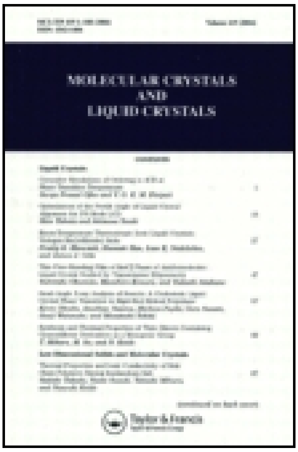

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# Photo Alignment of Liquid Crystals by an Azo Dye Doped Reactive Mesogen Layer

Alexia Blanchard-Lapierre [a] , Arutyun Bagramyan [a] & Tigran Galstian [a]

[a] Center for Optics, Photonics and Laser, Department of Physics, Engineering Physics and Optics, Laval University, Pav. d'Optique-Photonique, 2375 Rue de la Terrasse, Québec, Canada, G1V 0A6

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# Photo Alignment of Liquid Crystals by an Azo Dye Doped Reactive Mesogen Layer

ALEXIA BLANCHARD-LAPIERRE, ARUTYUN BAGRAMYAN, AND TIGRAN GALSTIAN*

Center for Optics, Photonics and Laser, Department of Physics, Engineering Physics and Optics, Laval University, Pav. d'Optique-Photonique, 2375 Rue de la Terrasse, Québec, Canada G1V 0A6

*Azobenzene dye doped reactive mesogen is used as thin photo control layer to align permanently nematic liquid crystal molecules. It is shown that, even in the case of a non mesogenic dye, the reactive mesogen matrix follows its photo induced reorientation rather efficiently. Polarimetric and electrooptic studies are performed to characterize this process. Storage, additional UV and thermal processing are then applied to evaluate, in a first approximation, the reliability of obtained layers.*

**Keywords** Azobenzene dye; liquid crystal; photo alignment; polymer; reactive mesogens; surface alignment

## Introduction

One of the most important applications of liquid crystals (LC) is the flat panel LC display (LCD) [1]. The continuous improvement of LCDs (performances and cost) requires, among others, the development of new methods of alignment of LCs and of their electrical driving algorithms. Particularly interesting are the orientational configurations having spatial (lateral) non uniformity, which are very difficult to make (if affordable in principle) by using traditional rubbing or vacuum deposition techniques [2]. Here is where the photo alignment method of LCs shows significant promise [3–5]. So far, there have been many approaches explored for photo alignment; however their acceptance is just starting to become reality in the LCD industry. Among several reasons (for this "resistance") were the sticking and the long term instability of such alignment layers. Thus, for example, if the photo alignment is achieved by the linearly polarized UV cleavage of molecular bonds (to create a preferential direction of LC alignment, or what is often called an "easy axis" of alignment [6]) then the continuous exposition of the LCD to even very week power of UV light during its operation (e.g., by the backlight of LCD or by powerful projection lamps) would create additional cleavage and would destroy that easy axis resulting in the loss of the initial (desired) LC alignment.

Different type of problem existed in the case of photo aligned but non stabilized dichroic dyes, such as azobenzenes [3a,7–9]. In fact, the linearly or circularly polarized

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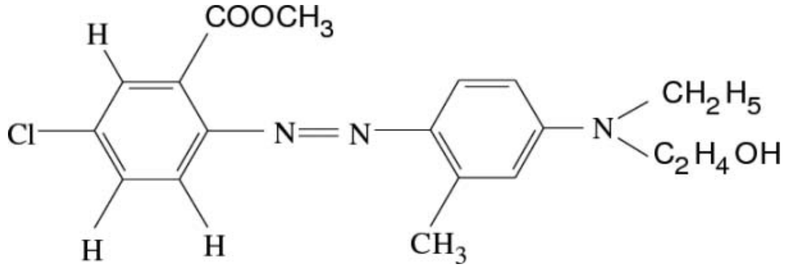
*Address correspondence to Tigran Galstian, Center for Optics, Photonics and Laser, Department of Physics, Engineering Physics and Optics, Laval University, Pav. d'Optique-Photonique, 2375 Rue de la Terrasse, Québec, Canada G1V 0A6. E-mail: galstian@phy.ulaval.ca light of appropriate wavelength (in the dichroic absorption band of the dye) was shown to generate (after multiple Trans ↔ Cis excitation processes) reorientation of the long axes of those molecules (typically, parallel to its dipole moment) towards the direction that is perpendicular to the plane of light field [10–12a]. However, if this reorientation is not fixed, then the thermal relaxation or further unpolarized light exposition may degrade the previous alignment during the operation of the LCD. This is not supposed to be the case when the azobenzene molecules are incorporated into various photo polymerizable matrices with the hope to fix definitively the light – created easy axis by the photopolymerization of the matrix. Thus, particularly interesting results have been already obtained in the case of mesogenic photo polymerizable (or otherwise called "reactive mesogen" / RM) matrices [12].

Recently we have developed such a mixture of azobenzene dye with an RM that was used mainly for a preliminary study of photo alignment and capillarity control processes [13]. The promise of this approach is related to the hypothesis that, once the photo alignment of azobenzene molecules generates a corresponding alignment of the RM molecules, then the UV photo polymerization of the whole matrix of RM could fix the obtained easy axis. Then, even if the azobenzene molecules might later relax back to their original alignment, the easy axis (defined by the polymerized RM matrix) would still maintain the desired alignment of LCs. The remnant alignment effect was demonstrated clearly [13], however the stability of this alignment was not studied. In the present work, we use a similar composition to further study its properties, including the thermal and UV stability aspects. As one can see further, the obtained results are rather disappointing since the UV exposition still degrades the photo alignment quality.

### *Photo Controlled Layer Fabrication*

**Material composition:** Our material composition consisted of a matrix of the "planar alignment" reactive mesogen RMS03-001C, purchased from Merck [14]. The RMS03-001C was supplied in a solution of PGMEA with the weight concentration of 30%. This solution was mixed with an azobenzene dye (further called AZD2, see the formula below, [15]) in concentration of 0.5% by weight. The final solution was mixed in an ultra sound bath (during 20 min) before its use.



**Film fabrication and photo alignment**: We have used commercial Indium Tin Oxide (ITO) coated glass plates (of 0.5 mm thickness) as substrates. Planar alignment Polyimide layer (PI-150, from Nissan) of approximate thickness of ≈0.1 $\mu$m was then spin coated on the ITO layer. The spin coating program used was 5 seconds at 500 rpm followed by 25 sec at 3000 rpm. The obtained layer of Polyimide was then heated during 15 minutes at 80°C followed by another heating stage of 60 minutes at 280°C. Then a standard unidirectional rubbing technique was used to generate the easy axis. Those substrates were used as *reference* substrates to build LC cells (see below).

Part of those reference substrates were further modified to obtain the photo alignment layers. Thus, another spin coating process was used to add a layer of AZD2 doped RM (with approximate thickness of $\approx 0.95\ \mu$m). The corresponding solution was spin coated on the top of the rubbed Polyimide surface in a double stage process (during 5 sec at 500 rpm and then during 25 sec at 3000 rpm). The obtained film was then heated at 60°C during 2 min.

The photo alignment layer was further *programmed* by first placing the obtained substrates in a Nitrogen container (to minimize the influence of the ambient oxygen on the photo polymerization process) with optical windows. Then a beam of circularly polarized CW Argon ion laser (operating at 514.5 nm) was used (at normal incidence) to reorient the molecules of the AZD2 (towards the normal of the substrate), and of RM molecules. This was done at room temperature ($\approx$20°C). The spot size of the laser beam in the plane of the photo alignment layer was $\approx$1.5 mm and its power was set to $\approx$750 mW. After 30 minutes of laser exposition, we started to expose the whole surface (including the laser exposed zone) of the photo alignment layer by a standard UV lamp ($\approx$65 mW/cm$^2$). This exposition lasted 35 minutes, while the laser exposition was maintained all the time (more than 1 hour).

### Liquid Crystal Cell Fabrication

The sandwich-like cells of LC were fabricated by using a standard "drop-fill" method. One reference substrate (with only rubbed Polyimide) and another substrate with the programmed photo alignment layer where used to build the cell. The reference substrate was positioned horizontally with its Polyimide layer facing up. Then a UV curable adhesive (containing spacer spheres of 30 $\mu$m diameter) was dispensed on the periphery of that substrate. The drop of a non reactive nematic LC MLC6080 (purchased from Merck) was disposed in the center of the reference substrate. Then the photo alignment substrate was pressed (with the photo programmed alignment layer facing down towards the Polyimide layer) on the top of the reference substrate and the peripheral adhesive was cured by UV exposition, the central part of the cell being protected by a mask.

### Experimental Results and Discussions

The transmission of the obtained (uniformly coated by AZD2/RM layer) substrates was first measured before their use for the LC cell fabrication. According to Merck [14], the pure RM is supposed to be aligned in the same direction as the rubbed Polyimide. Our hope was that the AZD2 molecules also will do so. The possible dichroism of absorption of obtained films (since the AZD2 dyes are dichroic and are supposed to be aligned in the RM matrix) was checked by positioning a broad band polarizer on the optical path of the spectrophotometer (model Varian Cary 500 scan). Then our samples were also placed (behind the polarizer) in the spectrophotometer with their rubbing direction being parallel and then perpendicular to the transmission axis of the polarizer. The detected transmission spectra were subtracted from the spectrum of the polarizer to obtain the differential transmission of our samples. As one can see, from the Fig. 1, the absorption spectra are clearly different for two input probe polarizations in the wavelength range corresponding to the resonant absorption band of the AZD2 [13,15]. Indeed, the transmission of the sample is lower when the probe polarization

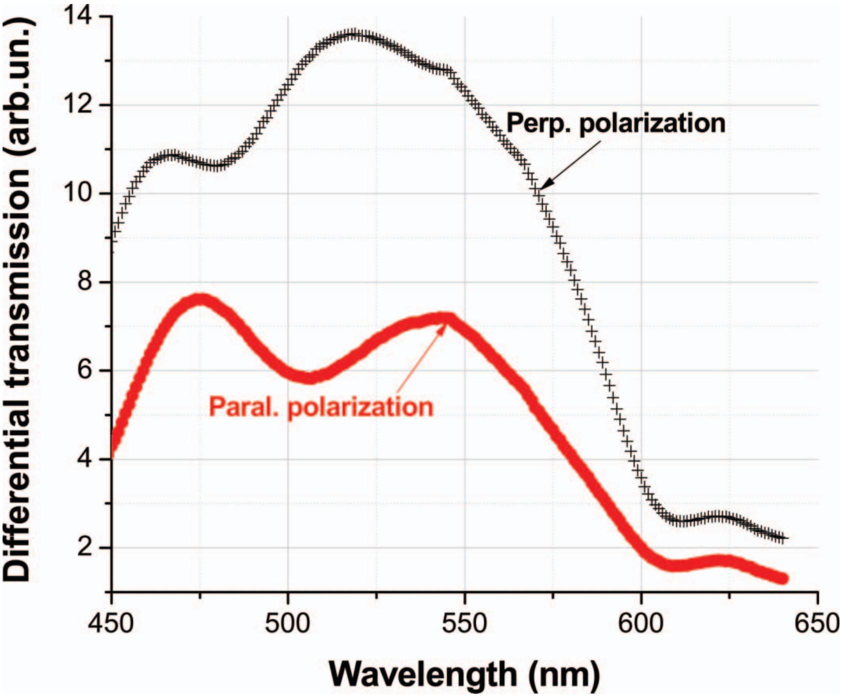


**Figure 1.** Demonstration of the relative dichroism of the AZD2/RM layer and thus of the alignment of the AZD2 dye by the reactive mesogen matrix (see the text for details).

is parallel with the rubbing direction of the Polyimide, which confirms the alignment of the dye's dipole moment by the RM matrix in the rubbing direction.

Another useful information that we obtain from those transmission spectra is the position of the Argon ion laser's wavelength (514.5 nm) with respect to the resonant absorption band of the dye. It is thus clear that, given its resonant position, we can use, e.g., the normally incident circularly polarized light of that laser to reorient AZD2 molecules in the direction of the normal of the substrate. Thus, in the LC cell zones, where the control substrates were exposed only to the UV light (laser non-exposed area), the average alignment of long molecular axes of LC molecules (so called "director," [6]) should remain parallel to the rubbing direction of the Polyimide. Then, the overall alignment of LC in those areas (in the LC sandwich – cell) should be uniform given that the opposed alignment surface is made by a reference substrate imposing the same direction of alignment of the director. In contrast, in the zones exposed to normally incident circularly polarized laser beam, the alignment of AZD2 and RM molecules should be changed towards the normal to the surface. Thus, in those zones, the alignment of LC in the sandwich – cell should be hybrid; planar at the Polyimide surface and reoriented towards the substrate's normal (say tilted at an angle $\theta_x$, further called as photo induced "pretilt angle") at the photo alignment surface.

In fact, the observations of the cell under Zeiss polarizing microscope confirm those hypotheses. As we can see, in the Fig. 2, the laser exposed and UV polymerized zone (left side area, ranging from the top left corner to the bottom middle point, approximately) has different alignment compared to the zone, which was simply UV polymerized (the

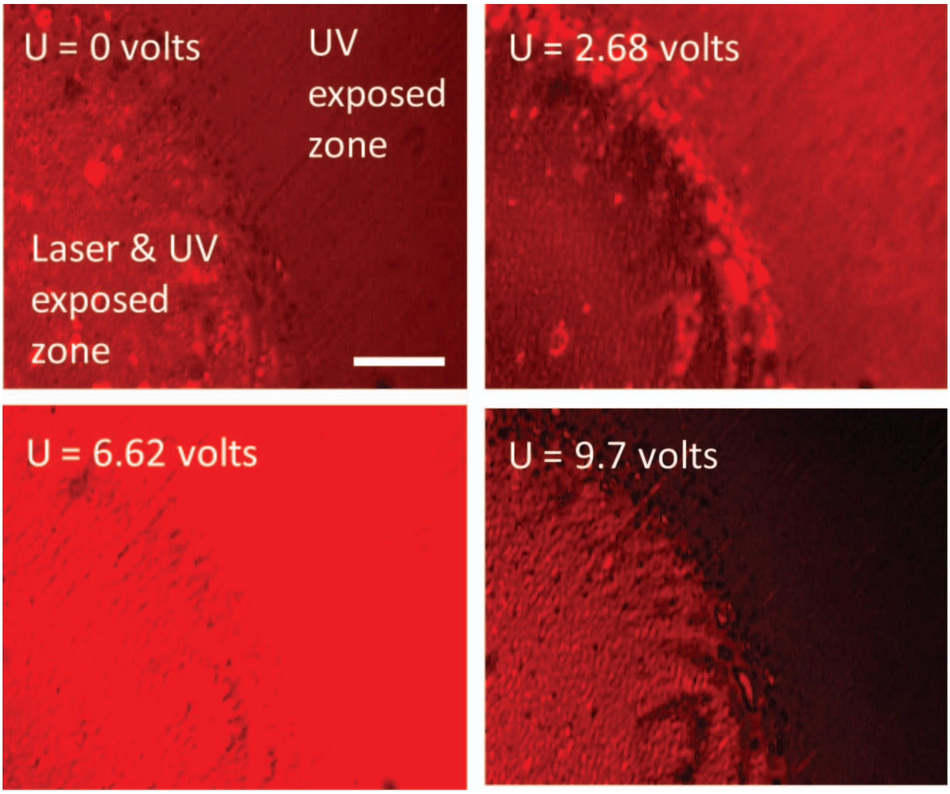


**Figure 2.** Micro photography (in red light) of the laser exposed and UV polymerized area (left bottom zone of pictures) versus only the UV polymerized area (right top zone of pictures) at different voltages (identified at the top left corner of pictures). The rubbing direction is at 45° with respect to the crossed polarizer and analyzer. The horizontal bar (in the bottom right of the top left picture) shows approximately a size of 250 um.

remaining top right area). There is also a significant difference of reaction (director's reorientation) of LC to the applied (to two ITOs) electrical voltage of 1 kHz frequency (AC, square shaped). One can see that the differential phase delay (between extraordinary and ordinary waves of the probe beam) changes quite differently in those zones depending upon the voltage applied. Interestingly, the light transmission shows a relatively abrupt character at the periphery of the laser exposed zone. Very likely this could be due to the generation of multiple zones of disclinations (abrupt variation lines of the director alignment [6]), related to the speckle character of the Argon ion laser beam. The impact of those non uniformities is more noticeable on the periphery of the area, exposed by laser beam, where the reorientation angle $\theta_x$ is still small (compared to the center of that area).

More detailed study (with smaller voltage steps) shows that the LC reorientation starts to be observable at already ≈0.5 V in the laser exposed and UV polymerized zones; while this value is ≈1.4 V in other zones exposed only to UV. The theoretical estimation of the reorientation threshold provides the approximate value of $U_{th} \approx 1.49$ V for a uniform planar aligned cell (filled by MLC6080) when using the well-known formula $U_{th} = \pi\sqrt{K_1/(\varepsilon_0\,|\Delta\varepsilon|)}$, (see, e.g.[16]), where $\varepsilon_0$ is the dielectric constant of vacuum,

$\Delta\varepsilon = 7.2$ is the dielectric anisotropy of the LC (at driving frequency) and $K_1 = 14.4$ pN is the splay deformation coefficient of the LC. Thus, while the experimentally measured threshold in the laser non-exposed areas is rather close to the theoretically estimated one, the significantly lower quasi-threshold in the laser exposed zone confirms the hybrid alignment of the LC in that zone.

We have tried to evaluate the photo induced pretilt angle $\theta_x$ in the center of the laser exposed area. We have used a simple (and very approximate) method of cell rotation by positioning our cell between two crossed polarizers. The cell was turned around the incidence point of the probe beam (obtained from a CW He-Ne laser, operating at 632.8 nm), with its substrates staying parallel to the surfaces of polarizers (in the vertical plane). The same experiment was made when the probe beam was passing through the laser exposed and non-exposed zones (as close as possible to each other to ensure similar cell thicknesses). There was no field applied to the cell. Given the anisotropy of those cells, the transmitted (through the second polarizer) light‘s intensity has shown typical oscillations with a rotation period of 90°. Given the different total phase delay, generated by the planar and hybrid orientations of the same thickness, the oscillation maximum values were different. The ratio of maximums of transmitted intensities through the non-exposed (planar) and exposed (hybrid) zones was equal to ≈4.3 ± 0.5. The oscillations of the polarimetric transmission for an anisotropic layer of LC may be described by the well-known formula $I = \sin^2(2\beta)\sin^2(\frac{\phi}{2})$, where $\phi = \frac{2\pi}{\lambda}\int_0^L (n_e(z) - n_\perp)dz$ is the accumulated (total output) phase delay between ordinary and extraordinary probe waves, z axis is aligned normal to the cell substrates, $n_e(z) \approx n_{II}n_\perp/\sqrt{n_{II}^2\sin^2\theta(z) + n_\perp^2\cos^2\theta(z)}$ and $n_\perp$ are the local extraordinary and ordinary refractive indices of the LC, respectively, $\beta$ is the angle between the input optical axis of the LC and the first polarizer's transmission axis, $\lambda$ is the wavelength of the probe beam in the vacuum (0.632 $\mu$m) and $L$ is the cell thickness (defined by spacers). Thus, given that there was no voltage applied to the cell, the observed oscillations (during the rotation process) are defined by the variation of the angle $\beta$ only. Modeling the molecular orientation configuration of the hybrid cell in a very approximate way as $\theta$(z) = $\theta_x$(1-z/L), where $\theta_x$ is the photo induced surface pretilt angle (at z = 0) in the center of the laser exposed zone, gives the same ratio 4.3 for the following fit parameters: the cell thickness is 32 $\mu$m (which is quite frequent when using spacers of 30 $\mu$m diameter) and the value of photo induced pretilt is equal to ≈85.6°, which is a rather important "pretilt" angle.

We have also tried to quantify, at least very approximately, the possible variation of anchoring energy of the LC and the AZD2/RM layer, versus other traditional alignment layers, e.g., the Polyimide. The corresponding experimental results were obtained by first applying strong voltage to the cell (ensuring saturated reorientation), which was then abruptly switched off. The typical transmission (through a laser non-exposed zone of the cell) relaxation dynamics may be seen at the Fig. 3. Using a simplified exponential relaxation model we find that the characteristic time of relaxation (averaged for data obtained at different positions of the cell) here is at the order of $\tau_R$≈1.2 sec. Supposing that the cell has hard boundary conditions (see, e.g., Ref.[17]), the orientation relaxation time may be estimated as $\tau_R \approx \gamma L^2/(K_1\pi^2)$, where $\gamma$ is the rotational viscosity of the LC. Supposing that there is no contamination and that the key physical parameters of the LC remain the same in the cell with the AZD2/RM surface ($\gamma = 157$ m Pa s and $K_1 = 14.4$ pN, at 20°C), we then find that its typical values (predicted theoretically) also should be at the order of $\tau_R \approx 1$ sec. Our experiments with cells having the same thickness and the same LC, but using two PI-150 (Nissan) alignment layers only (without AZD2/RMs), have done

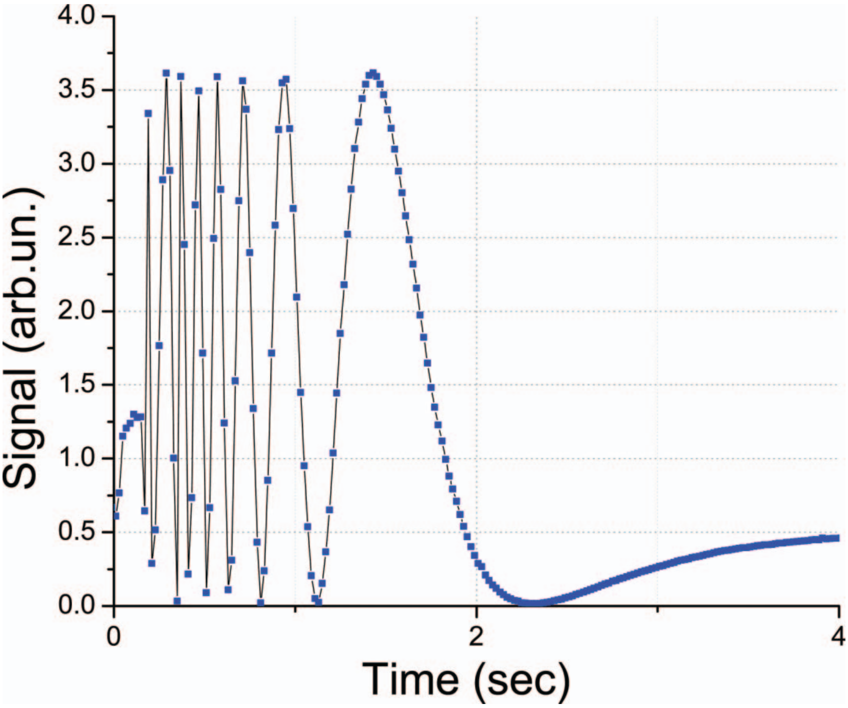


**Figure 3.** Demonstration of the relaxation process in the cell with photo controllable alignment layer (AZD2/RM) by using a typical polarimetric set-up.

the same number $\tau_R \approx 1.1$ sec. This indicates that the anchoring energy of our alignment material is weaker compared to the classical rubbed Polyimide, but there is no significant difference.

## Study of Stability of Photo Alignment

The fabricated samples were monitored periodically and their performance was found unchanged after 6 months in the conditions of their storage in ambient temperature and lighting.

To study the impact of UV exposure we have proceeded to additional uniform UV exposure ($\approx$87 mW/cm$^2$ during 25 minutes) of our cells. Those samples were then studied again by using the Zeiss polarizing microscope. As one can see, from the Fig. 4, the additional UV exposure has introduced two types of changes. The first one is the overall orientation change in the ground state (at 0 Volt), particularly visible in the laser exposed area (bottom left picture versus the top left picture taken before the additional UV exposure). There are also localized orientation defects both in the laser exposed and non-exposed zones. It must be noticed however that there is still a clearly observable difference of electro-optical behaviour in two zones. Thus the application of voltage demonstrates (top right picture versus bottom right picture) the fact that the reorientation difference is important. However, some small local defects are still visible even at the strongly reoriented state in

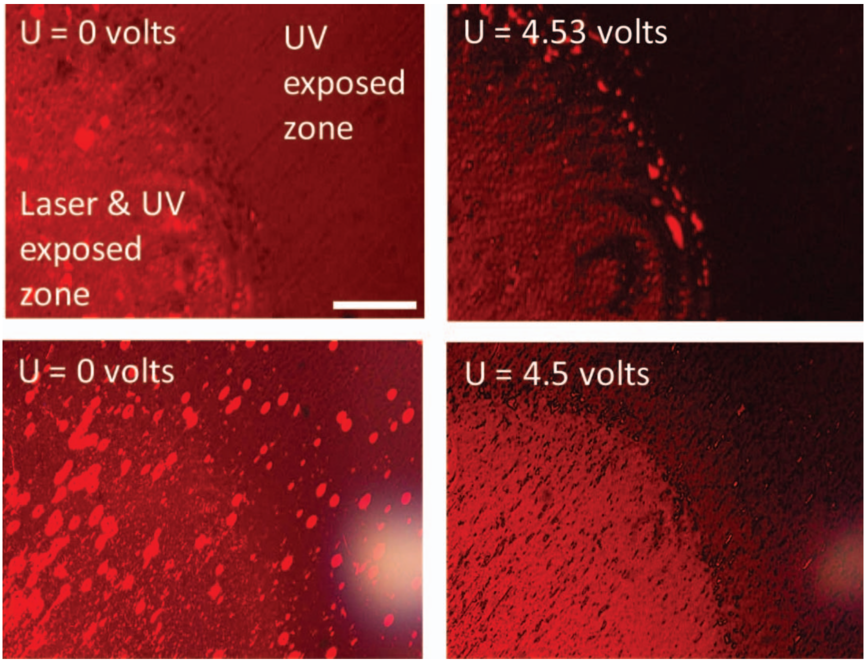


**Figure 4.** Demonstration of the impact of the additional "degrading" UV exposure on the alignment quality. Top pictures show the cell before the UV exposure, while the bottom pictures show the cell after it. The laser exposed and UV polymerized area is shown in the left bottom zone of pictures versus only the UV polymerized area that is shown in the right top zone of pictures (corresponding voltages are identified at the top left corner of pictures). The rubbing direction is at 45° with respect to the crossed polarizer and analyzer. The horizontal bar (in the bottom right of the top left picture) shows approximately a size of 250 um.

both laser exposed and non-exposed areas (bottom right picture, taken after the additional UV exposure).

Interestingly, we were able to partially recover the alignment properties of our layers by an additional thermal processing (Fig. 5). Those cells were heated up to 103°C (above

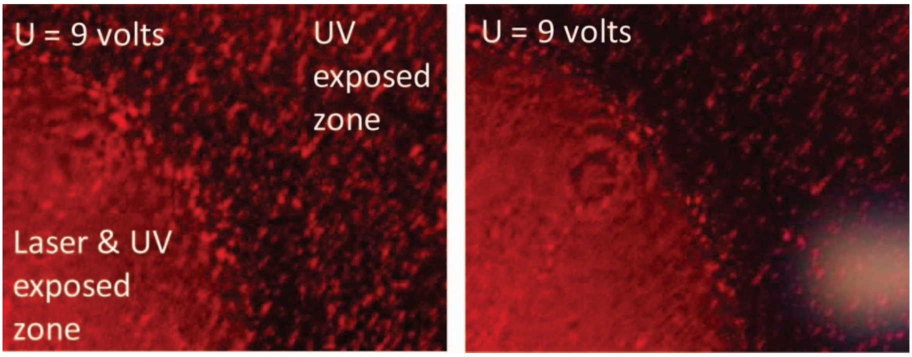


**Figure 5.** Demonstration of the partial thermal "repairing" (right side picture) after the degrading UV exposure of the cell (left side picture).

the nematic-isotropic phase transition temperature of the LC) and then cooled down by taking it out from the oven directly to the room temperature. As one can see, the alignment becomes relatively better defined and slightly more uniform (the right side figure) compared to the cell just after the UV exposure (left side figure). The small local defects are also decreased. This means that the UV induced damages were not permanent (at least not all of them) and perhaps the thermal processing could be further explored and used to improve the properties of our layers.

In conclusion, we have shown that we can align LC molecules rather efficiently by using light exposed alignment of azobenzene molecules doped into an RM matrix. Interestingly, even if the AZD2 is not mesogenic, the photo induced (via the AZD2's reorientation) collective reorientation of RM molecules is still very efficient. However, the UV exposure is a problem for the chosen material composition since some defects appear both in laser exposed and non-exposed areas. Finally, the appropriate thermal processing may partially "repair" the UV induced defects. For the moment, we don't know the underlying mechanism responsible for the observed alignment degradation by UV light.

## Acknowledgment

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