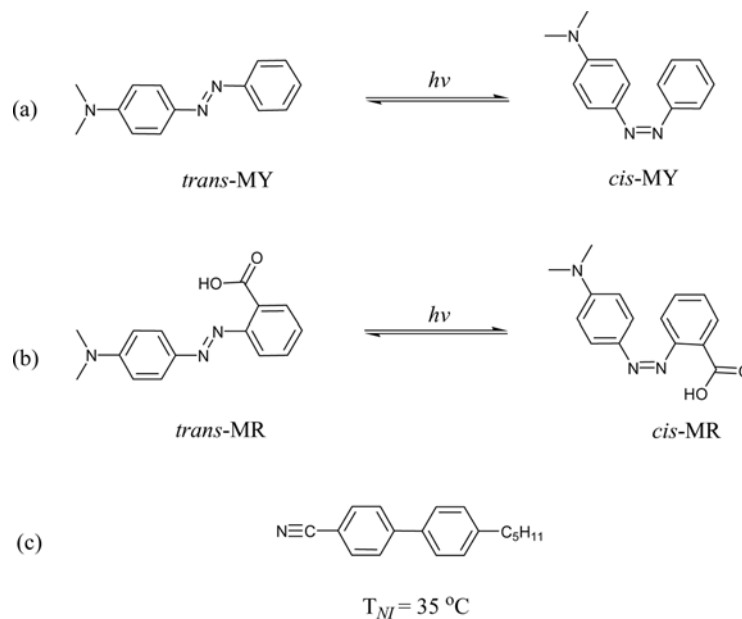


FIGURE 1 Molecular structures and photo-isomerization for (a) methyl yellow (MY) and (b) methyl red (MR); (c) is the molecular structure of the nematic liquid crystal 4-pentyl-4'-ciano-biphenyl (5CB).

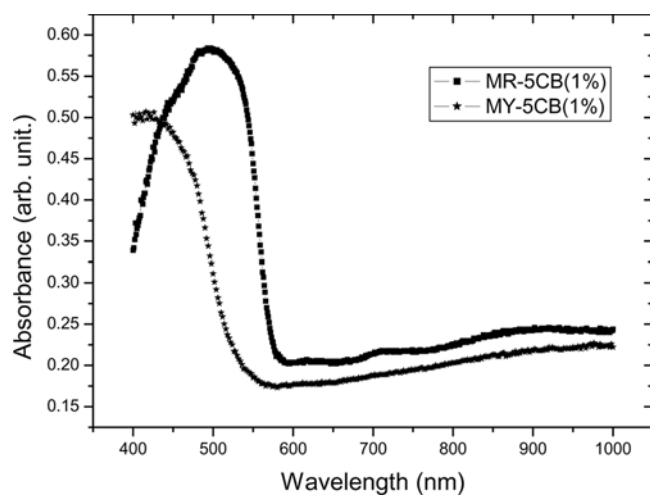


FIGURE 2 Absorption spectra of MY and MR in 5CB liquid crystal at 1% wt.

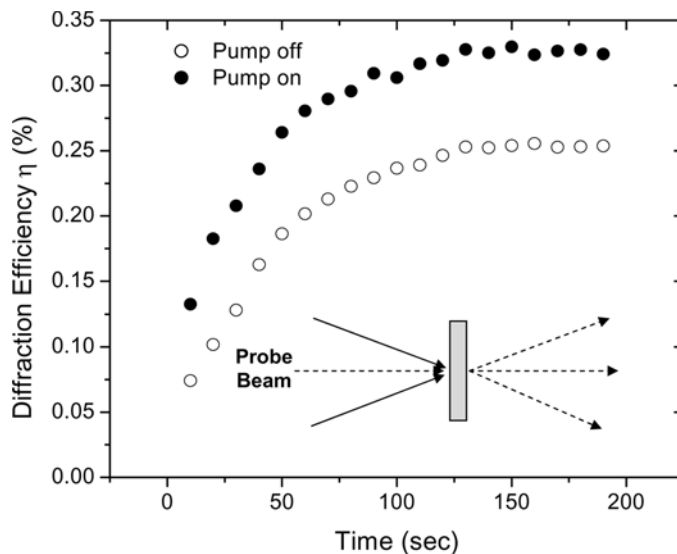


FIGURE 3 Permanent and reorientation grating in 5CB doped with methyl red at 0.3% wt 1.5 mW/cm². Inset shows the experiment setup: writing recording is performed with green (514.5 nm) and probing with red light (633 nm).

solution enhance the superficial density of -OH groups. A nematic liquid crystal 5CB (Merck) was used as the host liquid crystal material. MR and MY azo dyes (Sigma-Aldrich) were dissolved in the nematic host at different concentration per weight (0.3, 0.6 and 1.0%). The experiments were realized in a sandwiched glass cell ($d \approx 8\text{--}10 \mu\text{m}$) filled with the host-guest mixture. The sample is randomly oriented since no surfactants or aligning layers were deposited. Finally, some samples were prepared by dissolving MR and MY on isopropyl alcohol/dimethyl formamide *i*PrOH/DMF (1:1) solution in order to study the contribution of the dye adsorbed grating only to the total diffraction efficiency.

As the grating recording experiments concern, we used the conventional pump-probe geometry (see inset of Fig. 3). An Ar⁺ ion laser (wavelength $\lambda = 514.5 \text{ nm}$) was used to record $20 \mu\text{m}$ gratings period and a weak He-Ne laser (wavelength $\lambda = 633 \text{ nm}$) was used as probe beam with polarization parallel to grating recording beams and spot size with approximately 6 times smaller than the recording one.

2. RESULTS AND DISCUSSION

From our numerical simulations it was found that the dipole moment change upon photoisomerization for MY and MR are 2.72D and 1.97D,

TABLE 1 Dipolar Moment and Charge Parameters^a

	Methyl red		Methyl yellow	
	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
μ^b	2.59	4.56	1.73	4.46
$\Delta\mu_{\text{isom}}$	1.97		2.72	
E_{tot}^c	-702.166		-889.775	
	Atomic charge ^d			
N=N	-0.0876(N7)	-0.0678(N7)	-0.0929(N7)	-0.0721(N7)
	-0.1000(N8)	-0.0671(N8)	-0.1046(N8)	-0.0783(N8)
N=N ^e	-0.283(N7)	-0.2600(N7)	-0.2286(N7)	-0.3278(N7)
	-0.161(N8)	-0.3208(N8)	-0.2072(N8)	-0.3387(N8)
=O	-0.2136	-0.2145		
-O	-0.1898	-0.1948		

^aAll calculation were made at N31 6G** level. Charge calculations are giving as electrostatic potential.

^bDebye.

^cKcal/mol.

^delectrostatic potential: Mulliken-Lowdin.

^ePolarized continuum media charge (toluene).

respectively (Table 1). Furthermore, the dipolar moments in the *cis* conformation for both dyes are very similar (4.46D and 4.56D, respectively). These parameters are in good agreement with those reported by Komitov *et al.* [4]. The results showed that the dipole moment of *cis*-isomers become larger than those of *trans*-isomers, leading to a preferential *cis*-structure adsorption on the solid substrate. Based in these results, *cis*-MY species should give rise to a stronger dipole-dipole interaction and therefore stronger permanent gratings formation than *cis*-MR species. However, as we will show later, no permanent gratings were recorded in MY-doped liquid crystals whereas in MR-doped samples, permanently grating are easily written. We believe that the interaction between the polar carboxylic group of MR, so far not taken into account, and the substrate is very important and should be included in the interaction models.

In this context, an Atomic Charge Analysis (ACA) was carried out at the optimized structures in order to assess the charge distribution over each N atom on N=N group. The results show that charges in *cis*-MY conformation are larger than *cis*-MR (Table 1). Similar results were obtained in a polarizable continuum media (PCM-charges) in toluene. As mentioned before, and based on the N=N dipolar interaction model, it should be expected that 5CB doped with MY will have a better performance on grating recording. On the other hand,

according to the ACA analysis over oxygen atoms on MR-COOH group, it shows that in general, *cis* conformation charges are larger compared with *trans* isomer and almost three times larger than the N=N group. This analysis provides us information about a preferential interaction between the substrate and -COOH rather than N=N group, this interpretation is in agreement with the observed permanent grating on doped-MR liquid crystal cells.

A first approach to explain this apparently contradiction was to address the strong interaction between the polar group on MR and the hydrophilic surface through intermolecular forces (hydrogen bond, van der Waals, dipole interactions, etc.). Besides, it is well known that the orientation of a LC strongly depends on the surface properties of its substrate [8]. The interaction between the dye and the substrate will most likely occur through -OH on glass surface linked to Si [9]. Polar groups, such as -COOH, -OH, and -NH are associated with hydrogen bond interactions. Hydrogen bonds are widespread in chemistry and biology and have been the most reliable design elements in crystal engineering as the master-key of molecular recognition [10]. Based on results of the present study, it is wise to assume that molecules with a polar nature will interact strongly between the carboxylic acid group and the terminal -SiOH moieties of superficial glass substrate, this hydrogen bonding interaction could lead to much better perform in rendering permanent gratings formation.

In order to test our theoretical predictions we performed grating recording experiments on LC samples doped with MY and MR dyes. Figure 3 shows the diffraction efficiency of the probe beam at first order ($\eta = I_1/I_0$, where $I_{0,1}$ are the incident and first-order diffracted intensity, respectively) as function of the writing time for 5CB liquid crystal doped with MR at 0.3% wt. It should be pointed out that the response time for the formation of permanent gratings depends on the incident energy, so with sufficiently low power it is possible to write transient reorientation gratings only. In our case, illumination for $t < 10$ sec at $P = 1$ mW leads to no permanent gratings. Filled circles represent the diffraction efficiency when both writing beams are present and empty circles when the beams are off. The difference between the “off-grating” and the “on-grating” is due to the light-induced reorientation of the liquid crystal which disappears once the writing beams are switched off. As the Figure shows, the adsorbed dye on the substrate leads to a considerable volumetric reorientation of the liquid crystals. We notice that the diffraction efficiency scales linearly with the dye concentration in the range 0.3–1.0% wt concentration. We also notice that permanent gratings possess two contributions: i) one due to the adsorbed dye and

ii) another due to the adsorbed dye-induced reorientation of the liquid crystal molecules.

In this way and with the target to measure the contribution to the diffraction efficiency of the adsorbed dye in mind, we prepared some samples of the same thickness and dye concentration as those containing liquid crystal, by dissolving MR and MY in *i*PrOH/DMF (1:1) solution; thus, the maximum diffraction efficiency for MR at 0.3% wt in solvents is $4 \times 10^{-4}\%$, *i.e.* about eight hundred times smaller than the permanent grating in 0.3% wt MR doped liquid crystal cell. This fact emphasizes the strong effect on the volumetric reorientation due anchoring conditions controlled by the adsorbed dye. Heating of the sample above the clearing temperature (32°C for 1% wt MR doping) the diffraction efficiency decreases considerably. A few repeated heating cycles or even higher temperatures can erase the grating. At room temperature (25°C), the grating is so strong that even after six months they do not show signs of weakening. For MY doped samples (both in liquid crystals and solvent) was not possible to record permanent gratings by varying the laser power and the exposition time. However, transient reorientation gratings are easily recorded, indicating that MY binding energy of the dye and the -OH bonding may be smaller than the thermal energy. So, MY can be a suitable dye to enhance the nonlinear optical response of the liquid crystals but without the inconvenience of permanent phase changes. In addition, it is important to notice that at the same concentration (1% wt dye-doped LC), the diffraction efficiency for MR is almost two orders larger than MY while MR (1%) in *i*PrOH/DMF system produce a value of only $1.8 \times 10^{-3}\%$, once again, proving that surface-controlled anchoring conditions lead to increased nonlinear effects on the cell bulk.

As it is well known, molecules containing azo (N=N) moiety as photosensitive chromophore undergo a *trans-cis* isomerization upon exposure with laser light, concomitantly, the photo-isomerization process results in a changes of the molecular shape and also the magnitude and the orientation of the molecular form. According to our theoretical results, the *cis*-form appears to be higher polarity than the *trans* counterpart and therefore they will be more strongly attracted by the hydrophilic surfaces through dipolar interactions. Thus, the photoadsorption produces, by its light-induced reorientation, a nematic local order in the bulk of NLC with the director vector almost perpendicular to the substrate. A preliminary interpretation involving two-step strong adsorption of the MR on surface, as shown in Figure 4(b) unlike *trans*-MY that only dipolar interactions are present as can be observed in Figure 4(a); in *trans*-MR one of the first steps would be formed by an H-bonding of the O-H...O=C type

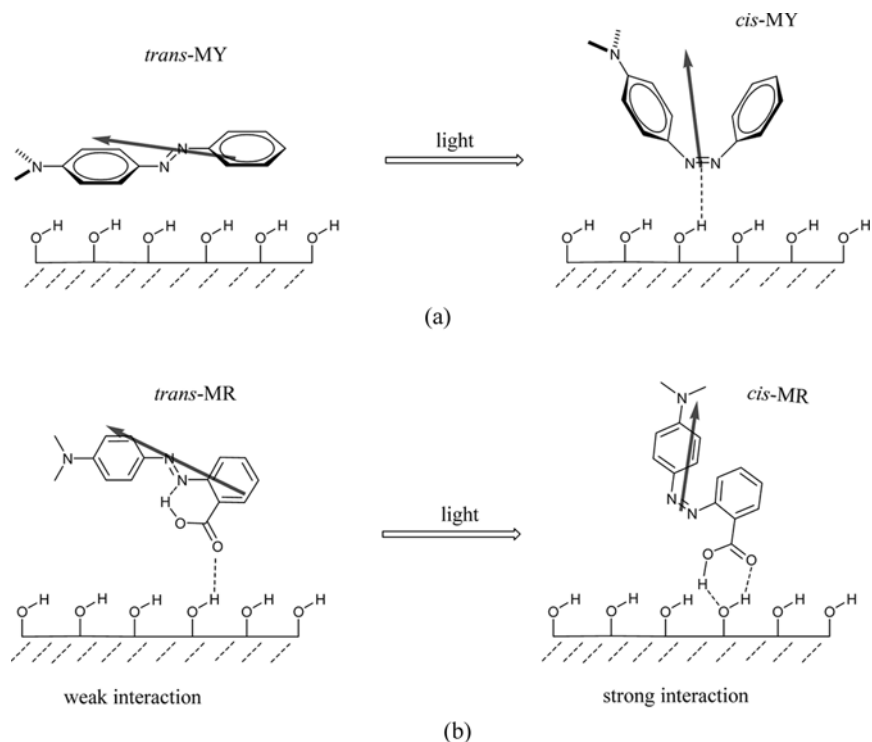


FIGURE 4 Different intermolecular interaction fashions for MY and MR. (a) between the surface and *trans-cis*-MY species only dipole interactions dominate. (b) Formation of hydrogen bonding on hydrophilic surface by MR molecules: left, *trans*-MR leads to single hydrogen bonding (weak interaction); right, double hydrogen bonding favored by *cis*-MR under photo-isomerization (strong interaction).

between -COOH and -OH species on the interface, this interaction is considerably stronger than dipolar factors solely. In second-step upon exposure with laser light, MR molecule quickly attain *cis*-isomer that generates a second hydrogen bond, as shown on right in Figure 4(b). Consequently, the molecules of MR are hardly tied to the hydrophilic surface by O-H...O=C and O-H...O double hydrogen bonding. The *cis*-phototransformed entity are oriented approximately perpendicular to the surface of substrate. The resulting molecular anchoring leads to reorientation on the bulk liquid crystal.

MR is widely used as an indicator in acid-base titrations and therefore, MR itself is subject to acid-base equilibrium. Both, acid and base forms of MR are ionic molecules. Preliminary molecular

modeling of the MR in its acid form reveals even larger charges and an unusual large dipole moment of 13.46D. This molecule in its ionic form will lead to very interesting results and better understanding of this mechanism. Efforts aimed to take advantage of the presented process for their applications are currently under development in our laboratory.

3. CONCLUSIONS

In summary, we have demonstrated that dipolar moment and the increase in N=N group charges on dyes with polar groups it is not enough to explain the adsorption of the dye to the substrate that in turn trigger the rearrangement of LC. Since no adsorption is observed on MY compared with MR, we conclude that the polar (acid) group in MR dye plays a very important role on dye adsorption, since -COOH hydrogen bond interaction are stronger compared with N=N interactions. We demonstrate that in addition to N=N interaction, H-bonding interaction facilitates stronger anchoring on the substrate, even more, our study suggest that strong interaction (ionic) will render better anchoring and in turn the dipole-dipole interaction to the LC will give more define and better grating formation. Finally, MY can be a suitable dye to enhance the nonlinear optical response of the liquid crystals on the blue region of the absorption spectra without the inconvenience of permanent gratings.

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