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Novel devices with photosensitive elements.

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ABSTRACT

Liquid Crystal (LC) devices with photosensitive elements have incredible scope for creating unique photo-induced optical devices.

The use of azobenzene based materials, which undergo a trans-cis isomerisation when irradiated with light of a specific wavelength, is firmly established in LC research. The trans conformation is an elongated rod-like shape, similar to LC mesogens, whilst the cis conformation is closer to a spherical (bent) shape, disrupting to the LC order. When these materials are doped into LC materials they are able to produce light induced responses, and therefore their application to photo-switchable optics and devices is undeniable. In this research paper the light induced order modification, rather than light induced reorientation, is utilized to produce an all-optical switchable laser protection device.

Upon irradiation of an azo-doped LC system with a continuous, low power (0.5 mW), laser threat ($\lambda=405$ nm) the trans-cis photoisomerisation process is triggered. This results in the trans-cis conformal shape change, lowering of the LC order, and causing the system to switch from the LC nematic phase (transmitting between crossed polarisers) to the isotropic liquid phase (blocking/dark between crossed polarisers). The optical properties of the azo-doped LC materials have been characterized and the response time dependence on azo-dopant concentration, system temperature, and laser threat intensity is thoroughly investigated.

Keywords: LCs, Photosensitive materials, Laser safety and eye protection, Azobenzene

1. INTRODUCTION

In recent years, the accessibility of high powered hand-held lasers is on the rise and subsequent reports of incidents involving dangerous and damaging use of laser, typically against aircraft, has increased dramatically. Laser powers as low as 5 mW can cause eyesight^{1, 2} or camera damage, whilst lower intensities still provide a dazzle threat. This later threat is especially relevant when attacks against pilots are considered. The development of novel liquid crystal (LC) optical protection devices which combat this problem are currently underway³⁻⁶, with the switchable optical properties of LCs providing an excellent basis for electrically switchable protective devices. Development of a passive switchable filter, which responds directly to the laser threat, is a bigger challenge that can be realized when incorporation of light sensitive azobenzene based mesogens into the LC system is considered.

Development of photo-sensitive azo-doped LC systems either requires the generation of an azobenzene based mesogen which itself exhibits a LC phase^{7, 8}, or, more simply doping of azobenzene based materials directly into a LC host system^{9, 10}. Upon irradiation of azobenzene-based materials, a reversible trans-cis photoisomerisation process occurs, figure 1(a). The irradiating light must be of a wavelength that corresponds to the azo π - π^* transition, typically UV wavelengths (though this can be manipulated through careful consideration of molecular chemistry). The trans-cis conformal switch results in the azobenzene based mesogen switching from a rod-like shape (considered anisotropic) to a bent/spherical mesogen (considered isotropic). If the material was a pure azo material which exhibited its own LC phase then irradiation whilst in the LC phase would result in an immediate reduction in order, almost certainly leading to a switch into the isotropic phase without changing the temperature of the system (an isothermal phase transition). However, if the azobenzene based material is doped into a LC host the resulting shape change disrupts the host packing and lowers the order of the system by a lesser degree. This will certainly change the LC properties, and if there is a large enough reduction in order can also result in an isothermal phase transition from liquid crystalline nematic to the isotropic state. This isothermal phase transition effect is utilised in the passive switchable protection device described in this paper.

Liquid crystals are well-known and the term describes states of matter that lie between solid crystal and isotropic liquid where the constituent molecules are anisotropic. The LC phase most used in devices and relevant to this application is

the calamitic nematic phase, in which the molecules can be considered rod-shaped with the molecular long axis on average aligned along the director, \hat{n} . The anisotropic nature of LC materials means that they exhibit some incredibly interesting electrical and optical properties. One such property utilised in this application is the birefringence, Δn , of the material. The birefringence means that the extraordinary and ordinary refractive indices differ for the material, and when a device of thickness d is observed between crossed polarisers (with the director, which defines the optic axis of the system, at 45°) a wavelength (λ) dependent transmission, T , is observed, $T = \sin^2(\Gamma/2) = \sin^2(\pi \Delta n d / \lambda)$. A nematic device between crossed polarisers, with a large cell gap ($d \sim 20 \mu\text{m}$), will transmit much of the incident light ($\sim 55\%$ for unpolarised light). If the LC material undergoes a transition into the isotropic phase, in which the birefringence is zero, the transmission is subsequently blocked by the crossed polarisers and the transmitted light intensity is purely determined by the polariser extinction ratio. This concept is the basis of our device.

2. MATERIALS AND METHODS

The azobenzene-based mesogen used in this device was 4-2-butyl-4'-2-alkoxyazobenzene (BAAB2), described in further detail by S. V. Serak et al.¹² and used in another embodiment of passive laser protection described by us recently⁴. BAAB2 was doped into the LC host 4-pentyl-4'-cyanobiphenyl (5CB) with varying concentration between 5 and 10% (w/w) (mix-5 to mix-10 respectively). These mixtures were filled into standard LC devices with a cell gap of $\sim 20 \mu\text{m}$ and the inner substrates treated for planar alignment (director parallel to the substrate). The planar alignment was achieved through rubbing of the SE3510 polyimide alignment layer. The absorption spectrum for BAAB2 is shown in figure 1(b) and the overlap between the "laser threat", chosen to be at 405 nm, and the azo $\pi-\pi^*$ absorption peak, ~ 350 nm, is clear.

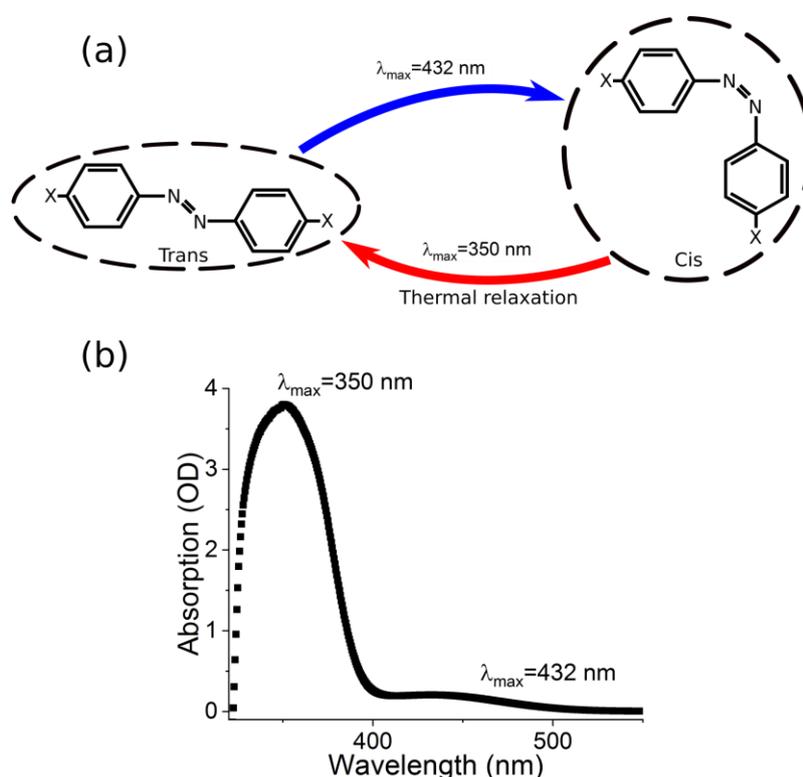


Figure 1. (a) Azobenzene based mesogens typical structure and conformal shapes. (b) Absorption spectrum of BAAB2 dissolved in acetone.

3. RESULTS AND DISCUSSION

The photosensitive nature of the azo-dopant means that the nematic to isotropic transition temperature, T_{NI} , will vary depending on the illumination conditions experienced. T_{NI} was measured for different conditions and the values are

summarized in figure 2. An increase in T_{NI} is observed with increasing BAAB2 concentration in both the differential scanning calorimetry method ($10\text{ }^{\circ}\text{Cmin}^{-1}$) and polarizing optical microscopy ($1\text{ }^{\circ}\text{Cmin}^{-1}$) coupled with a red filter to prevent lower broadband wavelengths from photoisomerising the system. This trend is expected as pure BAAB2 exhibits a higher T_{NI} at $83.5\text{ }^{\circ}\text{C}$ than 5CB at $35.8\text{ }^{\circ}\text{C}$. In all subsequent measurements T_{NI} relates to the transition temperature measured using polarizing optical microscopy coupled with the red filter. This will provide a higher relative accuracy for other measurements described as the same method and hot stage are employed.

Removal of the red filter will allow a small amount of photoisomerisation to occur due to the lower wavelengths of the broadband light source. This causes the transition temperature to decrease due to a lowering of the order in the system, an effect that would occur in day-to-day operation of the device. The result in figure 2(a) demonstrates a $\sim 5\text{ }^{\circ}\text{C}$ decrease in the transition temperature from focusing a 50 W broadband light source directly onto the sample. The reduction that would occur in day-to-day operation would in fact be lower as the ambient room lighting was measured to be $\sim 3.7\%$ of the microscope light intensity used. The variation in transition temperature due to broadband photoisomerisation is demonstrated in figure 2(b).

The fundamental operation of this device relies on the effect of continuous laser irradiation on the sample. The effect to the transition temperature was investigated through irradiation with 1 mWcm^{-2} and 5.2 mWcm^{-2} for 10 minutes before measurement of the transition temperature were conducted with continual irradiation (T_{Irr-NI}). A clear decrease in the transition temperature, $\sim 10\text{ }^{\circ}\text{C}$, was measured due to the photoisomerisation of the BAAB2 molecules. Increasing BAAB2 concentration causes a larger drop in transition temperature when under irradiation of the laser intensity, a direct result of the increase in cis conformer concentration.

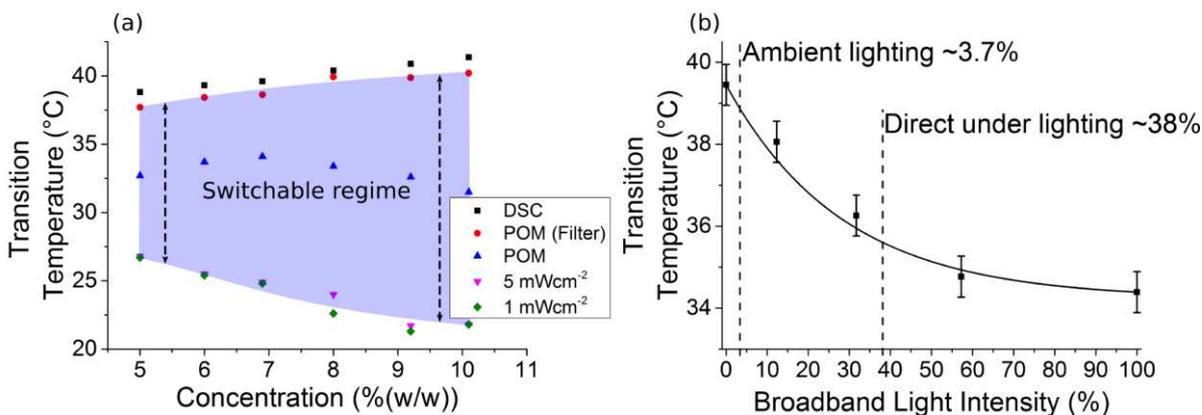


Figure 2. (a) Nematic to isotropic transition temperature for dark and irradiated conditions. (b) The transition temperature under varying broadband intensity.

The range between T_{NI} and T_{Irr-NI} is denoted the protection regime of this device. If the system is exposed the “laser threat”, whilst held in this temperature range, it will undergo an isothermal phase transition taking the device into the isotropic blocking state. Altering the LC host or azo-dopant concentration would allow this temperature range to be fine-tuned to device specifications.

To accurately predict how the transmission of the device between crossed polarisers, the wavelength dispersion of birefringence must be measured. An overall increase in birefringence was measured in the BAAB2 doped samples when compared with pure 5CB, figure 3(a). The extended Cauchy model¹³ was fit to the experimental data, $\Delta n = 3GS\lambda^{2\lambda^{*2}} / (2(\lambda^2 - \lambda^{*2}))$, where G is a proportionality constant, S is the order parameter, and λ^* is the mean resonance wavelength. The data demonstrates an increase in the mean resonance wavelength which corresponds to the higher π - π^* transition of BAAB2, $\lambda^* = 350\text{ nm}$, compared to pure 5CB, $\lambda^* = 210\text{ nm}$ ¹⁴.

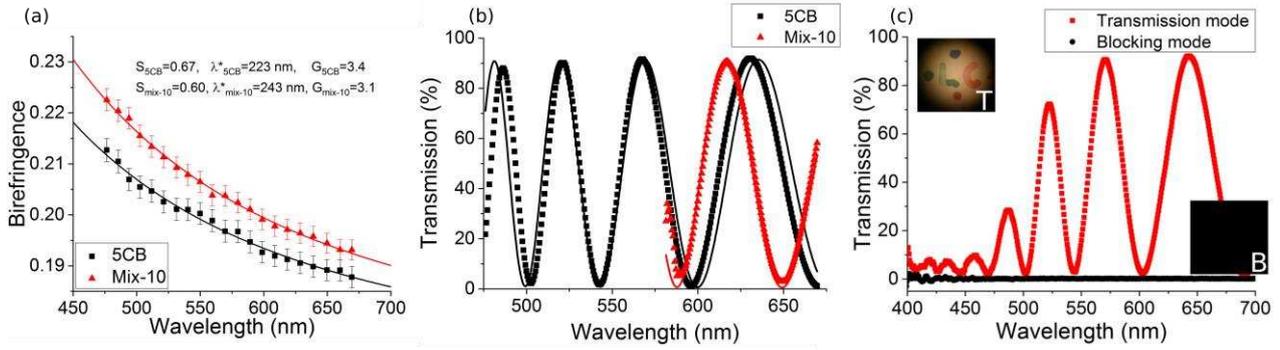


Figure 3. (a) The wavelength dispersion of birefringence for 5CB and mix-10. The extended Cauchy model is fit to the experimental data with fitting parameters included. (b) The experimental and fitted transmission spectra for 5CB and mix-10. (c) Visible transmission and blocking spectra for mix-10. Inserts show Nikon D7100 camera imaging through the device in the transmitting (T) and blocking (B) modes.

The device's transmission state spectra, with the director at 45° to the input polarisation, was measured using an Avantes Sensline Avaspec 2048-XL spectrometer, figure 3(b), coupled to the polarising microscope. An example of the experimental transmission data for 5CB and mix-10, measured over a restricted wavelength range (580-680 nm) to prevent photoswitching of BAAB2 is shown ($T=25^\circ\text{C}$), together with the transmission equation fit to the data (solid lines). The experimental data and theoretical fit show excellent agreement, with the small differences due to variations in the cell gap over the field of view.

When the device is held in the protective temperature regime the device will switch between transmitting and blocking modes when irradiated with the laser threat. The spectra for each state were also measured, with ambient light causing small amounts of photoswitching in the device, for mix-10, shown in figure 3(c). The data demonstrates the spectra and observations of objects through the device that would occur if it was implemented for CCD protection. The residual transmission in the blocking state is limited purely by the polarisation extinction ratio. Blocking of the laser radiation is therefore easily achieved through careful selection of a polariser with a high extinction at the required wavelength, in this case $\lambda=405$ nm.

The response speed of any switchable laser protection device is critical in considering its ability to protect against damaging exposure to laser light. The transmission of this device was measured with respect to time after the laser first irradiates the system, with the 10% transmission point taken as the time at which the system is in the blocking mode. The 10% value was selected to allow for a clear and robust comparison between samples, and is common in LC response time measurements.

The response time was measured as a function of temperature across each sample's protective temperature regime. A laser intensity of 5.2 mWcm^{-2} was used to trigger the switch. Figure 4(a) demonstrates that as the temperature is reduced further from T_{NI} , the response speed increases on average from ~ 2 s to ~ 60 s. This increase in response speed at lower temperatures is expected as a larger change in order is required to achieve the isothermal phase transition. At higher temperatures there is a negligible variation in the response times seen for different concentrations, though at lower temperatures the higher BAAB2 concentration mixtures have a clearly faster response speed. The response speed for each concentration can be further compared with the ratio of $(T_{NI}-T)/(T_{NI}-T_{Ir-NI})$, figure 4(b), where it can be seen that all the response speed measurements follow the same trend. When the temperature approaches T_{NI} for any mixture the ratio approaches 0 and the response speed approaches 0 s, as the system is already isotropic. As the temperature approaches T_{Ir-NI} the ratio approaches 1, and the response speed theoretically becomes infinitely long. When considering temperatures at the irradiated transition temperature it is clear that the system will no longer switch to isotropic and thus the response speed will tend to infinity.

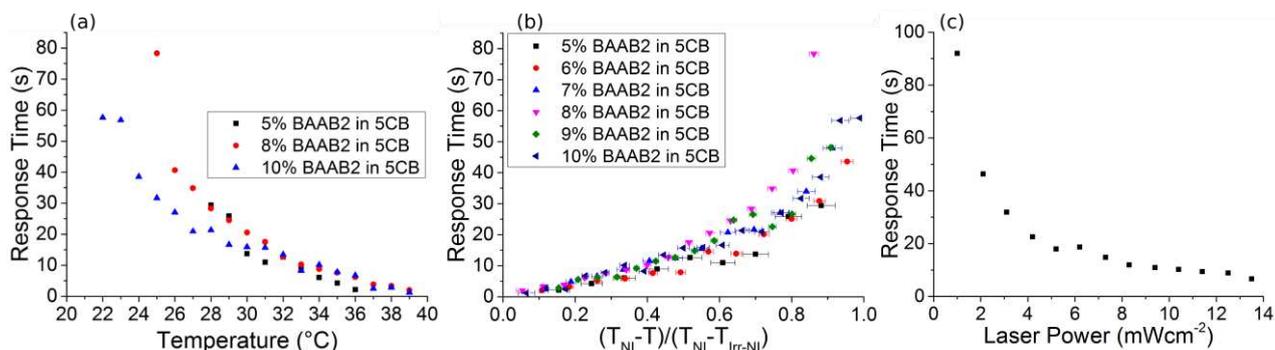


Figure 4. Mixture response time dependence on (a) temperature, (b) ratio of the reduced temperature and the difference between irradiated and non-irradiated transition temperatures, and (c) laser intensity.

The results indicate that an overall higher concentration of azo dopant will result in a faster response time, although the behavior is still temperature dependent. It is, however important to balance the increase in concentration with the reduction in transition temperature caused by ambient light conditions, described in figure 2. At sufficiently high concentrations, the reduction in switchable protection regime will render the system ineffective.

So far we have considered the response of the device to a rather low power ($\sim 5\text{mW}$) laser. It is clear that higher intensity laser irradiation will impact the switching speed of the device by further reducing it. Indeed by varying the incident laser power density, at $T=30^\circ\text{C}$, the response time was shown to rapidly improve from 92 s to 6.6 s, figure 4(c). The higher intensity laser irradiation results in an increased rate of photoisomerisation of the BAAB2 molecules and therefore a faster switch time into the isotropic state. Thus, if higher intensity “laser threats” are experienced, the exposure time to these threats would be lower, due to the higher switching speeds of the device. This would result in higher levels of protection.

The overlap between incident laser wavelength and the $\pi\text{-}\pi^*$ absorption peak is also important to consider. Here, a laser wavelength of 405 nm was used to trigger the trans-cis photoisomerisation in BAAB2 ($\lambda_{\text{max}}=350\text{ nm}$). The laser was chosen as it is a readily available hand-held laser, but the emission wavelength is close to the edge of the absorption peak, effectively capping the possible switch speed of the system. By matching the laser irradiation wavelength to the peak of the absorption band, faster response times could be easily be achieved.

It is important to consider whether the response of this simple device is sufficient to offer protection to a laser threat. Literature investigating the damage to CCD cameras from continuous laser irradiation shows that monochrome CCD cameras experience damage from laser intensities of 139 kWcm^{-2} after exposure times greater than 10 s^{15} . Considering the response times measured here we have shown that in specific temperature ranges for mix-10 a response time of $<10\text{ s}$ is easily achieved and therefore our simple device can provide an all-optical protection for CCD cameras against intensities $<139\text{ kWcm}^{-2}$.

It is also important to emphasize the low intensity nature of the irradiation in these measurements. In this paper the switching speed was measured with a low laser intensity of 5.2 mWcm^{-2} (27 times smaller than the damage threshold 139 kWcm^{-2}). Figure 4(c) shows how the response time improves with larger laser intensities and therefore the switching speeds measured here are actually much slower than would be exhibited by the device if exposed to irradiation of damaging intensities of 139 kWcm^{-2} . With the current testing the application of this all-optical device to CCD protection has been clearly demonstrated and improvements in the response time can be easily realized for higher laser intensities, as well as careful considerations of mixture parameters.

To further improve the response time of the device the orientation of the director with respect to the incident laser polarization can also be considered. The current device is oriented at a 45° angle with respect to the polarization of incident light. The absorption of the BAAB2 is polarization dependent, with a maximum when the long axis of the molecule is aligned with the polarization of light; at 45° the efficiency of absorption is half of the maximum. However, if a device is constructed with a twisted nematic geometry, the dye molecule effectively adopts all orientations with respect to incoming light, ensuring maximum absorption. We have recently shown that for such geometries, sub-second response times (51 ms) can be achieved, explored in detail by Jull et al.⁴

4. CONCLUSION

An all-optical switchable laser protection filter, comprising of an azobenzene-based material doped into a LC host has been shown, with the optical properties of the mixtures characterized. This two-mode device was clearly demonstrated, with the ability to switch between broadband transmission and protection, triggered directly by irradiation by the laser threat. The transmission mode provided excellent image quality, whilst the blocking state had a transmission limited purely by the polariser extinction ratio.

The response speed of the device was shown to depend on system temperature, BAAB2 concentration, and laser intensity. It has been clearly shown that the device would provide sufficient protection against laser intensities at damaging levels for CCD cameras and further improvement of the response time are clearly described. Thus, this azo-doped LC device has been shown to be an effective passive solution to negate damaging laser incidents.

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